

CARBON ISOTOPE MEASUREMENTS OF EXPERIMENTALLY-DERIVED HYDROTHERMAL MINERAL-CATALYZED ORGANIC PRODUCTS BY PYROLYSIS-ISOTOPE RATIO MASS SPECTROMETRY. Richard A. Socki¹, Qi Fu², Paul B. Niles³, and Everett K. Gibson, Jr.³. ¹ESCG, ³KR, Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058, and ²Lunar and Planetary Institute, Houston, TX 77058 (richard.a.socki@nasa.gov),

Introduction: We report results of experiments to measure the C isotope composition of mineral-catalyzed organic compounds derived from high temperature and high pressure synthesis. These experiments make use of an innovative pyrolysis technique designed to extract and measure C isotopes. To date, our experiments have focused on the pyrolysis and C isotope ratio measurements of low-molecular weight intermediary hydrocarbons (organic acids and alcohols) and serve as a “*proof of concept*” for making C and H isotope measurements on more complicated mixtures of solid-phase hydrocarbons and intermediary products produced during high temperature and high pressure synthesis on mineral-catalyzed surfaces. The impetus for this work stems from recently reported observations of methane detected within the Martian atmosphere [1-4], coupled with evidence showing extensive water-rock interaction during Martian history [5-7]. Methane production on Mars could be the result of synthesis by mineral surface-catalyzed reduction of CO₂ and/or CO by Fischer-Tropsch Type (FTT) reactions during serpentinization reactions [8,9]. Others have conducted experimental studies to show that FTT reactions are plausible mechanisms for low-molecular weight hydrocarbon formation in hydrothermal systems at mid-ocean ridges [10-12]. Further, recent experiments by Fu et al. [13] focus on examining detailed C isotope measurements of hydrocarbons produced by surface-catalyzed mineral reactions. Work described in this abstract details the experimental techniques used to measure intermediary organic reaction products (alcohols and organic acids). Our isotope measurements

utilize an analytical technique combining Pyrolysis-Gas Chromatography-Mass Spectrometry-Combustion-Isotope Ratio Mass Spectrometry (Py-GC-MS-C-IRMS) [Fig. 1]. For extraction and analysis of organic intermediaries (alcohols and organic acids), our initial data indicate that a measurable and consistent isotope offset accompanies these measurements.

Experiments: Reagent grade carboxylic acid consisting of C1-C6 acids, and reagent grade alcohols (C1-C4) were analyzed for their C isotope composition individually by the sealed-tube cupric oxide combustion technique [14], and again by Py-GC-MS-C-IRMS. The organic acids were mixed and the alcohols were mixed. Both mixtures were then analyzed separately by Py-GC-MS-C-IRMS (data are shown in the table below). Since our analytical technique allows for a gas chromatograph separation followed by gas effluent split, one split can be sent to the combustion furnace and subsequently analyzed by IRMS, while the other split is routed to the inlet of a DSQ-II quadrupole mass spectrometer, allowing for qualitative and semi-quantitative analyses. Chromatograms for organic acids and alcohols and are shown in figures 2 and 3.

The following experimental conditions were followed during the pyrolysis runs: **Sample:** .5 to 1.0 µl of alcohol/organic acid injected in pre-baked (850°C) quartz tubes; **GC:** 30 m poraplot Q column, 35°C held for 2 min., ramp to 210°C at 50°C/min., injector held at 180°C, He flow rate = 4.0 ml/min.; **Pyroprobe:** 50°C interface temperature, probe heated at 200°C for 30 sec., transfer line held at 150°C; **IRMS:** CF mode, 2 ref. injection at beginning of run, He P = 15psi, oxi-

ORGANIC ACIDS				Individual compound	Individual compound	Mixed compounds	
C# (Formula)	Acid Name	R.T (DSQ)	R.T. (IRMS)	CuO combust $\delta^{13}\text{C}^{\circ}/\text{oo}$	Pyrolysis $\delta^{13}\text{C}^{\circ}/\text{oo}$	Δ (py-combustion) ^{o/oo}	Pyrolysis $\delta^{13}\text{C}^{\circ}/\text{oo}$
C-1 (HCOOH)	methanoic (Formic)	6.15 min.	384 s.	-26.4	-21.6	4.8	-21.6
C-2 (CH ₃ COOH)	ethanoic (Acetic)	6.71 min.	415 s.	-21.2	-17.8	3.4	-17.4
C-3 (CH ₃ CH ₂ COOH)	propanoic (Propionic)	7.45 min.	458 s.	-32.6	-28.4	4.2	-27.9
	"			-32.6	-	4.2	-
C-4 (CH ₃ (CH ₂) ₂ COOH)	butanoic (butyric)	8.58 min.	527 s.	-26.2	-22.4	3.8	-23.9
	"			-26.4	-	4.0	-
C-5 (CH ₃ (CH ₂) ₃ COOH)	pentanoic (valeric)	10.80 min.	661 s.	-29.6	-24.4	5.2	-26.3
C-6 (CH ₃ (CH ₂) ₄ COOH)	hexanoic (caproic)	15.04 min.	919 s.	-35.1	-30.4	4.7	-31.2
	"			-34.9	-	4.5	-
					Avg Δ(py-combustion)	4.3	
ALCOHOLS				Individual compound	Individual compound	Mixed compounds	
C# (Formula)	Alcohol Name	R.T (DSQ)	R.T. (IRMS)	CuO combust $\delta^{13}\text{C}^{\circ}/\text{oo}$	Pyrolysis $\delta^{13}\text{C}^{\circ}/\text{oo}$	Δ (py-combustion) ^{o/oo}	Pyrolysis $\delta^{13}\text{C}^{\circ}/\text{oo}$
C-1 (CH ₃ OH)	methanol	5.41 min.	335 s.	-46.6	-45.2	1.4	-45.6
	"			-47.1	-	1.9	-
C-2 (C ₂ H ₅ OH)	ethanol	6.07 min.	375 s.	-12.7	-11.5	1.2	-11.4
	"			-12.3	-	0.8	-
	"			-12.5	-	1.0	-
C-3i ((CH ₃) ₂ CHOH)	i-propanol	6.54 min.	402 s.	-28.8	-27.2	1.6	-27.8
	"			-28.9	-	1.7	-
C-3n ((CH ₃)(CH ₂) ₂ OH)	n-propanol	6.79 min.	417 s.	-33.1	-32.5	0.6	-32.8
	"			-33.6	-	1.1	-
C-4 2 ((CH ₃) ₂ (CH ₂ CHOH))	sec-butanol	7.31 min.	449 s.	-26.3	-25.0	1.3	-26.1
	"			-26.3	-	1.3	-
C-4n ((CH ₃)(CH ₂) ₃ OH)	n-butanol	7.65 min.	469 s.	-31.2	-30.6	0.6	-32.0
	"			-31.4	-	0.8	-
					Avg Δ(py-combustion)	1.2	

ation $T = 940^{\circ}\text{C}$, reduction temp = 650°C .

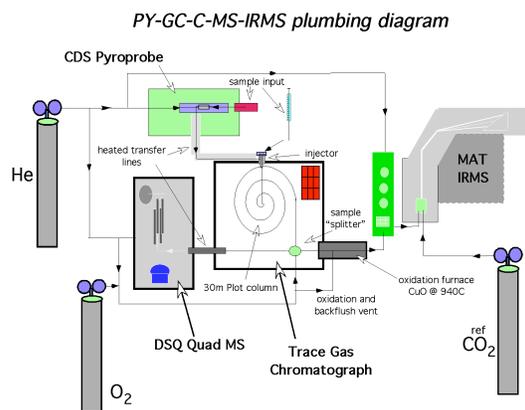


Fig. 1. Experimental apparatus showing the pyrolysis, gas chromatograph, quadrupole mass spectrometer, combustion, isotope ratio mass spectrometer. Samples (*liquid or solid*) are loaded in the pyroprobe and pyrolyzed. After GC separation, a split is sent to both the quadrupole mass spectrometer and the isotope ratio mass spectrometer for analyses, respectively.

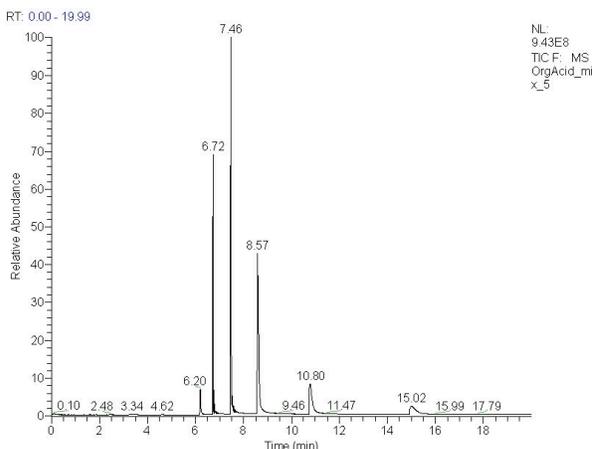


Fig. 2. DSQ-II chromatogram of C1-C6 organic acid mix showing retention times and relative abundances.

Results and Discussion: In order to evaluate the reliability of this technique we compared traditional carbon isotope extractions (sealed-tube combustion) with those extracted using the pyrolysis method described here (Table). Overall, the carbon isotope offset for the organic acids run by pyrolysis were $\sim 4.3\%$ heavier than those run by traditional extractions, with the largest offset occurring within the larger organic molecules (C5 and C6). For the alcohol runs the carbon isotope offset between traditional extractions and pyrolysis was much less ($\sim 1.2\%$). Both the organic acids and alcohols were offset in the same direction (i.e., pyrolyzed extractions were always isotopically heavier than the traditional extractions). We postulate that this isotope offset could be the result of incomplete thermal desorption during pyrolysis. We are con-

tinuing to investigate the reliability of this pyrolysis technique not only for correcting C isotope measurements, but also for measuring H isotopes of mineral surface-catalyzed organic compounds.

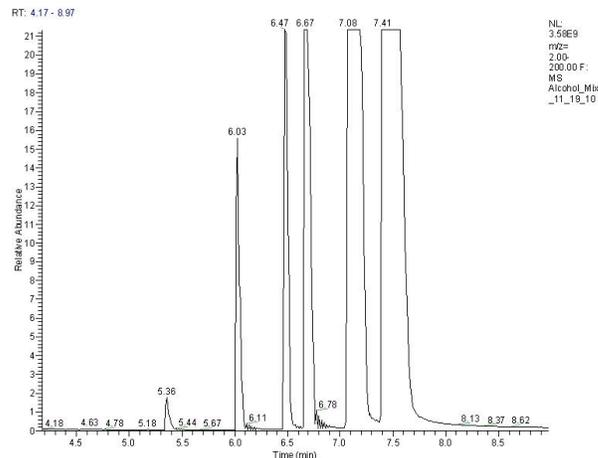


Fig. 3. DSQ-II chromatogram of C1-C4 alcohol mix showing retention times and relative abundances.

Conclusions: Our experiments make use of an innovative pyrolysis technique designed to extract and measure C isotopes from mineral-catalyzed organic compounds derived from high temperature and high pressure synthesis. These experiments serve as a “*proof of concept*” for making carbon isotope measurements on more complicated mixtures of solid-phase hydrocarbons and intermediary products. Initial data indicate that a measurable and consistent isotope offset accompanies these extractions.

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References: [1] Formisano V. et al. (2004) *Science*, 306, 1758–1761. [2] Krasnopolsky V. A. et al. (2004) *Icarus*, 172, 537–547. [3] Geminali A. et al. (2008) *Planetary and Space Science*, 56, 1194–1203. [4] Mumma M. J. et al. (2009) *Science*, 323, 1041–1045. [5] Poulet F. et al. (2005) *Nature*, 438, 623–627. [6] Bibring J. P. et al. (2006) *Science*, 312, 400–404. [7] Mustard J. F. et al. (2008) *Nature*, 454, 305–309. [8] Lyons J. R. et al. (2005) *Geophys. Res. Lett.*, 32, doi:10.10292004GL022161. [9] Oze C. and Sharma M. (2005) *Geophys. Res. Lett.*, 32, L10203. [10] Horita J. and Berndt M. (1999) *Science*, 285, 1055–1057. [11] McCollom T. M. and Seewald J. S. (2001) *Geochimica et Cosmochimica Acta*, 65, 3769–3778. [12] Foustoukos D. I. and Seyfried W. E. Jr. (2004) *Science*, 304, 1002–1005. [13] Fu, Q. et al. (*this LPSC volume*). [14] Schoell M. et al. (1983) *Organ. Geochem.*, 5, 3–6.