

## 科学研究費助成事業 研究成果報告書

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研究課題名(和文) 分子内同位体による新しい天然ガス起源推定法の開発

研究課題名(英文) Development of intramolecular isotope analysis for understanding the origin of natural gas hydrocarbons

研究代表者

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研究成果の概要(和文)：天然ガスの起源を理解する方法を開発しました。天然ガスは様々なプロセスから作られ、これらのプロセスを理解することは、化石エネルギー、生命の起源および他の惑星系の居住性を含むいくつかの意味を有する。この方法は、天然ガスからの炭化水素中の炭素の安定同位体比( $^{13}\text{C} / ^{12}\text{C}$ )の分析に基づいている。安定同位体は、所与の分子の起源および履歴を推測するために使用される。私たちが開発した方法はユニークで、天然ガスの起源に関する新しいタイプの情報をもたらします。特に、我々は生物学的生物から形成された炭化水素を化学的または無機的手段によって形成された炭化水素と区別することができた。

研究成果の概要(英文)：We developed a method to understand the origin of natural gas. Natural gas is made from various processes and understanding these processes has several implications, including fossil energy, origin of life and habitability of other planetary systems. The method is based on the analysis of stable isotope ratio of carbon ( $^{13}\text{C}/^{12}\text{C}$ ) in hydrocarbons from natural gas. Stable isotopes are used to infer the origin and history of a given molecule. The method we developed is unique and brings new type of information regarding the origin of natural gas. In particular, we were able to distinguish hydrocarbons that formed from biological organisms to those formed by chemical or inorganic means. In addition, we could understand the mechanism of formation of hydrocarbons in a Japanese hot spring (Hakuba-Happo, Japan). Overall, our work has implications to understand the origin of natural gas and will be used in the near future in other geological settings.

研究分野：Geochemistry

キーワード：Natural gas Stable isotopes hydrocarbons Analytical development

## 1. 研究開始当初の背景

**Development of a method for the determination of position-specific isotope composition of propane.** C<sub>2+</sub> hydrocarbons such as propane are made of isotopomers, namely molecules with a heavy atom in different positions.

The relative proportion of each isotopomer (called site-preference and expressed in ‰) is not stochastic and is governed by the processes they experienced. Theoretical approaches and mechanistic models suggest that significant differences of site-preference for thermogenic and abiogenic hydrocarbons should be expected, making site-preference a new potential indicator of abiogenic synthesis of hydrocarbons. Yet, this information was not accessible until recently due to technological difficulties.

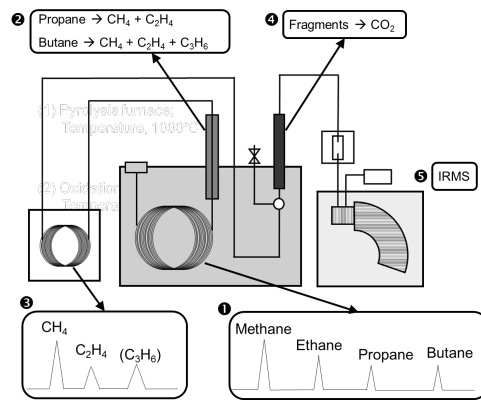
## 2. 研究の目的

During this project, we wanted to implement a device to measure the site-preference of propane and butane. The system is based on the breakdown of propane and subsequent analysis of the products formed (mainly methane and ethylene) from which the original site-preference of propane can be calculated. The relative ratio of propane central and terminal isotopomers (“site preference”, SP) has to be determined with a precision lower than 0.001 (1‰), and with a minimum required amount of 10 nmol (Article 2)).

## 3. 研究の方法

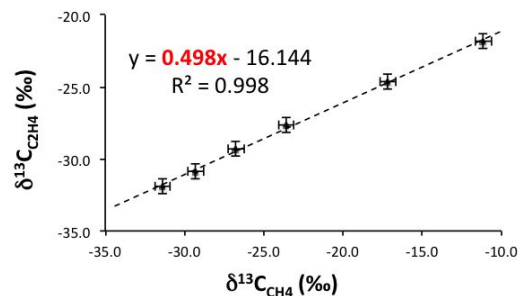
The experimental device that has been developed for our purpose consists in (Fig. 1):

1. A first gas chromatographic column to separate each individual hydrocarbon from natural gas
2. A pyrolysis furnace with variable temperature unit
3. A second gas-chromatographic column to separate pyrolytic fragments
4. A combustion furnace allowing the conversion of pyrolytic fragments into CO<sub>2</sub> for their isotopic analysis
5. An isotope ratio mass spectrometer to determine the isotopic composition  $\delta^{13}\text{C}$  of each pyrolytic fragment after their combustion to CO<sub>2</sub>.



**Figure 1.** Schematic view of the device used in our study (see text for detailed explanation).

**Accuracy of the method.** In order to ensure that there is no C-exchange during pyrolysis, we used 1-<sup>13</sup>C-propane to spike a natural abundance propane sample. We spiked our propane standard with different amounts of 1-<sup>13</sup>C-propane and check the isotopic composition of the pyrolytic fragments at different temperatures of pyrolysis (800°C to 950°C). The results show that: (i) methane arises only from the terminal C-atom position of propane and (ii) ethylene arise from an equal amount of the terminal and central C-atom positions of propane. This holds true for temperatures below or equal to 850°C. At temperatures above 900°C, C-scrambling starts to occur (see figure 2).

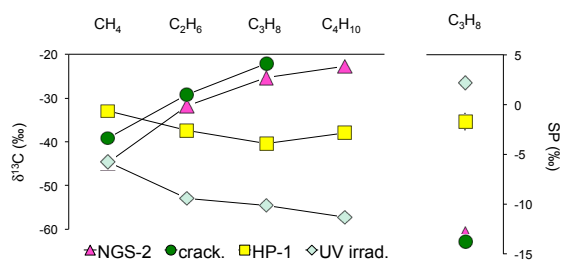


**Figure 2.** Graph showing the relationship between the <sup>13</sup>C values of fragments arising from the pyrolysis of propane at 850 °C (ethylene and methane). The slope of the curve indicates the filiation between the original C-atom positions in propane and the fragments. In an ideal case, the slope should be 0.5, which is the case here within the error (Article 2)).

## 4. 研究成果

**Abiotic production of organic matter revealed by new isotopic tracer.** Present-day geological settings such as hydrothermal systems can be used to study the formation of complex molecules from simple ones and thus to evaluate

the formation and supply of prebiotic molecules on the early Earth. Since most of these systems are now surrounded by biological organisms, one of the major difficulties relies on distinguishing molecules formed without the help of biology (“abiotic” molecules) from those derived from biology. Chemical and isotopic composition of hydrothermal fluids have shown that hydrocarbons - methane in particular - can be produced through abiotic synthesis (e.g.



Fischer-Tropsch-type reaction that implies  $\text{CO}_2$  reduction and subsequent  $\text{CH}_4$  polymerization). However, a clear distinction is often made difficult by mixing of different sources, secondary alteration (e.g. bacterial oxidation), and overlap of isotopic and chemical signatures from different sources. New lines of evidence would thus be helpful in order to clearly constrain abiotic production of organic molecules and the associated mechanisms.

**Figure 3.** Bulk  $^{13}\text{C}$  isotope composition of hydrocarbons as function of the carbon-chain length (left panel); Site-preference measured for propane (right panel). “NGS-2”: Thermogenic natural gas from field sampling (Apulian Basin, Italy); “crack.”: Thermogenic natural gas created artificially by thermal cracking of long-chain hydrocarbon n-C25; “HP-1”: Natural gas from serpentinite-hosted hydrothermal system, where abiotic production of hydrocarbons is suggested; “UV irradiation”: natural gas obtained from  $\text{CH}_4$  polymerization (simulation of abiotic formation).

As a proof-of-concept study, we conducted laboratory simulations as well as field sampling (including natural gas from serpentinite-hosted hydrothermal system Hakuba-Happo, Japan) and analyzed the formed hydrocarbons. Results show that significantly different SP values are obtained for abiotically synthesized propane compared with biologically-derived propane (Figure 1). For propane arising from thermal cracking of organic matter,  $^{13}\text{C}$  is preferentially located on the central position (SP < -10‰), whereas samples arising from  $\text{CH}_4$  polymerization show no site-preference

(SP  $\approx$  0‰) (Figure 3). In particular the results for Hakuba-Happo suggest that hydrocarbons are formed abiotically through rock-water reactions (Article 5)). In addition, it is likely that these hydrocarbons are used by microorganisms as the sole C-source, suggesting that **abiotic formation of organic molecules is a key process for the origins of life and also for life sustainability and planet habitability.**

## 5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文](計5件)

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- 2) A. Gilbert, K. Suda, K. Yamada, Y. Ueno, N. Yoshida. **Measurement of position-specific  $^{13}\text{C}$  isotopic composition of propane at the nanomole level** (*Geochim. Cosmochim. Acta*, **2016**, *177*, 205) DOI: 10.1016/j.gca.2016.01.017 (peer-reviewed)
- 3) A. Gilbert, K. Yamada, N. Yoshida. **Evaluation of an on-line pyrolysis system for the determination of site-specific isotope composition of short chain n-alkanes ( $\text{C}_6\text{-C}_{12}$ )** (*Talanta*, **2016**, *153*, 158) DOI: 10.1016/j.talanta.2016.03.014 (peer-reviewed)
- 4) K. Chandru, A. Gilbert, C. Butch, H. J. Cleaves. **The Abiotic Chemistry of Thiolated Acetate Derivatives and the Origin of Life** (*Sci. Rep.*, **2016**, *6*) DOI: 10.1038/srep29883 (peer-reviewed)
- 5) K. Suda, A. Gilbert, K. Yamada, N. Yoshida, Y. Ueno. **Compound- and position-specific carbon isotopic signatures of abiogenic hydrocarbons from on-land serpentinite-hosted Hakuba Happo hot spring in Japan** (*Geochim. Cosmochim. Acta*, **2017**, *206*, 201-215) DOI: 10.1016/j.gca.2017.03.008 (peer-reviewed)

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- 1) Alexis Gilbert, Gerald Remaud, Keita Yamada, Yuichiro Ueno, Richard Robins, Naohiro Yoshida “Recent insights into intramolecular  $^{13}\text{C}$  isotope composition of biomolecules” (AGU Fall meeting 2016; San Francisco, USA; 12-16 Dec

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2) Alexis Gilbert “Stable Isotopes in Biogeosciences” (ISI 2016; Nantes, France; 03-06 Oct 2016)

3) Alexis Gilbert, Keita Yamada, Yuichiro Ueno, Naohiro Yoshida “Position-specific isotope analysis by on-line pyrolysis coupled to IRMS” (AGU Fall meeting 2016; San Francisco, USA; 12-16 Dec 2016)

4) Alexis Gilbert, Keita Yamada, Yuichiro Ueno, Naohiro Yoshida “On-line pyrolysis combined with IRMS for <sup>13</sup>C intramolecular isotope determination” (ELSI/EON Pre-Goldschmidt Workshop; Tokyo, Japan; 25<sup>th</sup> June 2016)

〔図書〕(計 件)

〔産業財産権〕

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〔その他〕

ホームページ等

## 6. 研究組織

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なし

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