Hydrogen and carbon isotope compositions of hydrocarbons in hydrothermal carbon reduction processes

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To understand the reaction pathways and isotopic fractionation for abiotic organic synthesis under hydrothermal conditions, two experiments involving carbon dioxide reduction at 400°C, 500bar were carried out. Formic acid was used as carbon precursor in the first experiment, with magnetite as a catalyst. The second one was conducted by injecting CO_2 and then H_2 into the reaction cell, and magnetite was purified to remove potential organic contaminations prior to the experiment.

CO and hydrocarbons (C_1-C_4) were observed in both experiments. Only when the H_2/CO_2 ratio passed a critical threshold in the second experiment, did the formation of hydrocarbons from CO_2 reduction proceed. More CO and hydrocarbons were produced by adding more H_2. XPS analysis indicates carbon enrichment and hydrocarbon formation on magnetite surfaces following the reactions.

A pattern of carbon isotope depletion between C_1 - C_n has been debated as a potential indicator of abiogenic hydrocarbon synthesis. Recently it has become feasible to measure δ^2H isotope signatures as well. This presentation will show some of the first results for δ^2H isotope analysis of samples produced during hydrothermal solution experiments. In the first experiment, the hydrocarbon isotopic compositions were clearly impacted by mixing with biogenic hydrocarbons sorbed to the magnetite surface. After removal of this source of contamination in the second experiment, results do not show a pattern of C isotope depletion and H isotope enrichment, but rather a 5‰ enrichment between C_1 (-28.5‰) and higher hydrocarbons (C_2 and C_3) with identical $\delta^{13}C$ values. Results show a pattern of C isotope enrichment and H isotope depletion between C_1 and higher hydrocarbons in our experiments, suggesting that different abiogenic hydrocarbon formation reactions may well have different isotopic patterns associated with them.

Experimental investigation of organic acid carboxyl carbon exchange with aqueous CO_2

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Previous laboratory experiments have demonstrated rapid exchange of carboxyl carbon in organic acids with aqueous carbonate species during hydrous pyrolysis of petroleum source rocks (Dias 2000). To build on these initial findings, we conducted a series of experiments that constrain the roles of minerals, aqueous and vapor phase reactions, and temperature during carboxyl exchange reactions. Experiments were conducted at 250 to 350°C with and without a vapor phase present. All experiments initially contained 20 to 70 mmolal of C_2-C_5 straight chain organic acids and 100 mmolal H_2 and 99.9 % ^{13}C labeled CO_2. No minerals were added to the experiments.

Variations in the isotopic composition of C_2-C_5 organic acids revealed extensive exchange of carboxyl carbon at 250 to 350°C according to the reaction:

$$R^{12}COOH + {}^{13}CO_2 = R^{13}COOH + {}^{12}CO_2 \qquad (1)$$

The rates of reaction (1) increased with increasing temperature and decreased with increasing organic acid chain length. The rate of carboxyl exchange decreased slightly upon creation of a headspace, a likely result of reduced reaction rates for volatile acids that had partioned into the vapor phase. Rates of reaction observed during this study were comparable to rates during the mineral-bearing experiments of Dias (2000), suggesting carboxyl exchange via an aqueous reaction that is not mineral catalyzed.

Extensive reduction of aqueous organic acids to their corresponding n-alkanes resulted in the production of 13C labeled hydrocarbons during the experiments. Formation of these hydrocarbons demonstrates the availability of aqueous reaction pathways that may allow incorporation of carbonate carbon into petroleum hydrocarbons. Examination of carbon isotopic trends for short-chain *n*-alkanes, carboxylic acids, and CO_2 associated with petroleums from a variety of environments suggests similar exchange reactions may be occurring in nature. Accordingly, models that describe the isotopic evolution of short-chain hydorcarbons during the thermal maturation of petroleum may need revision to include the effects of carboxyl exchange reactions.

Reference

Dias R.F. (2000) Unpublished Ph.D. thesis, Penn. State Univ.