How clumped isotopes drive a deeper understanding of petrochemical processes

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What are Clumped Isotopes?

Principle Explained
“Classical” Isotopes of CO$_2$: 44, 45, 46

Single substitution
“Clumped” Isotopes of CO$_2$: 47, 48

Double substitution
“Clumped” Isotopes of CH₄

Δ¹³CH₃D

Mass 18

Δ¹²CH₂D₂

Mass 18

Double substitution
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

Clumped Carbonate Analysis

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

Thermo Scientific™ Ultra™ HR-IRMS

Clumped Methane Analysis
Clumped Carbonate
Principle and Applications
Clumped Carbonate: Typical Samples

Limestone  Forminifera  Speleothem  Corals  Travertine
Clumped Carbonate: Thermometry ($\Delta_{47}$)

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$\Delta_{47}$ data of travertines show an excellent correlation with temperature [...] and our calibration can be used to derive the deposition temperature of ancient carbonate deposits.
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Kele et al., 2015
Dual Clumped Carbonate Thermometry ($\Delta_{47} - \Delta_{48}$)

“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
Reconstructing Maximum Burial Temperature

“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
Clumped Methane: Typical Samples

- Wellhead gas
- Shale gas
- Gas hydrates
- Seeps
- Surface vents
Conventional Methane Analysis

Sample
Combustion / Pyrolysis
CO₂ / H₂
δ¹³C / δD

Source discrimination

Microbial fermentation
Microbial carbonate reduction
Thermogenic
Abiotic

Thermo Scientific™ EA Isolink™ IRMS System
Thermo Scientific™ GC Isolink™ IRMS System
Thermo Fisher Scientific Whitepaper (2021) WP30767
Clumped Methane Analysis

- Refined source discrimination
- Assessing maturity
- Process identification
- Thermometry

Thermo Scientific™ Ultra™ HR-IRMS

Sample
Preline (GC / Cryostat)
CH₄

δ¹³C / δD
Δ¹³CH₃D / Δ¹²CH₂D₂
HR-IRMS enables full peak separation of clumped methane isotopologues ($^{13}$CH$_3$D and $^{12}$CH$_2$D$_2$) from another and from ionization by-products ($^{13}$CH$_5$ and CH$_4$D).
Clumped Methane: Geothermometry

Experiments

\[ \Delta^{13}\text{CH}_3\text{D} \ [\%] \]

\[ \Delta^{12}\text{CH}_2\text{D}_2 \ [\%] \]

thermodynamic equilibrium

Δ\[12\text{CH}_2\text{D}_2 \ [\%] \] = thermodynamic equilibrium

Eldridge et al. (2019), ACS Earth Space Chem.
Clumped Methane: Geothermometry

Natural samples

\[ \Delta^{13}\text{CH}_3\text{D} \quad \%o \]

\[ \Delta^{12}\text{CH}_2\text{D}_2 \quad \%o \]

thermodynamic equilibrium

300°C

250°C

150°C

100°C

50°C

Shale gas

Conventional gas

Thermo Scientific Whitepaper (2021) WP30767
Clumped Methane: Geothermometry

Clumped Methane

\[ \Delta^{13} \text{CH}_3D \ [\%o] \]

\[ \Delta^{12} \text{CH}_2D_2 \ [\%o] \]

Fluid Inclusions

Homogenization Temperature [°C]

Clumped Methane Temperature [°C]

Mangenot et al. (2021), EPSL

Fluid Inclusions

1:1 line

Mangenot et al. (2021), EPSL
Clumped Methane: Source Discrimination
Clumped Methane: Source Discrimination

\[
\Delta^{12}\text{CH}_2\text{D}_2 \ [\%_o]
\]

\[
\Delta^{13}\text{CH}_3\text{D} \ [\%_o]
\]

\[
\Delta^{12}\text{CH}_2\text{D}_2 \ [\%_o]
\]

\[
\delta^{13}\text{C} \ [\%_o]
\]

After: Dong et al. (2021), GCA
Clumped Methane: Identification of Formation Mechanisms

After: Dong et al. (2021), GCA

\[ \Delta^{12}\text{CH}_2\text{D}_2 \, [\%_0] \]

\[ \delta^{13}\text{C} \, [\%_0] \]

Theoretical maturation model for an organic precursor with a given $\delta^{13}\text{C}$.
Clumped Methane: Assessing Maturity

Xie et al. (2021), GCA.
Clumped Methane: Safer Carbon Capture and Storage

Tyne et al. (2021), Nature.

Clumped Methane

$\delta^{13}C$ vs. CO$_2$/He

Tyne et al. (2021), Nature.
Future Perspectives: Clumped Hydrogen

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

\[ \Delta^{12}\text{CH}_2\text{D}_2 \text{ (methane)} \quad \text{[‰]} \]

\[ \Delta \text{DD}_{\text{(hydrogen)}} \quad \text{[‰]} \]
Clumped Hydrogen

Principle and Application Fields
Clumped Hydrogen: Thermometry

\[ \Delta \text{DD} \ [\text{‰}] \]

Temperature [°C]

Popa et al. (2019)
Clumped Hydrogen: Application Fields

Data from: Popa et al. (2019), Eldridge et al. (2019)
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 $\Delta_{30}$ constrains global denitrification rates.
Whitepaper: Clumped isotope analysis of methane using HR-IRMS

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!