CARBON ISOTOPE SYSTEMATICS IN MINERAL-CATALYZED HYDROTHERMAL ORGANIC SYNTHESIS PROCESSES AT HIGH TEMPERATURES AND PRESSURES. Qi Fu[1], Richard A. Socki[2], and Paul B. Niles[3], [1]Lunar and Planetary Institute, Houston, TX 77058 (fu@lpi.usra.edu), [2]ESCG, [3]KR, 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 CO_2 and/or CO during serpentization 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 water-rock 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 $\delta^{13}C$ 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 H_2 and CO_2 in the experiment due to its equimolar decarboxylation at high temperatures.

The experiments were conducted at 750 ^{o}C and 5.5 Kbars for 4 hours. The Au capsule was recovered after isobaric quench with a quench rate of > 50 $^{o}C/s$. 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-bearing compounds were detected, indicating that carbon contamination was below our detection limits.

Chemical compositions. The volatile carbon-bearing compounds in experimental products were dissolved CO_2, CH_4, and C_2H_6. Dissolved CO_2 was the dominant carbon species with its relative abundance of 88 mol%. The mole abundance ratio of CH_4 and C_2H_6 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 $\delta^{13}C$ value of the CO_2 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 ^{13}C with CH_4 and C_2H_6 having $\delta^{13}C$ values of -50.3‰ and -39.3‰, respectively (Fig. 1). The carboxylic acids were more enriched in ^{13}C and also showed increasing $\delta^{13}C$ values with carbon numbers. The formic and acetic acids were -37.4‰ and -25.1‰, respectively. The $\delta^{13}C$ value of ethanol at -14.4‰ was higher than the CO_2 source, while butanol had a value of -28.3‰ (Fig. 1).
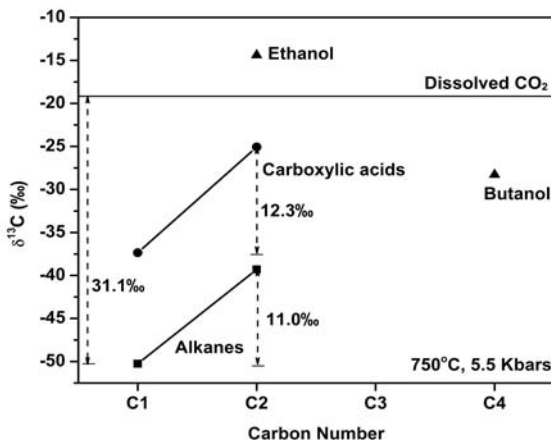
Fig. 1. C isotope compositions of carbon-bearing compounds obtained in mineral-catalyzed hydrothermal organic synthesis experiments at 750 $^{\circ}$C and 5.5 Kbars.

Discussion: The pattern of δ^{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 $^{\circ}$C [20]. This is also true for the ^{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 δ^{13}C values was observed for alkanes or carboxylic acids. Indeed, CH_4 was 11‰ less enriched in ^{13}C than C_2H_6, and formic acid was 12.3‰ less than acetic acid (Fig. 1). The δ^{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 δ^{13}C value decreased with increasing carbon numbers in a roughly parallel manner with carboxylic acids having higher δ^{13}C values than alkanes. Our results show a similar but opposite pattern: the δ^{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 $^{\circ}$C and 5.5 Kbars. Alkanes, alcohols and carboxylic acids were identified as organic compounds. No "isotopic reversal" of δ^{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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