How clumped isotopes drive a deeper understanding of petrochemical processes

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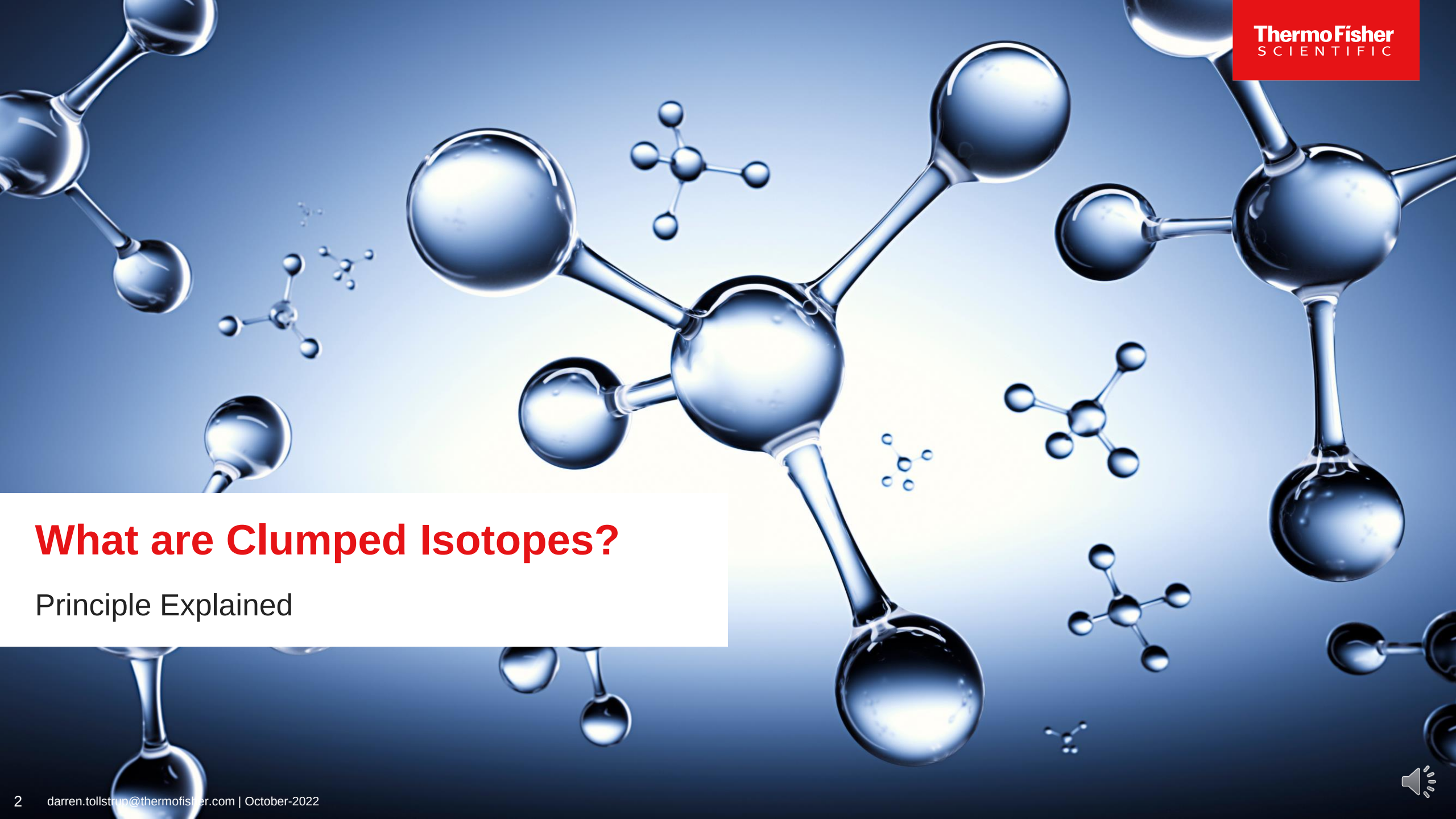
October 12th, 2022

The world leader in serving science



What are Clumped Isotopes?

Principle Explained

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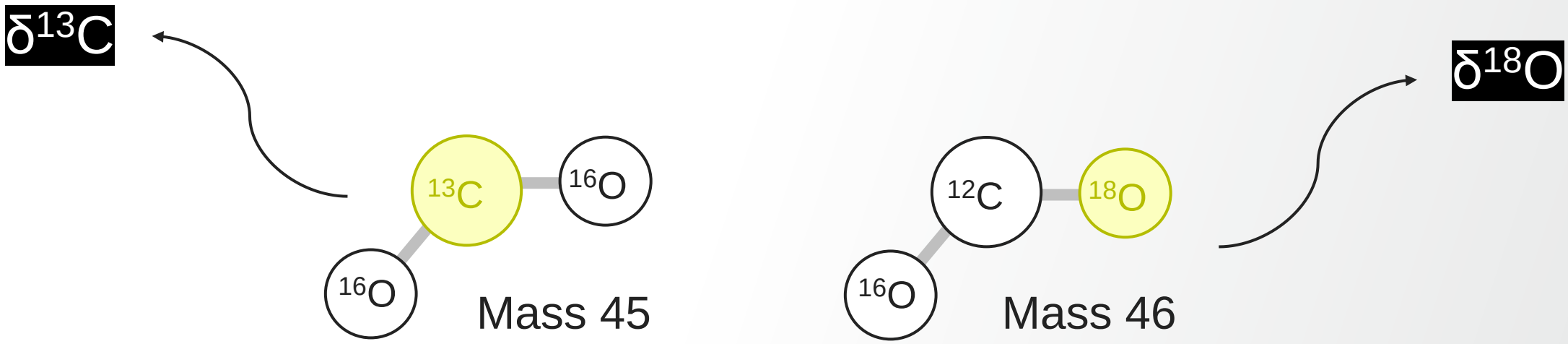
“Classical” Isotopes of CO_2: 44, 45, 46



Single substitution

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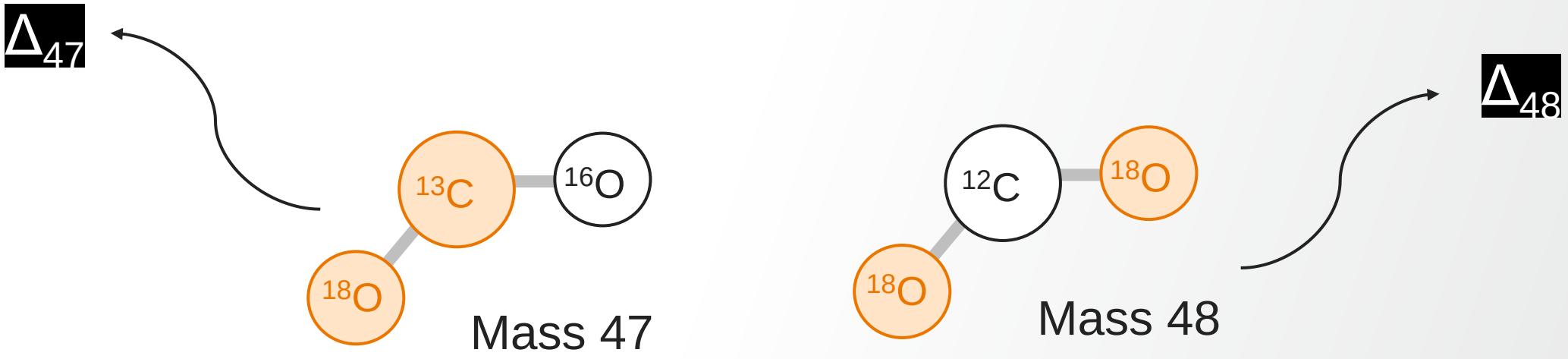
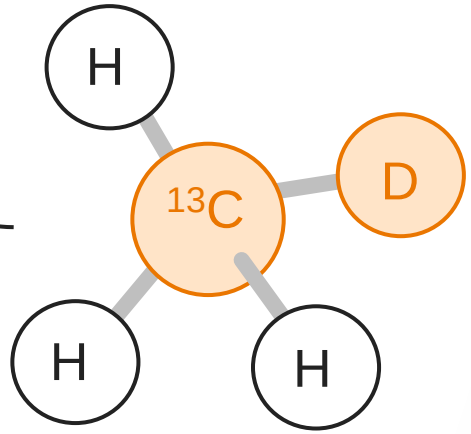
“Clumped” Isotopes of CO_2: 47, 48



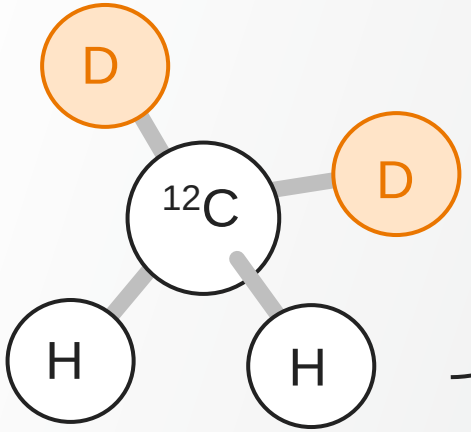
Double substitution

“Clumped” Isotopes of CH_4

$\Delta^{13}CH_3D$



Mass 18



Mass 18

$\Delta^{12}CH_2D_2$

Double substitution

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How are “Clumped Isotopes” useful?

- **The degree of “clumping”** of heavy isotopes in molecules is solely temperature dependent in thermodynamic equilibrium
- **Deviation from equilibrium clumping** indicates kinetic fractionation processes or mixing with non-equilibrated sources.
- **Clumped isotopes add new dimensions** to the classical isotope signatures and open new dimensions in for instance source apportionment and process identification.

Analytical Setup

Thermo Scientific™ 253 Plus™ 10 kV IRMS
Thermo Scientific™ Kiel IV Carbonate Device

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software

Thermo Scientific™ Ultra™ HR-IRMS

Clumped Carbonate Analysis

Clumped Methane Analysis

Clumped Carbonate

Principle and Applications

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Clumped Carbonate: Typical Samples

Limestone

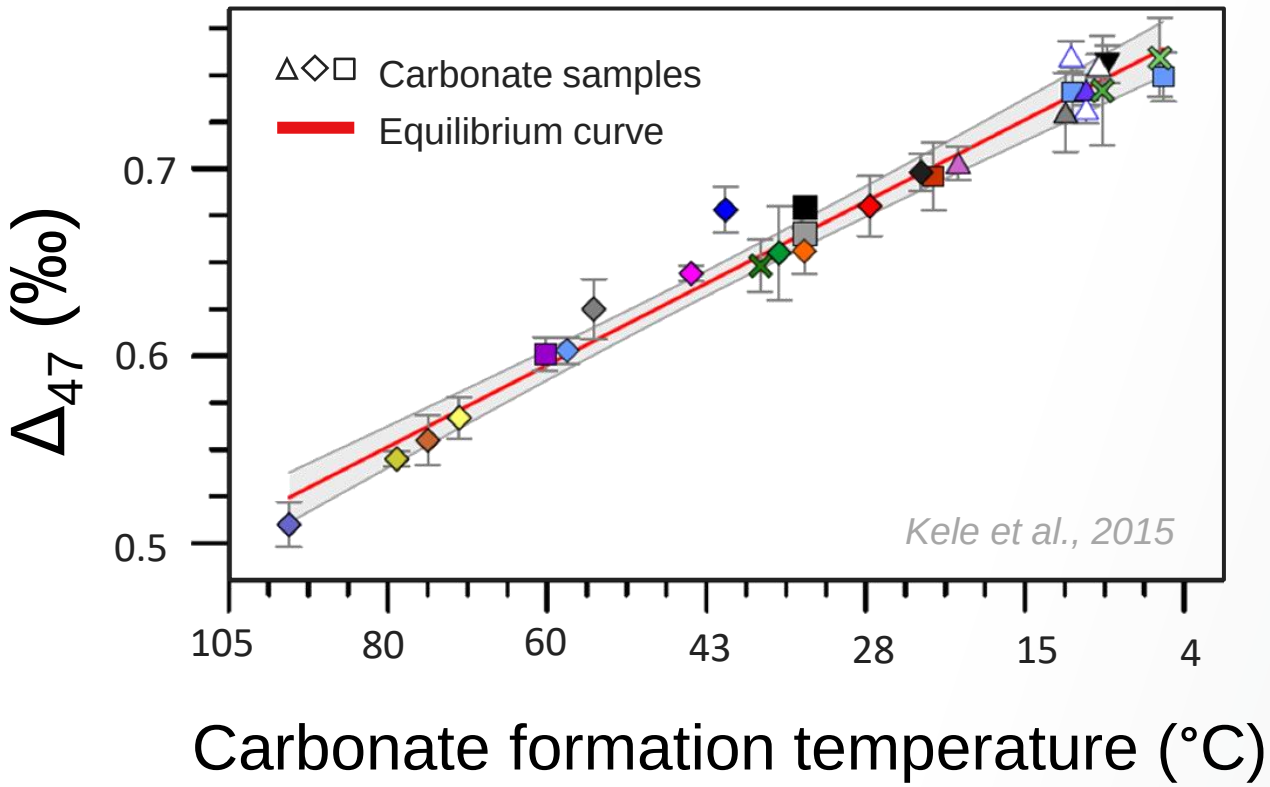
Forminifera

Speleothem

Corals

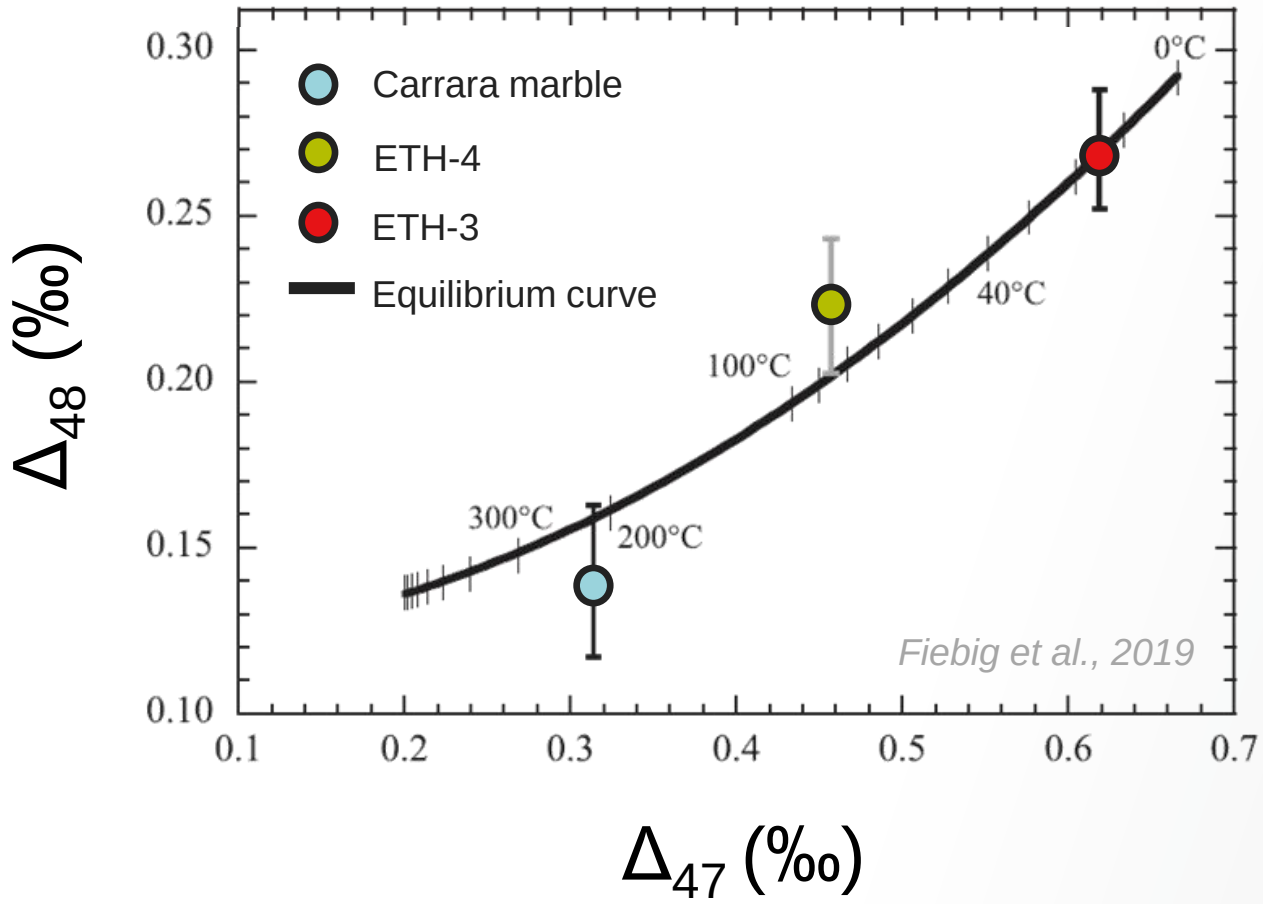
Travertine

Clumped Carbonate: Thermometry (Δ_{47})



"Δ_{47} data of travertines show an excellent correlation with temperature […] and our calibration can be used to derive the deposition temperature of ancient carbonate deposits." *Kele et al., 2015*

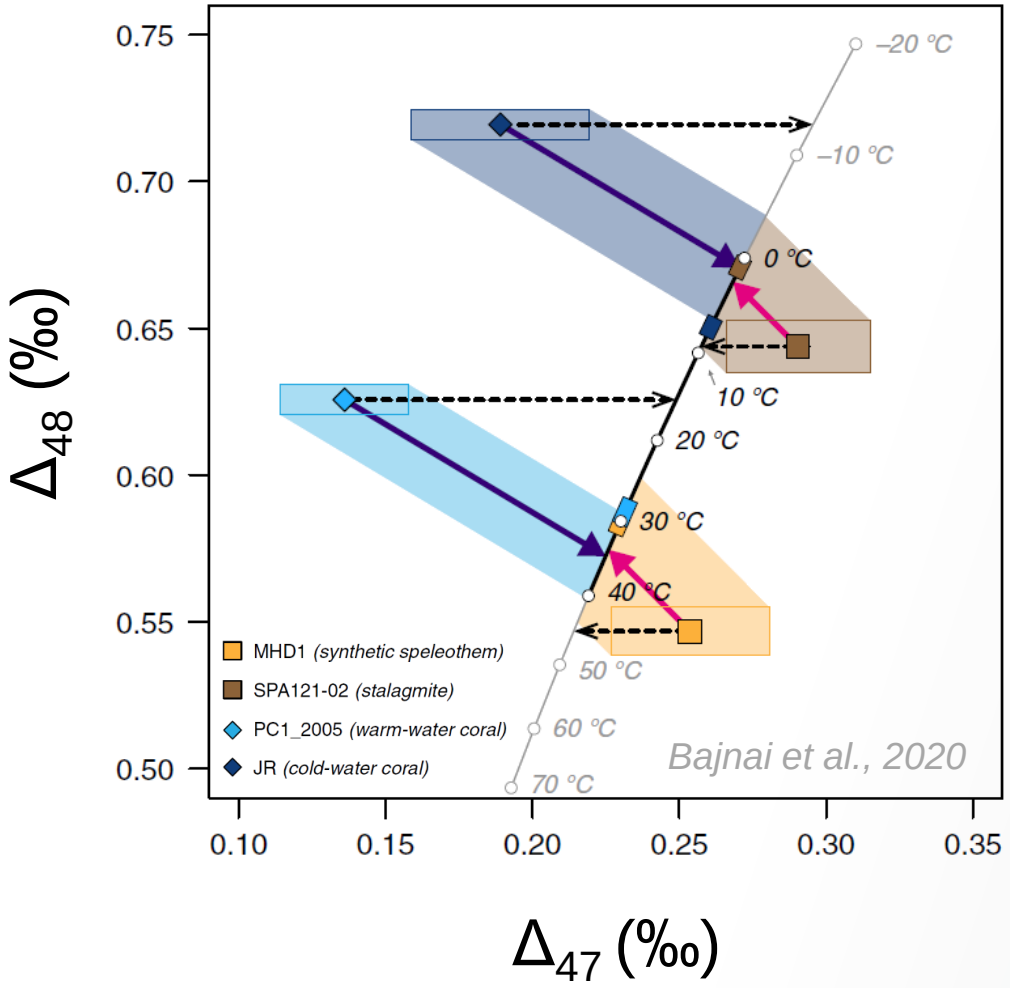
Dual Clumped Carbonate Thermometry (Δ_{47} - Δ_{48})



"Combined analysis of the abundances of mass 47 and mass 48 isotopologues in CO_2 […] has excellent potential for the determination of accurate and highly precise paleotemperatures as well as for the identification of rate-limiting kinetic processes involved in biomineralization."

Fiebig et al., 2019

Deciphering Kinetic Biases



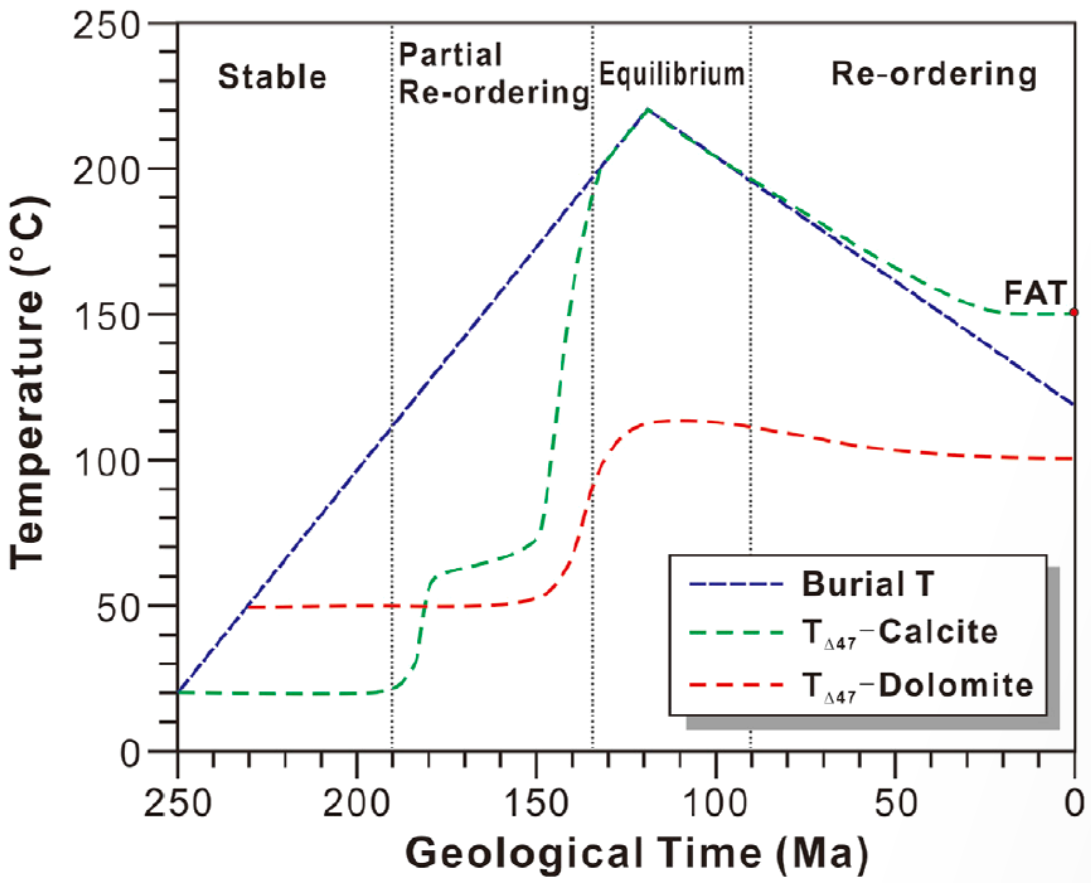
"We show that dual clumped isotope thermometry can achieve reliable palaeotemperature reconstructions, devoid of kinetic bias."

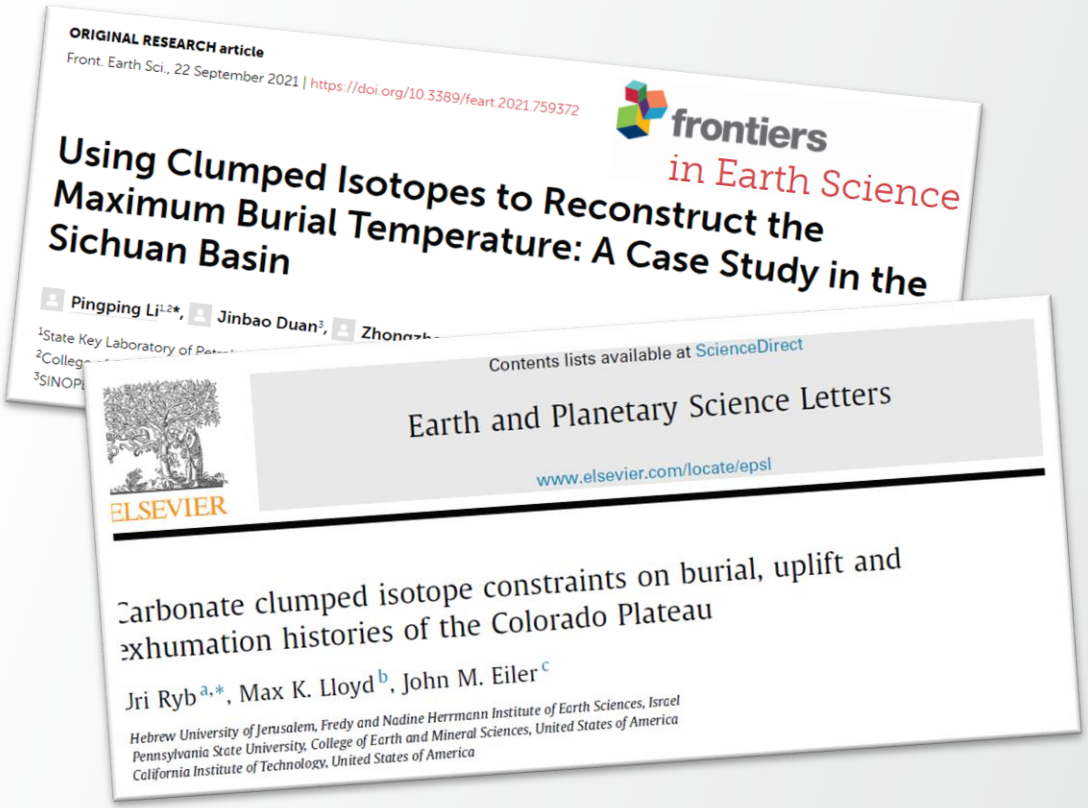
Bajnai et al., 2020

Temperature based on dual clumped isotope thermometry with 2 SE*

Temperature based on Δ_{47} only

Reconstructing Maximum Burial Temperature





ORIGINAL RESEARCH article
Front. Earth Sci., 22 September 2021 | https://doi.org/10.3389/feart.2021.759372

frontiers in Earth Science

Using Clumped Isotopes to Reconstruct the Maximum Burial Temperature: A Case Study in the Sichuan Basin

Pingping Li[1,2]*, Jinbao Duan[3], Zhongz...

[1]State Key Laboratory of Pet...
[2]Colleg...
[3]SINOP...

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

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ELSEVIER

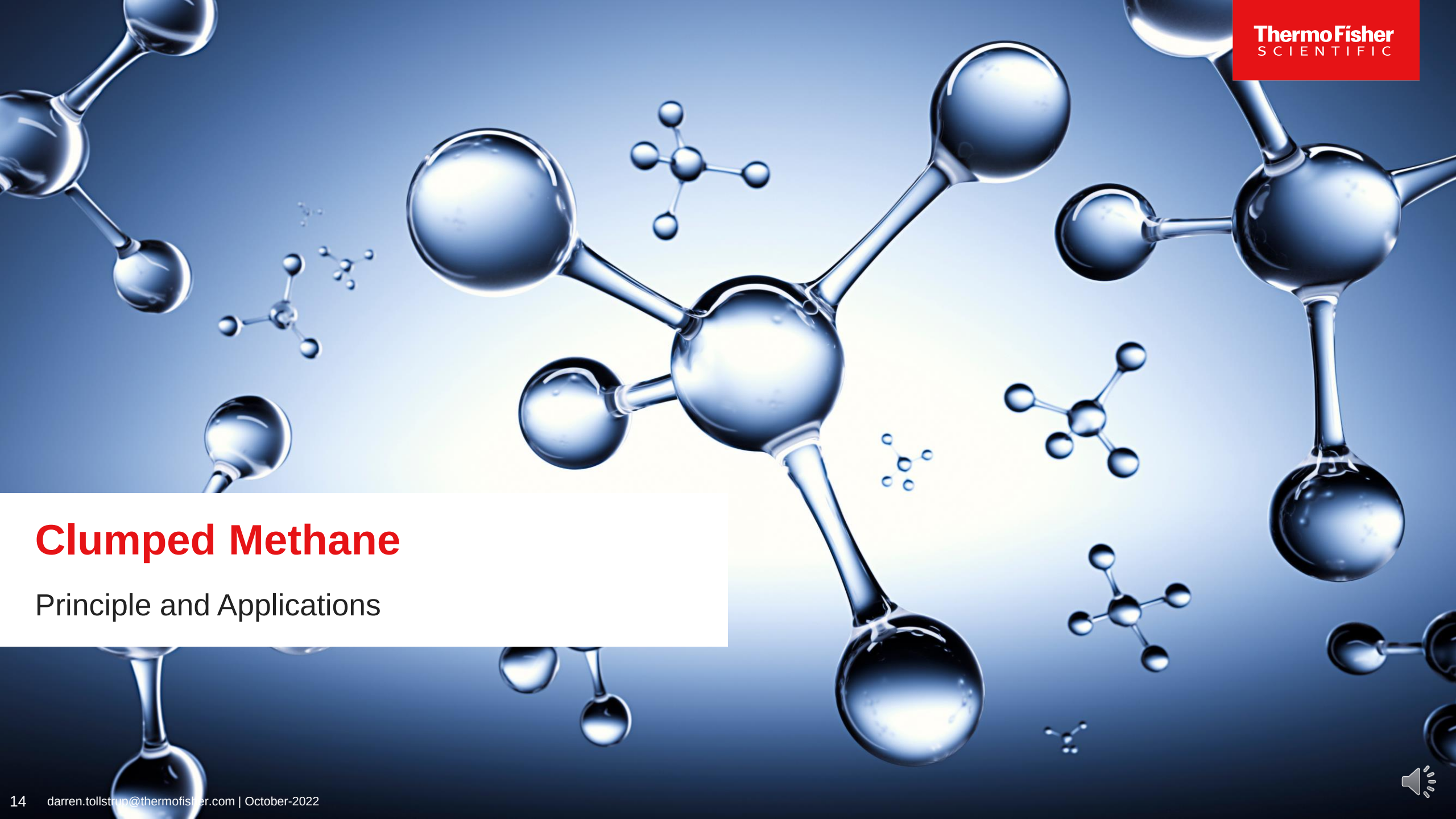
Carbonate clumped isotope constraints on burial, uplift and exhumation histories of the Colorado Plateau

Jri Ryb[a,*], Max K. Lloyd[b], John M. Eiler[c]

[a]Hebrew University of Jerusalem, Fredy and Nadine Herrmann Institute of Earth Sciences, Israel
[b]Pennsylvania State University, College of Earth and Mineral Sciences, United States of America
[c]California Institute of Technology, United States of America

"The case study [...] suggests that Δ47 can be used to reconstruct the MBT of ancient carbonate strata lacking vitrinite and detrital zircon data."

Li et al. (2021)



Clumped Methane

Principle and Applications

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Clumped Methane: Typical Samples

Wellhead gas

Shale gas

Gas hydrates

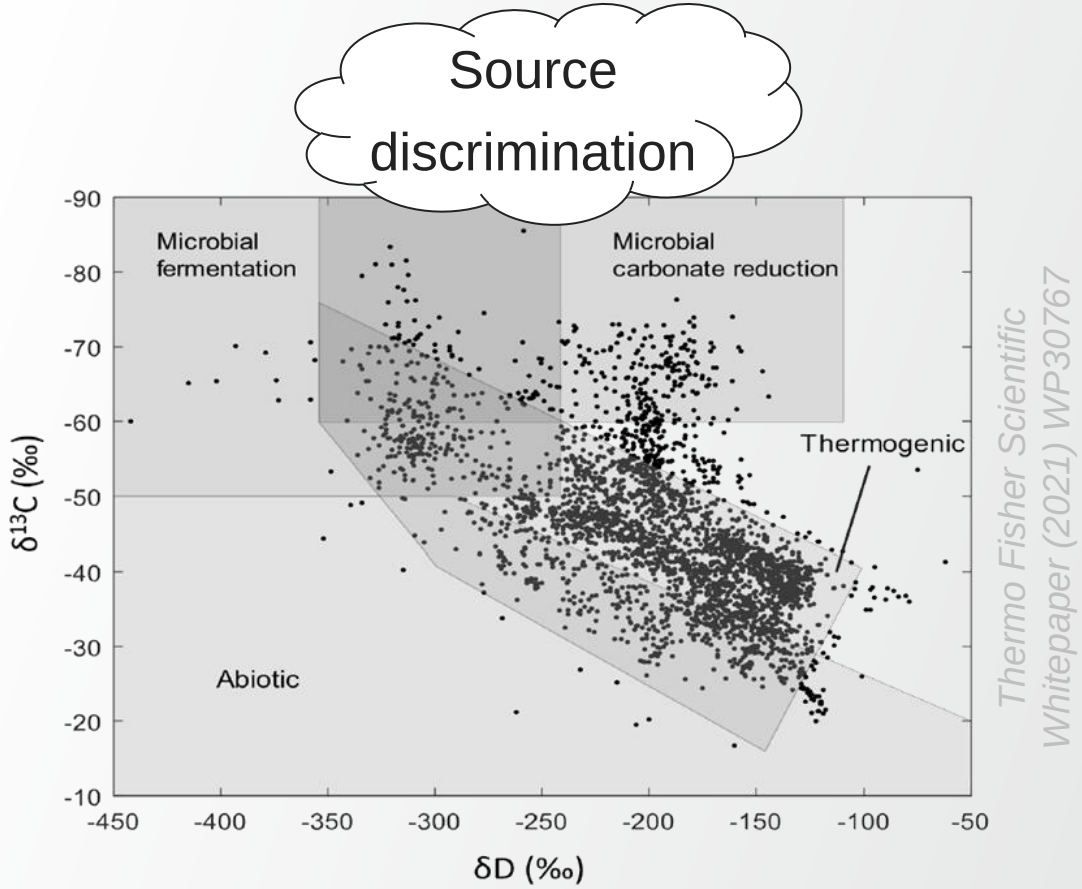
Seeps

Surface vents

Conventional Methane Analysis

Thermo Scientific™
EA Isolink™ IRMS System

Thermo Scientific™
GC Isolink™ IRMS System



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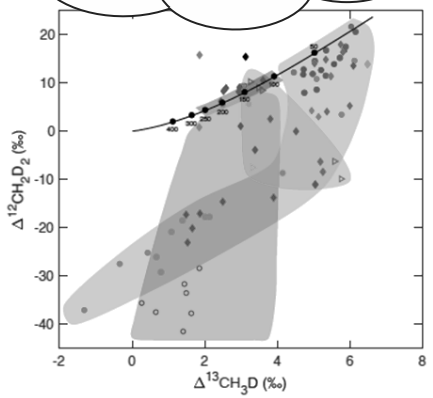
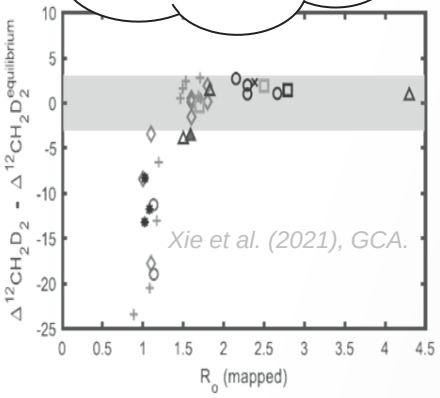
Sample → Combustion / Pyrolysis → CO_2 / H_2 → $\delta^{13}C$ / δD

Clumped Methane Analysis

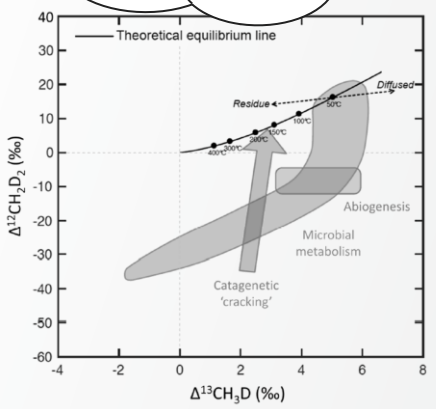
Refined source discrimination



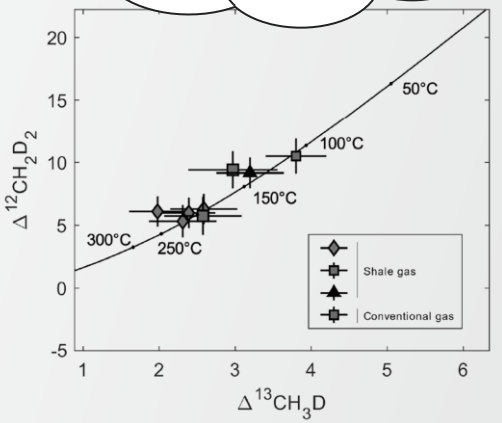
Assessing maturity



Process identification



Thermometry

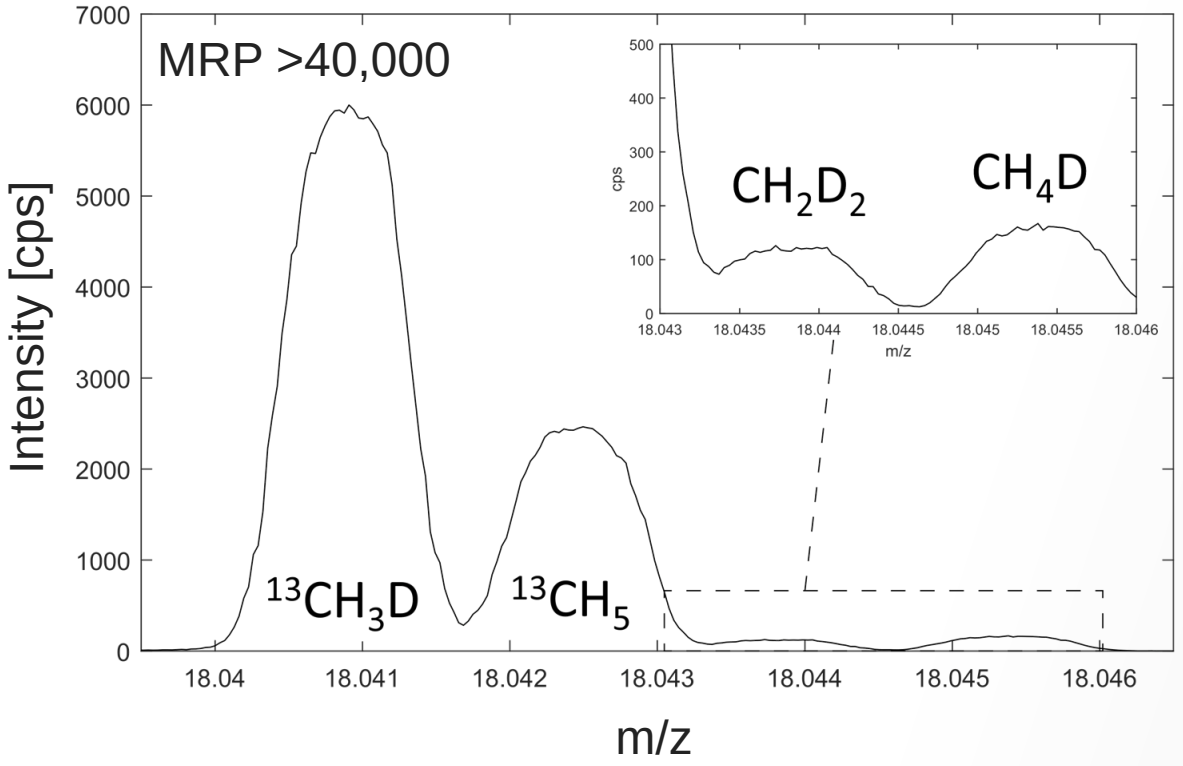


Thermo Scientific™ Ultra™ HR-IRMS

Sample → Prepline (GC / Cryostat) → CH_4 → $\delta^{13}C$ / δD $\Delta^{13}CH_3D$ / $\Delta^{12}CH_2D_2$

Thermo Fisher Scientific White Paper (2021) WP30767

The Benefit of High Resolution IRMS



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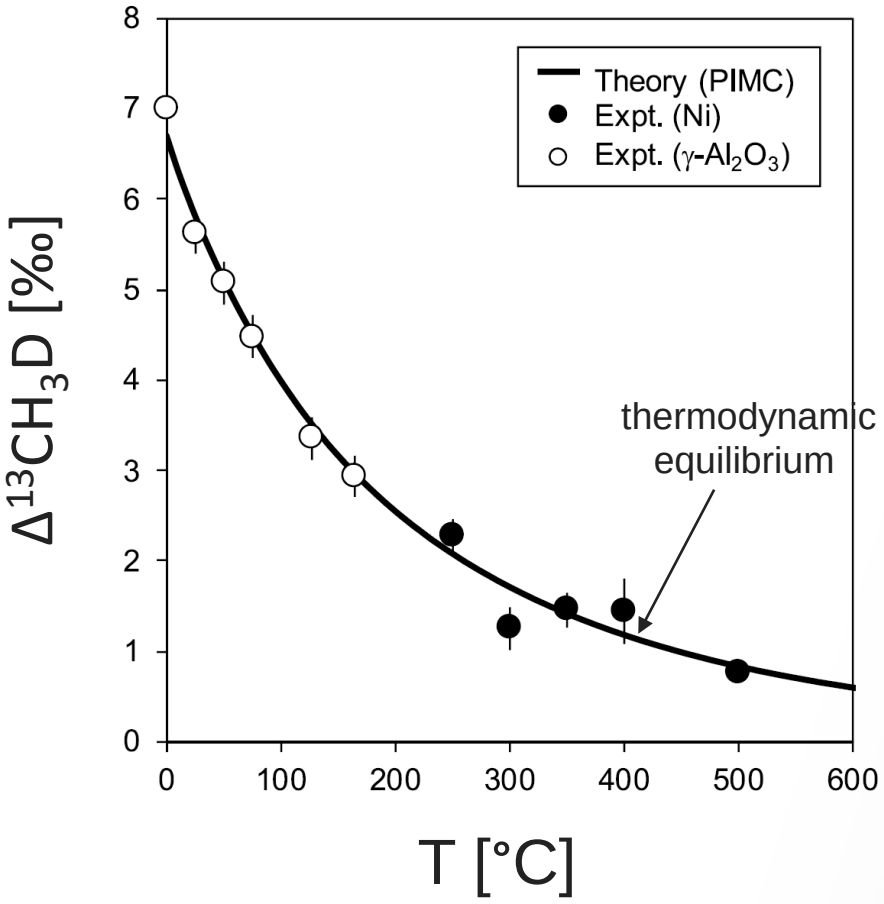
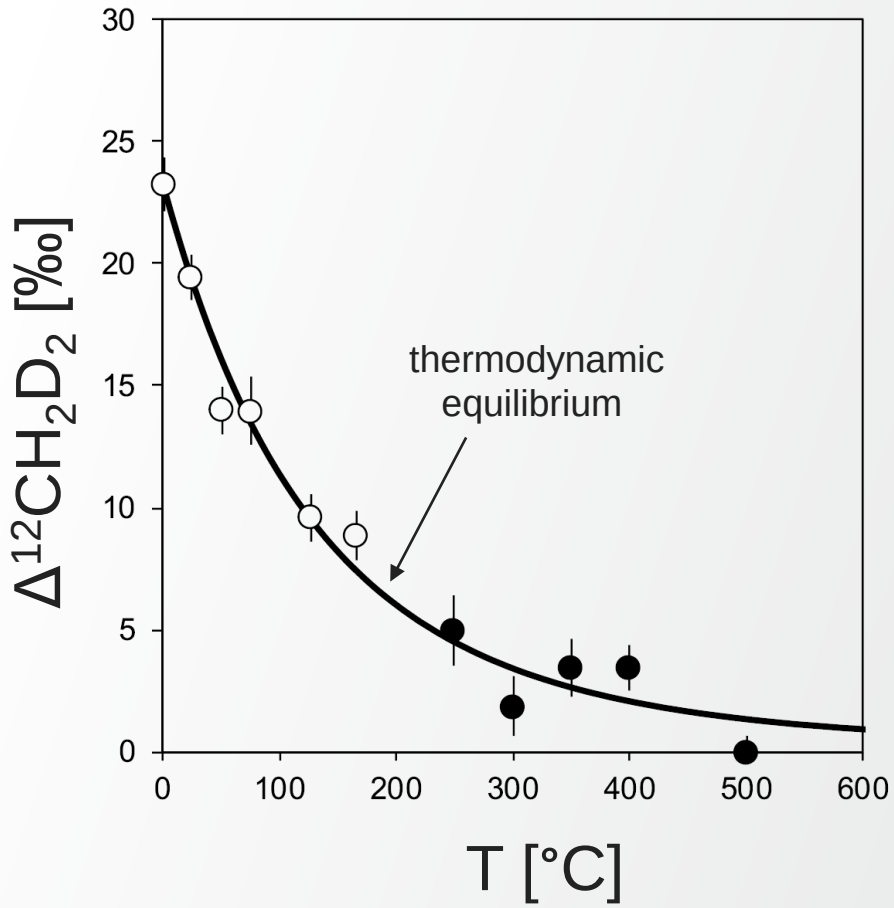
HR-IRMS enables full peak separation of clumped methane isotopologues ($^{13}CH_3D$ and $^{12}CH_2D_2$) from another and from ionization by-products ($^{13}CH_5$ and CH_4D).

Clumped Methane: Geothermometry

Experiments

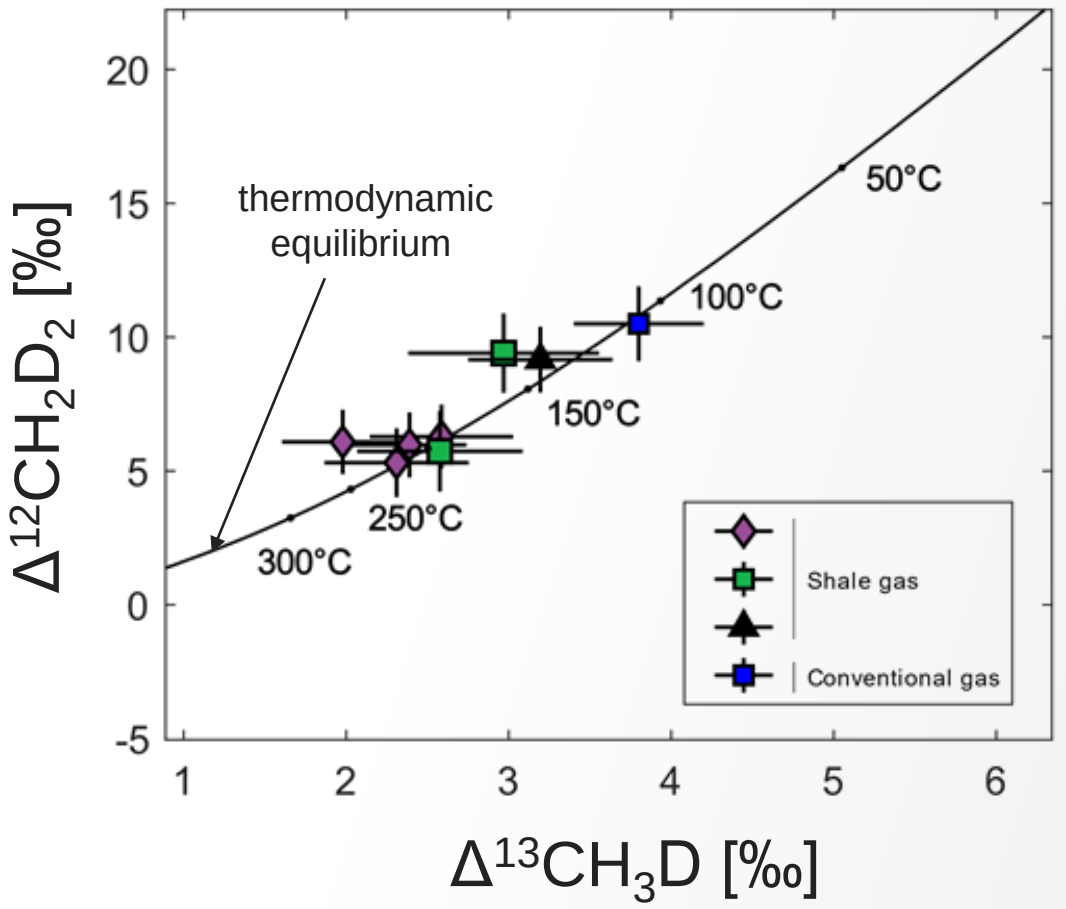




Eldridge et al. (2019), ACS Earth Space Chem.

Clumped Methane: Geothermometry

Natural samples



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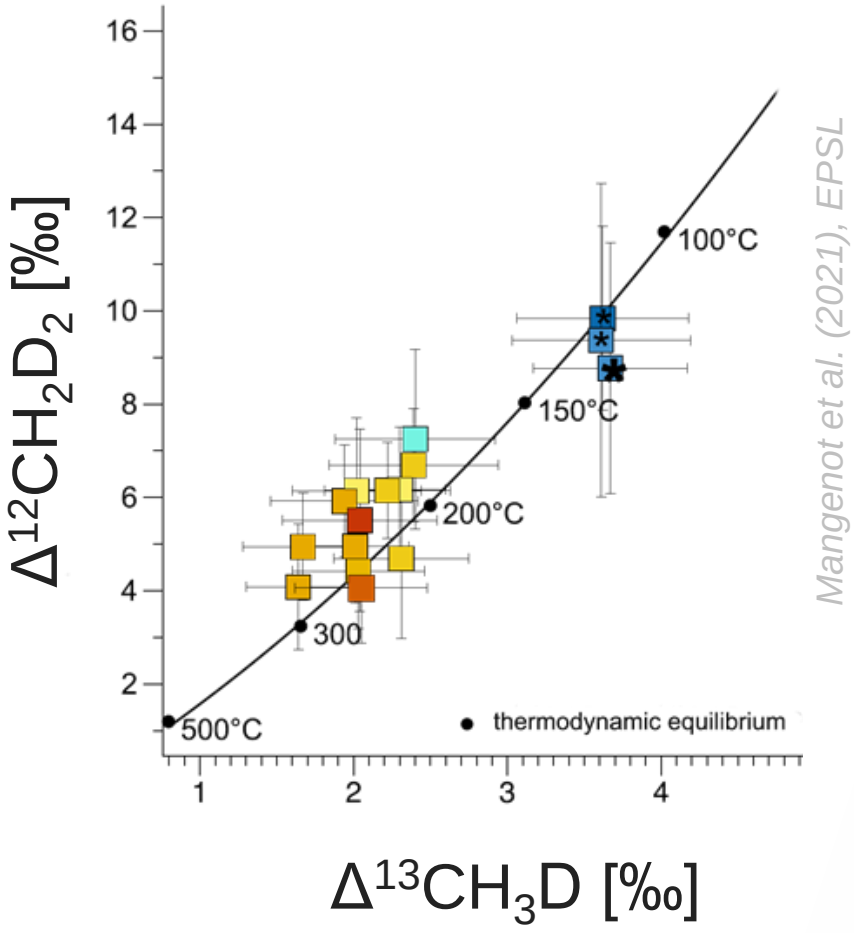
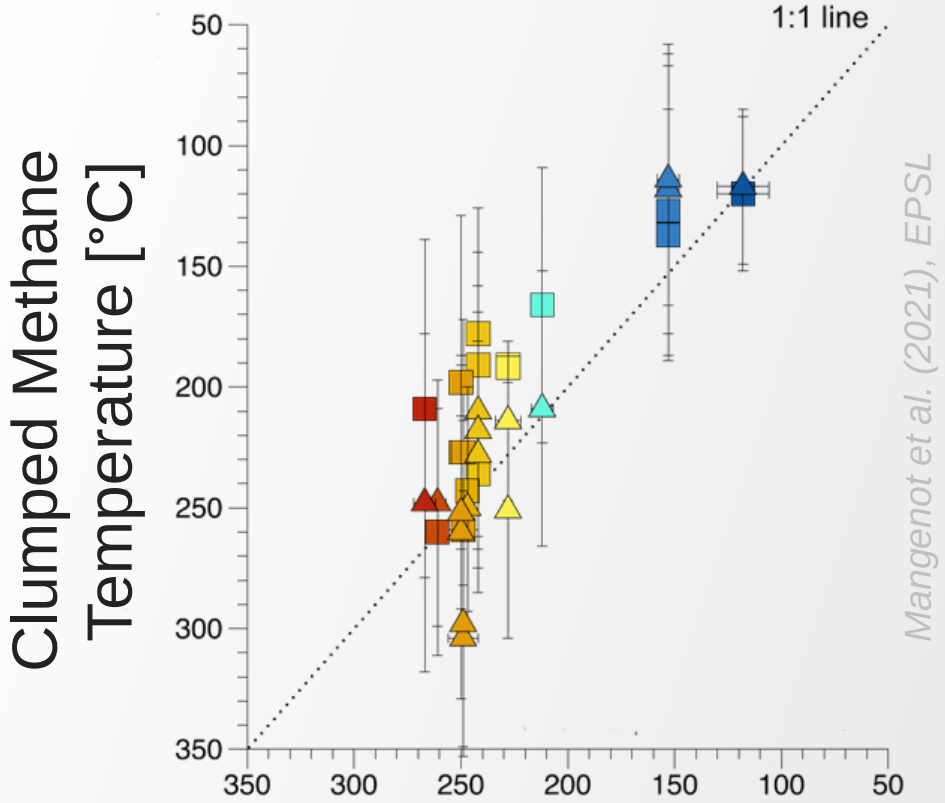
Clumped Methane: Geothermometry

Clumped Methane



Fluid Inclusions



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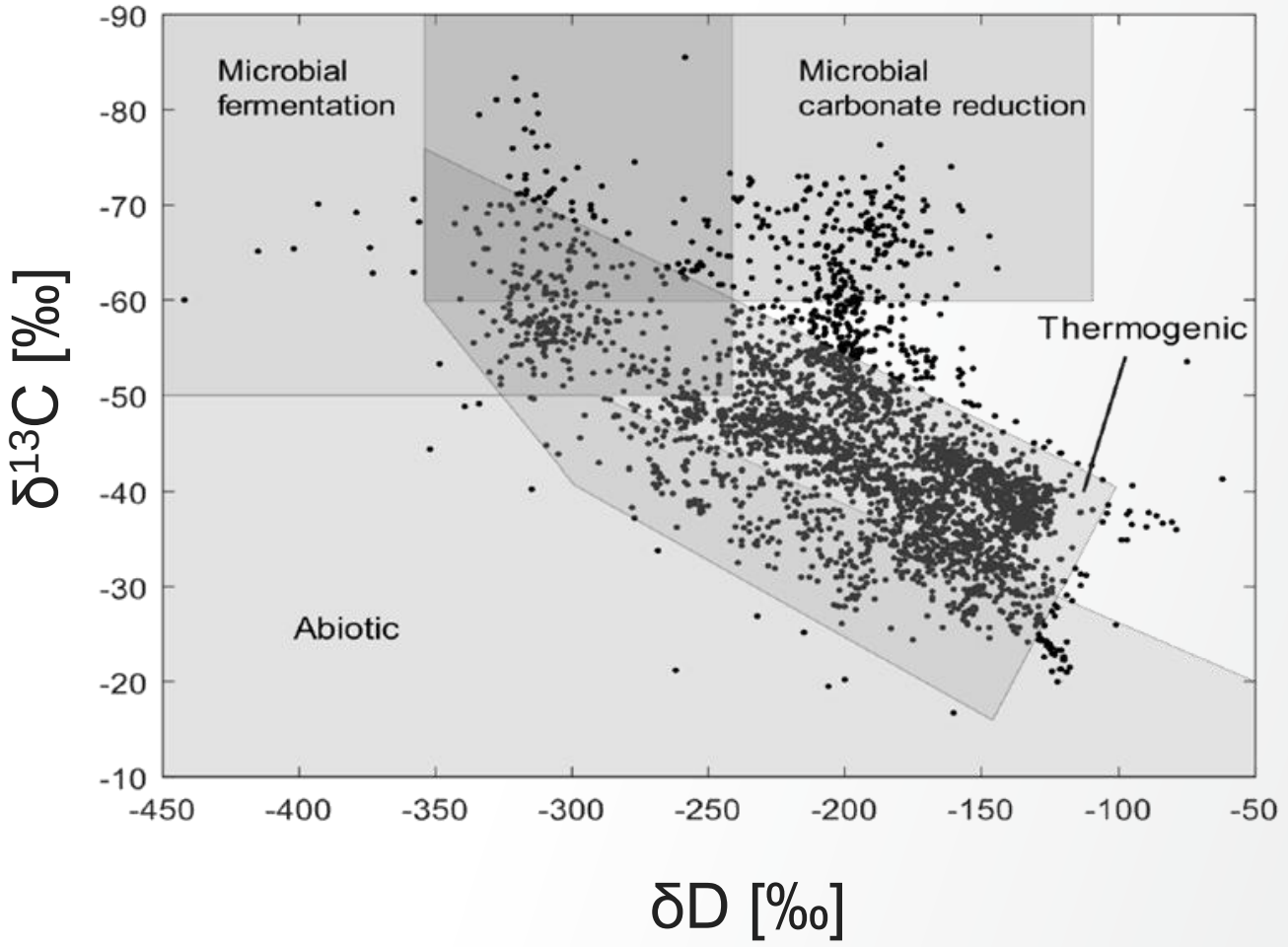
Clumped Methane: Source Discrimination



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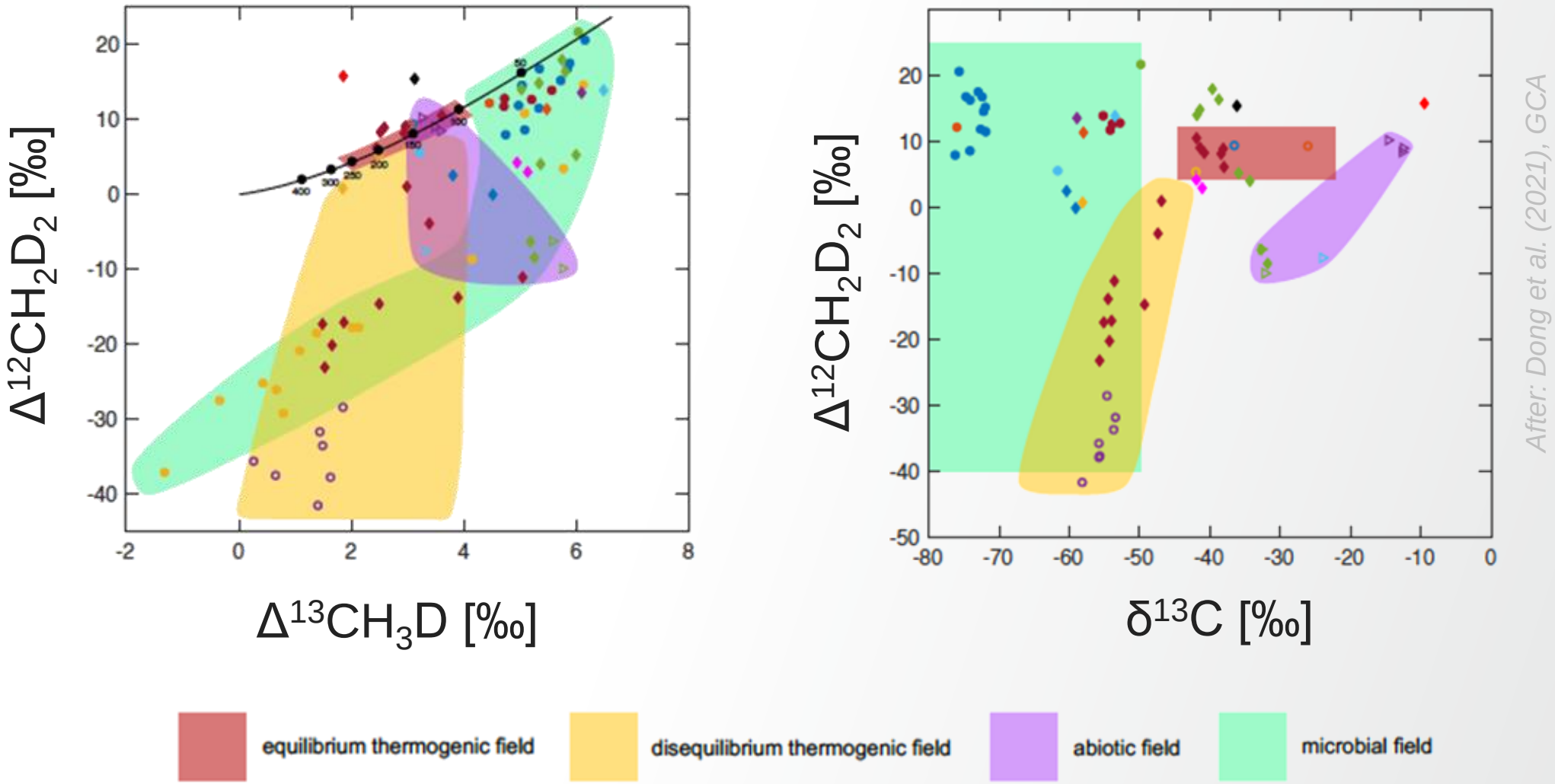
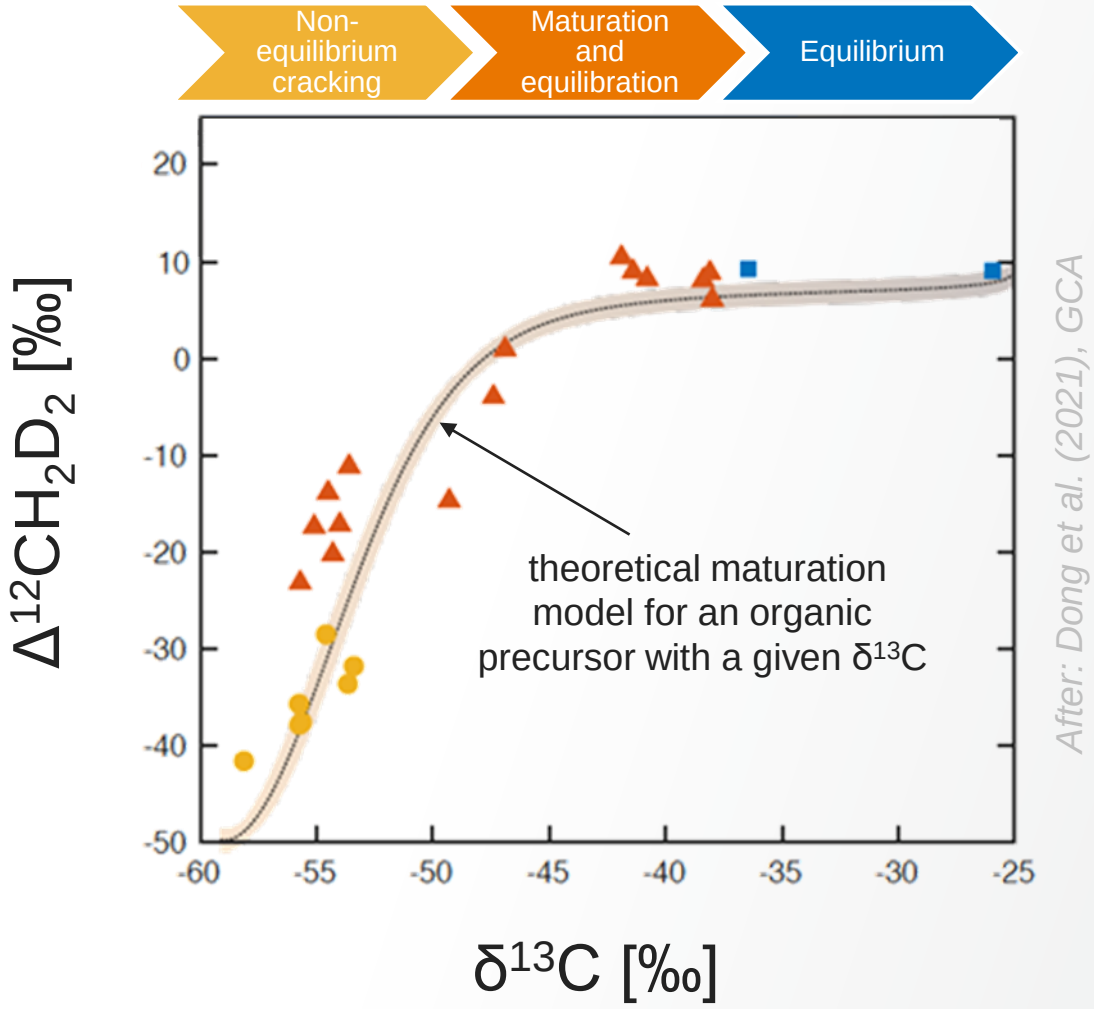
Clumped Methane: Source Discrimination

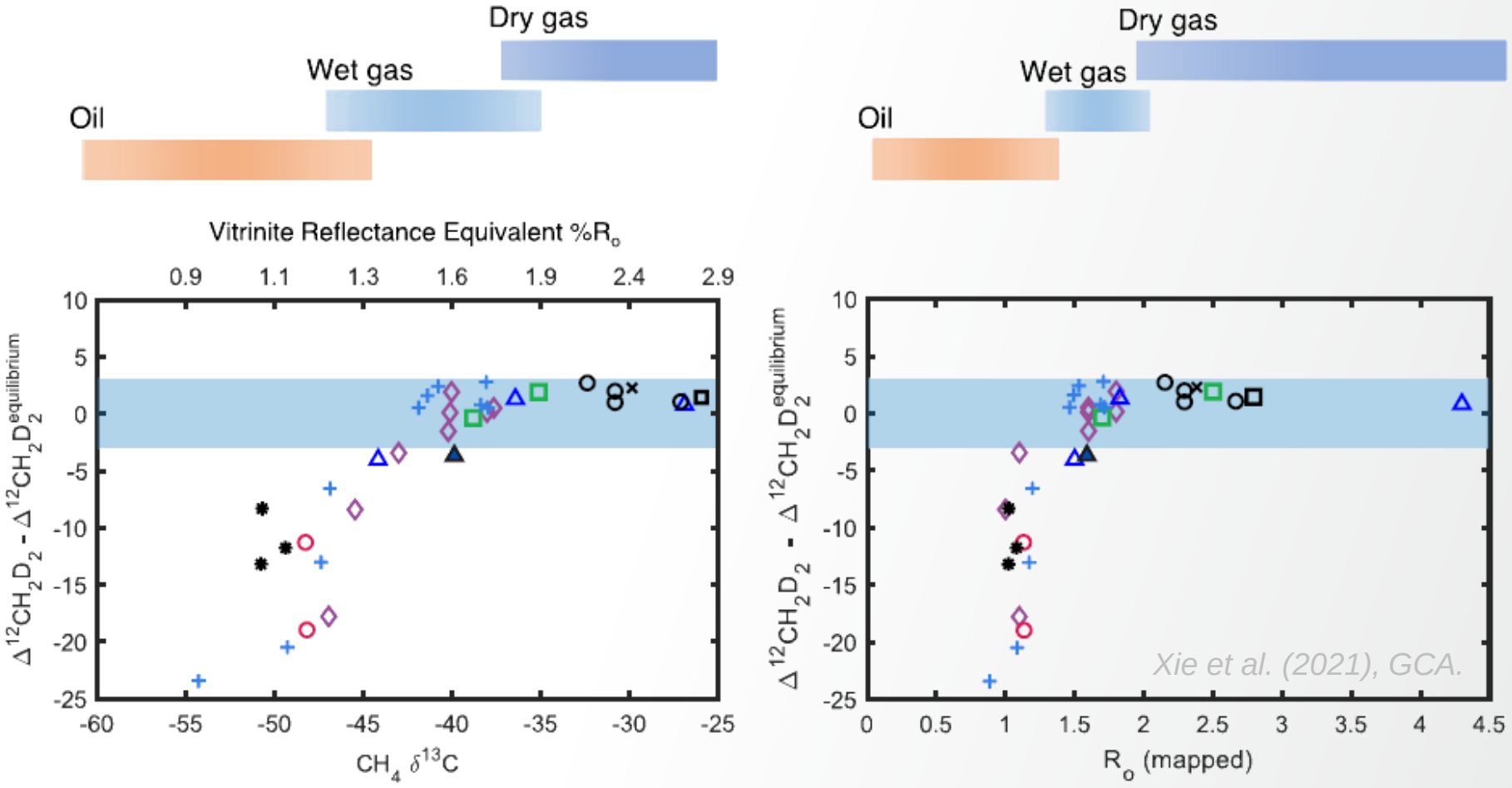


After: Dong et al. (2021), GCA

Clumped Methane: Identification of Formation Mechanisms



Clumped Methane: Assessing Maturity



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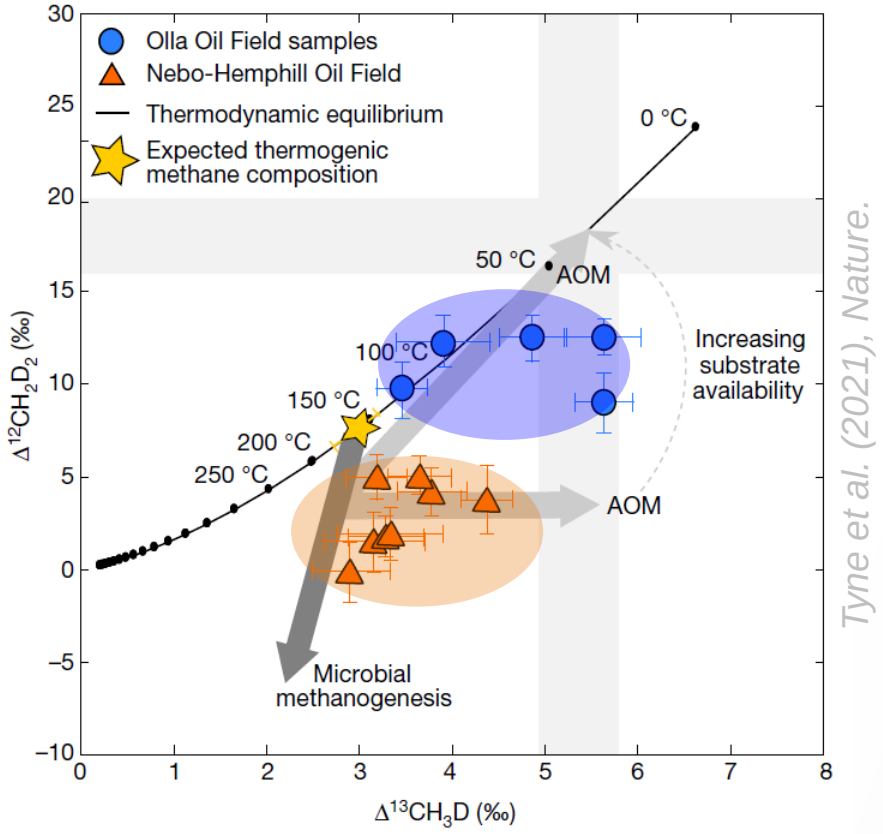
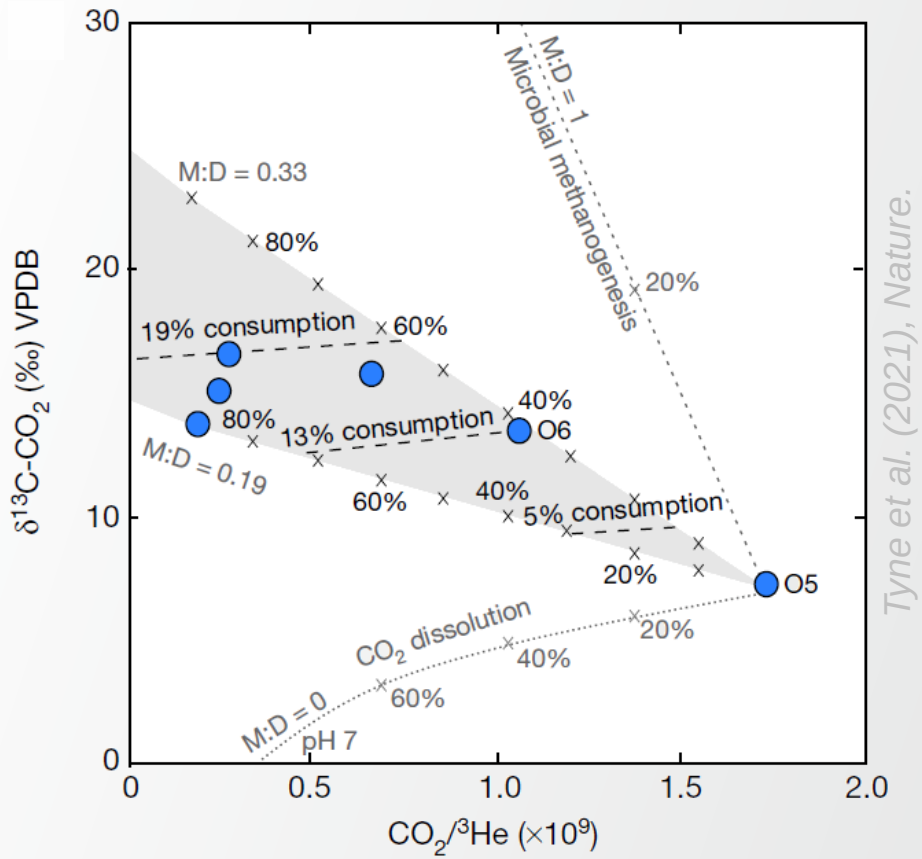
Clumped Methane: Safer Carbon Capture and Storage

Clumped Methane



Tyne et al. (2021), Nature.

$\delta^{13}C$ vs. $CO_2/^3He$



Tyne et al. (2021), Nature.

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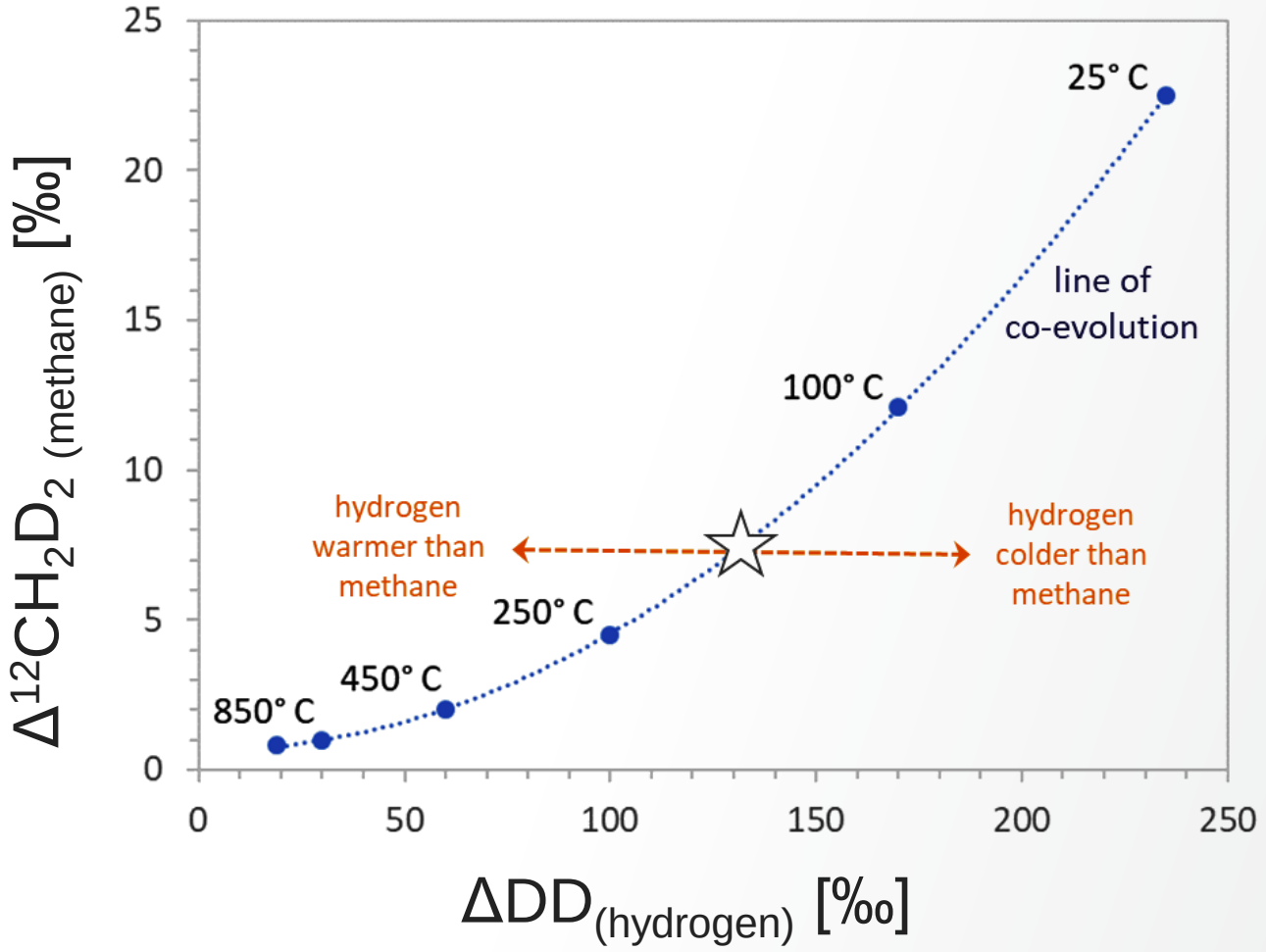
Future Perspectives: Clumped Hydrogen



Data from: Popa et al. (2019), RCMS, Eldridge et al. (2019) ACS Earth Space Chem

Clumped Hydrogen

Principle and Application Fields

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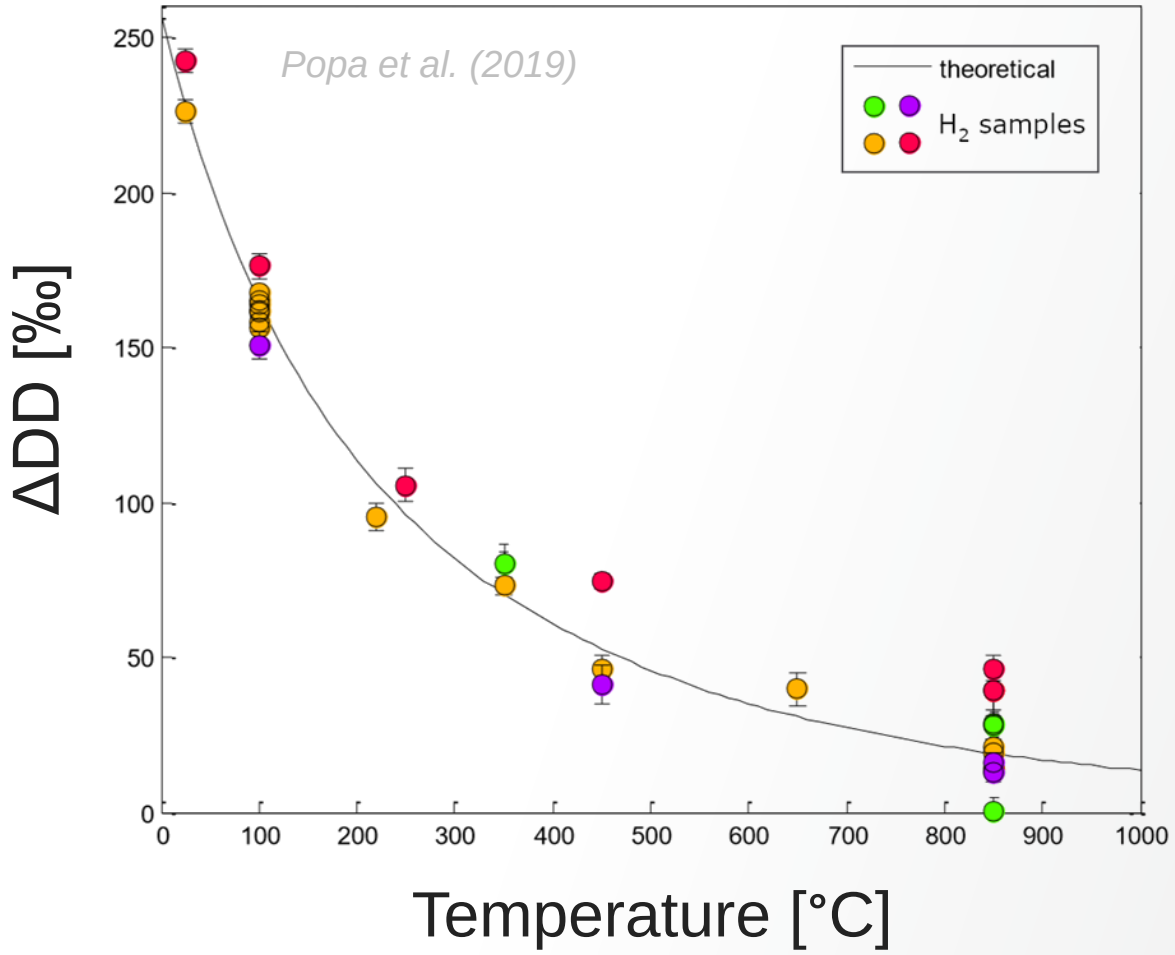
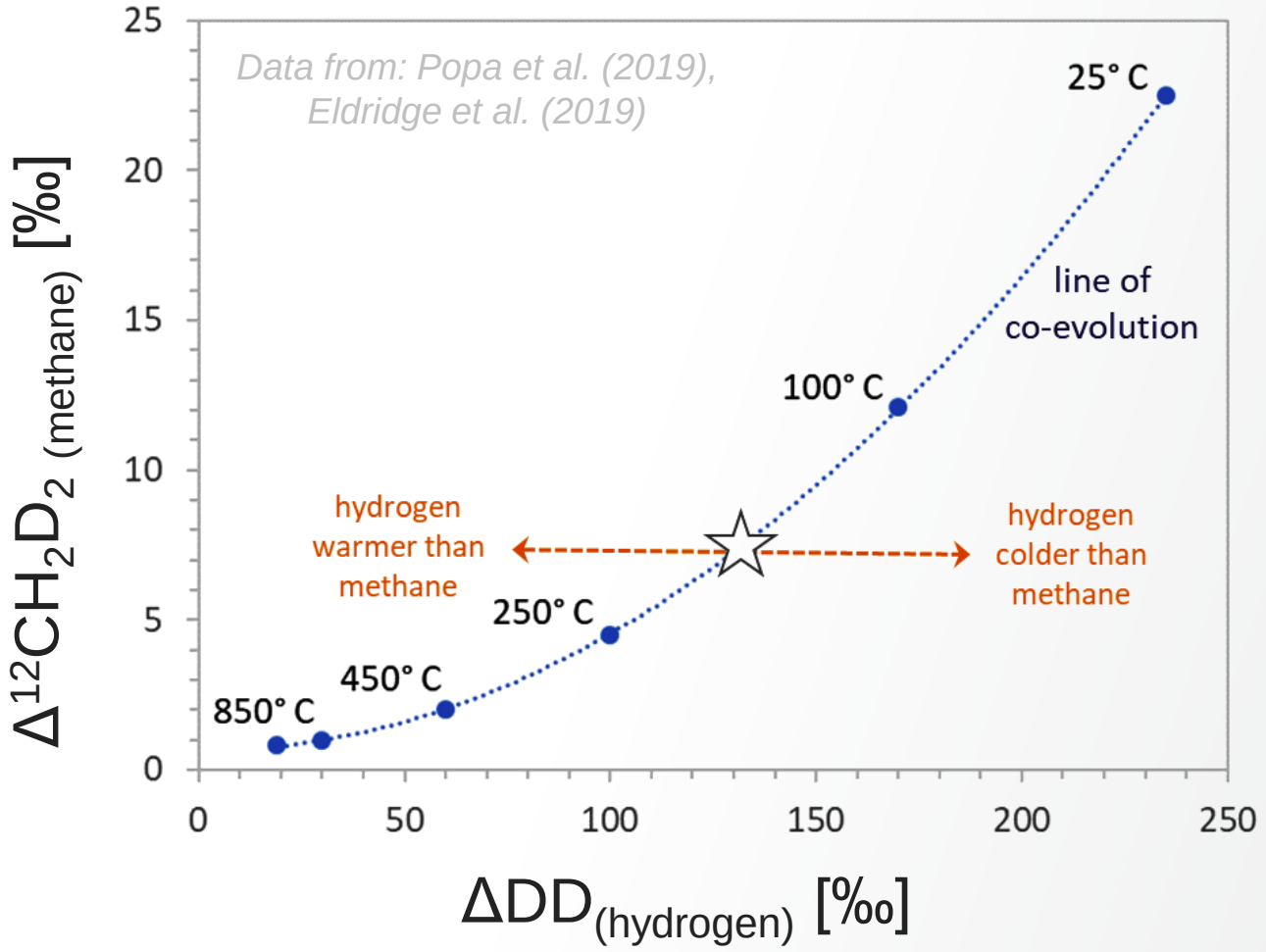
Clumped Hydrogen: Thermometry



Clumped Hydrogen: Application Fields



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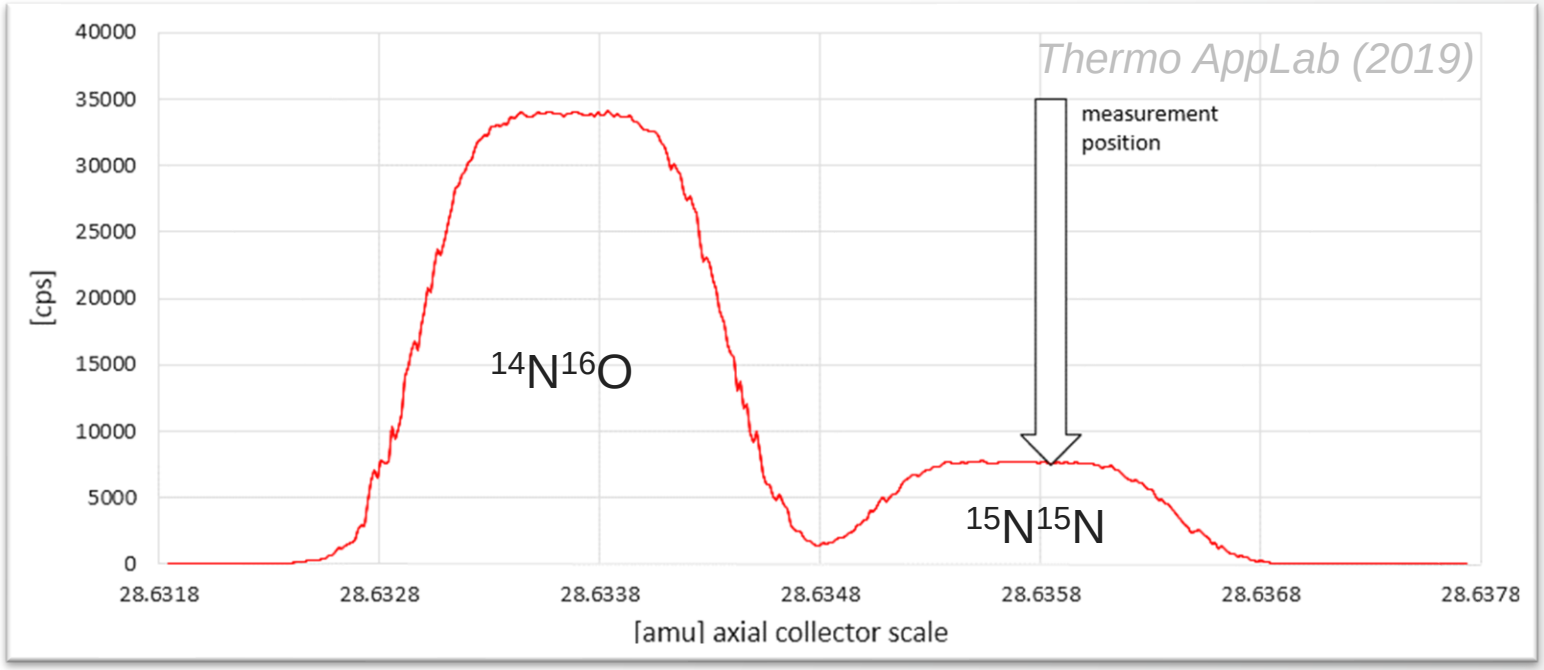
Clumped Nitrogen

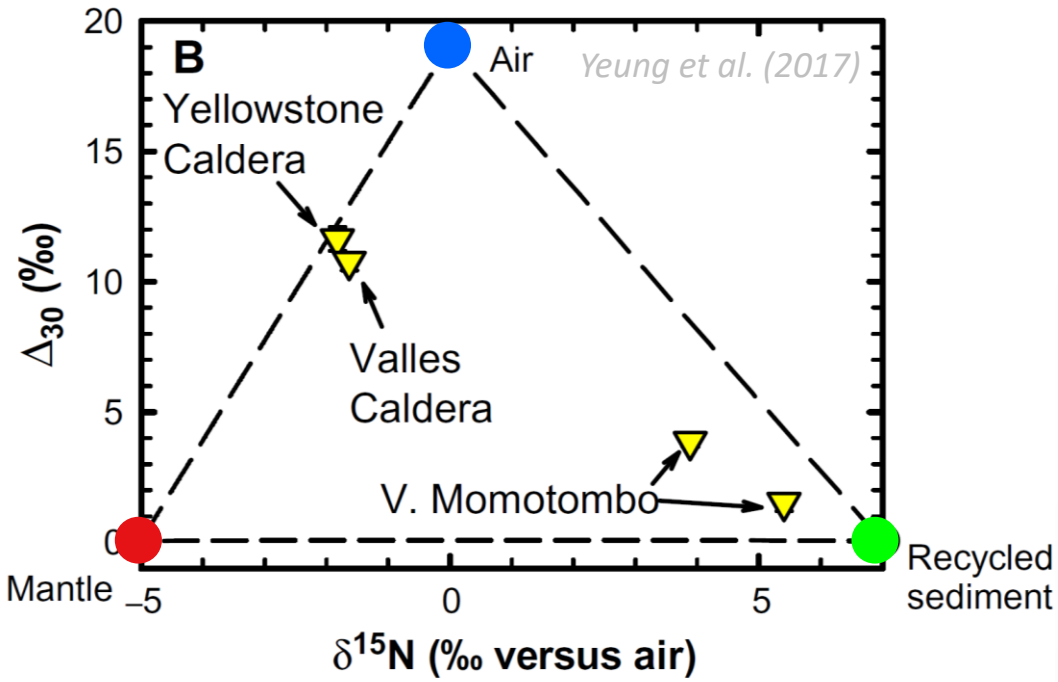
Principle and Application Fields

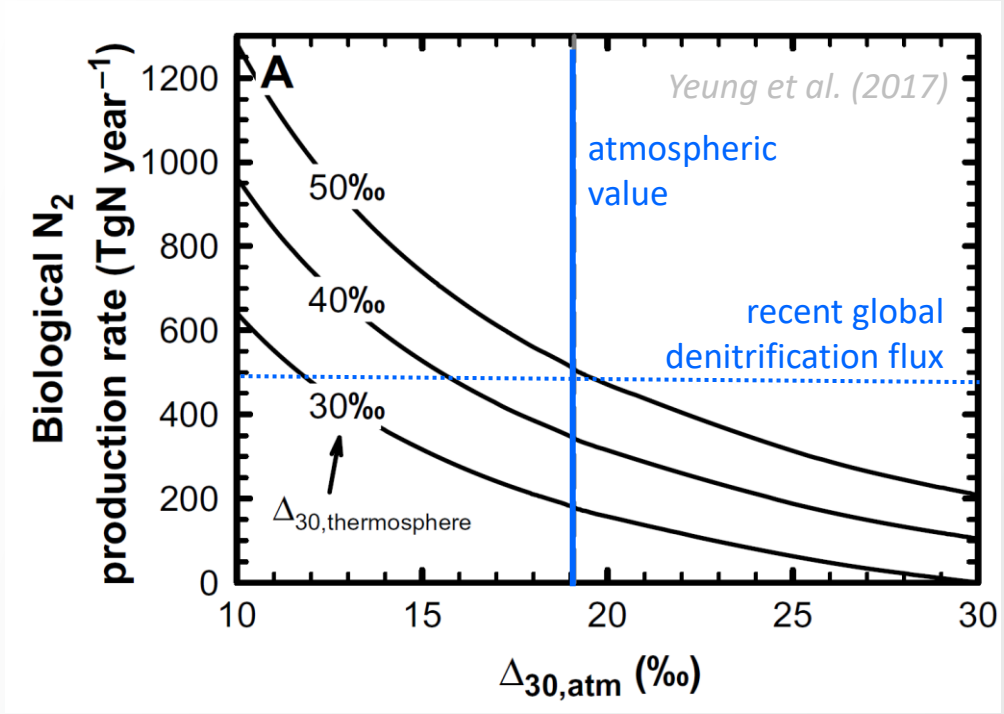
Clumped Nitrogen: HR-IRMS Mass Scan



HR-IRMS enables full peak separation of species which share the same cardinal mass.

Clumped Nitrogen: Application Fields

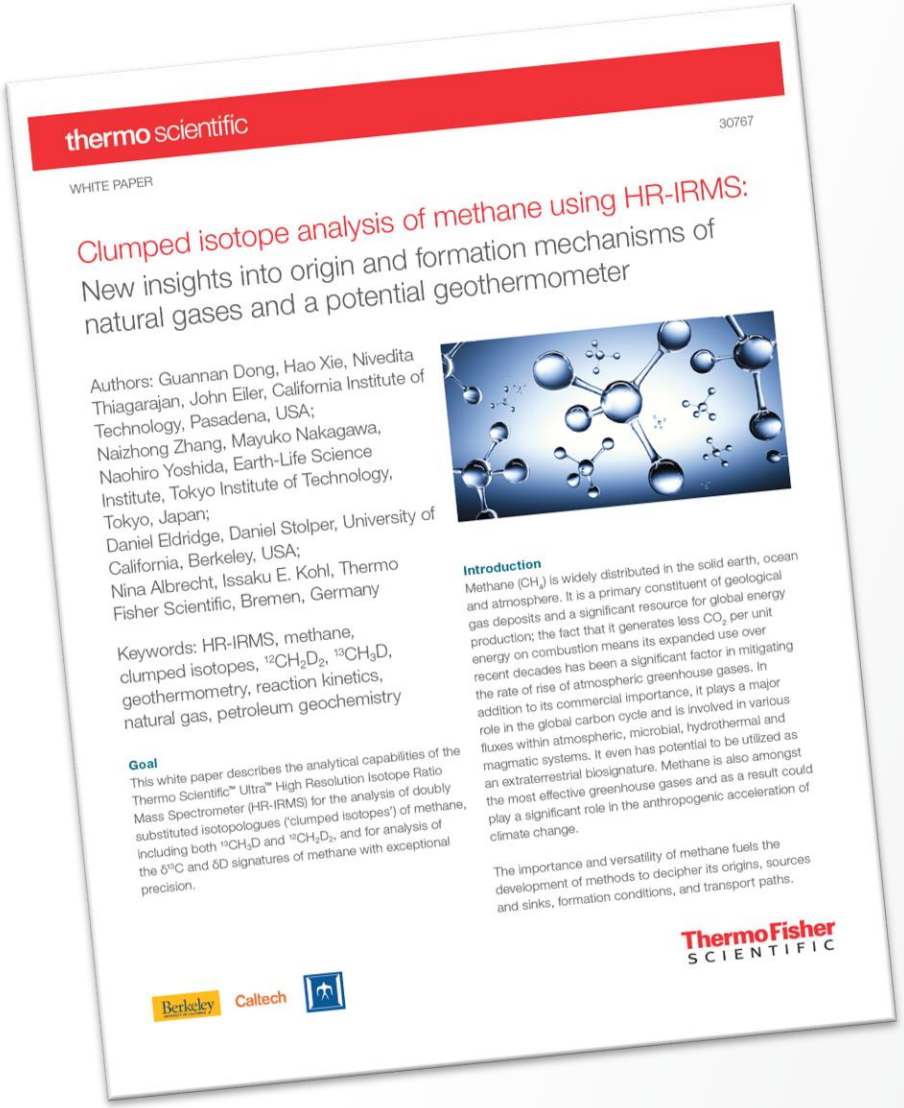




Linking nitrogen sources to volcanic N_2 outgassing in combination with classical $\delta^{15}N$

Modelling of thermospheric Δ_{30} constrains global denitrification rates.

Whitepaper: Clumped isotope analysis of methane using HR-IRMS



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30767

WHITE PAPER

Clumped isotope analysis of methane using HR-IRMS:
New insights into origin and formation mechanisms of natural gases and a potential geothermometer

Authors: Guannan Dong, Hao Xie, Nivedita Thiagarajan, John Eiler, California Institute of Technology, Pasadena, USA;
Naizhong Zhang, Mayuko Nakagawa, Naohiro Yoshida, Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan;
Daniel Eldridge, Daniel Stolper, University of California, Berkeley, USA;
Nina Albrecht, Issaku E. Kohl, Thermo Fisher Scientific, Bremen, Germany

Keywords: HR-IRMS, methane, clumped isotopes, $^{12}CH_2D_2$, $^{13}CH_3D$, geothermometry, reaction kinetics, natural gas, petroleum geochemistry

Goal

This white paper describes the analytical capabilities of the Thermo Scientific™ Ultra™ High Resolution Isotope Ratio Mass Spectrometer (HR-IRMS) for the analysis of doubly substituted isotopologues ('clumped isotopes') of methane, including both $^{13}CH_3D$ and $^{12}CH_2D_2$, and for analysis of the $\delta^{13}C$ and δD signatures of methane with exceptional precision.

Introduction

Methane (CH_4) is widely distributed in the solid earth, ocean and atmosphere. It is a primary constituent of geological gas deposits and a significant resource for global energy production; the fact that it generates less CO_2 per unit energy on combustion means its expanded use over recent decades has been a significant factor in mitigating the rate of rise of atmospheric greenhouse gases. In addition to its commercial importance, it plays a major role in the global carbon cycle and is involved in various fluxes within atmospheric, microbial, hydrothermal and magmatic systems. It even has potential to be utilized as an extraterrestrial biosignature. Methane is also amongst the most effective greenhouse gases and as a result could play a significant role in the anthropogenic acceleration of climate change.

The importance and versatility of methane fuels the development of methods to decipher its origins, sources and sinks, formation conditions, and transport paths.

ThermoFisher SCIENTIFIC

Berkeley Caltech

Written in collaboration with Caltech, Berkeley, and Tokyo Tech.

Free to download at thermofisher.com/ultra

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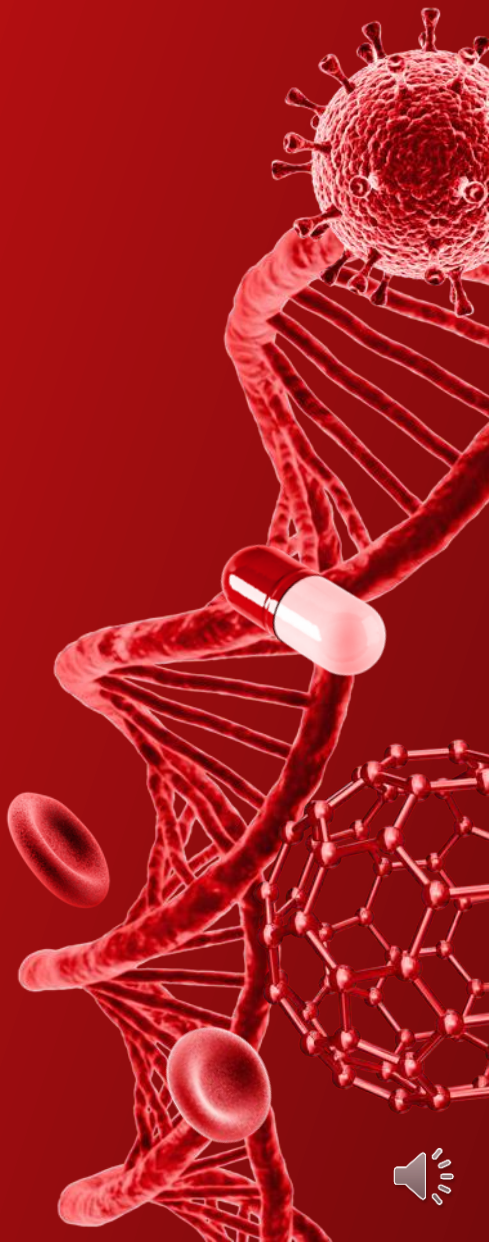
Thank you

Questions are welcome!



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