hardcore stable isotope laboratory@MIT

Earth Resource Laboratory
2020

Generation temperature of methane estimated from doubly substituted isotopologue ($^{13}CH_3D$)

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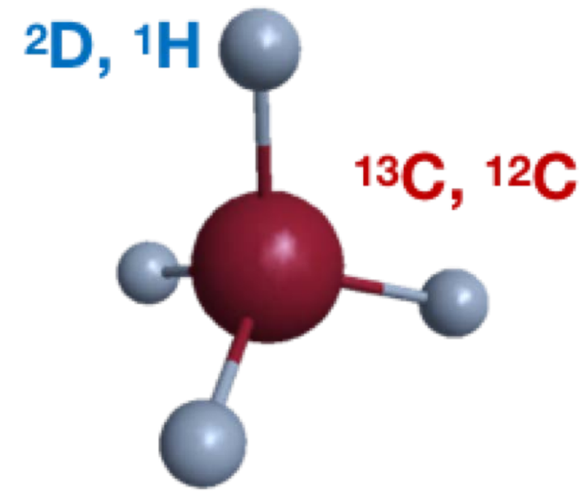
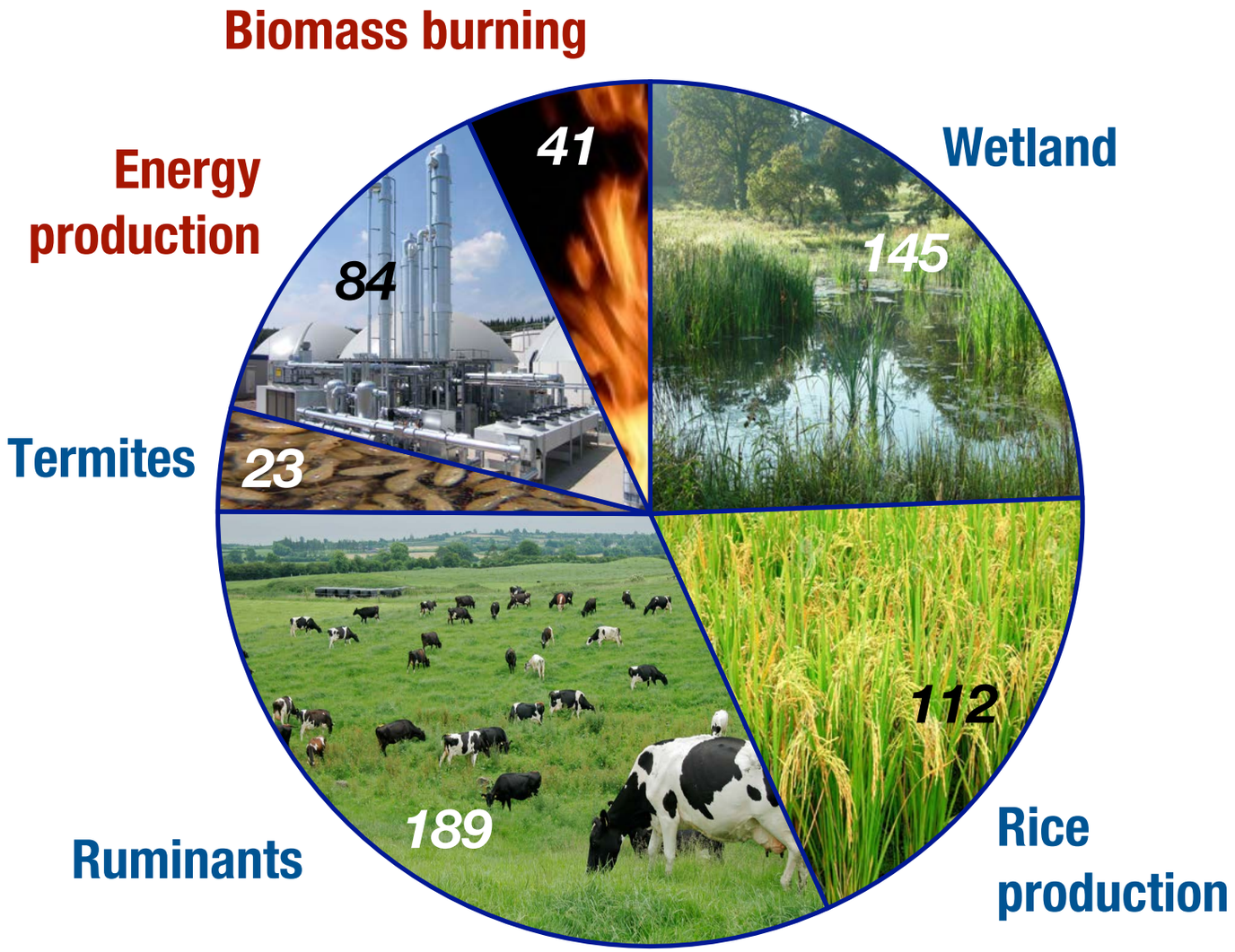
David D. Nelson, Joanne Shorter, J. Barry McManus
Aerodyne Research Inc.



*Isotopologue: molecule with different isotope configurations

Sources of methane to the atmosphere



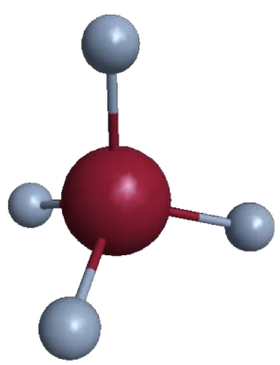
Atmospheric methane sources in Tg CH_4 per year
Source: Chen and Prinn, 2006, *JGR*, 111

1) Microbial methane

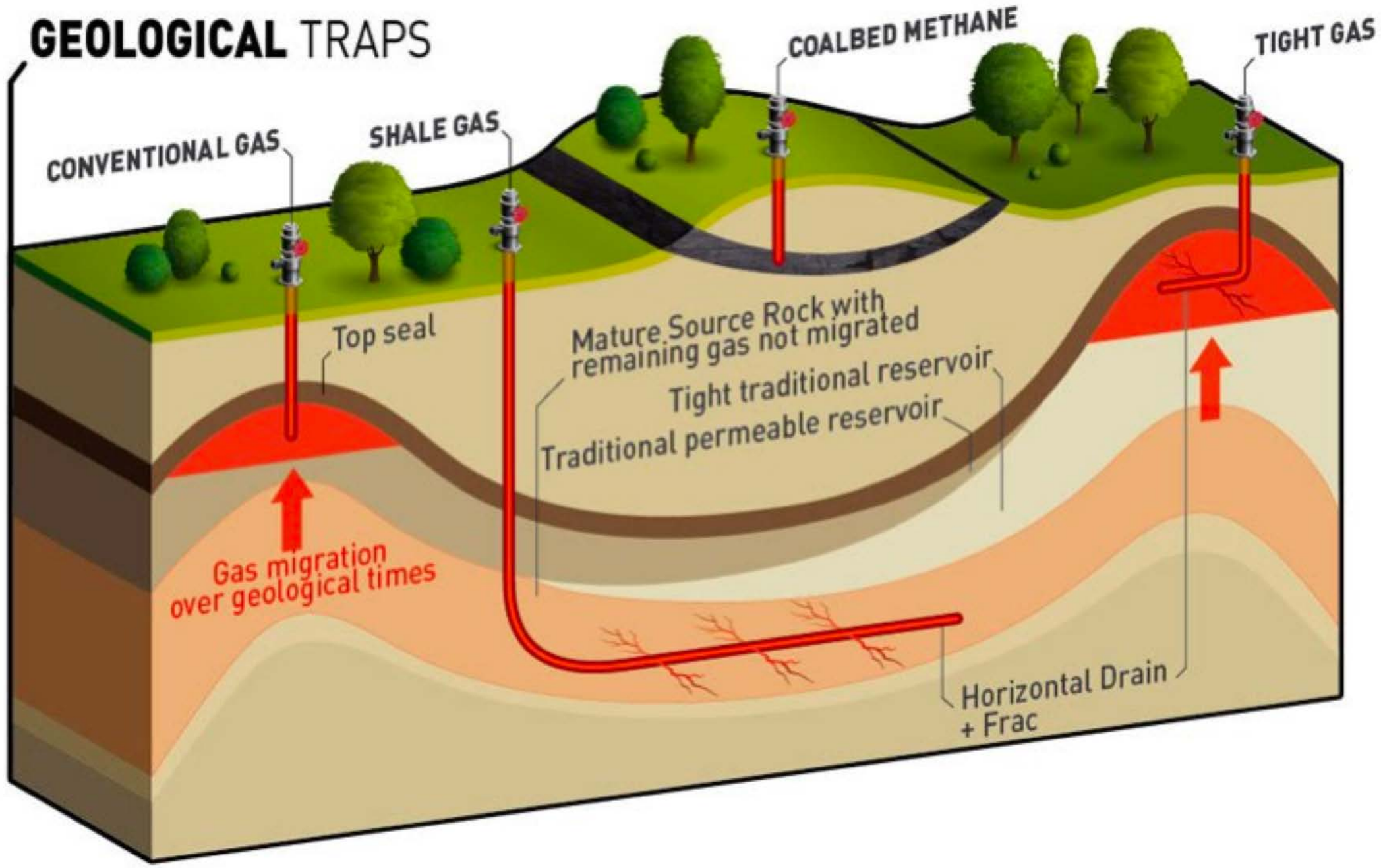
Microbes produce methane from CO_2 and H_2 or from acetate, formate, methanol, etc (T <121°C).

2) Thermogenic methane

Major source of natural gas. Formed from thermal cracking of organic materials at > 150°C.

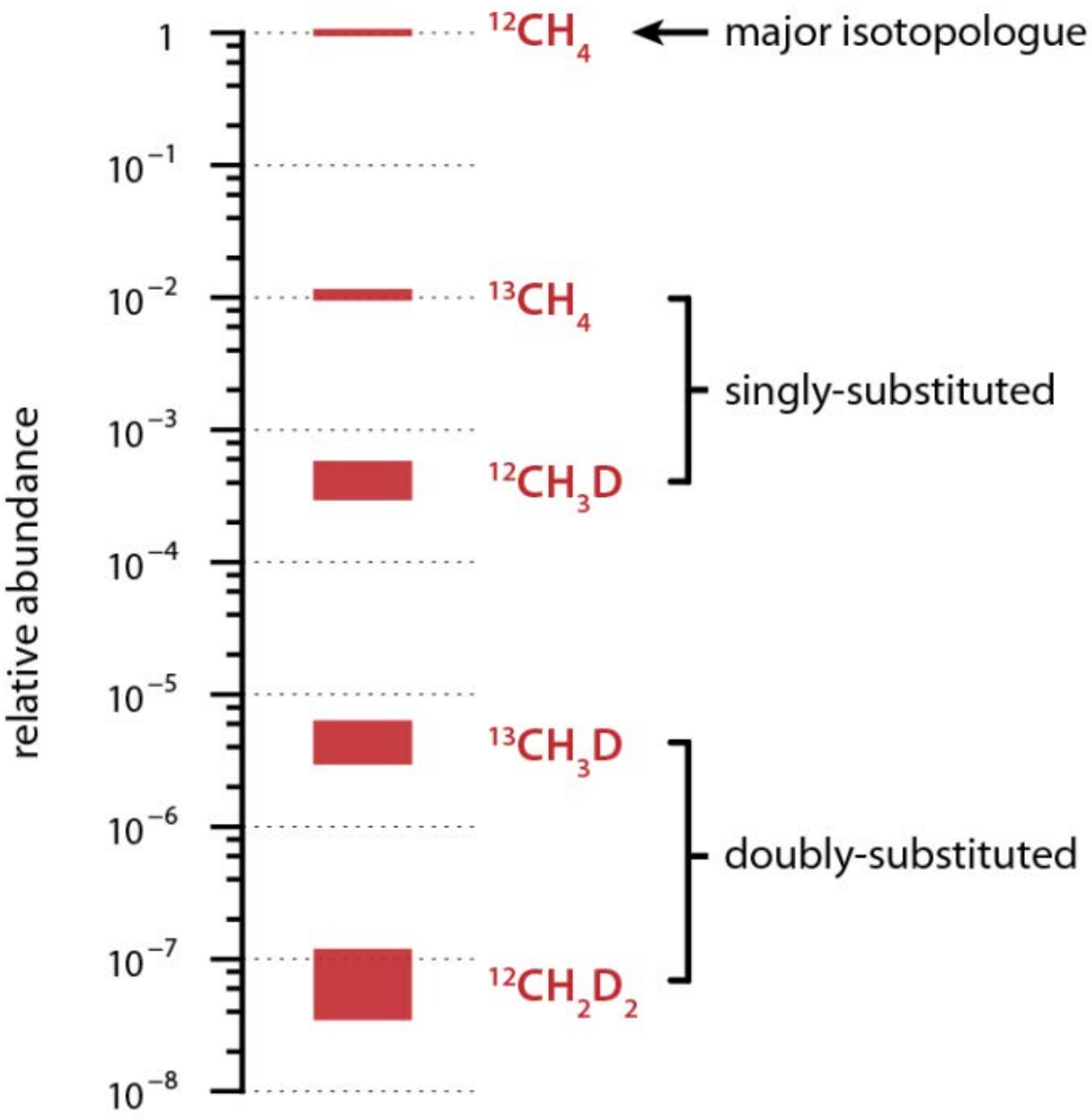


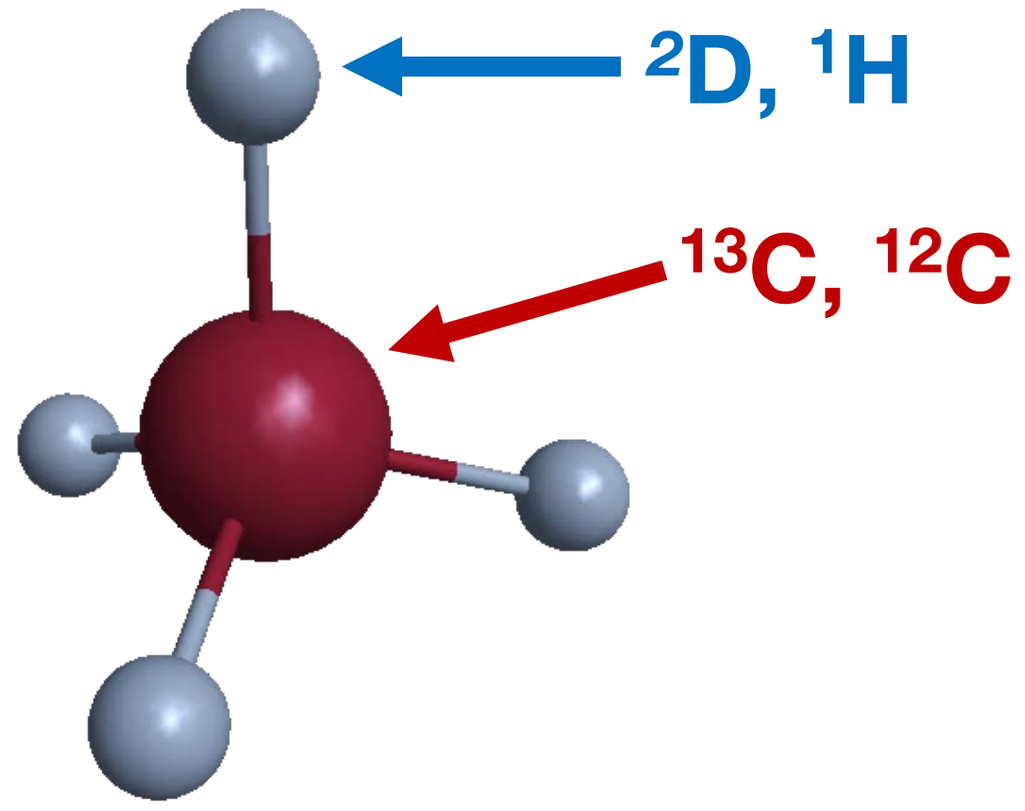
Methane migrates in subsurface environment



Typical Reservoirs: Tight Gas, Shale Gas, and Coal bed Methane -Credit: Total.com

Isotopic flavors of methane



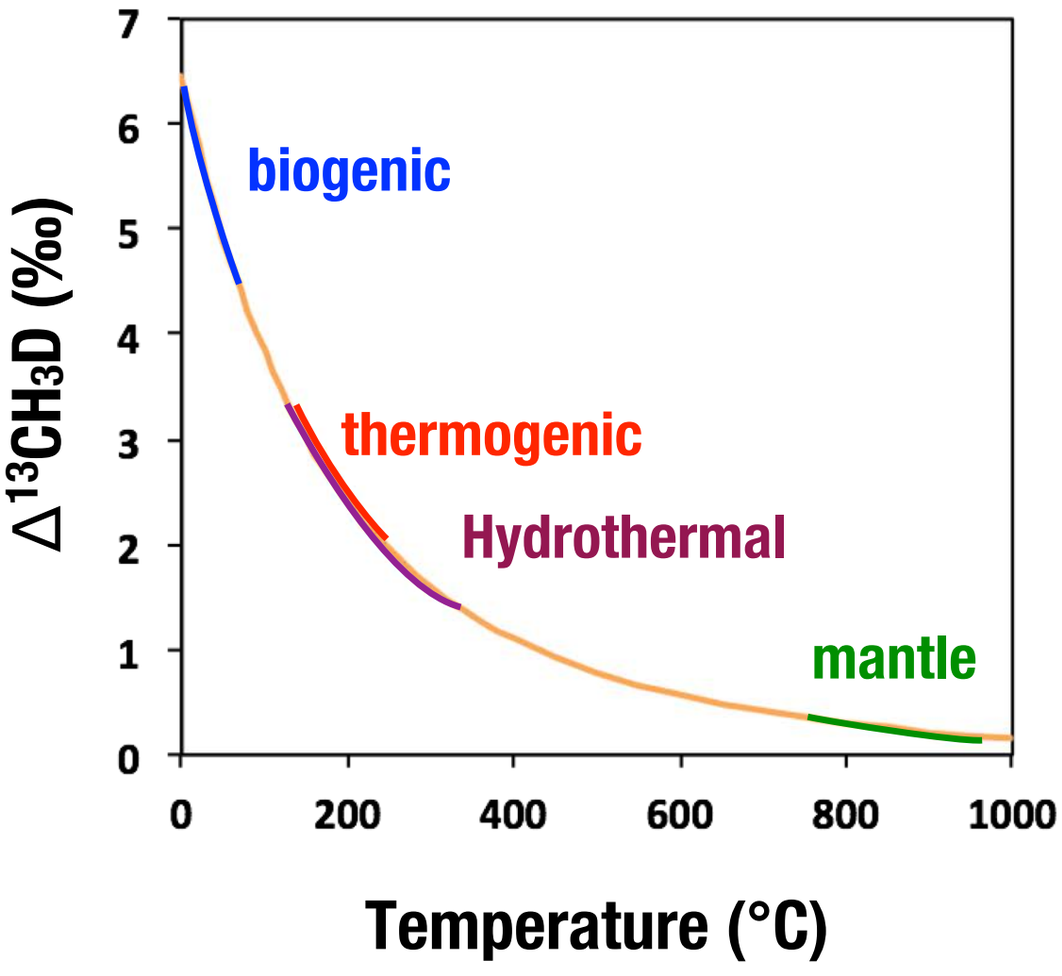


* bars represent approximate ranges of natural variability of isotopologue abundances

Isotopologues: molecules with different isotope configurations

Principles of $^{13}CH_3D$ "clumped" methane thermometry

$$^{13}CH_4 + {}^{12}CH_3D \rightleftarrows {}^{13}CH_3D + {}^{12}CH_4, \quad K(T)$$



K = 1.0057 at 25°C

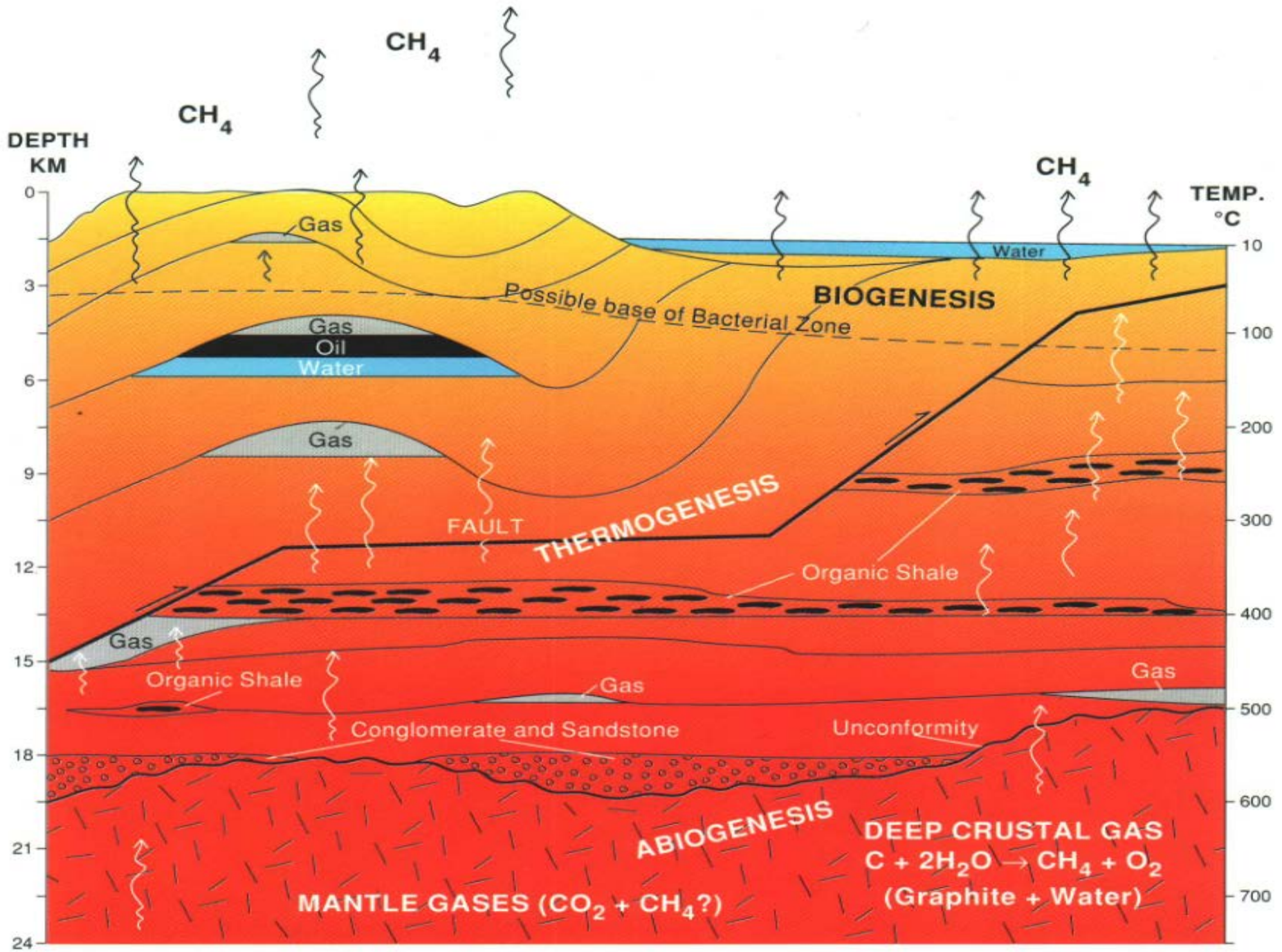
= 1.0011 at 400°C

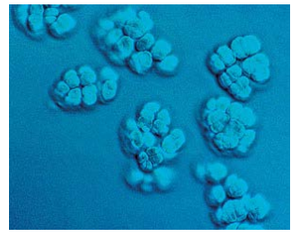
$$\Delta^{13}\mathrm{CH_3D} = \frac{^{13}\mathrm{CH_3D}}{^{12}\mathrm{CH_3D}} \cdot \frac{^{12}\mathrm{CH_4}}{^{13}\mathrm{CH_4}} - 1$$

* ***We need to measure all four isotopologues at better than 0.3 ‰ precision (6 ppm of ±0.3‰ = ± 2 ppb).***
* ***Thermometer works if CH_4 was generated under near-equilibrium process.***

Eiler (2006), Ma et al. (2008), Stolper et al. (2014), Ono et al. (2014)

Promise: locate the depth of CH_4 generation





Methanogen up to 122 °C
Takai et al., 2008

Gas Window (> ~ 150 °C)

Howell et al., 1993

Double focusing high-resolution isotope ratio mass spectrometry
Panorama at UCLA (made by Nu instrument in UK)

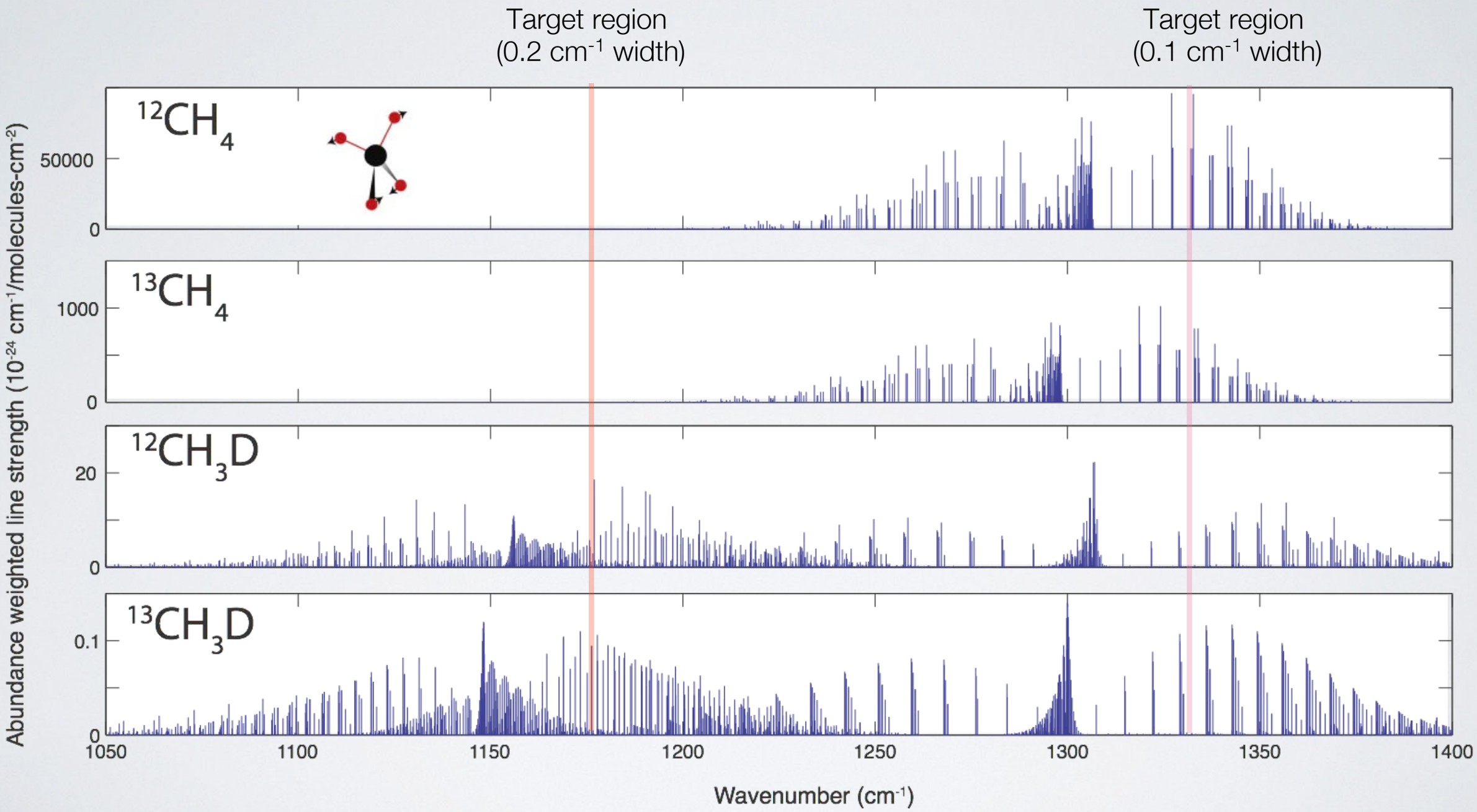
Ion Species	Mass (Da)
$^{13}CH_3D^+$	18.04093
$^{13}CH_5^+$	18.04248
$^{12}CH_2D_2^+$	18.04386

Effective radius is 140cm, it separates $^{13}CH_3D^+$ and $^{12}CH_2D_2^+$ by 200μm!

Young et al., 2016, *IJMS*, 401, 1-10

Infrared spectroscopy of methane isotopologues

Rotation-vibration absorption bands at ~1300cm^{-1}

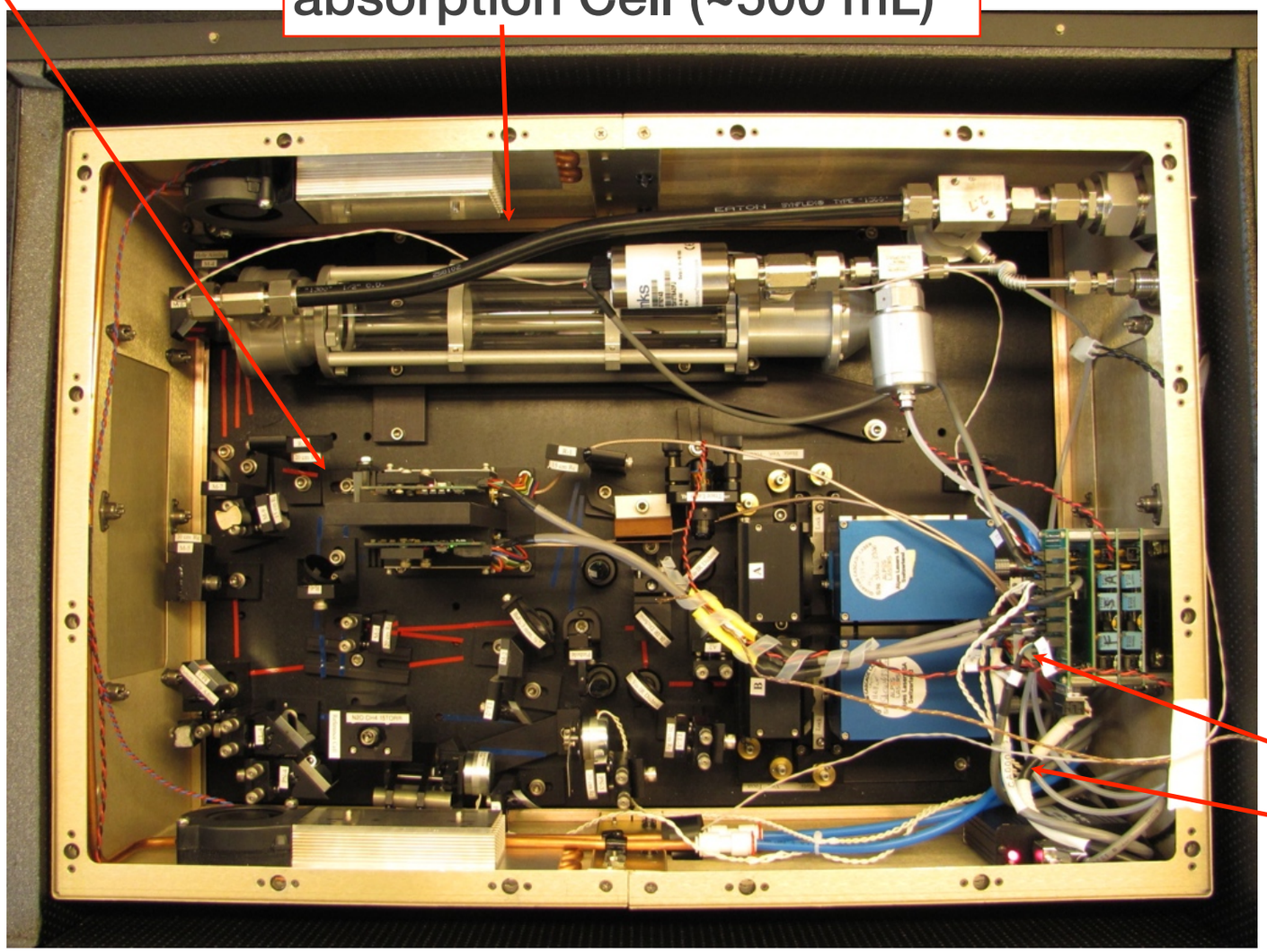


Line strength from From HITRAN database (Rothman et al., 2009)

Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS)

HgCdTe detector

76 m multi-pass Herriott absorption Cell (~500 mL)



21“

27”

MADE IN U. S. A.

Aerodyne Research

National Science Foundation WHERE DISCOVERIES BEGIN

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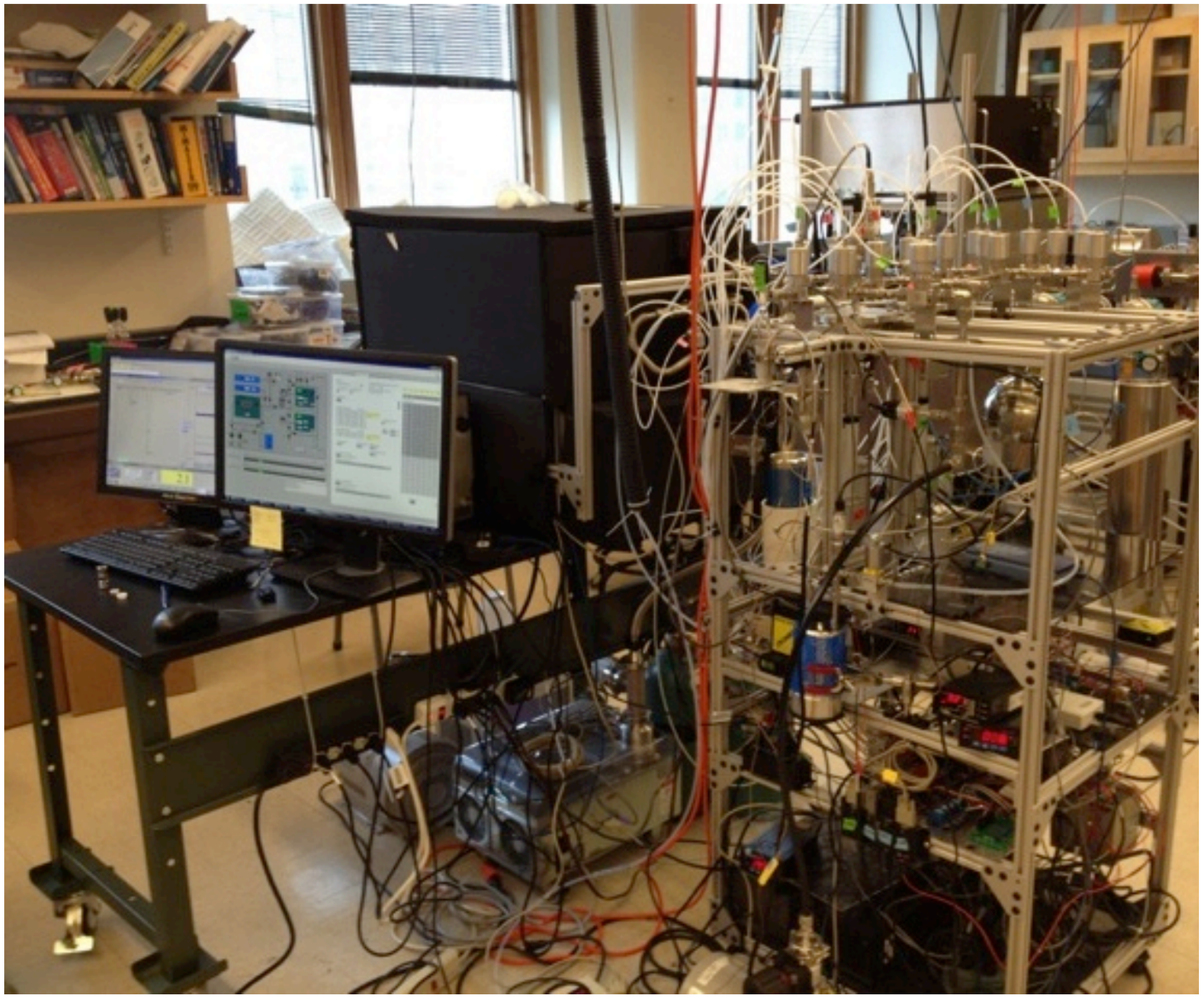
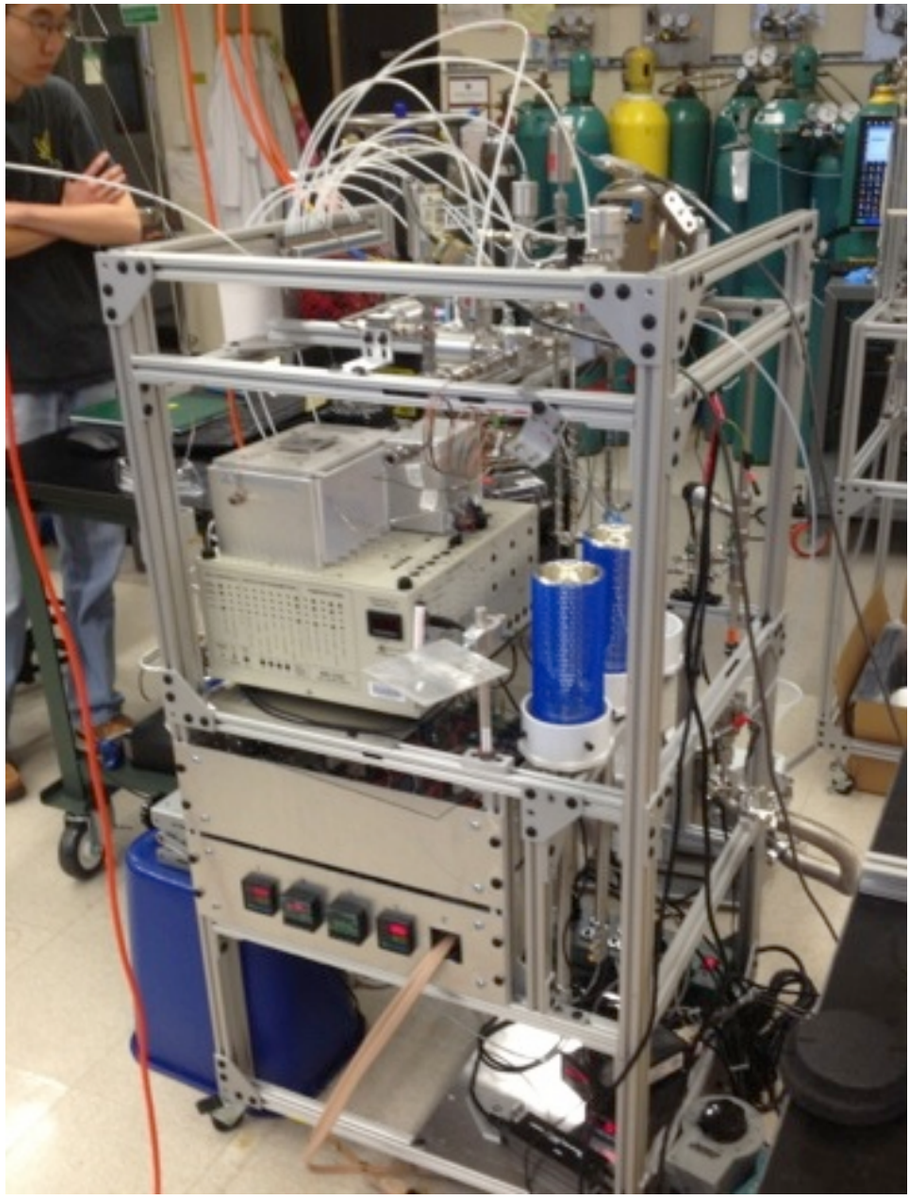
Two continuous-wave quantum cascade lasers

TILDAS + dual inlet manifold at MIT

We measure pure CH_4 (~1mL STP) at constant pressure



TILDAS with Gas Inlet System



Preparatory GC system

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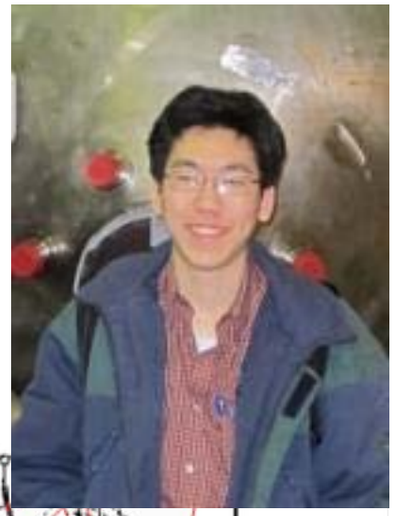
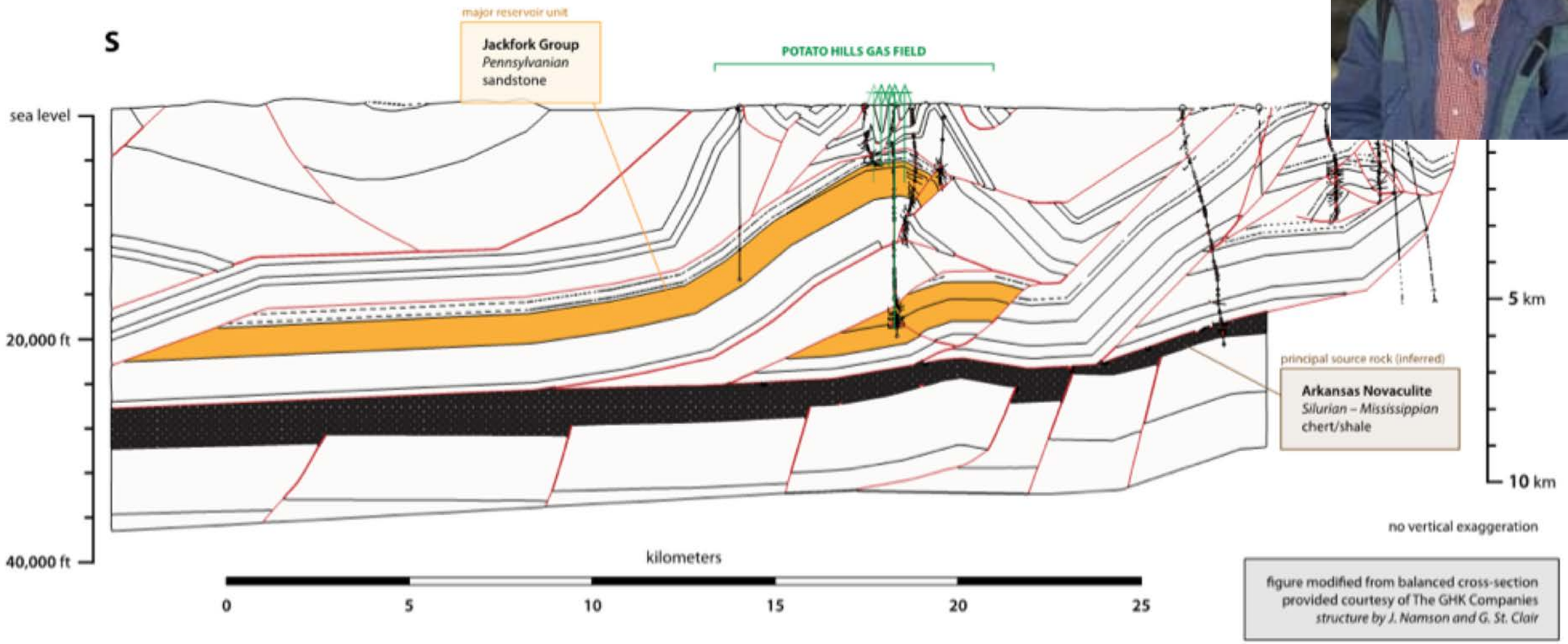
Application 1
$^{13}CH_3D$ temperature of thermogenic methane

The Potato Hills Gas Field, Oklahoma
"migrated gas"



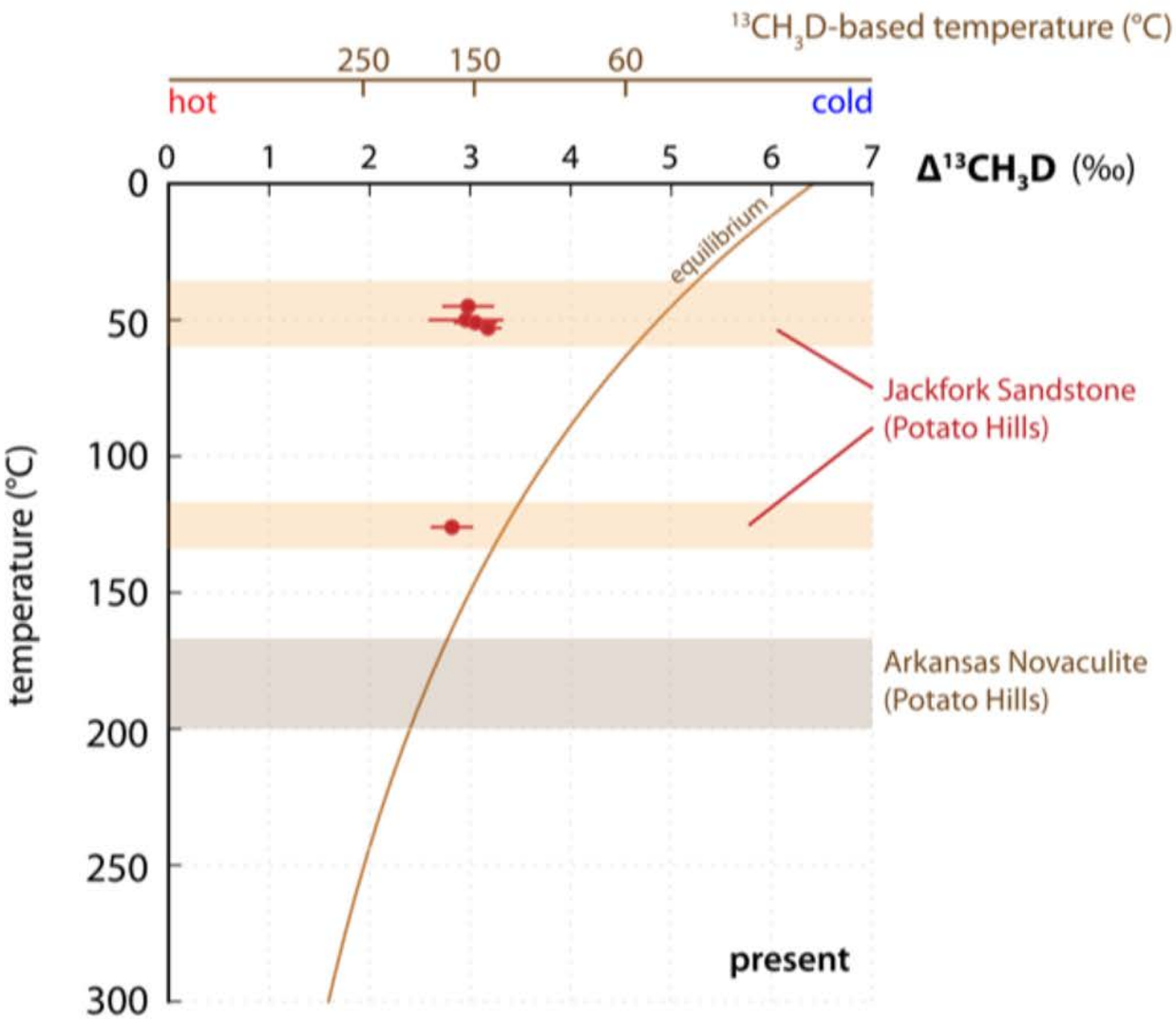


Potato Hills, Ouachita Mtns.
migrat

Work by
David Wang*, Shuhei Ono, MIT, Jeff Seewald, WHOI
***Upstream Research Company, ExxonMobil**

MITei
MIT Energy Initiative

$^{13}CH_3D$ abundance corresponds to generation not reservoir T



- **$^{13}CH_3D$ yielded T of 145±15 °C, reasonable for gas window.**
- **$^{13}CH_3D$ signal did not reset at the reservoirs**

Potato Hills, Ouachita Mtns.
migrated gases

Work by
David Wang, Shuhei Ono, MIT, Jeff Seewald, WHOI

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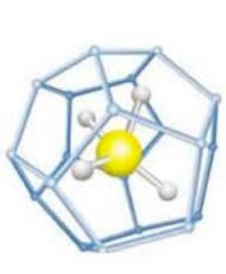
MIT Energy Initiative

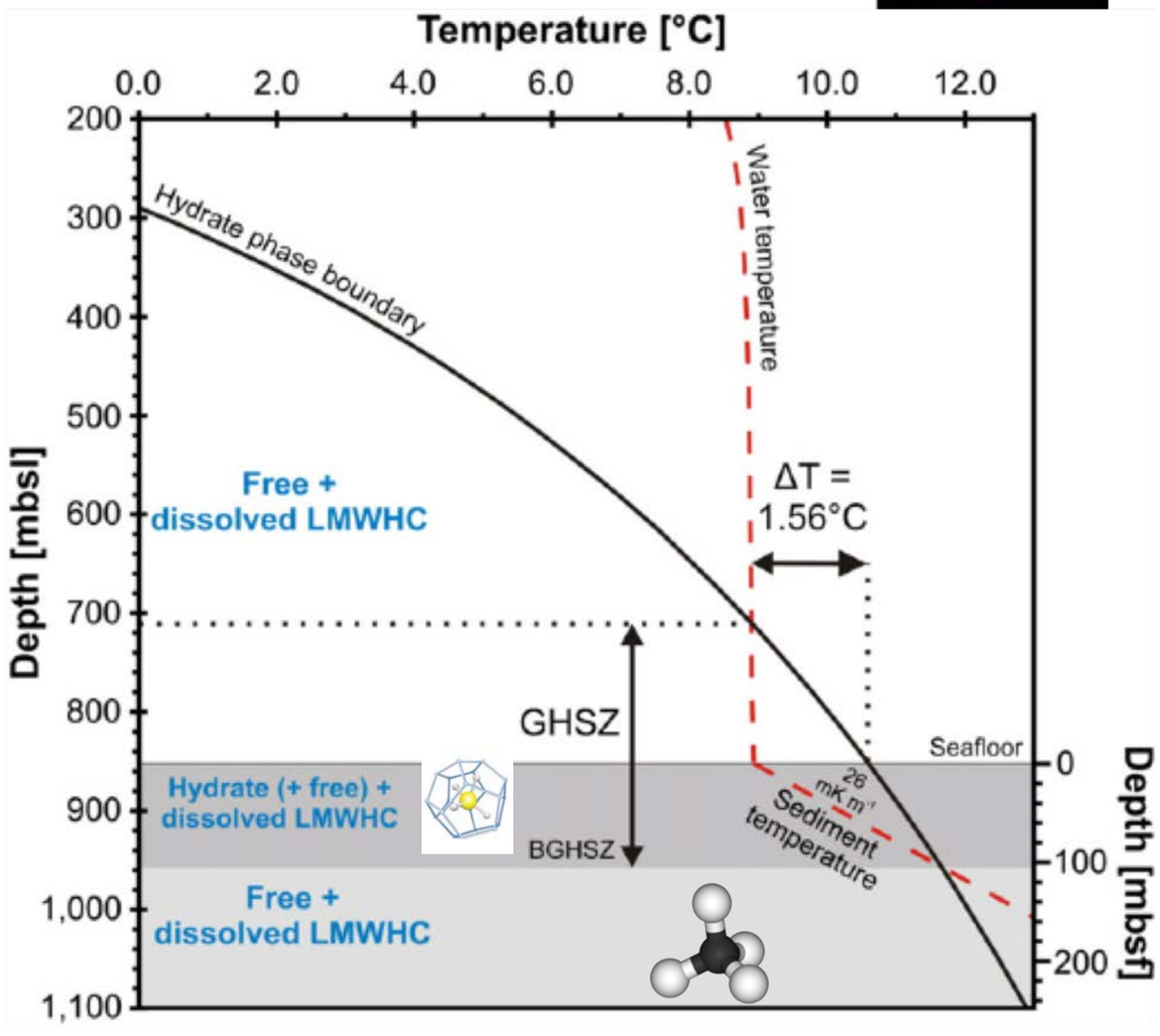
Application 2
How deep is the source of methane in hydrates?

CH_4 from mud volcanoes in Sorokin Trough Sailing et al., (2009)



Danielle Gruen, MIT

CH_4 hydrate in eastern Black Sea
Pape et al., (2009) *EPSL*
Reitz et al. (2011) *GCA*

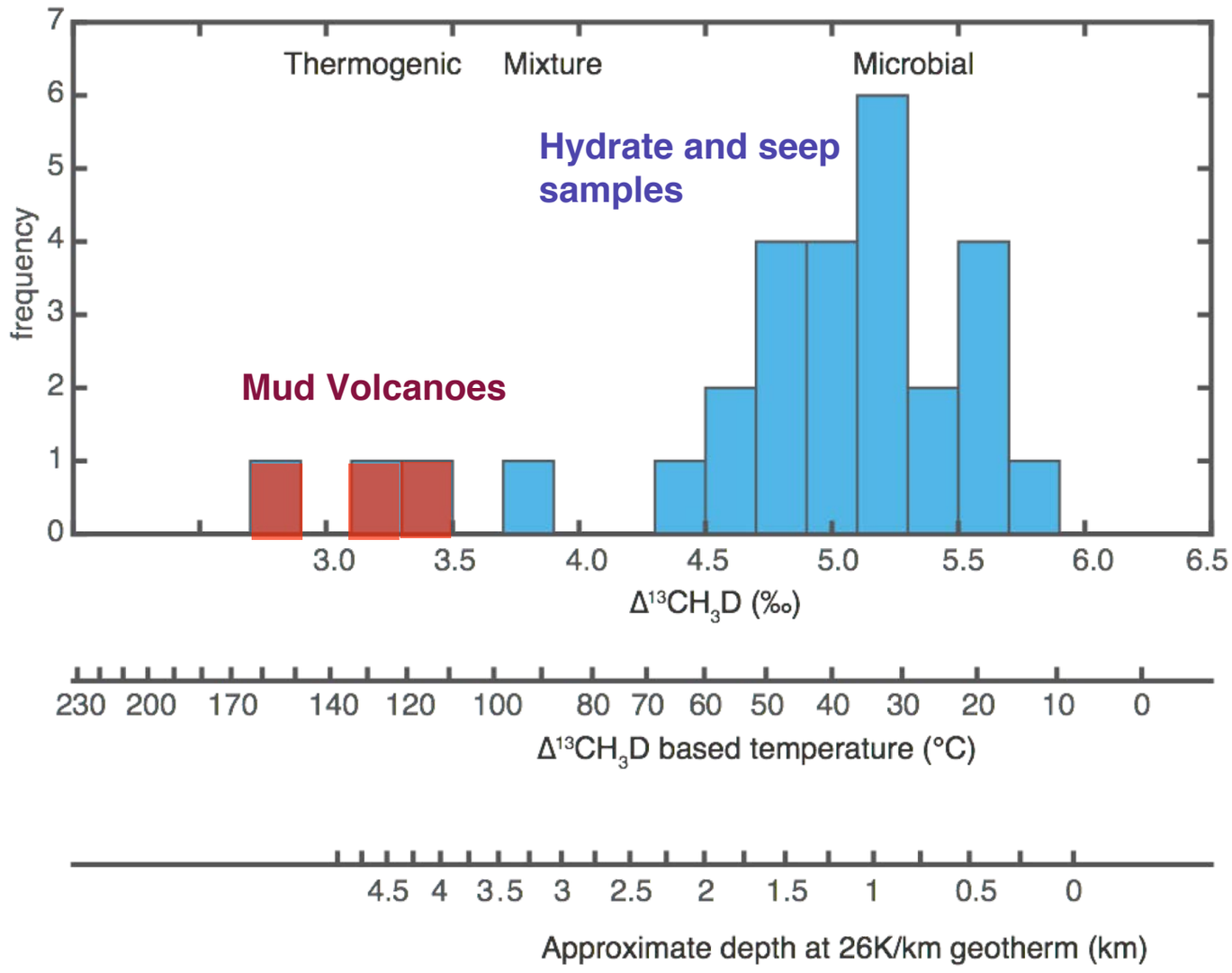


Danielle Gruen, Jen Karolewski, Shuhei Ono (MIT)
Thomas Pape, Gerhard Bohrmann (MARUM U. of Bremen).

Methane Hydrate Stability zone is upper 100 m sediments in the eastern Black Sea.

Pape et al. (2009) *EPSL*

$^{13}CH_3D$ geothermometry of methane hydrates



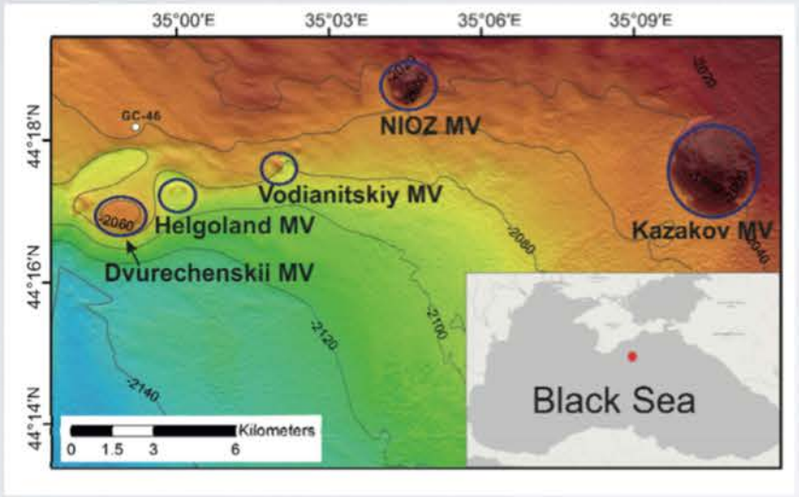
Clumped CH_4 isotopologue temperatures of marine methane hydrate, vent gas and mud volcanoes from Black Sea

Danielle Gruen, Jen Karolewski, Shuhei Ono (MIT)

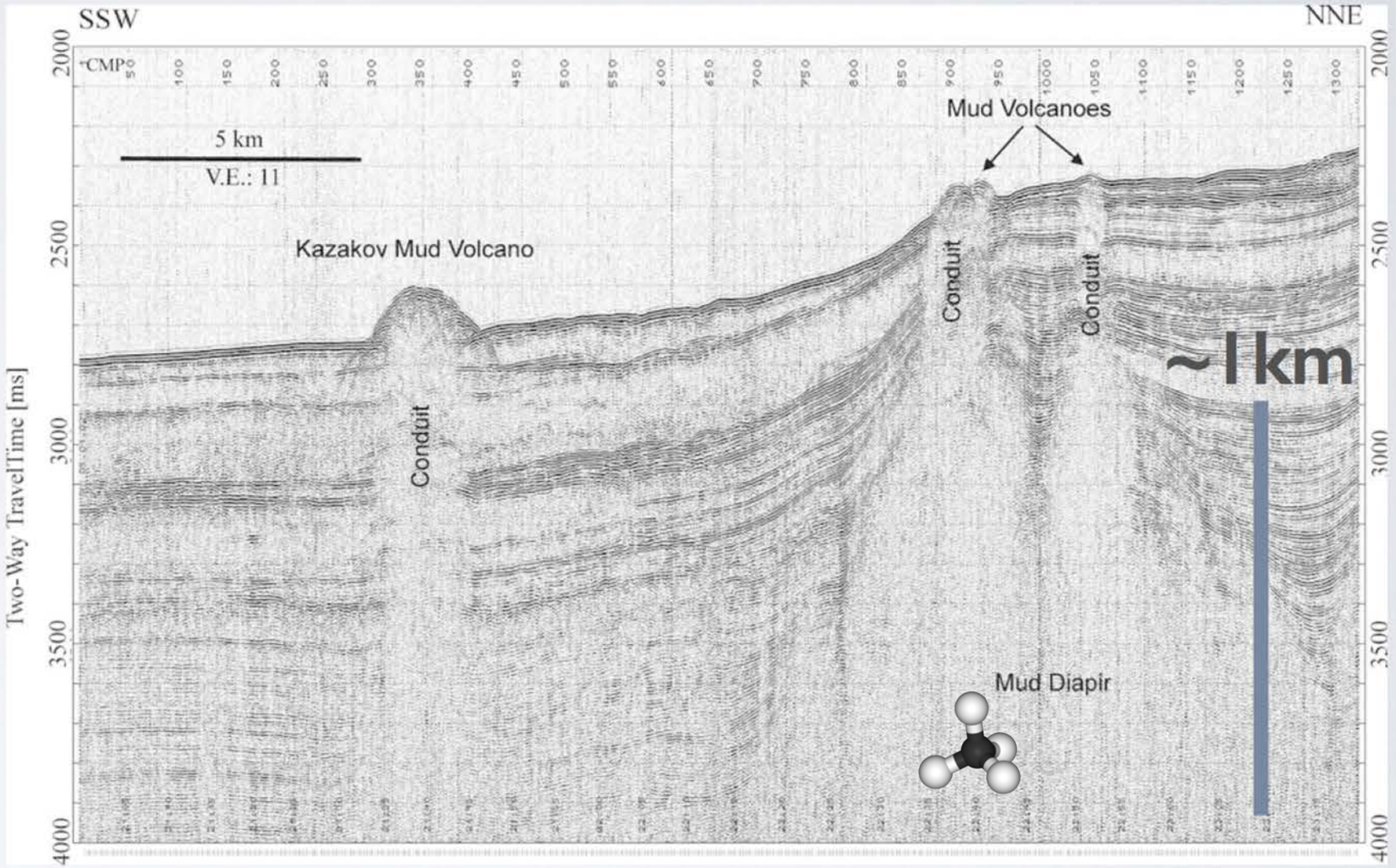
Thomas Pape, Gerhard Bohrmann (MARUM U. of Bremen).

Deep roots (>2 to 7km) for mud volcanoes in the Sorokin Trough, Black Sea

125±25°C is consistent with very deep (>4km?) methane source

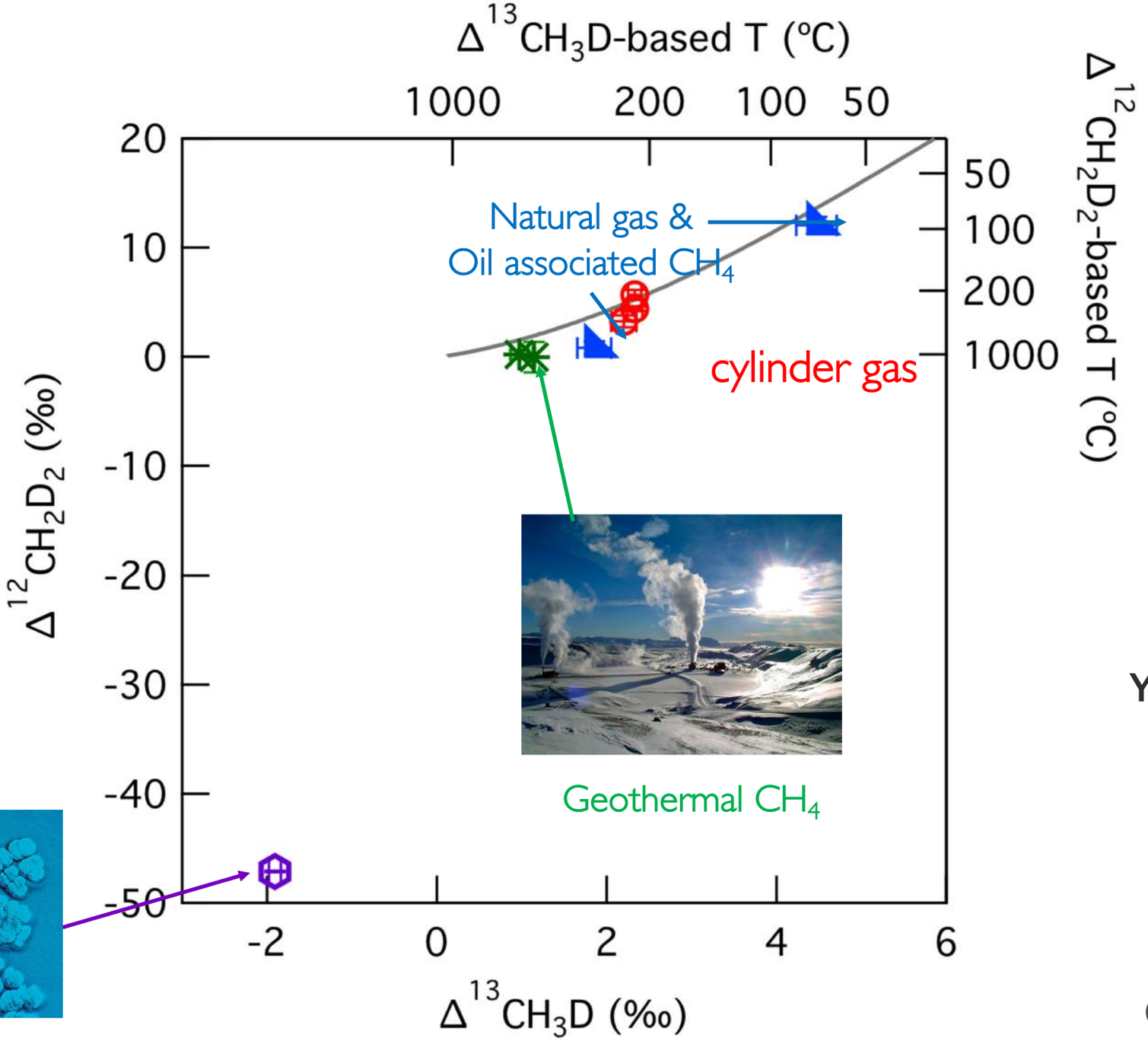


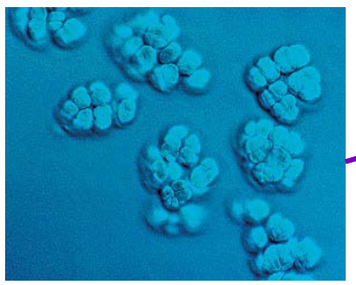
Wu, 2015



Krastel et al., 2003, *Geo-Mar Lett*

CH_2D_2 can be used to detect kinetic signals for natural samples





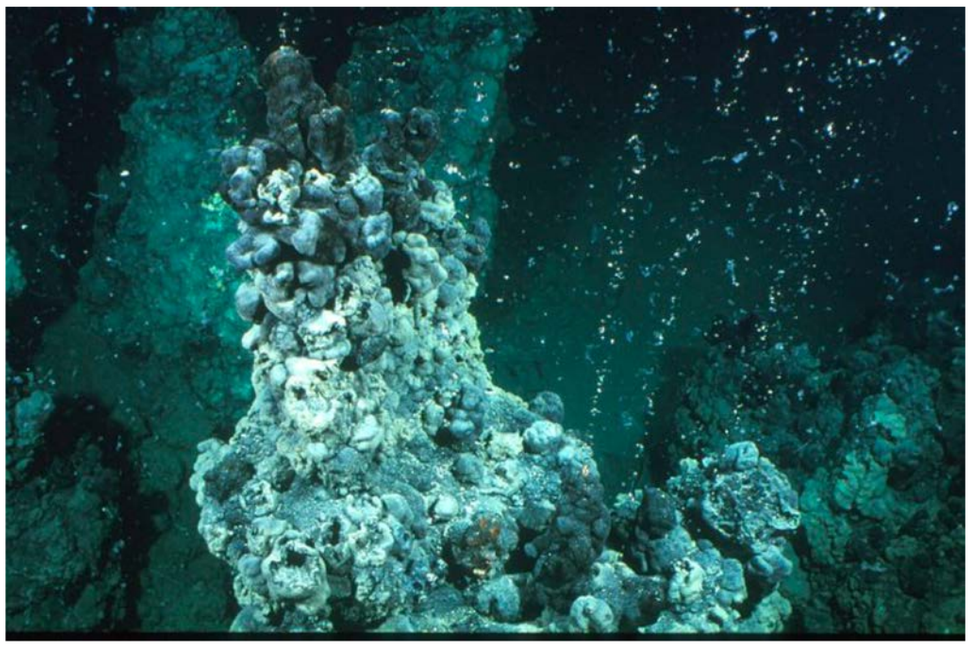
Methanogen culture

Yenny Gonzalez Ramos

ExxonMobil

Gonzales et al., 2019
also Young et al., 2017

Summary and prospects



Methane seep in Black Sea
From National Academy of Sciences

- Precise measurements of the methane isotopologue, $^{13}CH_3D$, can be used to infer the generation temperature.

- This tool was used to trace methane sources in subsurface; methane often migrates upward over kms.

Acknowledgements

Ono lab 2019

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