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研究課題名（和文）プロパンの重水素置換種分析に基づく天然ガス生成温度の推定

研究課題名（英文）Estimation of natural gas production temperature based on deuterium isotopologues propane

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研究成果の概要（和文）：天然プロパンの内部2H分布を測定するシステムを実装しました。このシステムでは、従来の方法と比較して、0.5%の精度で天然プロパンの内部2H分布を測定できます。メソッドの精度を推定するために、特定の位置でわずかに2 Hに富んだプロパンを使用しました。
テストでは、システムで使用されている高温変換ではH原子が完全にスクランブルされないこと、およびプロパンの元の「h内部分布は熱分解フラグメントのそれから計算できることが明らかになりました。天然ガスサンプルからのプロパンの分析は、起源に応じて異なるシグネチャが得られることを示しています。これは、天然ガス内の炭化水素のソースとシンクの追跡に有望です。

研究成果の学術的意義や社会的意義
開発されたアプローチは最先端であり、炭化水素の2H内部分布を測定できる研究室は世界中にほとんどありません。 それは、有機分子の起源を明らかにすることを目的とする私たちのグループの進歩、したがって重要な地球と生命の相互作用を追っています。
概して、エネルギー探査、気候変動、地下の隠された生物圏など、さまざまな分野にわたる質問に光を当てます。
長期的には、この手法は堆積物の炭化水素に使用され、過去の年代の気温を推定することができます。

研究成果の概要（英文）：We implemented a system for the measurement of internal 2H-distribution in natural propane. The system is based on that used for 13C measurement. The system allows measurement of internal 2H distribution of natural propane with a precision of 0.5%, comparable with conventional methods.
We used slightly 2H-enriched propane at specific position to estimate the accuracy of the method. The tests revealed that the high-temperature conversion used in our system do not scramble completely H-atoms and that the original "h internal distribution of propane can be calculated from that of the pyrolytic fragments. Analysis of propane from natural gas samples shows that depending on the origin a different signature is obtained, which is promising for tracing sources and sinks of hydrocarbons in natural gas.

研究分野：Biogeochemistry

キーワード：Natural gas　Propane　isotope　Biogeochemistry

１．研究開始当初の背景

Stable isotopes are used in a wide range of scientific disciplines such as geochemistry, biochemistry or forensics. Conventionally, ^{2}H and ^{13}C are measured at the molecular scale after the transformation of the molecule to simple gases such as CO_2 or H_2. Recent theoretical calculations show that non-conventional isotope measurements such as "clumped" isotopes of methane ($^{13}CH_3D$ vs $^{12}CH_4$) or position-specific isotope analysis (PSIA) of propane (CH_2D-CH_2-CH_3 vs CH_3-CHD-CH_3) can be used to assess the temperature of formation of natural gas. The former has been technically achieved through high-resolution mass spectrometry on methane (Stolper et al., 2014). Yet, clumped isotopes of methane can be altered when biological processes such as biodegradation are involved (Wang et al., 2015).

In this project, we explore the potential of ^{2}H PSIA of propane as a new temperature indicator. ^{2}H PSIA of organic molecules requires isolating and quantifying each isotopomer species of the given molecule (CH_2D-CH_2-CH_3 vs CH_3-CHD-CH_3 for propane) which is technically challenging. This type of analysis was until now conducted using Nuclear Magnetic Resonance, which is not adapted to gaseous molecules and requires a substantial amount of compound (> 10 millimoles), making it very limited for geochemical applications. Here, we use the method we developed for ^{13}C PSIA of propane (Gilbert et al., GCA, 2016) and adapt it to ^{2}H measurements. The approach has the advantage to be sensitive, namely nanomoles of propane can be analyzed.

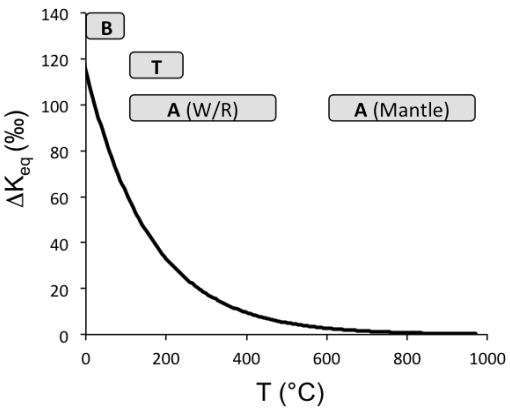

Figure 1. Deviation (ΔK_{eq}) from the random distribution of the deuterium abundance at the central position of propane as a function of the equilibrium temperature. The formation temperature can be estimated by determining the equilibrium constant ΔK_{eq} by hydrogen PSIA. Temperature ranges for different propane formation mechanisms are shown: B=biological origin, T=pyrolysis origin, A(W/R)=mineral origin from hydrolith reaction, A(Mantle)=mineral origin from mantle. (Drawing based on data from Piasecki et al., (2016)).

２．研究の目的

Here, we aim at developing a temperature indicator based on ^{2}H-internal distribution in propane. Theoretical calculations have shown that the position-specific D/H ratios (terminal vs central positions) depends on the temperature at which propane is formed. Therefore if ^{2}H-internal distribution can be measured in propane, the temperature of formation can be estimated. However, measuring internal 2H distribution at natural abundance is not trivial and requires specific instruments or methods. The goal of the project is to **develop a method to measure ^{2}H internal distribution in propane**.

３．研究の方法

We use a system that was already developed for ^{13}C internal distribution of propane (Gilbert et al., 2016). The system uses a pyrolysis furnace to convert propane into smaller fragments from which internal isotope distribution can be calculated. In order to have access to D/H isotope composition of each position of propane, we thermally degrade it into fragments through a pyrolysis furnace. Through thermal degradation, propane forms methane, ethylene, propylene and hydrogen gas H_2 (Fig 2). Methane and ethylene form from the C-C bond breaking while propylene and H_2 form through direct dehydration of propane:

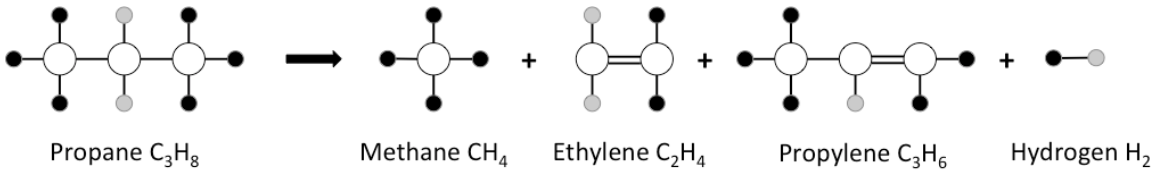

Figure 2. Schematic view of propane thermal degradation. Large circles represent C-atom and small circles H-atoms. Central and Terminal H-atoms are represented by grey and black circles respectively.

Each fragment is then separately analyzed for its D/H isotope composition through an isotope ratio mass spectrometer. The apparatus we will use is similar to that used by our group for ^{13}C analyses (Gilbert et al., 2016). If thermal degradation occurs through single bond breaking and if no rearrangement occurs, we have the following equations (Fig. 2):

$$D/H_{CH4} = D/H_{terminal}$$

$$D/H_{C2H4} = (D/H_{terminal} + D/H_{central})/2$$

and we can calculate the deviation from a random distribution ΔK_{eq}:

$$\Delta K_{eq} = D/H_{terminal}/D/H_{central} = [(2 \times D/H_{C2H4}/D/H_{CH4}) - 2] \times 1000$$

４．研究成果

The implemented system allows measurement of internal ^2H distribution of natural propane with a precision of 0.5%, comparable with conventional methods.

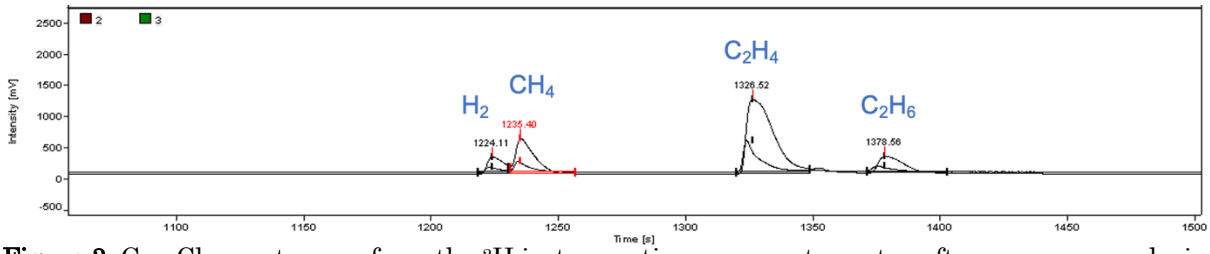

Figure 3. Gas Chromatogram from the ^2H isotope ratio mass spectrometry after propane pyrolysis. Fragments are separated by a chromatographic column before their D/H ratio is being measured.

We used slightly ^2H-enriched propane at specific position to estimate the accuracy of the method. The tests revealed that the high-temperature conversion used in our system do not scramble completely H-atoms and that the original ^2H internal distribution of propane can be calculated from that of the pyrolytic fragments.

Table 1. Isotope composition (as δ^2H = (D/Hsample / D/H standard -1) x 1000) of propane from different natural gas samples. Thermogenic = propane formed from pyrolysis of *n*-C_{25} at 400°C. Abiotic = putative abiotic samples from Kidd Creek Mine, Canada (Courtesy of Prof. Barbara Sherwood Lollar; Sherwood Lollar et al., 2002).

Sample	δ^2H_{CH4} (‰)	δ^2H_{C2H4} (‰)	δ^2H_{CH4}- δ^2H_{C2H4} (‰)
Standard	-276	-233	-43
Thermogenic From pyrolysis (400C)	-292	-407	115
Abiotic Kidd Creek mine 1 (Canada) Kidd Creek mine 2 (Canada)	 -381 -393	 -155 -139	 -226 -254

Analysis of propane from natural gas samples shows that depending on the origin a different signature is obtained, which is promising for tracing sources and sinks of hydrocarbons in natural gas. In particular, thermogenic propane from a long chain alkane pyrolysis at 400°C shows significantly different ^{2}H internal signature compared with putative abiotic propane (Table 1). The values thus obtained will have to be calibrated to temperature scale by conducting H-exchange experiments at different temperatures.

References:

Gilbert et al. *GCA* **2016** *177*, 205; Piasecki et al *GCA* **2016** *190*, 1; Stolper et al *Science* **2014** *344*, 1500; Suda et al. *GCA* **2017** *206*, 201; Wang et al. *Science* **2015** *348* 428; Sherwood Lollar et al., *Nature* **2017** *416*, 522

５．主な発表論文等

〔雑誌論文〕　計4件（うち査読付論文　4件／うち国際共著　4件／うちオープンアクセス　1件）

１．著者名 A. Gilbert, B. Sherwood Lollar, F. Musat, T. Giunta, S. Chen, Y. Kajimoto, C. J. Boreham, N. Yoshida, Y. Ueno	４．巻 14
２．論文標題 Intramolecular isotopic evidence for bacterial oxidation of propane in subsurface natural gas reservoirs	５．発行年 2019年
３．雑誌名 PNAS	６．最初と最後の頁 6653-6658
掲載論文のDOI（デジタルオブジェクト識別子） https://doi.org/10.1073/pnas.1817784116	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 T. Giunta, E. D Young, O. Warr, I. Kohl, J. L. Ash, A. Martini, S. O. C. Mundle, D. Rumble, I. Perez-Rodriguez, M. Wasley, D. E. LaRowe, A. Gilbert, B. Sherwood Lollar	４．巻 245
２．論文標題 Methane sources and sinks in continental sedimentary systems: New insights from paired clumped isotopologues 13CH3D and 12CH2D2	５．発行年 2019年
３．雑誌名 Geochim. Cosmochim. Acta	６．最初と最後の頁 327-351
掲載論文のDOI（デジタルオブジェクト識別子） https://doi.org/10.1016/j.gca.2018.10.030	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 N. Kitadai, R. Nakamura, M. Yamamoto, K. Takai, Y. Li, A. Yamaguchi, A. Gilbert, Y. Ueno, N. Yoshida, Y. Oono.	４．巻 4
２．論文標題 Geoelectrochemical CO production: Implications for the autotrophic origin of life	５．発行年 2018年
３．雑誌名 Science Advances	６．最初と最後の頁 1-7
掲載論文のDOI（デジタルオブジェクト識別子） https://doi.org/10.1126/sciadv.aao7265	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 M. Julien, A. Gilbert, K. Yamada, R. J. Robins, P. Hohener, N. Yoshida, G. S. Remaud.	４．巻 176
２．論文標題 Expanded uncertainty associated with determination of isotope enrichment factors: Comparison of two-point calculation and Rayleigh-plot	５．発行年 2018年
３．雑誌名 Talanta	６．最初と最後の頁 367-373
掲載論文のDOI（デジタルオブジェクト識別子） https://doi.org/10.1016/j.talanta.2017.08.038	査読の有無 有
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〔学会発表〕　計3件（うち招待講演　3件／うち国際学会　1件）

1．発表者名 Gilbert Alexis
2．発表標題 Position-specific isotope composition of natural gas hydrocarbons: recent insights and future prospects
3．学会等名 Goldschmidt 2018; Aug 12-17 2018, Boston USA（招待講演）（国際学会）
4．発表年 2018年

1．発表者名 Gilbert Alexis
2．発表標題 Position-specific isotope analysis of biomolecules by isotopic 13C Nuclear Magnetic Resonance
3．学会等名 Stable Isotopes in the Biosphere workshop 2019, Jan 20-25 2019, Xi ' an China（招待講演）
4．発表年 2019年

1．発表者名 Gilbert Alexis
2．発表標題 Position-specific isotope analysis of natural gas hydrocarbons
3．学会等名 Stable Isotopes in the Biosphere workshop 2019, Jan 20-25 2019, Xi ' an China（招待講演）
4．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

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