

Site specific D/H in natural propanes: a new tool for constraining thermal history of petroleum systems

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Hydrogen isotope compositions of n-alkanes, including intermolecular fractionations, site-specific intramolecular fractionations, and ¹³C-D or D-D ‘clumping’, can potentially provide geothermometers that constrain the temperature histories of petroleum systems (i.e., conditions of hydrocarbon formation, migration, and/or storage). We experimentally constrained the rates of hydrogen isotope exchange at low temperatures (down to 100 °C) between propane and water and internally within propane, in the presence and absence of catalysts and for the two non-equivalent sites on propane. Results indicate that over geologic time, hydrogen exchange with water in the presence of clay can control the hydrogen isotope contents of alkanes even at the low temperatures of natural petroleum systems.

Then we analyzed the D/H of the central and terminal positions of natural propanes from a number of oil and gas fields globally. Results reveal two groups of samples that we infer to have experienced different mechanisms of exchange. The first group of samples exhibit center—end hydrogen isotope fractionation with a distinct correlation with the reservoir temperature from which each sample was collected. At the higher temperature ranges (ca. 150°C), the center—end fractionations approach the theoretical equilibrium fractionation. This finding suggest the possibility that thermogenic propanes may be formed out of equilibrium with respect to its site-specific hydrogen isotope structure but then evolve toward equilibrium as the temperature increases. A process that might promote such equilibration is intra- or inter-molecular hydrogen isotope exchange, catalyzed by co-existing materials (e.g., water, clay) as revealed by our experiments. A second group of samples also lie on the predicted equilibrium trend but at lower temperatures (ca. 60 °C). These gas samples were collected from oil fields that are shown to have experienced biodegradation by active microbial communities. Our initial results are encouraging and suggest that further exploration of the position specific D/H in natural gases can provide additional constrains on the history of petroleum systems.