HYDROGEN ISOTOPE MEASUREMENTS OF ORGANIC ACIDS AND ALCOHOLS BY PYROLYSIS-GC-MS-TC-IRMS: APPLICATION TO ANALYSIS OF EXPERIMENTALLY DERIVED HYDROTHERMAL MINERAL-CATALYZED ORGANIC PRODUCTS.

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Introduction: We report results of experiments to measure the H isotope composition of organic acids and alcohols. These experiments make use of a pyroprobe interfaced with a GC and high temperature extraction furnace to make quantitative H isotope measurements. This work compliments our previous work that focused on the extraction and analysis of C isotopes from the same compounds [1]. Together with our carbon isotope analyses our experiments serve as a "*proof of concept*" for making C and H isotope measurements on more complex mixtures of organic compounds on mineral surfaces in abiotic hydrocarbon formation processes at elevated temperatures and pressures. Our motivation for undertaking this work stems from observations of methane detected within the Martian atmosphere [2-5], coupled with evidence showing extensive water-rock interaction during Mars history [6-8]. Methane production on Mars could be the result of synthesis by mineral surface-catalyzed reduction of CO_2 and/or CO by Fischer-Tropsch Type (FTT) reactions during serpentization [9,10]. 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 [11-13]. Our H isotope measurements utilize an analytical technique combining Pyrolysis-Gas Chromatograph-Mass Spectrometry-High Temperature Conversion-Isotope Ratio Mass Spectrometry (Py-GC-MS-TC-IRMS). This technique is designed to carry 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 separated organic compounds, therefore both chemical and isotopic measurements can be carried out simultaneously on the

ORGANIC ACIDS ***C# (Formula)***	***Acid Name***	***R.T (DSQ)***	***R.T. (IRMS)***	***Individual compound Pyrolysis*** $\delta D^{o}/_{oo(V\text{-}SMOW)}$	***Average STDEV*** $\delta D^{o}/_{oo(V\text{-}SMOW)}$
C-1 (HCOOH)	methanoic (Formic)	6.20 min.	384 s.	-80.9	**-81.5**
		"	"	-84.2	1.8
		"	"	-80.2	
		"	"	-80.7	
C-2 (CH_3COOH)	ethanoic (Acetic)	6.71 min.	415 s.	-63.1	**-68.0**
		"	"	-68.9	3.4
		"	"	-68.8	
		"	"	-71.0	
C-3 (CH_3CH_2COOH)	propanoic (Propionic)	7.45 min.	458 s.	-82.9	**-84.1**
		"	"	-81.7	3.2
		"	"	-87.8	
C-4 ($CH_3(CH_2)_2COOH$)	butanoic (butyric)	8.58 min.	527 s.	-84.1	**-79.2**
		"	"	-73.7	5.2
	"	"	"	-79.8	
C-5 ($CH_3(CH_2)_3COOH$)	pentanoic (valeric)	10.80 min.	661 s.	-72.7	**-72.7**
					0.0
C-6 ($CH_3(CH_2)_4COOH$)	hexanoic (caproic)	15.04 min.	919 s.	-213.8	**-211.8**
	"			-209.8	2.8
ALCOHOLS ***C# (Formula)***	***Alcohol Name***	***R.T (DSQ)***	***R.T. (IRMS)***	***Individual compound Pyrolysis*** $\delta D\ ^{o}/_{oo}$	***Average STDEV*** $\delta D^{o}/_{oo}$
C-1 (CH_3OH)	methanol	5.36 min.	335 s.	-201.3	**-202.2**
		"	"	-202.7	0.8
		"	"	-202.7	
C-2 (C_2H_5OH)	ethanol	6.03 min.	375 s.	-247.9	**-247.5**
		"	"	-247.1	0.6
C-3i ($(CH_3)_2CHOH)$)	i-propanol	6.47 min	402 s.	-167.0	**-166.7**
		"	"	-167.3	0.8
		"	"	-165.8	
C-3n ($(CH_3)(CH_2)_2OH)$)	n-propanol	6.67 min.	415 s.	-171.0	**-169.2**
		"	"	-170.6	2.1
		"	"	-166.3	
		"	"	-168.8	
C-4 2 ($(CH_3)_2(CH_2CHOH)$)	sec-butanol	7.08 min.	449 s.	-101.4	**-101.0**
		"	"	-100.6	0.6
C-4n ($(CH_3)(CH_2)_3OH)$)	n-butanol	6.41 min.	465 s.	-176.5	**-182.5**
	"	"	"	-183.1	5.7
	"	"	"	-187.9	

TABLE 1. Hydrogen isotope data from organic acids and alcohol standards analyzed by Py-GC-MS-TC-IRMS.

same sample [Fig. 1].

Experiments: Reagent grade carboxylic acid (C1-C6) and reagent grade alcohols (C1-C4) were analyzed for their H isotope composition individually by Py-GC-MS-TC-IRMS. Data are shown in Table 1. Examples of Chromatograms for organic acids and alcohols and are shown in figures 2 and 3.

The following experimental conditions were followed: **Sample size**: 0.5 to 1.0 µl of alcohol/organic acid injected in pre-baked (850°C) quartz tubes; **GC conditions**: 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 to 200°C for 30 s., transfer line held at 150°C; **IRMS:** CF mode, 2 ref. injections, He P = 15psi, conversion T = 1450°C.

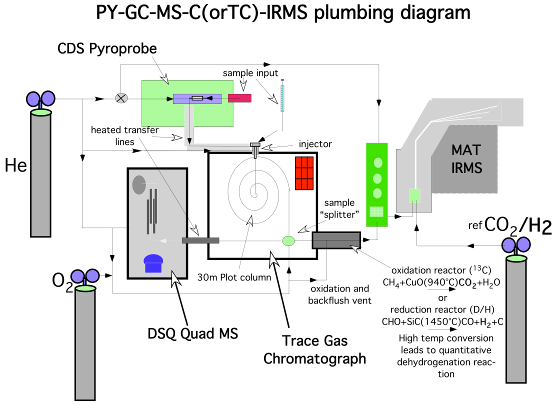

Fig. 1. Experimental apparatus showing the pyrolysis, gas chromatograph, quadrupole mass spectrometer, high temperature conversion, isotope ratio mass spectrometer.

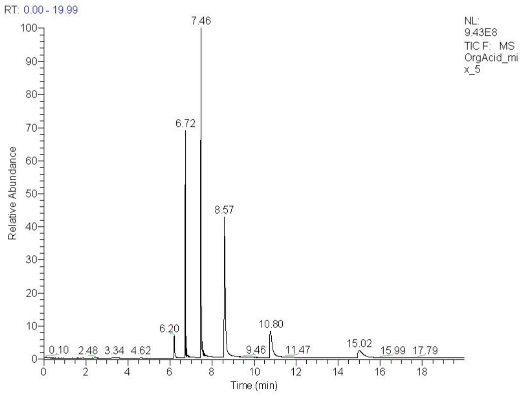

Fig. 2. DSQ-II chromatogram of C1-C6 organic acid mix showing retention times and relative abundances.

Results and Discussion: In order to evaluate the reliability of this technique organic acid and alcohol internal standards were analyzed repeatedly [Table 1]. Average δD values range from -247.5‰ (V-SMOW) for ethanol, to -68‰ (V-SMOW) for ethanoic acid. Reproducibility using this method is typically better than ±5.2‰ for organic acids and ±5.7‰ for alcohols. The largest standard deviation between runs is seen in the C-4 organic acid standard and the C-4 alcohols. We postulate that this high standard deviation could be the result of incomplete thermal desorption during pyrolysis. We continue to investigate the reliability of this technique for making H isotope measurements of mineral surface-catalyzed organic compounds.

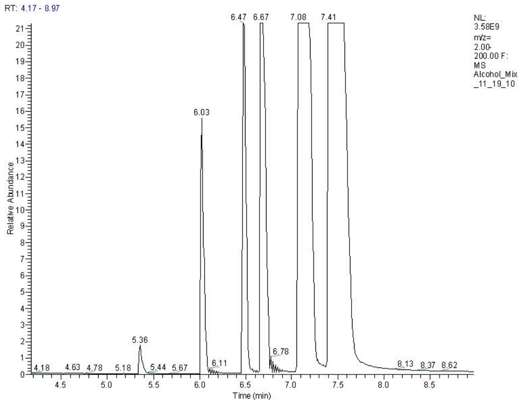

Fig. 3. DSQ-II chromatogram of C1-C4 alcohol mix showing retention times and relative abundances.

Conclusions: Our experiments utilize pyrolysis to extract and measure hydrogen isotopes from organic acids and alcohols. These experiments serve as a "*proof of concept*" for making hydrogen isotope measurements on more complicated mixtures of solid-phase hydrocarbons and intermediary products. Initial data indicate that reproducible hydrogen isotope measurements can be made using this technique.

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