Hydrogen (H) Isotope Composition of Type II Kerogen Extracted by Pyrolysis-GC-MS-IRMS: Terrestrial Shale deposits as Martian Analogs

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Described here is a technique for H isotope analysis of organic compounds pyrolyzed from kerogens isolated from gas- and liquids-rich shales. Application of this technique will progress the understanding of the use of H isotopes not only in potential kerogen occurrences on Mars, but also in terrestrial oil and gas resource plays. H isotope extraction and analyses were carried out utilizing a CDS 5000 Pyroprobe connected to a Thermo Trace GC interfaced with a Thermo MAT 253 IRMS. Also, a split of GC-separated products was sent to a DSQ II quadrupole MS to make qualitative and semi-quantitative compositional measurements of these products.

Kerogen samples from five different basins (type II and II-S) were dehydrated (heated to  $80^{\circ}\text{C}$  overnight under vacuum) and analyzed for their H isotope compositions by Pyrolysis-GC-MS-TC-IRMS. This technique takes pyrolysis products separated via GC and reacts them in a high temperature conversion furnace (1450°C), which quantitatively forms H<sub>2</sub>. Samples ranging from  $\sim 0.5$  to 1.0mg in size, were pyrolyzed at  $800^{\circ}\text{C}$  for 30s. and separated on a Poraplot Q GC column.

H isotope data from all kerogen samples typically show enrichment in D from low to high molecular weight.  $H_2O$  average  $\delta D = -215.2\%$  (V-SMOW), ranging from -271.8% for the Marcellus Shale to -51.9% for a Polish shale. Higher molecular weight compounds like toluene ( $C_7H_8$ ) have an average  $\delta D$  of -89.7‰, ranging from -156.0% for the Barnett Shale to -50.0% for the Monterey Shale. We interpret these data as representative of potential H isotope exchange between hydrocarbons and sediment pore water during basin formation. Since hydrocarbon H isotopes readily exchange with water, these data may provide some useful information on gas-water or oil-water interaction in resource plays, and further as a possible indicator of paleoenvironmental conditions. Alternatively, our data may be an indication of H isotope exchange with water and/or acid during the kerogen isolation process. Either of these interpretations will prove useful when deciphering H isotope data derived from kerogen analyses. Understanding the role that these H-bearing compounds play in terrestrial shale paleo-environmental reconstruction may also prove useful as analogs for understanding the interactions of water and potential kerogen/organic compounds on the planet Mars.