CARBON ISOTOPE SYSTEMATICS IN MINERAL-CATALYZED HYDROTHERMAL ORGANIC SYNTHESIS PROCESSES AT HIGH TEMPERATURES AND PRESSURES. Qi Fu1, Richard A. Socki2, and Paul B. Niles3, 1Lunar and Planetary Institute, Houston, TX 77058 (fu@lpi.usra.edu), 2ESCG, 3KR, Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058.

Introduction: Observation of methane in the Martian atmosphere has been reported by different detection techniques [1–4]. Reduction of CO2 and/or CO during serpentinization by mineral surface catalyzed Fischer-Tropsch Type (FTT) synthesis may be one possible process responsible for methane generation on Mars [5, 6]. With the evidence a recent study has discovered for serpentinization in deeply buried carbon rich sediments [7], and more showing extensive waterrock interaction in Martian history [8–10], it seems likely that abiotic methane generation via serpentinization reactions may have been common on Mars.

A number of experimental studies have been conducted to validate FTT reactions as mechanisms of hydrocarbon formation in subseaﬂoor hydrothermal systems at mid-ocean ridges [11-13]. The limited range of temperature and pressure conditions at which those experiments were performed, and general lack of knowledge on reaction pathways of hydrothermal FTT synthesis, however, precludes an unambiguous evidence to constrain the origin and evolution of methane on Mars.

It is rapidly becoming evident that carbon isotope measurements of homologs of organic compounds can be used as an effective tool for the recognition of different reaction pathways [14]. For example, the decrease of δ13C values of n-alkanes with carbon numbers (“isotopic reversal”) has been attributed to a kinetic fractionation effect during polymerization reactions that produce alkanes [15-17]. Recent experimental studies, however, have shown that different reaction pathways (e.g., polymerization vs. depolymerization) during abiotic hydrocarbon formation processes may have different carbon isotopic patterns [14], and that pressure could also be a crucial factor affecting fractionation of carbon isotopes [18]. Under high pressure conditions, no experimental data are available describing carbon isotope fractionations during mineral catalyzed FTT synthesis. Thus, hydrothermal experiments present an excellent opportunity to provide the requisite carbon isotope data for examining reaction pathways.

Experiments: A set of hydrothermal experiments involving organic synthesis by FTT were performed using piston cylinder apparatus in the Multi-Anvil and High Pressure Lab at NASA Johnson Space Center. Gold capsules (2 mm O.D. × 10 mm L) were used owing to the deformability and adequately chemical inertness of gold under experimental conditions. Magnetite, the mineral catalyst, was synthesized from inorganic compounds following the method described in Schwertmann and Cornell (1991) [19], and was characterized by XRD. Formic acid (HCOOH) was the source of dissolved H2 and CO2 in the experiment due to its equimolar decarboxylation at high temperatures.

The experiments were conducted at 750 °C and 5.5 Kbars for 4 hours. The Au capsule was recovered after isobaric quench with a quench rate of > 50 °C/s. The volatile products were retrieved by puncturing the capsule in an evacuated container. The chemical and carbon isotope compositions of volatiles, carbon compounds on mineral surfaces and in solution were determined by a Pyrolysis-GC-MS system installed in parallel with a combustion isotope ratio mass spectrometer system in the Light Element Analysis Laboratory at JSC.

Results: To evaluate carbon background on magnetite surfaces and in the whole reaction system, a control experiment was performed at the same T and P conditions with no formic acid present. No carbon-bear compounds were detected, indicating that carbon contamination was below our detection limits.

Chemical compositions. The volatile carbon-bearing compounds in experimental products were dissolved CO2, CH4, and C2H6. Dissolved CO2 was the dominant carbon species with its relative abundance of 88 mol%. The mole abundance ratio of CH4 and C2H6 was 15:1.

Alcohols (ethanol and butanol) and carboxylic acids (formic acid and acetic acid) were the main phases detected on mineral surfaces and in solution. Semi-quantitative analysis showed that the abundance of the organic compound decreases with carbon numbers in each class, i.e., ethanol is more abundant than butanol, and formic acid is more abundant than acetic acid.

Carbon isotopes. The δ13C value of the CO2 derived from decarboxylation of formic acid was -19.2‰, which served as the carbon source in all of the experiments. The alkanes were the most depleted in 13C with CH4 and C2H6 having δ13C values of -50.3‰ and -39.3‰, respectively (Fig. 1). The carboxylic acids were more enriched in 13C and also showed increasing δ13C values with carbon numbers. The formic and acetic acids were -37.4‰ and -25.1‰, respectively. The δ13C value of ethanol at -14.4‰ was higher than the CO2 source, while butanol had a value of -28.3‰ (Fig. 1).
Discussion: The pattern of $\delta^{13}C$ values between CO$_2$ and CH$_4$ is consistent with their equilibrium pattern (CO$_2$ > CH$_4$). The magnitude of this fractionation (31.1‰), however, is much higher than the theoretical isotopic equilibrium prediction of 8.9‰ at 750 °C [20]. This is also true for the $\delta^{13}C$ fractionation between CO$_2$ and acetic acid. The difference of 5.9‰ between CO$_2$ and acetic acid is higher than the value of 4.0‰ expected from theoretical prediction. No calculated theoretical fractionation data are available for formic acid, ethanol, or butanol.

No “isotopic reversal” of $\delta^{13}C$ values was observed for alkanes or carboxylic acids. Indeed, CH$_4$ was 11‰ less enriched in $^{13}C$ than C$_2$H$_6$, and formic acid was 12.3‰ less than acetic acid (Fig. 1). The $\delta^{13}C$ value of ethanol, however, was 13.9‰ higher than butanol which has a higher carbon number.

Yuen et al. (1984) studied carbon isotopes of alkanes and monocarboxylic acids (C1-C5) in the Murchison meteorite [21]. For both classes, the $\delta^{13}C$ value decreased with increasing carbon numbers in a roughly parallel manner with carboxylic acids having higher $\delta^{13}C$ values than alkanes. Our results show a similar but opposite pattern: the $\delta^{13}C$ value increases with carbon numbers for both classes of compounds (Fig. 1). This suggests that the formation process of alkanes and carboxylic acids in the Murchison meteorite may feature some similar reaction steps to those in our experiments.

The hypothesized reaction pathway of generation of organic compounds observed in our experiments includes the following steps: 1) alcohols are formed as organic intermediaries on mineral catalyst surfaces, and alcohol chain growth continues by kinetically controlled polymerization reactions. 2) Partial oxidation of alcohols result in formation of carboxylic acids. 3) Dissolved H$_2$ reacts with acids to generate alkanes. It also serves as the chain terminator to break C-C bonds (i.e., depolymerization), generating carboxylic acids and alkanes with lower carbon numbers.

Conclusions: Experiments involving mineral-catalyzed hydrothermal organic synthesis processes were conducted at 750 °C and 5.5 Kbars. Alkanes, alcohols and carboxylic acids were identified as organic compounds. No “isotopic reversal” of $\delta^{13}C$ values was observed for alkanes or carboxylic acids, suggesting a different reaction pathway than polymerization. Alcohols were proposed as intermediaries formed on mineral surfaces at experimental conditions.

Carbon isotope data were used in this study to unravel the reaction pathways of abiotic formation of organic compounds in hydrothermal systems at high temperatures and pressures. They are instrumental in constraining the origin and evolution history of organic compounds on Mars and other planets.

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