

## Hydrogen isotope measurements of organic acids and alcohols by Pyrolysis-GC-MS-TC-IRMS

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One possible process responsible for methane generation on Mars is abiotic formation by Fischer-Tropsch-type (FTT) synthesis during serpentinization reactions. Measurement of carbon and hydrogen isotopes of intermediary organic compounds can help constrain the origin of this methane by tracing the geochemical pathway during formation. 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 hydrogen isotope measurements. Reported here are results of experiments to characterize the hydrogen isotope composition of low molecular weight organic acids and alcohols. The presence of these organic compounds has been suggested by others as intermediary products made during mineral surface catalyzed reactions. This work compliments our previous study characterizing the carbon isotope composition of similar low molecular weight intermediary organic compounds (Socki, et al, American Geophysical Union Fall meeting, Abstr. #V51B-2189, Dec., 2010). Our hydrogen isotope measurements utilize a unique analytical technique combining Pyrolysis-Gas Chromatograph-Mass Spectrometry-High Temperature Conversion-Isotope Ratio Mass Spectrometry (Py-GC-MS-TC-IRMS). Our technique is unique 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 separated organic compounds, therefore both chemical and isotopic measurements can be carried out simultaneously on the same sample.

Samples of carboxylic acid (C1 through C4) and alcohols (C1 through C4) were pyrolyzed at 200°C on a CDS Analytical, Inc. Model 5200® pyroprobe and passed through a Thermo Electron® GC-MS-TC-IRMS system operating in continuous flow mode. The High Temperature Conversion step (1450°C) converts organic compounds directly to hydrogen gas (Burgoyne and Hayes, Anal. Chem. 70, p. 5136 [1998]). Average  $\delta D$  values range from -247.5‰ (V-SMOW) for ethanol, to -68‰ (V-SMOW) for ethanoic acid. Reproducibility using this method is typically better than  $\pm 3.4\%$  for organic acids and  $\pm 8\%$  for alcohols. We are continuing to investigate the reliability of this pyrolysis technique for making hydrogen isotope measurements of mineral surface catalyzed organic compounds.