

Position-specific hydrogen isotope distribution in natural propanes: thermal cracking, equilibration and biodegradation

HAO XIE¹, CAMILO PONTON², MICHAEL J FORMOLO³, MICHAEL LAWSON⁴, ALEX L SESSIONS¹, JOHN M EILER¹

¹Division of Geological and Planetary Sciences, California Institute of Technology, CA, USA (hxie@caltech.edu)

²Geology Department, Western Washington University, WA, USA

³ExxonMobil Upstream Research Co., TX, USA

⁴ExxonMobil Exploration Co., TX, USA

The natural occurrence of propane and other light hydrocarbons is of great economical importance. Novel intramolecular isotope observations, such as clumping and position specific fractionation, provide new proxies for the formation temperature and formation and destruction pathways of these hydrocarbons. In this study, we explore the position-specific hydrogen isotope distribution in propane. We analyzed propane samples from 10 different petroleum systems with high-resolution molecular mass spectrometry.

Our results show that central—terminal hydrogen isotope fractionation of natural propanes ranges from -100‰ to +200‰, much bigger than the range of thermodynamic equilibrium at their source and reservoir temperature (~40‰). Based on these findings, we propose that the hydrogen isotope structure of propane is largely controlled by irreversible process, expressing kinetic isotope effects (KIEs). Disequilibrium of the intra-molecular D/H distribution in immediate products of cracking is supported by a hydrous pyrolysis experiment using the Woodford shale as substrate. This initial cracking KIE signature is simulated in a kinetic Monte-Carlo model for different types of kerogens. In contrast, unconventional shale fluids or hot conventional reservoirs, contain propane with an isotopic structure close to equilibrium, presumably reflecting internal and/or heterogeneous exchange during high temperature storage (ca. 150C). In relatively cold (<100C) conventional gas accumulations, propane can discharge from its source to a colder reservoir, rapid enough to preserve disequilibrium.

Propane is also susceptible to microbial uptake in both oxic and anoxic environments. Biodegradation of propane in Keathley Canyon and Diana Hoover oil fields (Gulf of Mexico) result in strong increases in central-terminal fractionation. This reflects preferential attack on the central position.