

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

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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.