Analysis of 13C-13C isotopologue of ethane and ethanol by a fluorination method

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Doubly-substituted isotope species (“clumped isotopes”) of a molecule potentially records important biogeochemical information such as its temperature of formation and/or its (bio)synthetic pathway. The abundance of clumped isotopologue can be viewed as a deviation from its stochastic abundance, conventionally denoted as a D value (i.e., $D = (R_{sample}/R_{stochastic} - 1)$). Notably, when an isotope exchange reaction occurs at equilibrium, the abundance of clumped isotopologue reflects its temperature and thus is used as a geothermometer. Recentlly, ^{18}O-^{18}O species in oxygen and ^{15}N-^{15}N in nitrogen have been measured and their abundance helped distinguishing between atmospheric, volcanic and biological sources [1,2]. Recently, Clog et al [3] measured ^{13}C-^{13}C species of ethane from natural gas, highlighting the potential of the approach to study thec biogeochemistry of organic molecules.

Yet, measuring ^{13}C-^{13}C species at natural abundance is not trivial. The common method used to measure the bulk ^{13}C isotopic composition of ethane consists in its combustion to CO_2, which leads to the loss of ethane molecules, and thus of its ^{13}C-^{13}C isotopologue. Clog et al (2018) measured the abundance of clumped isotopologue in ethane in natural gasusing high-resolution gas source mass spectrometer (MAT253 Ultra) which allows the sepoaration and quantification of ^{13}C-^{13}C isotopologues of ethane.

Here, we propose a new alternative method for measuring ^{13}C-^{13}C isotopologue of C2 molecules - not only to ethane but also potentially applicable to various organic compounds - using a conventional isotope ratio mass spactrometer. Because fluorine has only one stable isotope, ^{13}C-^{13}C isotope species in C_2 molecules were measured as C_2F_6 arising from the fluorination of C_2 molecules. This method is applicable to ethane from natural gas samples but also to ethanol from the fermentation of sugars. Ethanol is first converted into ethene through dehydration reaction then fluoridated to C_2F_6.

The fluorination reaction is first conducted at 77K for 10min and then at 173K for 30min using ice ethanol slush adding liquid nitrogen into ethanol. During the fluorination, the mild condition at low temperature is critical to avoid to break the C-C bonding. On the other hand, further fluorination of the intermediate requires higher temperature up to 298K. Therefore, the sample was thawed back to room tempareture for a quantitative conversion.

The yield of fluorination cannnot be strictly contorolled and varies within 5% around the average value. In order to estimate the effect of the conversion efficiency on the $D^{13}C^{13}C$ values, fluorination reactions were conducted at lower yields by changing the amount of fluorine against the starting ethene/ethane. Whereas the $D^{13}C^{13}C$ values of ethane are affected at low yields, the $D^{13}C^{13}C$ valies are constant at the yield above 50%. On the other hand, the $D^{13}C^{13}C$ values of ethene are constant for all yields. Therefore, we can obtain the reproducible $D^{13}C^{13}C$ values at a yield commonly reached 60% or 80% for ethene and ethane, respectively.

Reproducibility of the whole prorocol, including chemical modification steps and measurement of C_2F_6 isotopologues is 0.14‰ for all the compounds. We applied this method to sevral C_2 molecules: ethane from natural gas (thermogenic and abiotic), biologically derived ethanol, as well as abiotic ethane produced experimentally by diverse processes (UV irradiation, spark discharge, Fischer-Tropsch synthesis and Gamma ray irradiation).

Ethane from thermogenic natural gas samples and biologically derived ethanol show a narrow range of D^{13}C^{13}C values varying from 0.72‰ to 0.90‰. In contrast, abiotic ethane, either from natural samples or from experiments shows D^{13}C^{13}C values systematically lower than those of biotic origin. C-C clumping provides new potential (a)biomarkers to the biogeochemistry field.

Reference

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Keywords: Clumped isotope, Fluorination, Isotopologue

