

Abiotic formation of methane by oxidation of sulfur species under hydrothermal conditions

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In recent years, abiotic reactions have been considered as one of the potential mechanisms for the formation of reduced carbon species (i.e., CH₄, ..) in hydrothermal systems at seafloor. Because the fluid flux through deep-sea hot-springs represents a potentially significant source of carbon and energy to support microbial activities in surface and sub-surface habitats, the possibility that abiotic processes may influence the speciation of carbon in vent fluids has direct implications for the maintenance of life in present-day hydrothermal environments. Although aqueous carbon compounds have significant role in broad spectrum of geochemical and biological processes, reactions to produce abundant aqueous hydrocarbons at seafloor hydrothermal environment are poorly understood.

Abiotic synthesis of hydrocarbons in hydrothermal environments is attributed to Fischer-Tropsch type processes, which are characterized by the reduction of CO₂ or CO by H₂ on catalytic mineral surfaces including magnetite (Anderson, 1984). These reactions are also thought to occur in association with serpentinization of mantle peridotites, which produces H₂ and Fe₃O₄. Previous experimental studies under hydrothermal conditions (e.g., Foustoukos et al. 2004) succeeded in production of H₂ and abiotic CH₄. For example, Foustoukos et al. (2004) reported the production of 208 mmol/kg of H₂ and 39 μmol/kg of CH₄ by the olivine hydration over 1000 hours; however, the concentration of CH₄ gas was quite low than those observed in natural ultramafic-hosted hydrothermal vent fluid, for example, 0.13 ~2.2 mmol/kg of CH₄ from the hydrothermal vent at the Lost City.

In this study, we focused on sulfur species as reducing agent, based on Putri et al. (2011), which reported high H₂ generation rate (64.3 mmol/kg in an hour) in the system of H₂S and H₂O. We conducted a series of hydrothermal experiments with H₂S to generate H₂ by reduction of H₂O. We used Na₂S • 9H₂O for H₂S species, NaHCO₃ for CO₂ species, and Fe₃O₄ for catalyst of Fischer-Tropsch type CH₄ synthesis. The initial concentration of H₂S and CO₂ species were set to be 10 mmol/kg and 40 mmol/kg, as analogue of hydrothermal vent fluids. The experiments were conducted at 300 degree C, and initial pH was controlled at 9.9~10.0 with NaOH. After 168 hours experiment, the concentration of H₂ gas was 39.7 mmol/kg, which means almost H₂S species was consumed by the reduction of H₂O. The generated H₂ gas was used for the second reaction CH₄ gas. The CH₄ gas concentration was 30.3 μmol/kg in 168 hours, 6.3 times higher than that from serpentinization experiment (Foustoukos et al., 2004). In the same condition except for absence of Fe₃O₄, the gas concentration of H₂ were 40.14 mmol/kg and 4.91 μmol/kg, respectively. The experiment without Fe₃O₄ generated CH₄ gas and the concentration of CH₄ was quite lower than the experiment using Fe₃O₄, that indicates Fe₃O₄ takes the role of catalyst in the formation of CH₄, while other catalytic effect should be considered in the system.

References

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