論文 / 著書情報
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Clumped isotope geochemistry is a new field of study using multiple isotopic substitutions within a molecule and potentially provides information for origins of organic molecules on Earth and beyond. However, due to technical difficulty, its measurement in organic molecules is still limited to a few simple molecules.

Here, we have developed a new fluorination method for measuring ^{13}C-^{13}C clumped isotopologue abundances ($\Delta^{13}C^{13}C$) in ethane, ethene, and ethanol (Chapter 2). Reproducibility of the whole protocol, including chemical modification steps and measurement of isotopologues, is better than ±0.09‰. We reported the ^{13}C-^{13}C clumped isotopologues of ethanol produced by the fermentation of glucose from C3, C4, and CAM plants. All these bio-ethanol show a very narrow range of $\Delta^{13}C^{13}C$ values irrespective to their $\delta^{13}C$ variation, suggesting that the glucose tends to "scramble" C-atoms through the Calvin-Benson-Bassham (CBB) cycle, eventually leading to a constant ^{13}C-^{13}C distribution in sugars.

The developed method was standardized and calibrated against a stochastic reference scale using isotopically enriched ^{13}C-^{13}C-labeled ethanol (Chapter 3). We found that the chemical reaction steps in the fluorination method could change the ^{13}C distribution in ethene, leading to a scale compression for observed Δ values. Thus, we provided the empirical transfer function to standardize the $\Delta^{13}C^{13}C$ values. After standardization of the fluorination method, we constructed a stochastic reference frame assuming that the clumped isotopologues distribution in biogenic glucose assuming isotopic equilibrium (+0.2‰ against stochastic distribution) at 25°C through carbon scrambling during the CBB cycle. The equilibrium $\Delta^{13}C^{13}C$ value in glucose was calculated using density functional theory. Consequently, the reference scale for $\Delta^{13}C^{13}C$ analysis was established.

To understand actual varioation of ^{13}C-^{13}C clumping in nature, we have measured various ethane (C_2H_6) samples (Chapter 4). Most natural ethane gas from various geological settings show similar $\Delta^{13}C^{13}C$ values compared to the bio-ethanol. On the other hand, abiotically-synthesized ethane from CH_4 in laboratory shows distinctively low ^{13}C-^{13}C abundances compared to the stochastic distribution (anti-clumping) as well as the thermogenic ethane. We modeled the abiotic ethane formation reaction using a collision frequency of isotopologues and found that the collisional frequency model predicts the anti-clumping in abiotic ethane. Remarkably, the model prediction matches with a few putative abiotic ethane from natural geological settings, such as Kidd Creek Mine. Therefore, $\Delta^{13}C^{13}C$ analysis can provide additional evidence for abiological origin of some natural gas on Earth.

To understand the change in $\Delta^{13}C^{13}C$ during thermal clacking, we conducted hydrothermal experiments for about two years using lignin and docosane ($C_{22}H_{46}$) as starting materials (Chapter 5). The results demonstrated that thermogenic ethane has a relatively high ^{13}C-^{13}C abundance compared to stochastic distribution, which matches thermogenic ethane from various geological settings. Also, we modeled the ethane formation from the thermal cracking of precursor organics and demonstrated that ^{13}C distribution in thermogenic ethane is inherited from the C-C bonding in the precursor molecule (i.e., bio-glucose). In addition, if thermal maturity increases further, the ^{13}C-^{13}C distribution in ethane may shift toword equilibrium at the temperature of formation.

To understand the tolerance of the ^{13}C-^{13}C clumped isotope signature against ethane decomposition, we conducted theoretical calculations for the ^{13}C-^{13}C clumped isotopic fractionation through an ethane dissociation ($C_2H_6 \rightarrow CH_3 + CH_3$) reaction using quantum chemical calculations and transition state theory (Chapter 6). We found that the ^{13}C-^{13}C clumped isotopic fractionation during ethane dissociation reactions does not show significant variation at plausible geological temperatures in the subsurface on Earth, even though isotope fractionation occurs in the thermal cracking. The observed $\Delta^{13}C^{13}C$ variations in natural gas ethane may reflect mixing between reservoirs of different maturity levels.

Finally, the established systematics of clumped ethane isotopologues was applied for distinguishing the origins of hydrocarbons from serpentinite mud volcanos at the Mariana forearc region (Chapter 7). The Mariana hydrocarbons are potentially abiotic in orign, though thermogenic origin has not been discarded because subducting slabs contain organic-rich sediment (i.e., potential source of thermogenic ethane). Using the ^{13}C-^{13}C clumped isotope signatures, we demonstrated that hydrocarbons are mainly of thermogenic origin. In summary, the approach distinguishes biogenic, abiotic, and thermogenic organic compounds and can provide an important step forward for discrimination of the origin of organic molecules on Earth and in extra-terrestrial environments.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。
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