

Carbon isotope characterization of organic intermediaries in hydrothermal hydrocarbon synthesis by Pyrolysis-GC-MS-C-IRMS

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We report results of experiments designed to characterize the carbon isotope composition of intermediate organic compounds produced as a result of mineral surface catalyzed reactions. The impetus for this work stems from recently reported detection of methane in the Martian atmosphere coupled with evidence showing extensive water-rock interaction during Martian history. Abiotic formation by Fischer-Tropsch-type (FTT) synthesis during serpentinization reactions may be one possible process responsible for methane generation on Mars, and measurement of carbon and hydrogen isotopes of intermediary organic compounds can help constrain the origin of this methane. Of particular interest within the context of this work is the isotopic composition of organic intermediaries produced on the surfaces of mineral catalysts (i.e. magnetite) during hydrothermal experiments, and the ability to make meaningful and reproducible isotope measurements. Our isotope measurements utilize a unique analytical technique combining Pyrolysis-Gas Chromatograph-Mass Spectrometry-Combustion-Isotope Ratio Mass Spectrometry (Py-GC-MS-C-IRMS). Others have conducted similar pyrolysis-IRMS experiments on low molecular weight organic acids (*Dias, et al, Organic Geochemistry, 33 [2002]*). Our technique differs in that it carries a split of the pyrolyzed GC-separated product to a Thermo DSQ-II® quadrupole mass spectrometer as a means of making qualitative and semi-quantitative compositional measurements of the organic compounds.

A sample of carboxylic acid (mixture of C1 through C6) was pyrolyzed at 100°C and passed through the GC-MS-C-IRMS (combusted at 940°C). In order to test the reliability of our technique we compared the $\delta^{13}\text{C}$ composition of different molecular weight organic acids (from C1 through C6) extracted individually by the traditional sealed-tube cupric oxide combustion (940°C) method with the $\delta^{13}\text{C}$ produced by our pyrolysis technique. Our data indicate that an average 4.3‰ \pm 0.5‰ (V-PDB) apparent isotopic fractionation accompanies the pyrolysis extractions. We postulate that this isotope offset could be the result of incomplete thermal desorption during pyrolysis. We are continuing to investigate the reliability of this pyrolysis technique for correcting carbon isotope measurements of mineral surface catalyzed organic compounds.