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Isotopomer approaches to the detection of anaerobic oxidation of natural gas hydrocarbons

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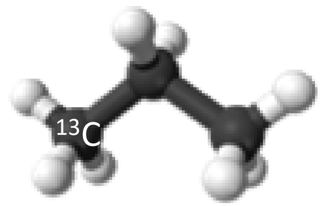
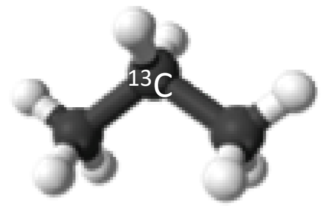
EGU 2020

Anaerobic oxidation of hydrocarbons (AOH)

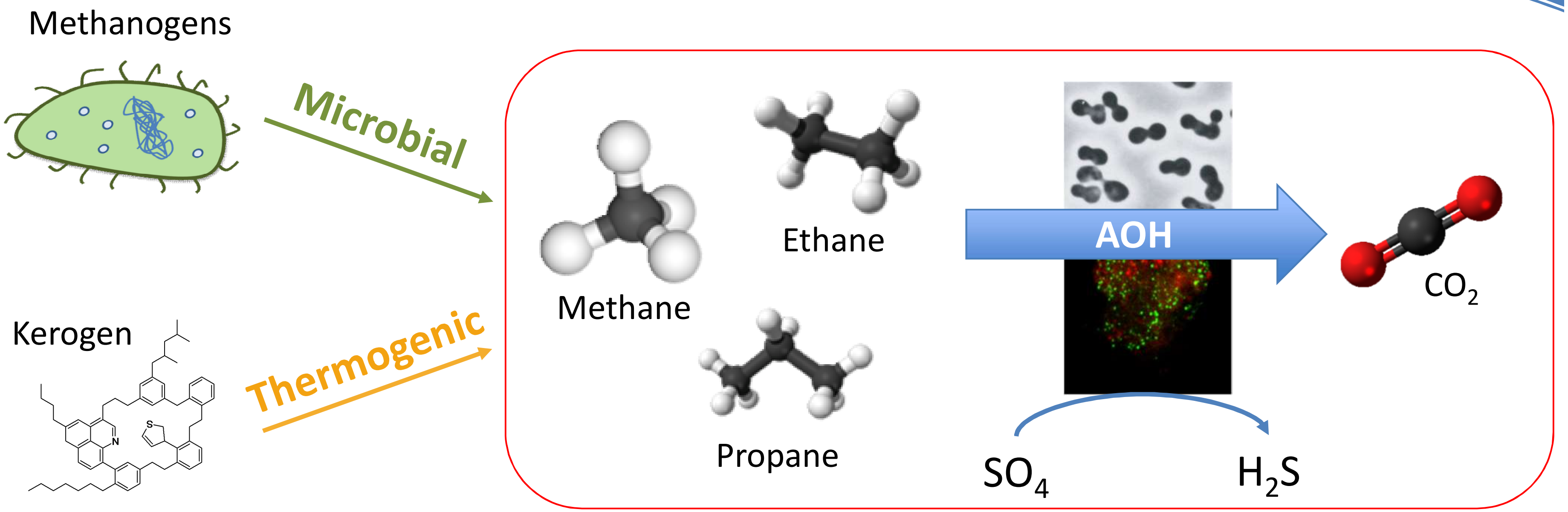
Can we use isotopomers of hydrocarbons to detect their oxidation *in situ*?



1-^{13}C-propane
(Terminal)



2-^{13}C-propane
(Central)



Kniemeyer et al 2007; Laszlo-Perez et al 2016

Anaerobic oxidation of non-methane hydrocarbons

nature Vol 449|18 October 2007|doi:10.1038/nature06200

LETTERS

2007 Bacteria

Anaerobic oxidation of short-chain hydrocarbons by marine sulphate-reducing bacteria

Olaf Kniemeyer[1]†, Florin Musat[1], Stefan M. Sievert[2], Katrin Knittel[1], Heinz Wilkes[3], Martin Blumenberg[4], Walter Michaelis[4], Arno Classen[5], Carsten Bolm[5], Samantha B. Joye[6] & Friedrich Widdel[1]

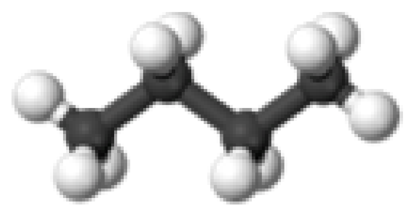
ARTICLE

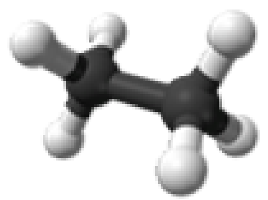
2016 Archea

doi:10.1038/nature20152

Thermophilic archaea activate butane via alkyl-coenzyme M formation

Rafael Laso-Pérez[1,2], Gunter Wegener[1,2,3], Katrin Knittel[1], Friedrich Widdel[1], Katie J. Harding[1]†, Viola Krukenberg[1,2], Dimitri V. Meier[1], Michael Richter[1], Halina E. Tegetmeyer[2,4], Dietmar Riedel[5], Hans-Hermann Richnow[6], Lorenz Adrian[6], Thorsten Reemtsma[6], Oliver J. Lechtenfeld[6] & Florin Musat[1,6]





LETTER

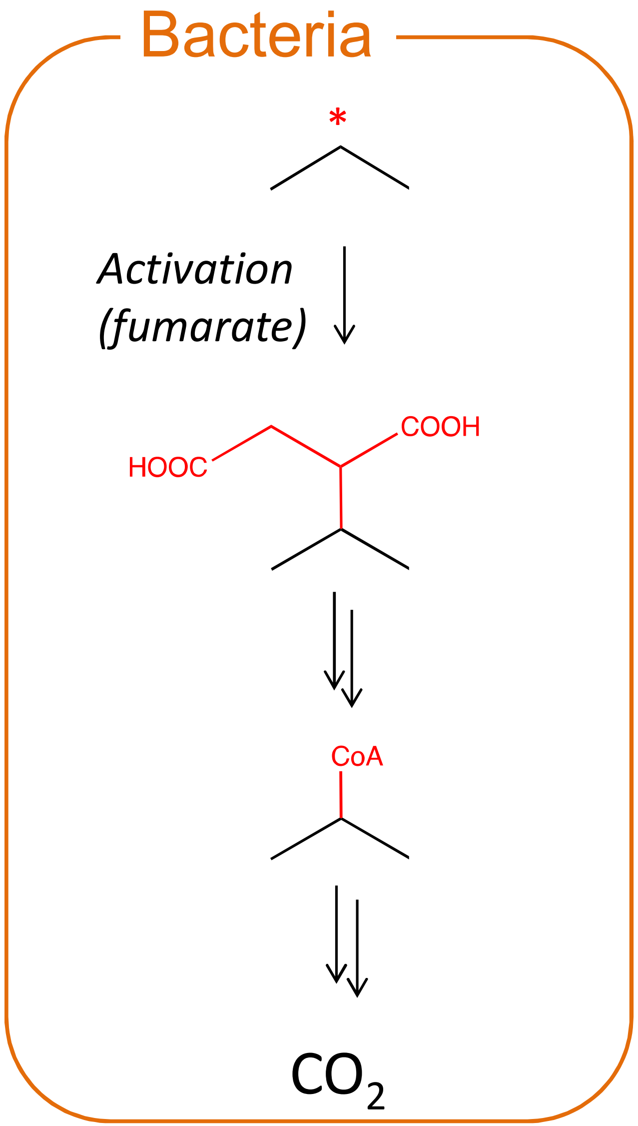
2019 Archea

https://doi.org/10.1038/s41586-019-1063-0

Anaerobic oxidation of ethane by archaea from a marine hydrocarbon seep

Song-Can Chen[1,2], Niculina Musat[1], Oliver J. Lechtenfeld[3], Heidrun Paschke[3], Matthias Schmidt[1], Nedal Said[1], Denny Popp[4], Federica Calabrese[1], Hryhoriy Stryhanyuk[1], Ulrike Jaekel[5,8], Yong-Guan Zhu[2,6], Samantha B. Joye[7], Hans-Hermann Richnow[1], Friedrich Widdel[5] & Florin Musat[1,5]*

Culture experiments with propane



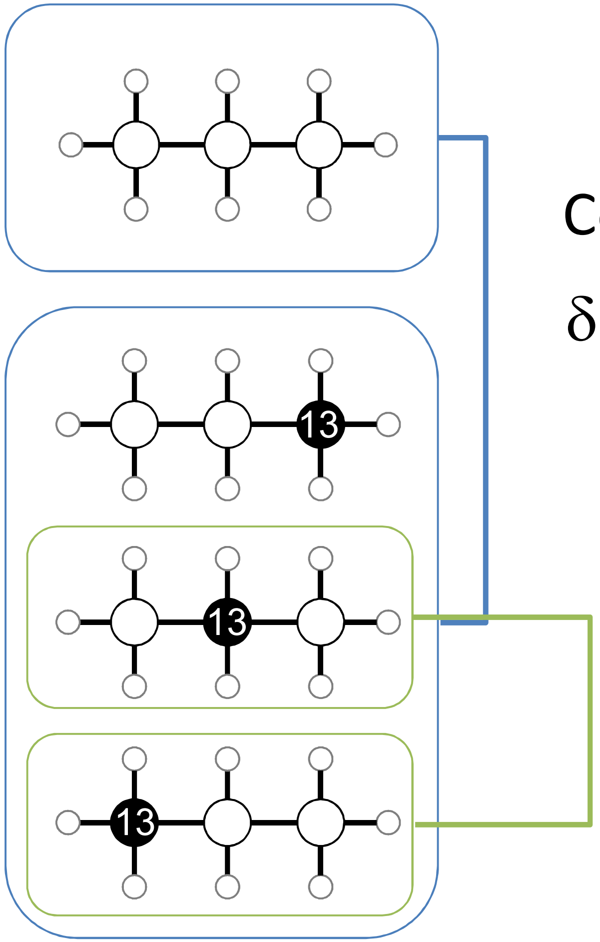
Propane oxidation starts with fumarate addition on the central C-atom

→ **An isotope fractionation on the central position is expected (Kniemeyer et al., 2007)**

Bacteria incubated with propane (gas phase) and sulfate (liquid phase)

Culture experiments conducted by **Florin Musat & Songcan Chen** (UFZ, Germany)

Position-specific isotope composition



Conventional: ^{13}C vs ^{12}C

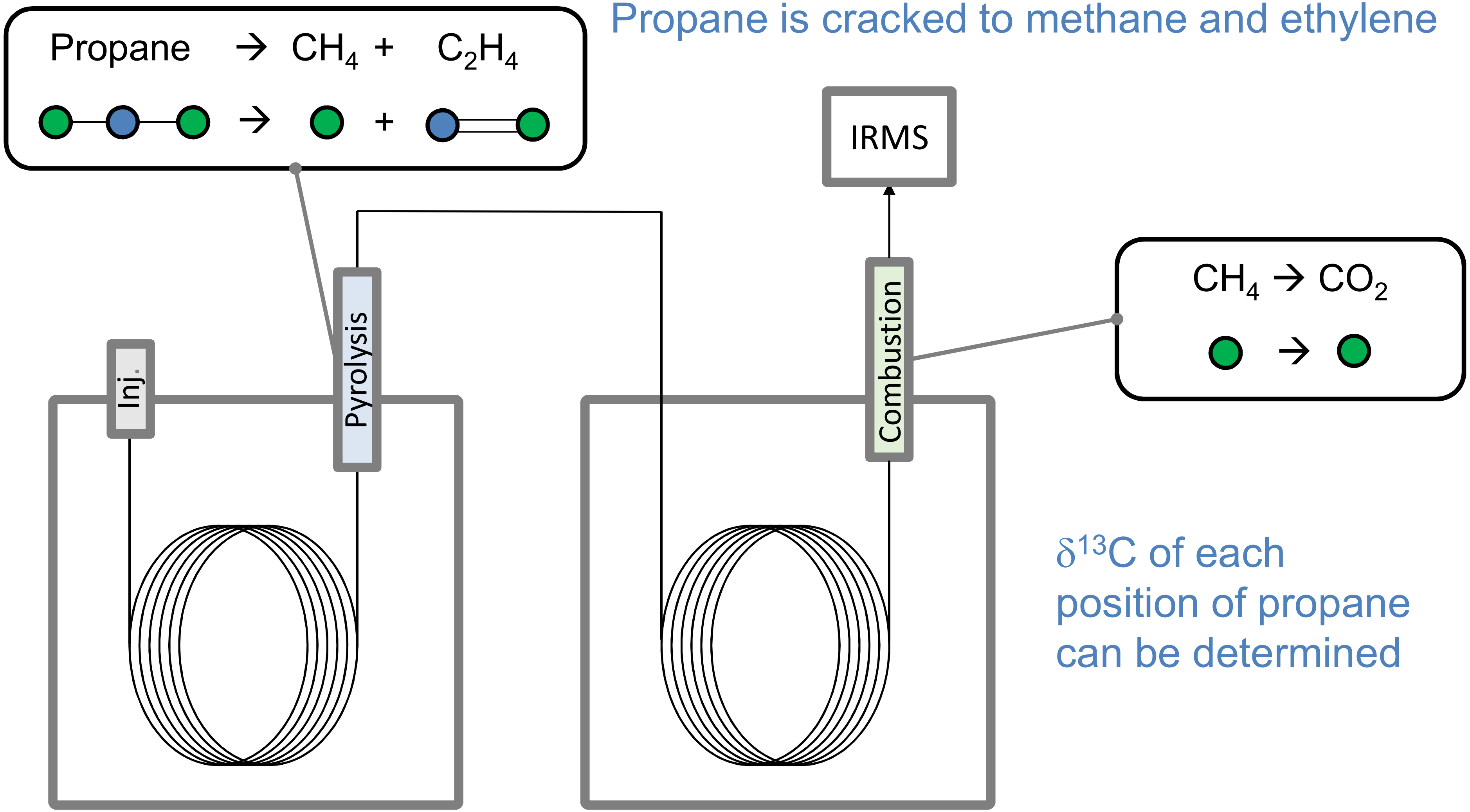
$\delta^{13}C_{propane}$

Position-specific: Central vs Terminal

$$\Delta^{13}C_{central} = \delta^{13}C_{central} - \delta^{13}C_{terminal}$$

On-line pyrolysis for position-specific isotope analysis (propane)

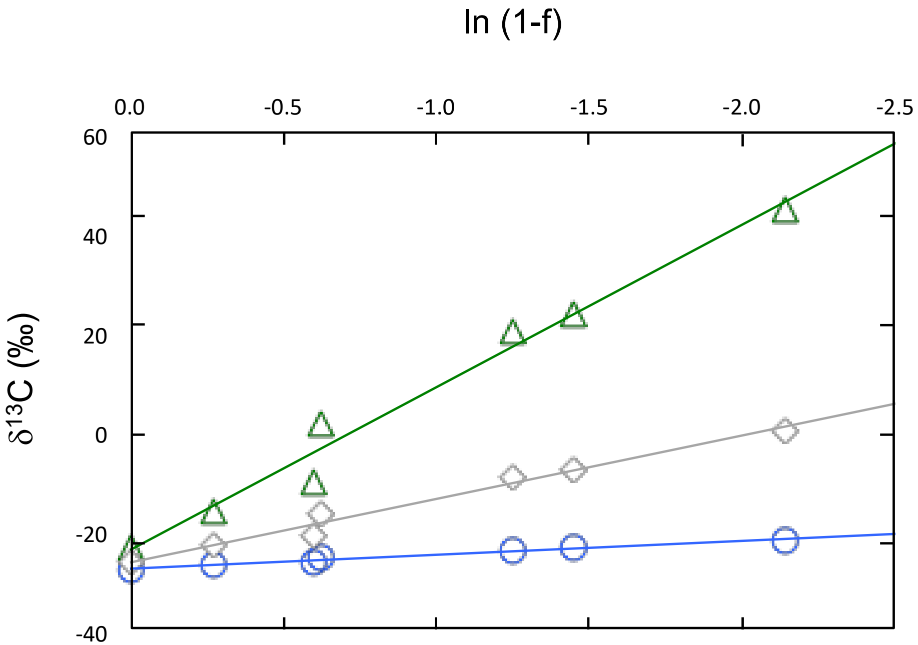
Propane is cracked to methane and ethylene



$\delta^{13}C$ of each position of propane can be determined

Corso & Brenna **1997** PNAS; Gilbert *et al.* **2016** GCA; Li *et al.* **2018** Org. Geochem.

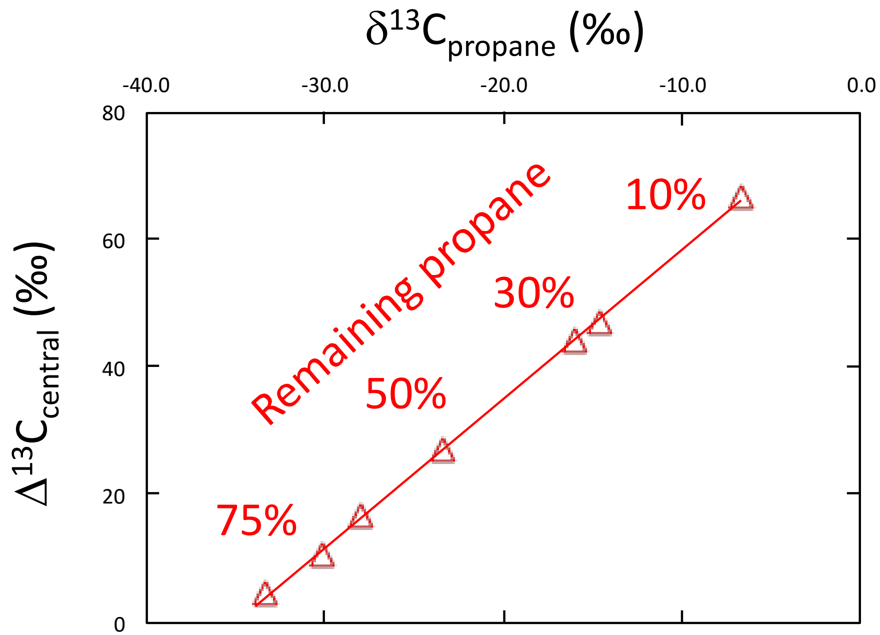
Position-specific ^{13}C Kinetic isotope effect



Central ε = 33 ± 2‰

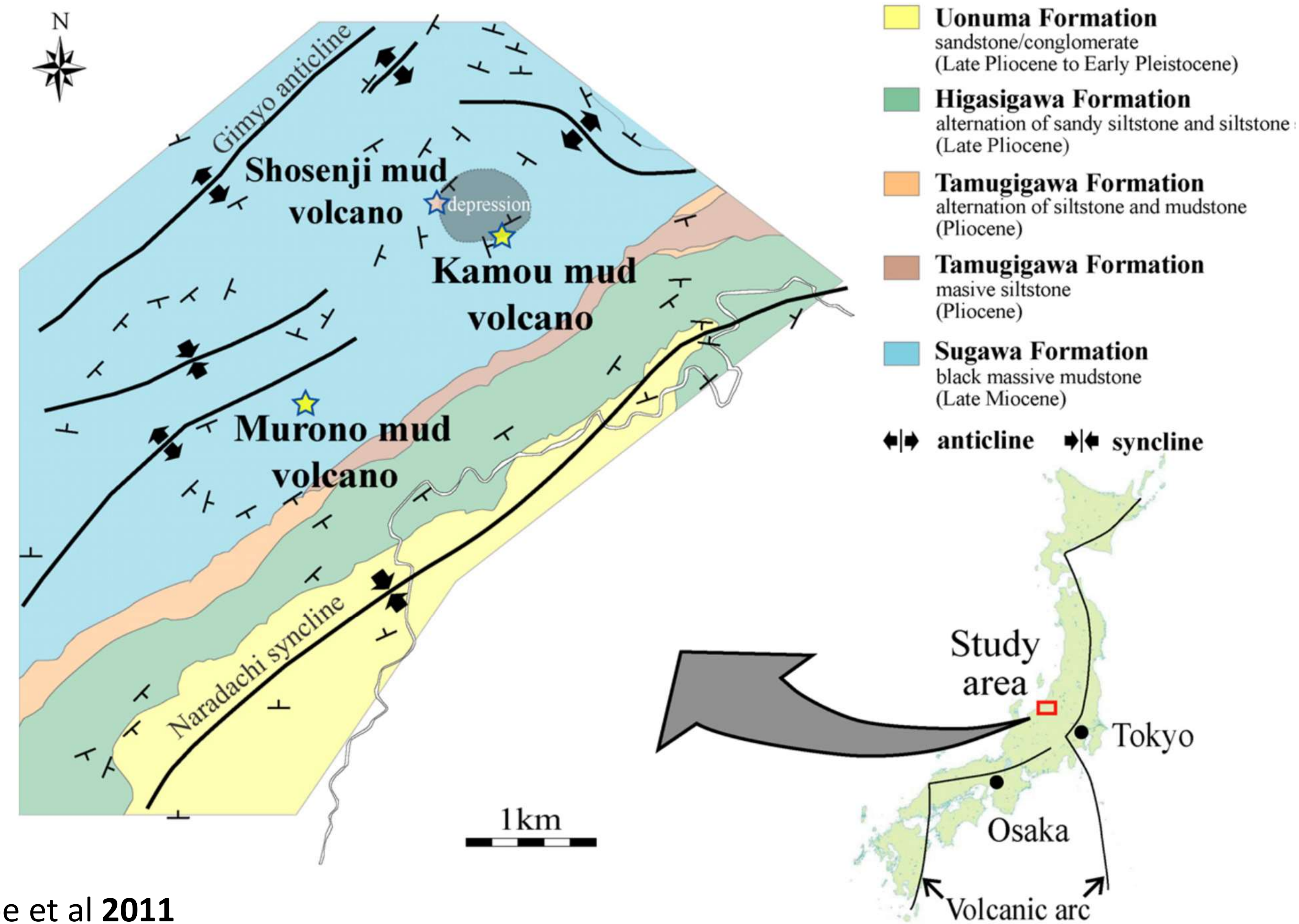
Bulk ε = 11.8 ± 0.8‰

Terminal ε = 2.8 ± 0.3‰



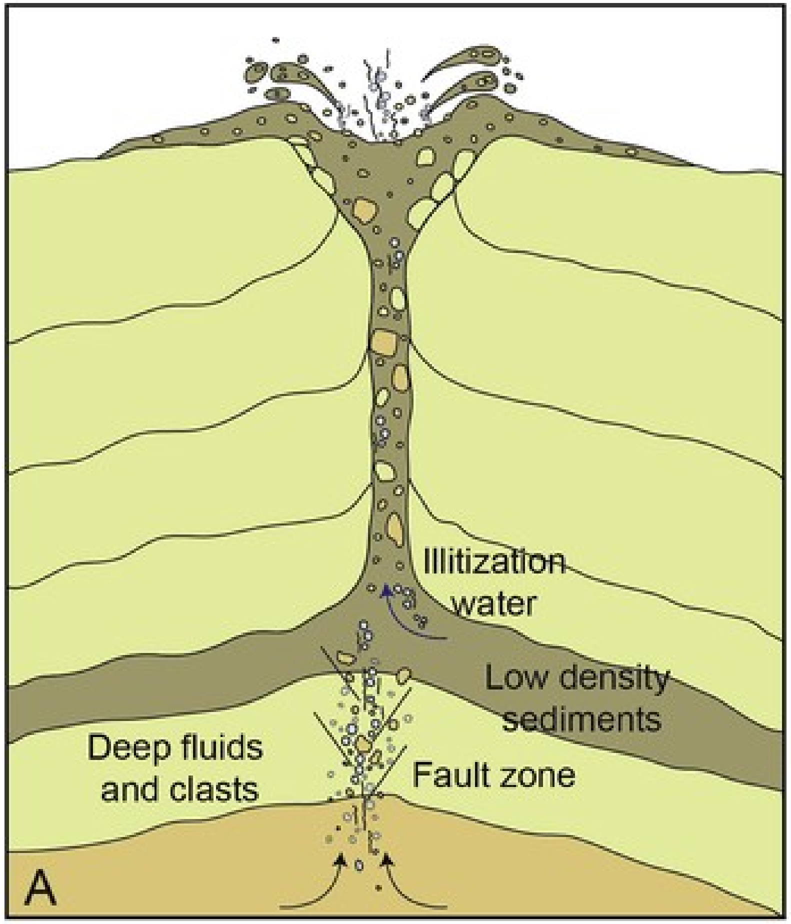
$$\Delta^{13}C_{central} = \delta^{13}C_{central} - \delta^{13}C_{Terminal}$$

Sampling: Tokamachi mud volcano (Niigata Pref.)



Etiope et al **2011**

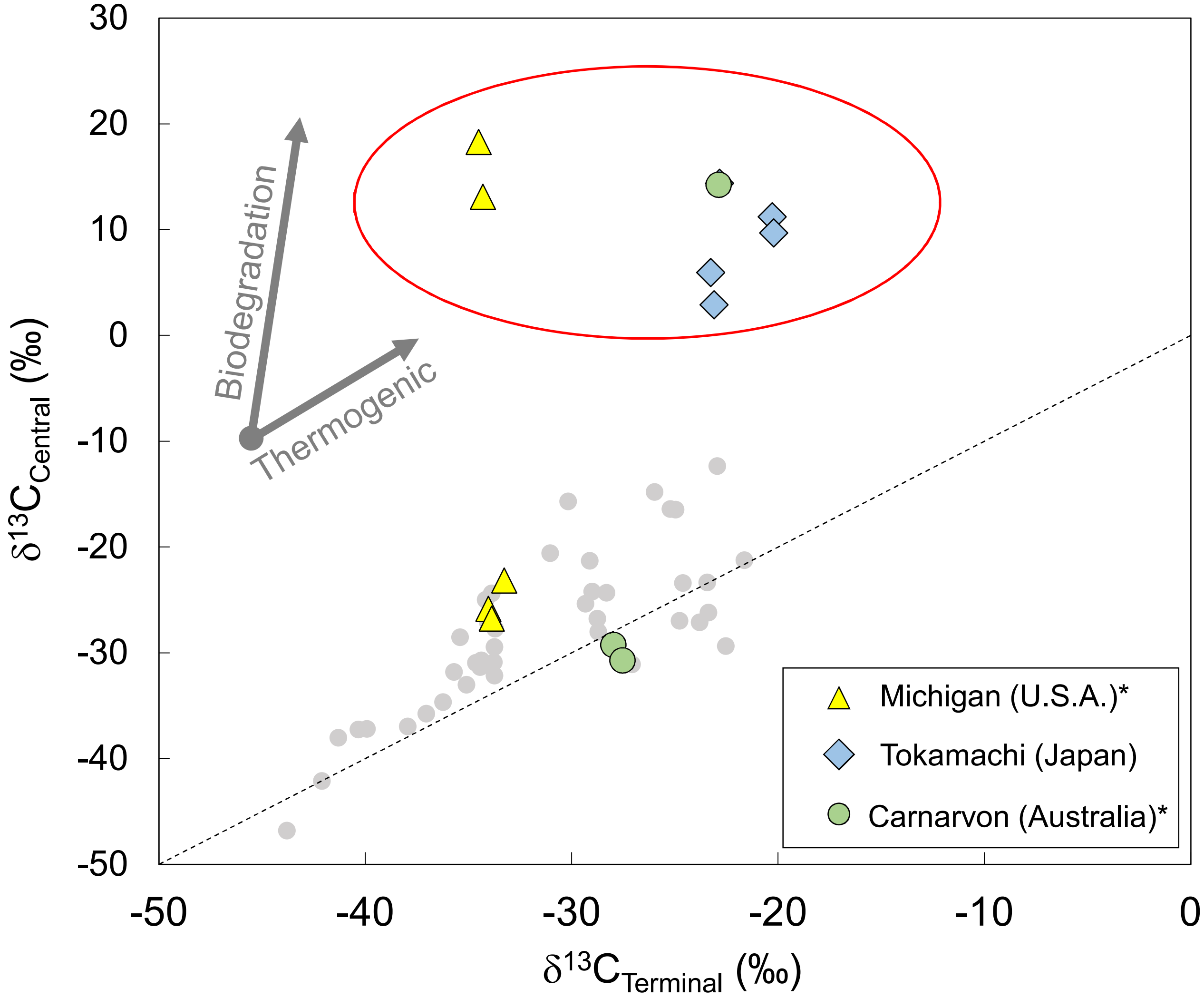
Sampling at Tokamachi mud volcano (Niigata pref.)



N. Yoshida, A. Gilbert, M. Nakagawa, K. Taguchi

Etiope et al **2011;** Collignon et al **2017**

Results: $\delta^{13}C_{Terminal}$ vs $\delta^{13}C_{Central}$ of propane

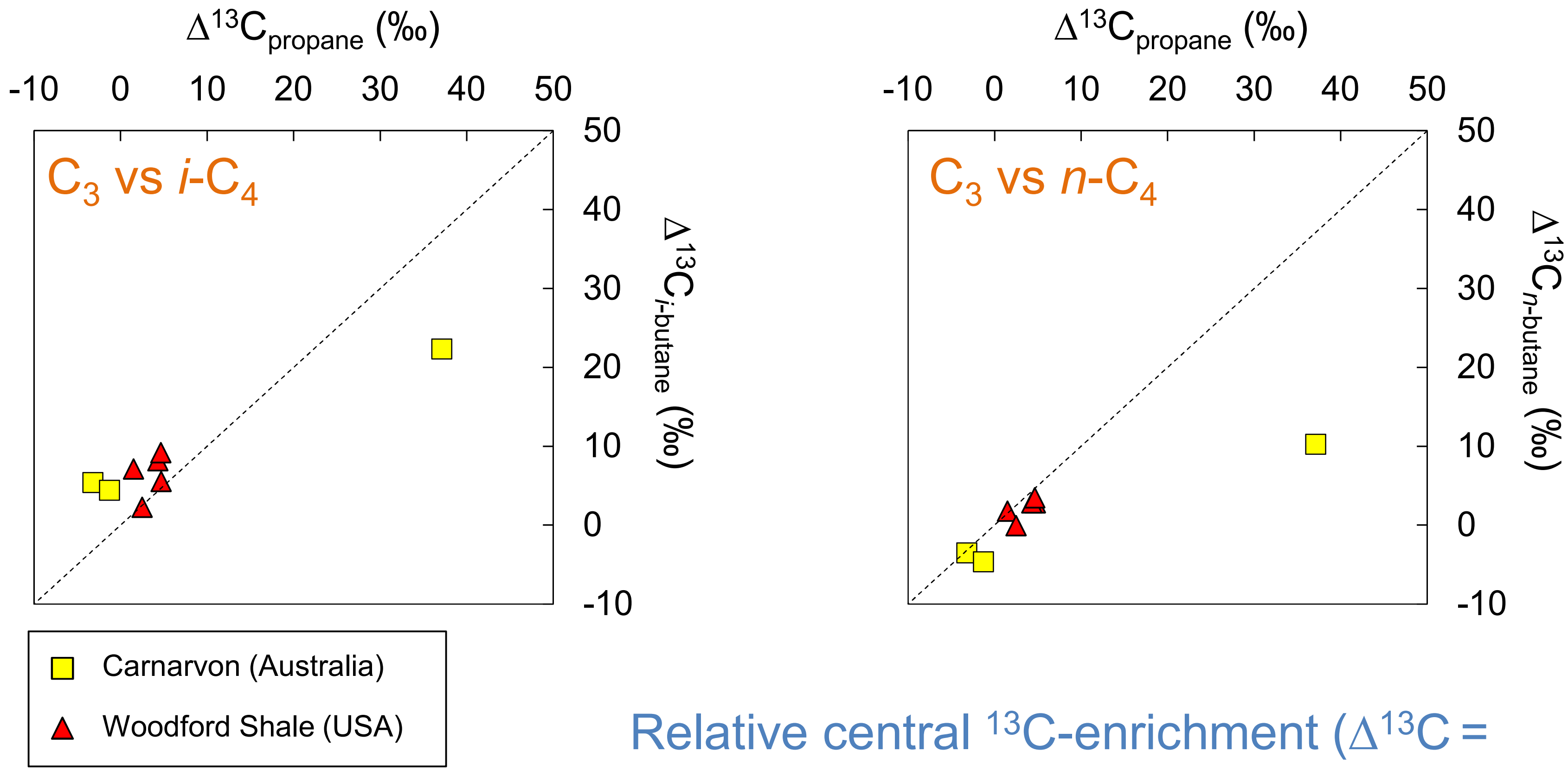


The strong ^{13}C-enrichment in the central position suggests biodegradation of propane in natural gas reservoirs (Gilbert et al **2019** *PNAS*)

*Samples kindly provided by **Thomas Giunta** & **Barbara Sherwood Lollar** (Univeristy of Toronto, Canada) and **Chris Boreham** (Geoscience Australia)

Multi-compound PSIA: propane vs butanes

The method developed for propane also works for *n*-butane and *i*-butane



Relative central ^{13}C-enrichment ($\Delta^{13}C = \delta^{13}C_{central} - \delta^{13}C_{terminal}$) shows biodegradation of both *n*-butane and *i*-butane

Julien et al **2020** *Chem. Geol.*

Acknowledgements

The Tokyo Tech Team

Koudai Taguchi

Maxime Julien

Image credit Nerissa Escanlar

Yuichiro Ueno

Keita Yamada

Image credit Nerissa Escanlar

Naohiro Yoshida

Image credit Nerissa Escanlar

Mayuko Nakagawa

University of Toronto
Barbara Sherwood Lollar
Thomas Giunta

UFZ Leipzig
Florin Musat
Songcan Chen

Geoscience Australia
Chris Boreham

MIT
Mark Goldman

Tokyo Institute of Technology

科研費 KAKENHI

NASA