

Doubly ^{13}C -substituted ethane in shale gases

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Ethane (C_2H_6) is present in most natural gas reservoirs, and is critically important as a source of ethylene for petrochemical industries. It is also the simplest molecule abundant in nature which can manifest multiple ^{13}C substitutions. We focus here on natural gases, where the abundance of $^{13}\text{C}_2\text{H}_6$ can be modified by multiple processes: inheritance from larger biomolecules that produce oil and natural gas during thermal cracking; kinetic fractionation during thermal cracking; homogeneous isotope exchange reactions at thermodynamic equilibrium; mixing of gases with different bulk isotopic composition; secondary gas cracking or biodegradation; or a combination of these. There is little basis for *a priori* predictions on which of these factors will dominate in natural ethane.

Ethane samples from shale gas reservoirs were analyzed for their bulk isotopic composition (δD and $\delta^{13}\text{C}$) as well as for the abundance of $^{13}\text{C}_2\text{H}_6$. To resolve isobaric interferences, we use a prototype gas source isotope ratio mass spectrometer, the Thermo 253-Ultra, capable of achieving a mass resolution ($M/\Delta M$) of up to 27000. This high mass resolution is key to separating or peak-stripping contaminants, such as O_2 or CH_3OH at $m/z=32$, but also to discriminating between $^{13}\text{C}^{12}\text{CH}_6$ and $^{12}\text{C}_2\text{DH}_5$ at $m/z=31$ and $^{13}\text{C}_2\text{H}_6$ from $^{13}\text{C}^{12}\text{CDH}_5$ at $m/z=32$. Based on these mass spectrometric data, we calculate the excess of $^{13}\text{C}_2\text{H}_6$ compared to a stochastic distribution ($\Delta^{13}\text{C}_2\text{H}_6$, defined as $1000 * ((^{13}\text{C}_2\text{H}_6/\text{C}_2\text{H}_6) / (^{13}\text{C}_2\text{H}_6/\text{C}_2\text{H}_6)_{\text{stochastic}}) - 1$), with an external reproducibility of better than 0.25 per mil.

We will present measurements of natural samples from shale gas reservoirs that display a range in $\Delta^{13}\text{C}_2\text{H}_6$ of 4 per mil. Thermodynamic equilibrium gives rise to clumped isotope fractionations of less than 1 per mil for geologically reasonable temperatures, and hence cannot be the dominant process controlling the abundance of $^{13}\text{C}_2\text{H}_6$. Two scenarios could be invoked to potentially explain the non-equilibrium isotope fractionation observed: (i) a combination of kinetic effects and inheritance from larger biomolecules, or (ii) secondary cracking and/or biodegradation of ethane. Using relationships between $\Delta^{13}\text{C}_2\text{H}_6$ with percent methane