

Experiments constraining blocking temperatures of H isotope exchange in propane and ethane

Camilo Ponton¹, Hao Xie¹, Aditi Chatterjee², Nami Kitchen¹, Max Lloyd¹, Michael Lawson³, Michael J. Formolo³, John M. Eiler¹

¹*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, USA*

²*Department of Geology and Geophysics, Indian Institute of Technology, Kharagpur, India*

³*ExxonMobil Upstream Research Company, Spring TX, USA*

Email: ponton@caltech.edu

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). The ability of such fractionations to record temperature depends critically on the ‘blocking temperatures’ of relevant exchange processes. Prior work on this problem has focused on temperatures far in excess of natural petroleum systems, and/or on mixed materials (oils, kerogens) where it is unclear what species are or are not exchangeable. Here we experimentally constrain the rates of hydrogen isotope exchange at low temperatures (down to 100 °C) between ethane, propane and water, with or without catalysts, including experiments that examine whether rates of exchange differ between non-equivalent sites in propane. A motivation for studying the kinetics of exchange at this level of detail is that we speculate blocking temperatures of different compounds and sites may differ from one another, such that the H isotope distributions between and within the alkanes may record several events or conditions.

We performed experiments heating propane and ethane vapor exposed to deuterated water ($\delta D=1,1419\text{ ‰}$), either alone or in the presence of Ni catalyst or clay, at temperatures between 100 and 400 °C. Ethane is not exchangeable at time scales of weeks in the presence of water alone at temperatures up to 400 °C, nor in the presence of Ni or clay catalysts at 100 or 160 °C, but has an exchange rate of $\sim 10^{-4}\text{ hr}^{-1}$ in the presence of Ni at 200 °C. Similarly, propane is not exchangeable in the presence of water alone at 200 °C or below, nor in the presence of catalysts at 160 °C or below, but exchanges vigorously in the presence of Ni at 200 °C ($\sim 10^{-3}\text{ hr}^{-1}$). Under these conditions hydrogen isotope exchange of the central CH₂ group of propane is significantly faster ($\sim 2x$) than that of the terminal CH₃ group. Propane exchange in the presence of clay at 200 °C is measurable for the CH₂ group ($\sim 10^{-5}\text{ hr}^{-1}$), but not observable for the CH₃ group.

Results from this study indicate that hydrogen exchange with water can control the hydrogen isotope contents of alkanes even at the low temperatures of natural petroleum generating systems. In the presence of Ni catalysts, both ethane and propane are sufficiently exchangeable that geological blocking temperatures should be less than 100 °C; at least the central site of propane is also likely exchangeable at low temperatures over geological time scales in the presence of clay. These findings have important implications for the possible uses of inter- and intramolecular fractionations involving natural hydrocarbons as a large family of geothermometers. But they highlight the essential role of catalysis in controlling the blocking temperatures of these systems. Our ongoing work on this problem focuses on understanding the activity of more naturally relevant catalysts in the T and P range of natural systems.