

Compound Specific Hydrogen Isotope Composition of Type II and III Kerogen Extracted by Pyrolysis-GC-MS-IRMS

Richard A. Socki, NASA-JSC-ESCG 2224 Bay Area Blvd., Houston, TX 77058, Denet Pernia, BP America, Inc. Houston, TX 77079, Michael Evans, Texas A&M University. Dept of Oceanography, College Station, TX 77834; Qi Fu. NASA-JSC, Code KR, 2101 NASA Rd, Houston, TX 77058, Kadry K. Bissada, University of Houston, Petroleum Systems Research Institute, 312 Science and Research 1, Houston, TX 77204, Joseph A. Curiale, Chevron, 1500 Louisiana St, Houston, TX 77002, and Paul B. Niles, NASA-JSC, Code KR, 2101 NASA Rd, Houston, TX 77058.

The use of Hydrogen (H) isotopes in understanding oil and gas resource plays is in its infancy. Described here is a technique for H isotope analysis of organic compounds pyrolyzed from oil and gas shale-derived kerogen. Application of this technique will progress our understanding. This work complements that of Pernia et al. (2013, *this meeting*) by providing a novel method for the H isotope analysis of specific compounds in the characterization of kerogen extracted by analytically diverse techniques. Hydrogen isotope analyses were carried out entirely "on-line" utilizing a CDS 5000 Pyroprobe connected to a Thermo Trace GC Ultra interfaced with a Thermo MAT 253 IRMS. Also, a split of GC-separated products was sent to a DSQ II quadrupole MS to make semi-quantitative compositional measurements of the extracted compounds.

Kerogen samples from five different basins (type II and III) were dehydrated (heated to 80°C overnight in 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 H₂, following a modified method of Burgoyne and Hayes, (1998, *Anal. Chem.*, 70, 5136-5141). Samples ranging from ~0.5 to 1.0mg in size, were pyrolyzed at 800°C for 30s. Compounds were separated on a Poraplot Q GC column.

Hydrogen isotope data from all kerogen samples typically show enrichment in D from low to high molecular weight compounds. Water (H₂O) average $\delta D = -215.2\text{‰}$ (V-SMOW), ranging from -271.8‰ for the Marcellus Shale to -51.9‰ for the Polish Shale. Higher molecular weight compounds like toluene (C₇H₈) have an average δD 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 formation within each basin. 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 paleo-environmental 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 analysis. More experiments are planned to discern these two or other possible scenarios.