

Evolution of natural gas reservoirs using site-specific carbon isotopes

ALISON PIASECKI¹, JOHN EILER² AND MICHAEL LAWSON³

¹piasecki@gps.caltech.edu

²eiler@gps.caltech.edu

³michael.lawson@exxonmobil.com

Stable isotope studies of natural gas generally use bulk isotopic analyses that average over all positions in a molecule, potentially obscuring information that may be recorded by isotopic differences between non-equivalent molecular sites. ‘Site-specific’ carbon isotope variations can arise from biosynthetic processes and potentially be passed on to products of catagenesis, and might be modified or created by kinetic isotope effects associated with thermal degradation of biomolecules.

$\delta^{13}\text{C}$ values of small n-alkanes are often interpreted along the lines of the model of, Chung et. al 1988, which assumes isotopic variations reflect kinetic isotope effects during C-C bond cleavage, and reservoir effects (i.e., product alkanes must approach the composition of the reactant kerogens as reaction progress increases). This model can be used to make predictions about site-specific C isotope variations; for propane, we predict that increasing thermal maturation will be associated with increasing $\delta^{13}\text{C}$ of the terminal carbon positions, whereas the center C position will remain unchanged across a range of thermal maturities.

We test this prediction using mass spectrometric analysis of fragments of propane that differentially sample the terminal vs. central carbon positions, examining propanes produced by thermal ‘cracking’ of Woodford shale or recovered from samples of two natural gas suites that sample a range in gas maturity.

Our findings differ significantly from our predictions, principally because the central position C in propane varies markedly in $\delta^{13}\text{C}$ with increasing maturity, both in experiments and natural samples. In experiments, we find the central position initially increases in $\delta^{13}\text{C}$ faster than the terminal position, followed by more rapid change in the terminal position at higher maturities. In conventional and shale gases, we observe approximately equal increases in $\delta^{13}\text{C}$ of terminal and central C positions with increasing maturity (with more complex second order variations).

We suggest three factors contribute to our findings: changing relative contributions from substrates that differ in carbon isotope structure (i.e., primary vs. secondary cracking, and perhaps more subtle, previously unrecognized changes in proportions of reactants); ‘cleavage’ kinetic isotope effects and reservoir effects, as predicted by the Chung model; perhaps also complemented by secondary isotope effects during cleavage reactions.