

EXPERIMENTAL STUDY OF ABIOTIC SYNTHESIS PROCESSES IN A HYDROTHERMAL FLOW SYSTEM: IMPLICATIONS FOR ORGANIC MATTER FORMATION IN EXTRATERRESTRIAL ENVIRONMENTS. Q. Fu^{1,*} and W. E. Seyfried Jr.¹, ¹Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455, *Present address: Lunar and Planetary Institute, Houston, TX 77058 (fu@lpi.usra.edu).

Introduction: Hydrocarbons with an apparent abiotic origin are found in hydrothermal fluids from vents on unsedimented mid-ocean ridges. In particular, fluids from ultramafic-hosted hydrothermal systems contain significant quantities of many organic species other than methane [1-3]. Generation of significant amounts of long chain hydrocarbons was not reported in previous experimental studies [4-7]. This might be attributed to unknown critical factors that control abiotic formation of organic compounds in hydrothermal systems, and limited experimental strategies in closed systems as well. Therefore, experimental studies in hydrothermal flow system are needed to systematically identify the chemical and physical factors that contribute to the formation of reduced carbon species at elevated temperatures and pressures. Furthermore, the similar reactions of methane and organic matter formation might occur in extraterrestrial environments. With the existence of organic compounds in meteorites [8-9] and detection of methane in Martian atmosphere [10], it is of importance to understand factors controlling abiotic organic synthesis.

Experiments: Two experiments were conducted using a newly-designed hydrothermal flow-through system. A fixed volume (~100 ml) titanium reactor represents the central unit of the flow system. It is linked to a high-pressure fluid delivery system (Shimadzu LC-10AT VP HPLC pump) that maintains constant flow rate during the experiments. The outlet side of the reactor is connected to a computer-controlled regulating valve that keeps the total pressure at a fixed value. A magnetic stirrer in the system permits the mineral reactant to be kept in suspension. Temperature control is provided by band heaters outside the reactor. The continuous inflow of fluid reactants combined with the same volumetric outflow rate of products provides a thermodynamically open system, in which the steady state can be sustained.

Experiments were performed at 250 bars total pressure and at two different temperatures: 250 °C and 300 °C. In each experiment, the reactor contained five grams of magnetite as a catalyst. The source fluid for all experiments was an aqueous NaCl solution at 0.5 mol/kg, equivalent to that of sea water. The source fluid was modified by addition of HCl, to make sure that the *in-situ* pH was ~5. H₂ gas was delivered to the system through a high pressure gas-injection valve,

while CO₂ gas was dissolved in the source fluid before being pumped into the reaction cell. Subsequent step-wise changes in dissolved H₂ were made to achieve different redox conditions (H_{2(aq)}/CO_{2(aq)} ratios). The flow rate of input fluid was kept at three different values (0.5, 0.3, and 0.15 ml/min) for certain amounts of time in each experiment. Fluid samples were analyzed for total organic carbon (TOC), volatile components and dissolved carboxylic acids.

Results and Discussion: Magnetite was pretreated with hydrogen peroxide to eliminate organic carbons chemisorbed on the surface before each experiment. As an additional step to exclude carbon from magnetite and the inside wall of the reactor, deionized water with ~15 mmol/kg H_{2(aq)} was used to flush the system at experimental T, P conditions. No carbon background was detected by TOC and GC analysis.

Volatile carbon species. In both experiments, dissolved CO and CH₄ were detected. For example, at 250 °C and the flow rate of 0.5 ml/min, when dissolved CO₂ was kept constant at ~15.5 mmol/kg, the increase in dissolved H₂ (from 29 to 75 mmol/kg) caused the concentrations of CO and CH₄ to increase from 10 to 43 μmol/kg, and zero to 0.3 μmol/kg, respectively. This is consistent with previous experimental observation in closed systems: the positive relationship between the H_{2(aq)}/CO_{2(aq)} ratio and coexisting dissolved concentrations of reduced carbon species (CO and alkanes) [7].

Thermodynamic calculations indicated that CO reached chemical equilibrium with CO₂ and H₂ at different H_{2(aq)}/CO_{2(aq)} ratios when the flow rate is 0.5 ml/min, while the amounts of CH₄ were far below theoretical predictions. The relatively slow overall rate of CH₄ generation was confirmed by adjusting the fluid flow rate, i.e. the residence time of fluid in the system. With the same H_{2(aq)}/CO_{2(aq)} ratio of ~5, dissolved concentration of CH₄ increased from 0.3 to 0.7 μmol/kg when the flow rate decreased from 0.5 to 0.3 ml/min. Further decreasing the flow rate to 0.15 ml/min made the concentration of CH₄ reach 1.6 μmol/kg, which is 5 times more than the concentration at flow rate of 0.5 ml/min. At 300 °C, the same trend was also observed. The concentration of CH₄ increased from 0.2 to 0.3 μmol/kg when the flow rate decreased from 0.5 to 0.15 ml/min with the constant H_{2(aq)}/CO_{2(aq)} ratio of ~9. At the same flow rate, the concentration of

CH₄ at higher temperature, however, is lower even with higher H_{2(aq)}/CO_{2(aq)} ratio.

TOC and carboxylic acids. Analyses showed that TOC increased with H_{2(aq)}/CO_{2(aq)} ratio and residence time. The increase is significant at higher temperature. At 300 °C and flow rate of 0.5 ml/min, TOC increased from 0.44 to 0.62 mmol/kg when the H_{2(aq)}/CO_{2(aq)} ratio increased from 4 to 9 (Figure 1). TOC then increased to 0.74 mmol/kg when flow rate decreased to 0.15 ml/min. At 250 °C, TOC increased from 0.36 to 0.42 mmol/kg with the increase of H_{2(aq)}/CO_{2(aq)} ratio from 2 to 5. It increased to 0.47 mmol/kg when flow rate was 0.15 ml/min.

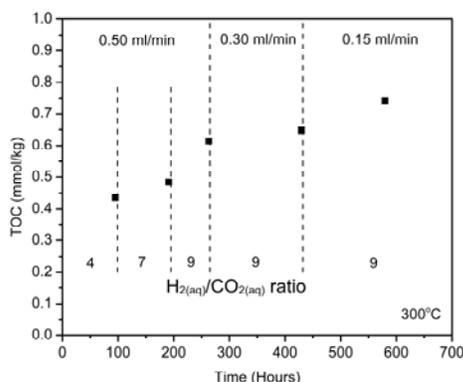


Figure 1. Measured TOC as a function of time in the hydrothermal carbon reduction experiment at 300 °C and 250 bars. Dashed lines indicate changes in redox condition (H_{2(aq)}/CO_{2(aq)} ratio) or fluid flow rate.

C1-C8 carboxylic acids were identified in both experiments. Formic acid (C1) was the dominant species. At 250 °C, the concentration of formic acid increased from 32.5 to 79.3 μmol/kg when the H_{2(aq)}/CO_{2(aq)} ratio increased from 2 to 5. It then increased to 144.5 μmol/kg when the flow rate decreased from 0.5 to 0.15 ml/min. At 300 °C, however, the concentration of formic acid was ~35 μmol/kg throughout the whole experiment. There was no significant change in concentration with adjustments of H_{2(aq)}/CO_{2(aq)} ratio or fluid flow rate. This might be due to two competing reactions: the generation and decomposition of formic acid.

The total concentration of carboxylic acids (C1-C8), however, was less than the measured TOC con-

centration, indicating the existence of other unidentified organic compounds in solution. At 250 °C, the total amount of carboxylic acids only account for ~65% of measured TOC, while ~48% at 300 °C.

Conclusions: Carbon reduction experiments were conducted using a hydrothermal flow-through reactor at 250 and 300 °C. Magnetite was used as the mineral catalyst. The redox state (H_{2(aq)}/CO_{2(aq)} ratio) controls the generation of methane and other organic compounds. The rate of methane generation is slower than that of CO. The relatively low concentration of CH₄ at higher temperature is consistent with thermodynamic prediction of methane generation by direction reduction of CO/CO₂ by H₂. Carboxylic acids (C1-C8) were observed in both experiments. The total amount of carboxylic acids was less than the concentration of TOC, indicating the existence of other unidentified organic species.

The detection of methane in the atmosphere of Mars, combined with the ever increasing evidence for extensive water-rock interaction in Mars' past, makes understanding abiotic synthesis at elevated temperature and pressure conditions a primary goal for Martian science and astrobiology. Abiotic synthesis may also have played a significant role during hydrothermal alteration on meteorite parent bodies. Experimental studies in hydrothermal flow systems provide invaluable evidence for evaluating abiogenic synthesis of organic compounds on Mars and other planetary bodies.

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Acknowledgments: We thank Allan Treiman (LPI) and Paul Niles (NASA JSC) for comments and suggestions.