

# Intramolecular Isotope Geochemistry of Propane and Butane Isomers from Natural Gases

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Recent advances in analytical techniques of position-specific (PS), intramolecular isotope compositions of light hydrocarbons have opened up a new potential to better decipher the origins and history of natural organic molecules in the subsurface, including fundamental chemical and kinetic processes during the transformation of sedimentary organic matter to petroleum hydrocarbons. However, many PS data sets reported in the literature still lack in accuracy. Here, we summarize and discuss the state-of-the-art data set of PS carbon and hydrogen isotope compositions of propane (C<sub>3</sub>) and butane isomers (normal/iso-C<sub>4</sub>), including natural gases of likely thermogenic origins and from laboratory maturation experiments.

The PS isotope data generated to date clearly show that <sup>13</sup>C and <sup>2</sup>H distribute non-stochastically between the two different C and H sites within C<sub>3</sub> and n/i-C<sub>4</sub> molecules and that the  $\Delta_{C-T}$  (=  $\delta_{\text{center}} - \delta_{\text{terminal}}$ ) values vary widely; -9 to +42 ‰ (<sup>13</sup>C of C<sub>3</sub>), -2 to +15 ‰ (<sup>13</sup>C of n-C<sub>4</sub>), -2 to +21 ‰ (<sup>13</sup>C of i-C<sub>4</sub>), and -200 to +150 ‰ (<sup>2</sup>H of C<sub>3</sub>). It is very likely that <sup>13</sup>C and <sup>2</sup>H do not distribute randomly within parental macromolecules of biogenic origins (kerogens), reflecting their biosynthesis and early diagenesis processes. Complex thermogenic processes for the generation of C<sub>3</sub> and n/i-C<sub>4</sub> gases in natural and laboratory maturation processes also induce PS isotope fractionation from macromolecules. Various post-generation, organic-inorganic reactions in the subsurface, including hydrogen isotope exchange with formation waters and others, could modify the PS isotopes of natural light hydrocarbons. It has also been demonstrated that microbial biodegradation processes can induce very large PS isotope fractionation, resulting in unique PS isotope signatures of biodegraded gases.

To realize the potential of PS isotope geochemistry of light hydrocarbons, we first need to establish certified PS isotope reference materials for traceability to accuracy and interlaboratory comparison. Then, synergistic efforts of natural studies, laboratory experiments, and theoretical/simulation studies of key reactions and processes would significantly improve the utility of PS isotope compositions, including as possible abiotic signatures of various organic molecules in terrestrial and extraterrestrial environments.