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the world in a whole new way

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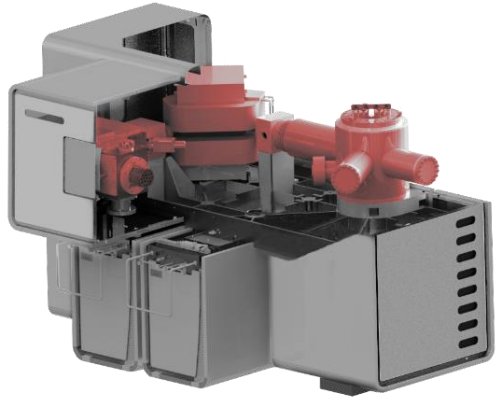
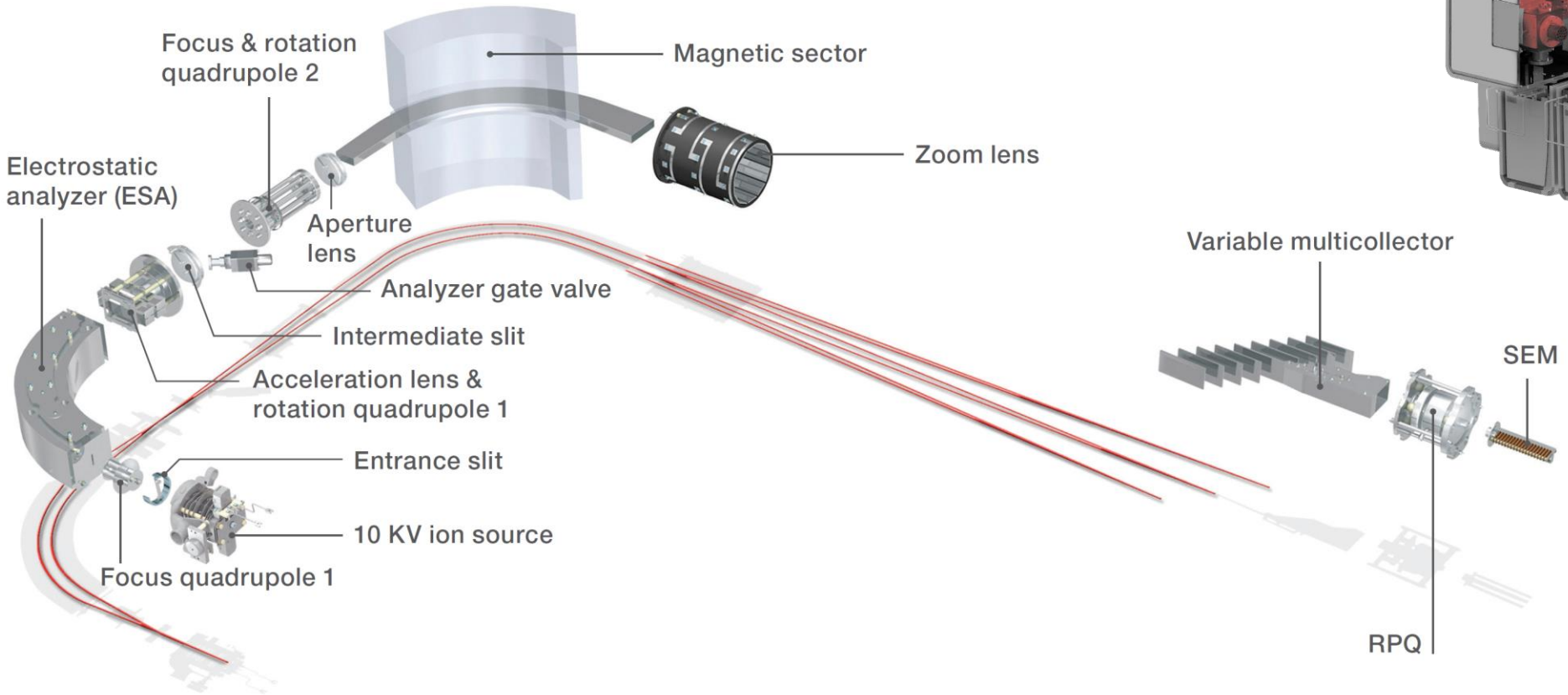
Latest Applications of HR-IRMS

Revolutionizing Clumped Isotope Research

Dr. Nina Albrecht (Product Specialist HR-IRMS)

Ultra™ HR-IRMS – A double-focusing gas source mass spectrometer





Ion beam path

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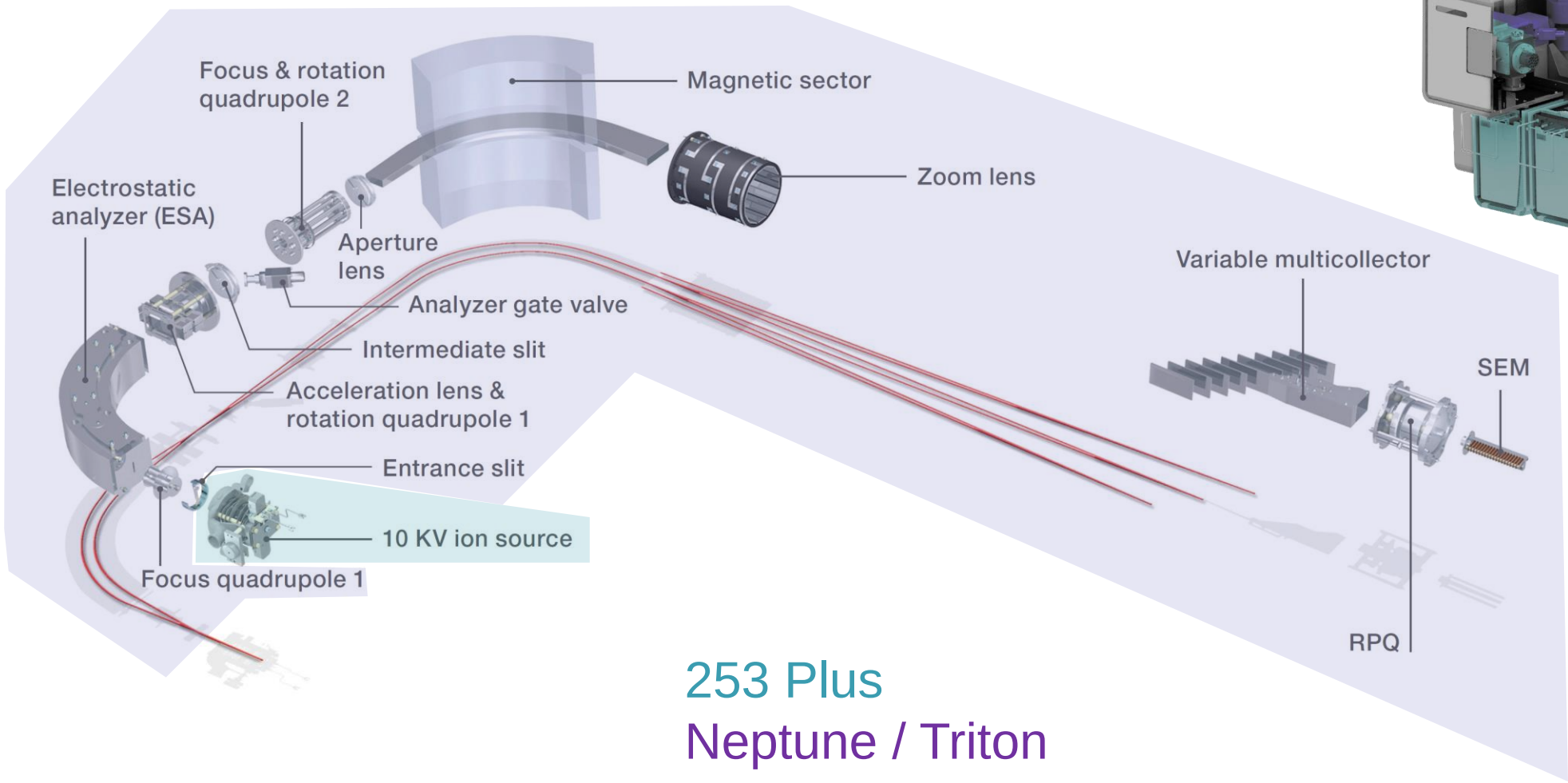
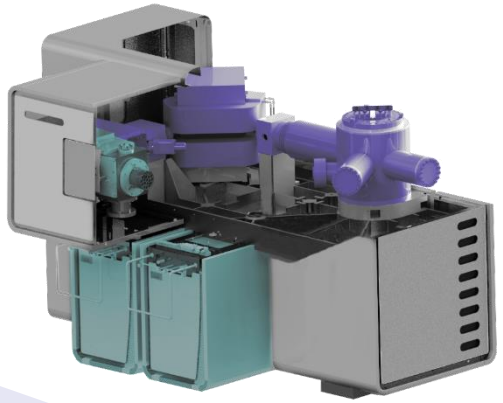
Ultra™ HR-IRMS – Uniting field-proven high-end technologies





253 Plus

Neptune / Triton

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Ultra™ HR-IRMS Benefits

Separation of isobaric interferences

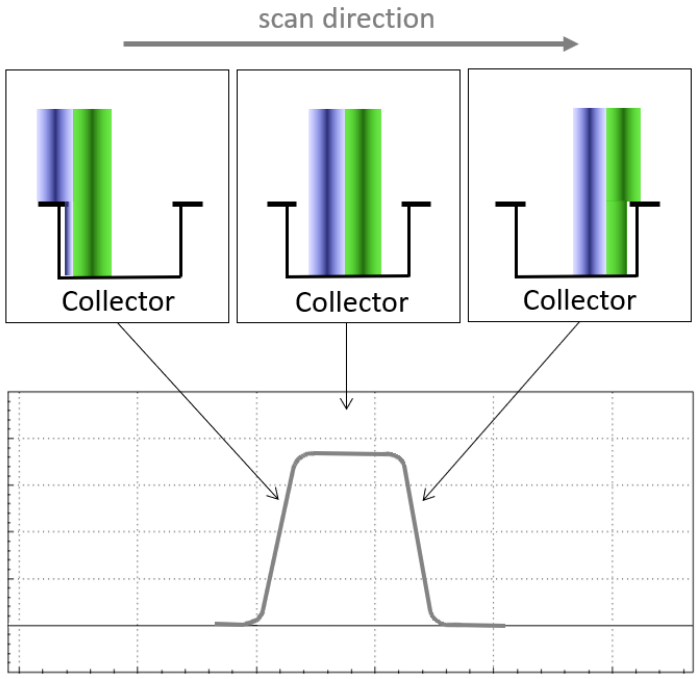
Guaranteed mass resolving power >30,000 (50,000 reported) is sufficient to fully resolve the clumped isotopologues of methane $^{13}CH_3D$ and $^{12}CH_2D_2$ from another and from adducts which share the same cardinal mass.

Analysis of super rare isotopologues

The system is optimized for the detection of smallest signals, such as clumped isotopologues of methane (and many more). It employs a high-end vacuum system to provide lowest backgrounds, optional $10^{13}\Omega$ amplifier technology for enhanced measurement precision of low intensity signals, as well as ion counters for the detection of smallest ion beams.

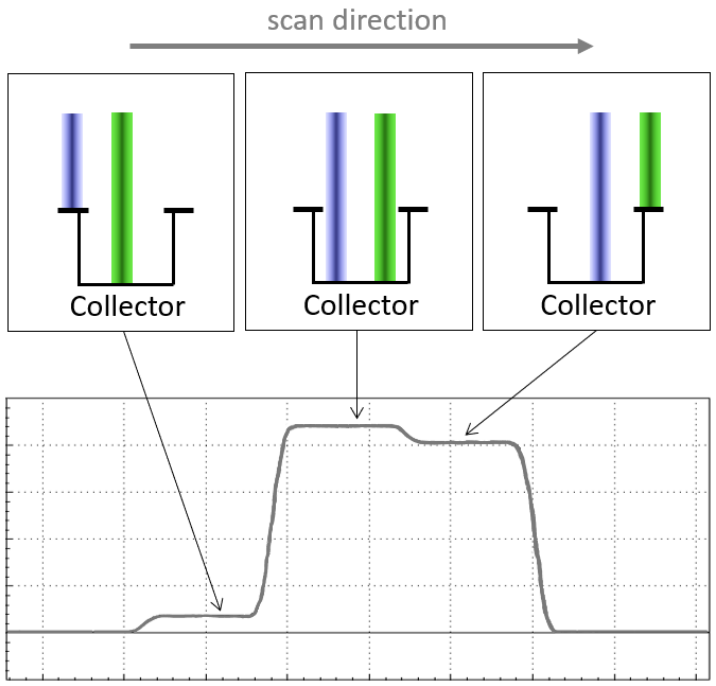
Ultra™ HR-IRMS Resolution Modes Explained

Maximum Transmission



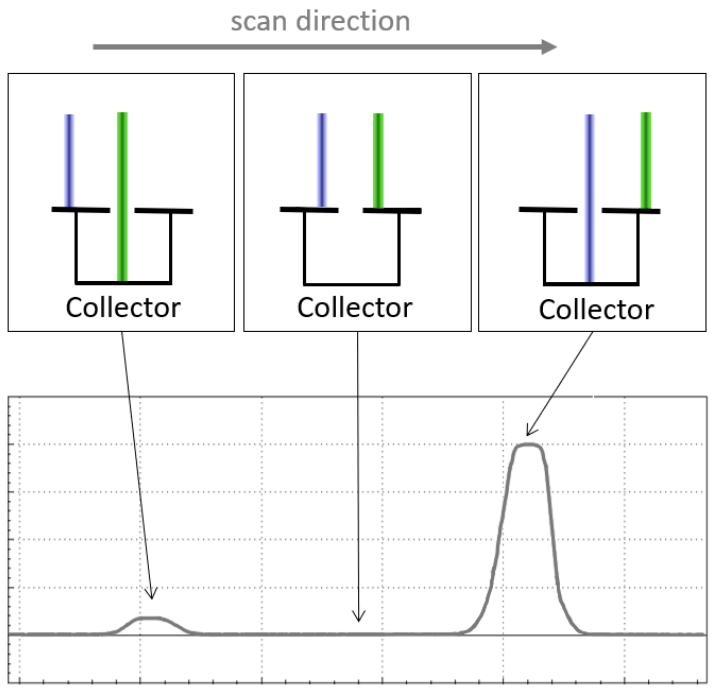
- wide source slit
- wide ion beams
- wide collector slit

High Resolving Power



- Medium or narrow source slit
- narrow ion beams
- wide collector slit

Full Peak Separation



- narrow source slit
- narrow ion beams
- narrow collector slit

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HR-IRMS Research Fields

N_2 H_2 O_2 Kr Xe SO_2F_2

CH_4 CO N_2O

Ne

C_3H_8 C_2H_6 He CO_2 Ar SF_6

Petroleum Geology

Atmospheric Sciences

Climate Change Research

Paleoclimate Reconstruction

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HR-IRMS Applications

Clumped Isotopes

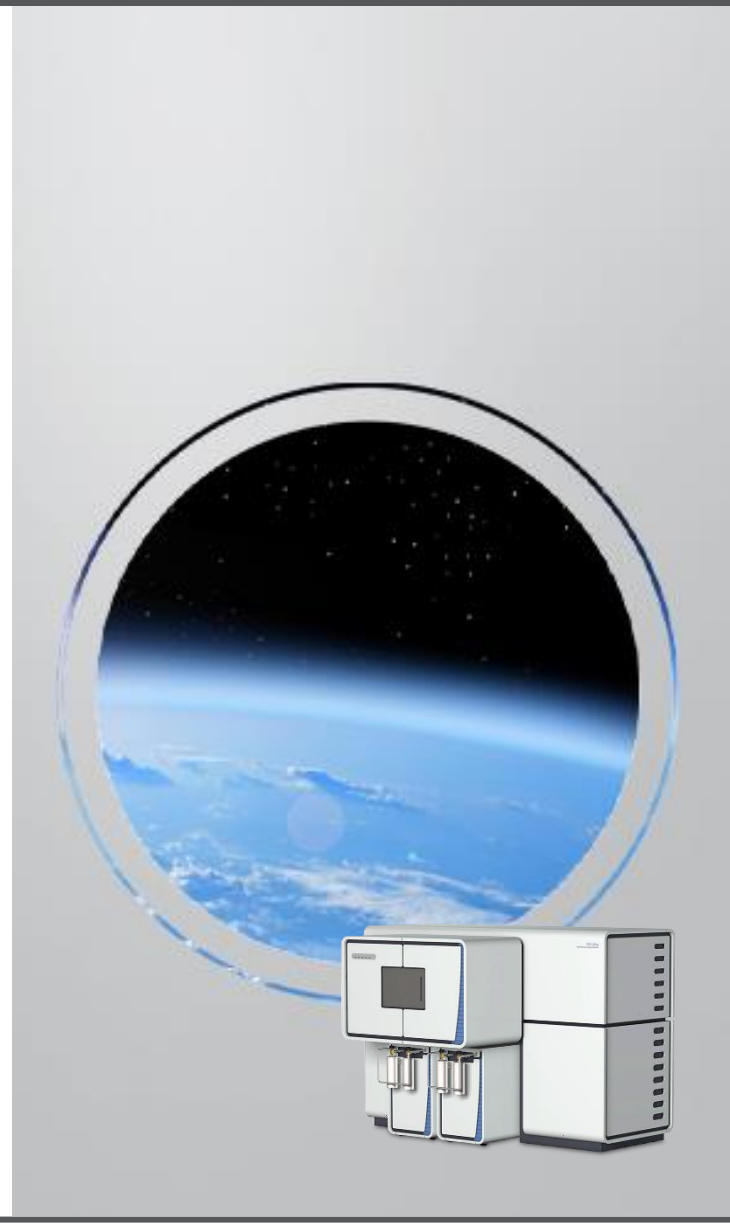
- **Methane**: $\Delta^{12}CH_2D_2$, $\Delta^{13}CH_3D$, $\delta^{13}C$, δD
- **Hydrogen**: ΔDD, δD
- **Nitrogen**: $\Delta_{30}N_2$, $\delta^{29}N_2$
- **Oxygen**: $\Delta_{35,36}O_2$, $\delta^{18}O$, $\delta^{17}O$
- **Ethane**: $\Delta^{13}C_2H_6$
- **Nitrous Oxide**: $\Delta^{14}N^{15}N^{18}O$
- **Sulfates (SO_2F_2)**: $\delta^{34}S$, $\Delta^{33}S$, $\delta^{18}O$

Classical Stable Isotopes “Revisited”

- **Carbon Dioxide**: $\delta^{18}O$, $\delta^{17}O$, $\delta^{13}C$
- **Hydrogen**: δD

Position-Specific Isotopes

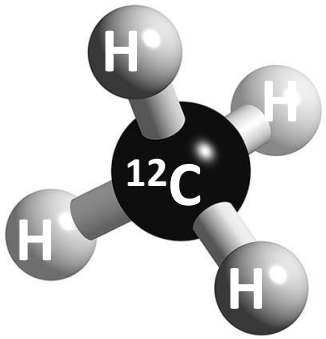
- **Ethane**, **Propane**: ^{13}C, D
- **Nitrous Oxide**: ^{18}O, ^{15}N



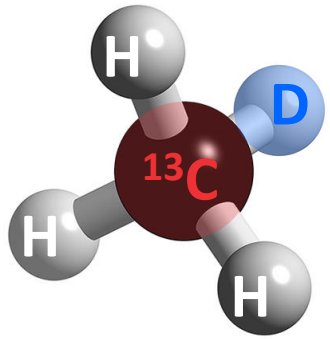
Proprietary & Confidential

What are Clumped Isotopes?

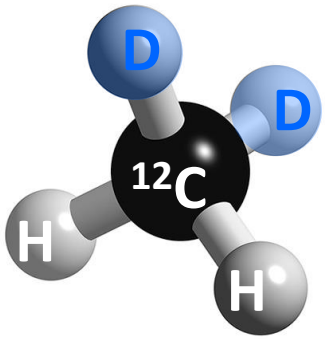
- **Clumped Isotopes** are multiply-substituted isotopologues.
- **Multiply-substituted isotopologues** are isotopologues that contain two or more rare (heavy) isotopes.
- **Thermodynamic equilibrium** provided, the deviation of a gasses clumped isotopic composition from a purely statistic distribution (i.e., the degree of molecular “clumping” of heavy isotopes) is temperature dependent.
- **Kinetic fractionation** mechanisms can cause deviation from thermodynamic equilibrium clumping.



CH_4



$^{13}CH_3D$



$^{12}CH_2D_2$

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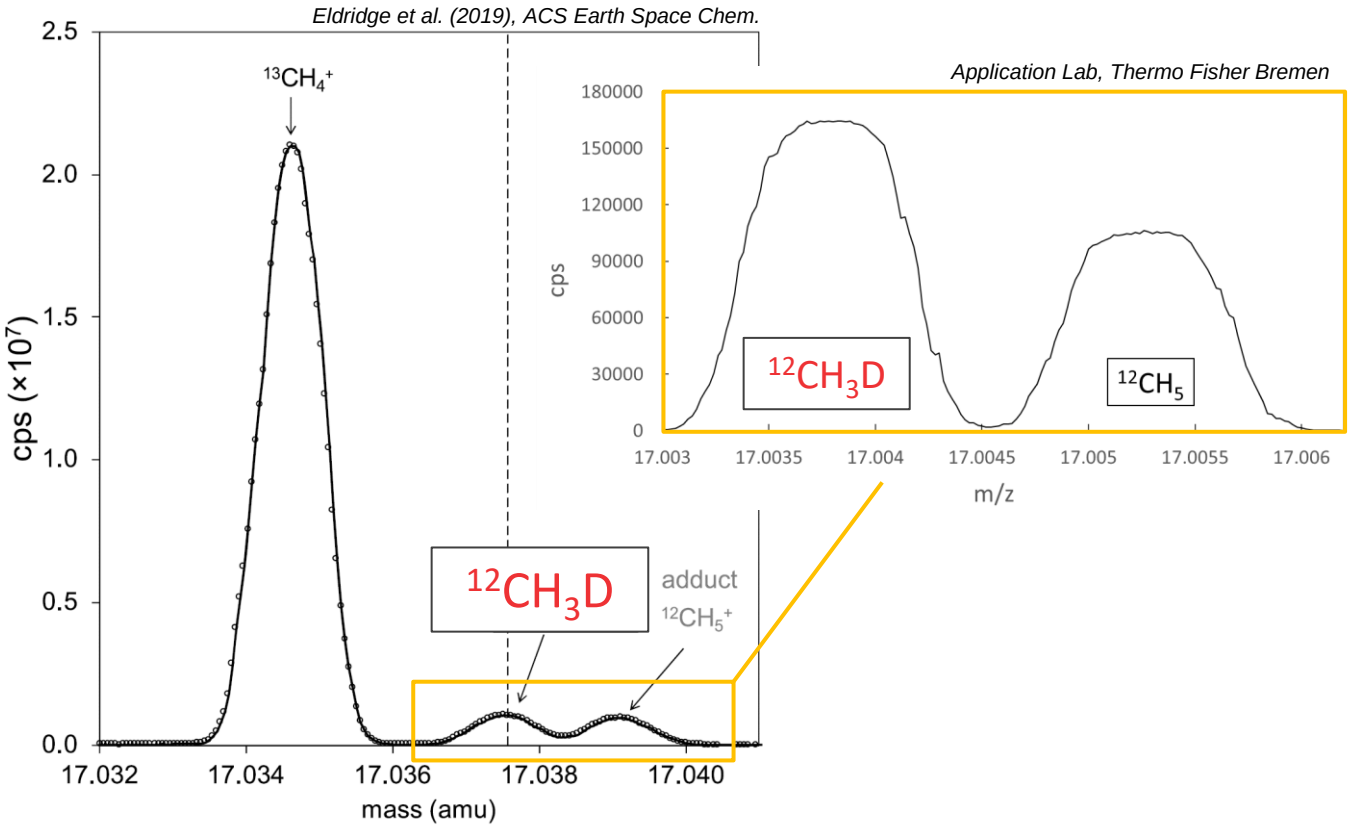
Methane: $\delta^{13}C$ and δD

The traditional molecule-average („bulk“) isotopic compositions $\delta^{13}C$ and δD of methane are determined through the ratios of $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$



“full peak separation”

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

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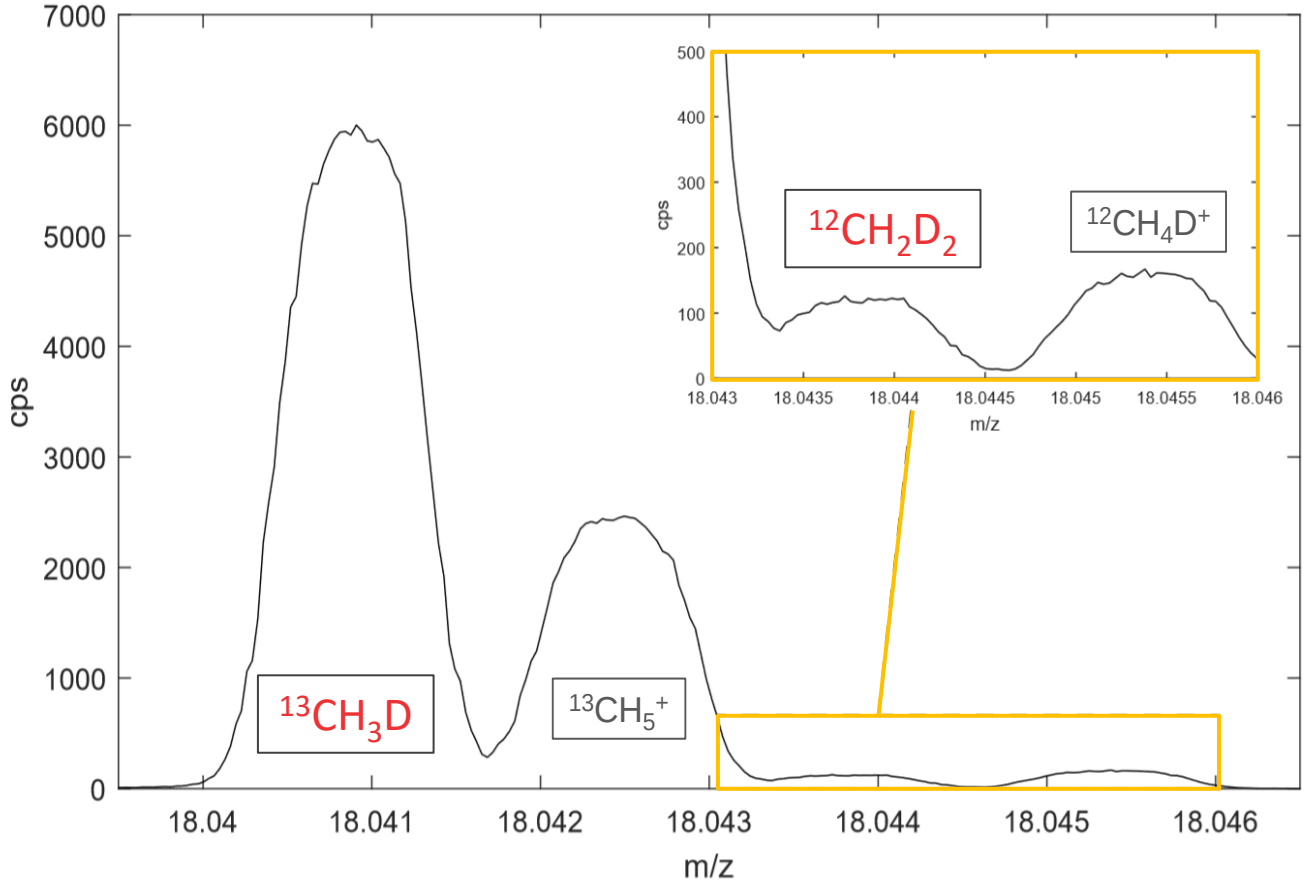
Methane: $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$

The clumped isotopic compositions $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ of methane are determined through the ratios of $^{13}CH_3D$ /$^{12}CH_4$ and $^{12}CH_2D_2$/$^{12}CH_4$



Red: Clumped isotopes

Black: Adducts

Hao Xie et al. (2019), Caltech, unpublished proprietary data.

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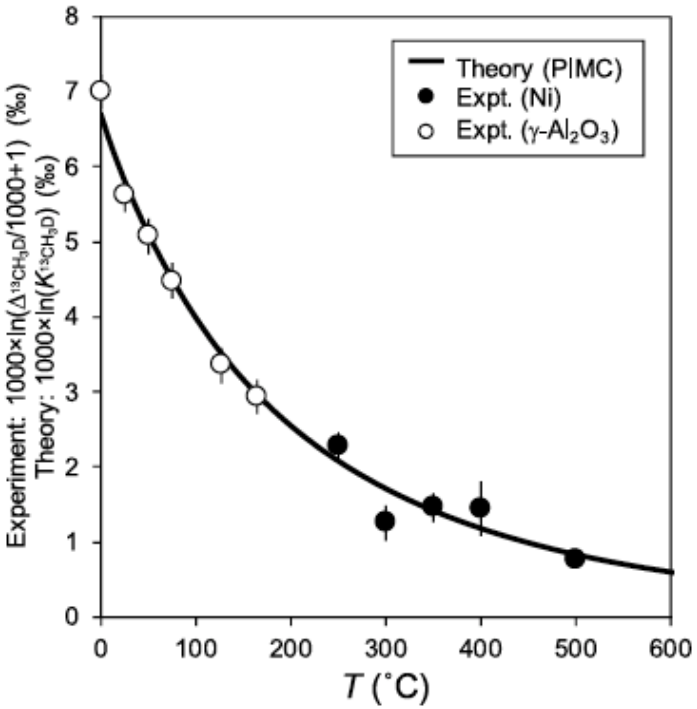
Methane: Geochemical Use of Methane Clumped Isotopes

Geothermometry

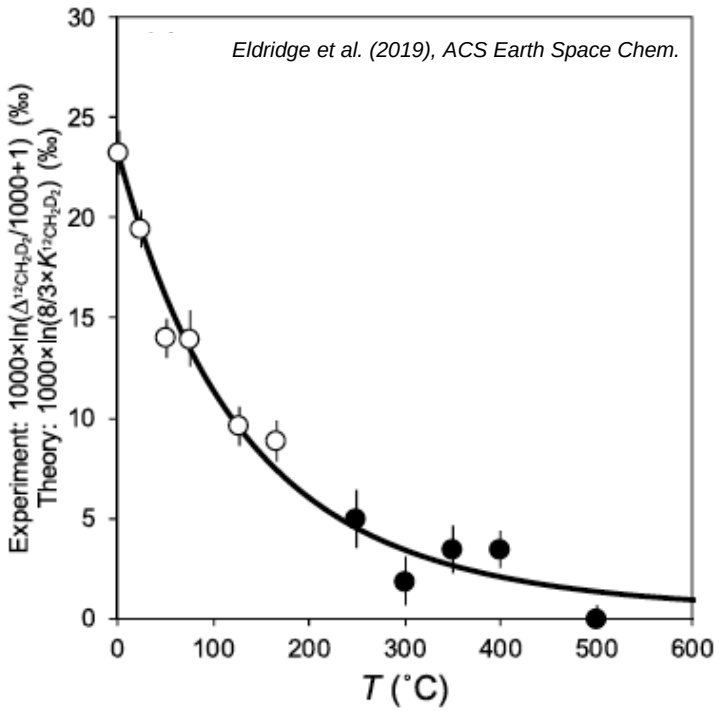
In methane that has formed in thermodynamic equilibrium with its surroundings (i.e., the $^{13}CH_3D$ – $^{12}CH_2D_2$ composition of a methane sample meets the line of simultaneous consistency with the trends on the shown diagrams) the clumped isotope composition provides a direct and absolute measurement of formation temperature.

In methane where the clumped isotopologues $^{13}CH_3D$ and $^{12}CH_2D_2$ are not in thermodynamic equilibrium, one can deduce the contribution of kinetic processes, or mixing with non-equilibrated methane sources.

"$\Delta^{13}CH_3D$"



"$\Delta^{12}CH_2D_2$"



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

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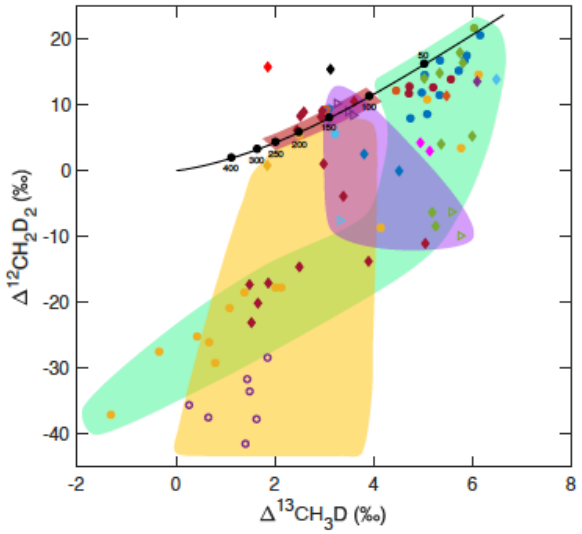
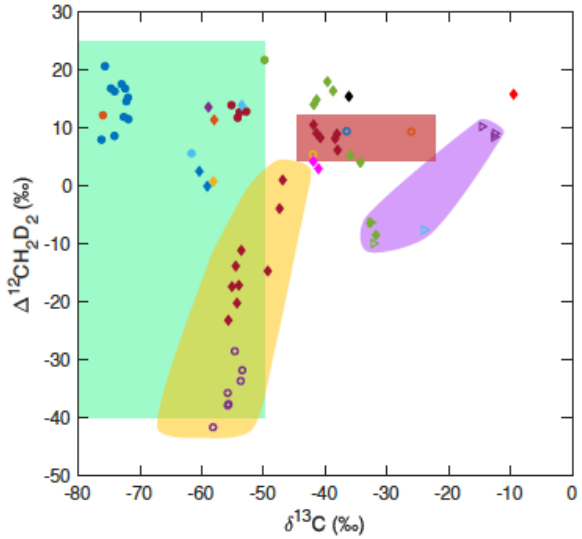
Methane: Geochemical Use of Methane Clumped Isotopes

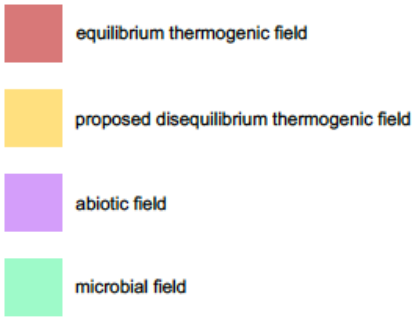
Forensic Discrimination

The isotope geochemical toolbox is expanded by the two clumped isotope signatures $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$. Along with the traditional $\delta^{13}C$ and δD, we now have 4 isotopic “fingerprints” available to discriminate different methane sources.

When combined, these 4 tools can make visible what was hidden before.







John Eiler, Guannan Dong (2020), Caltech, unpublished proprietary data.

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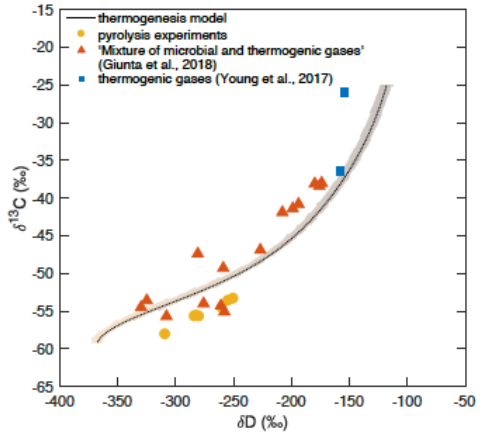
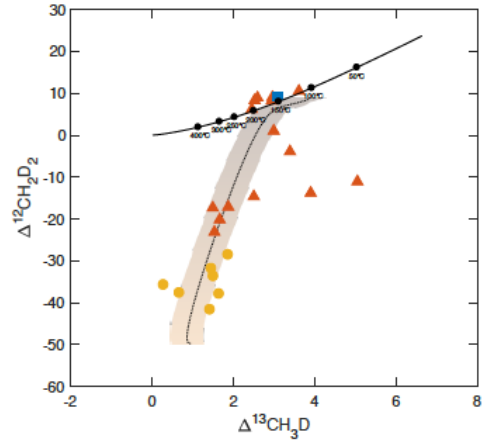
Methane: Geochemical Use of Methane Clumped Isotopes

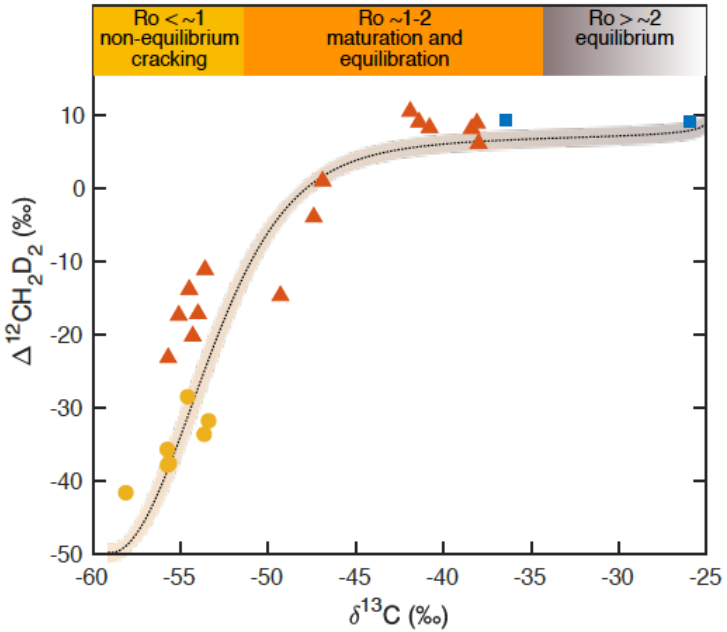
Formation Mechanisms

Kinetically controlled methane formation mechanisms, such as pyrolysis of aliphatic hydrocarbons, biological hydrogenotrophic CO_2 reduction and abiotic CO_2 reduction, are associated with distinctive fractionations that depart from the thermogenic equilibrium curve.

Bulk and clumped signatures, when combined, can identify and trace different formation mechanisms as well as mixing, and have potential to shed light on the isotopic composition of the substrate of methanogenesis.







Guannan Dong (2020), Caltech, unpublished proprietary data.

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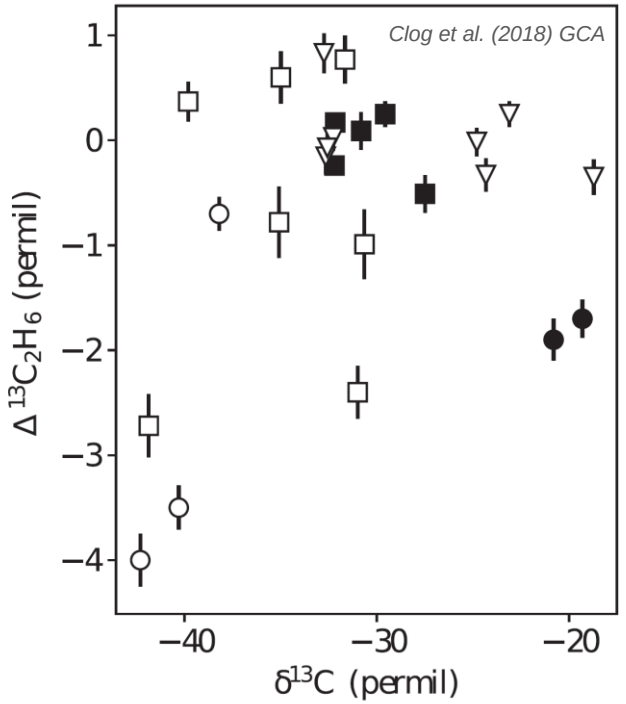
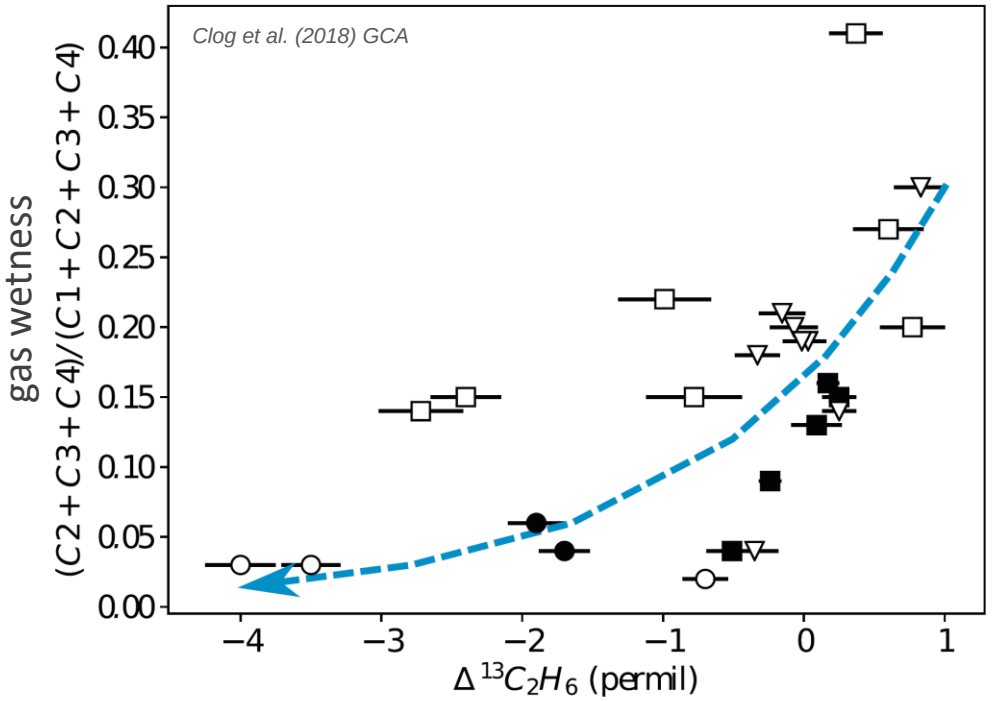
Ethane: Carbon Clumping $\Delta^{13}C_2H_6$



Large variations bear potential to discriminate different sources



Expected path of ethane which is thermally cracked, based on propane pyrolysis experiments

Clog et al. (2018) GCA

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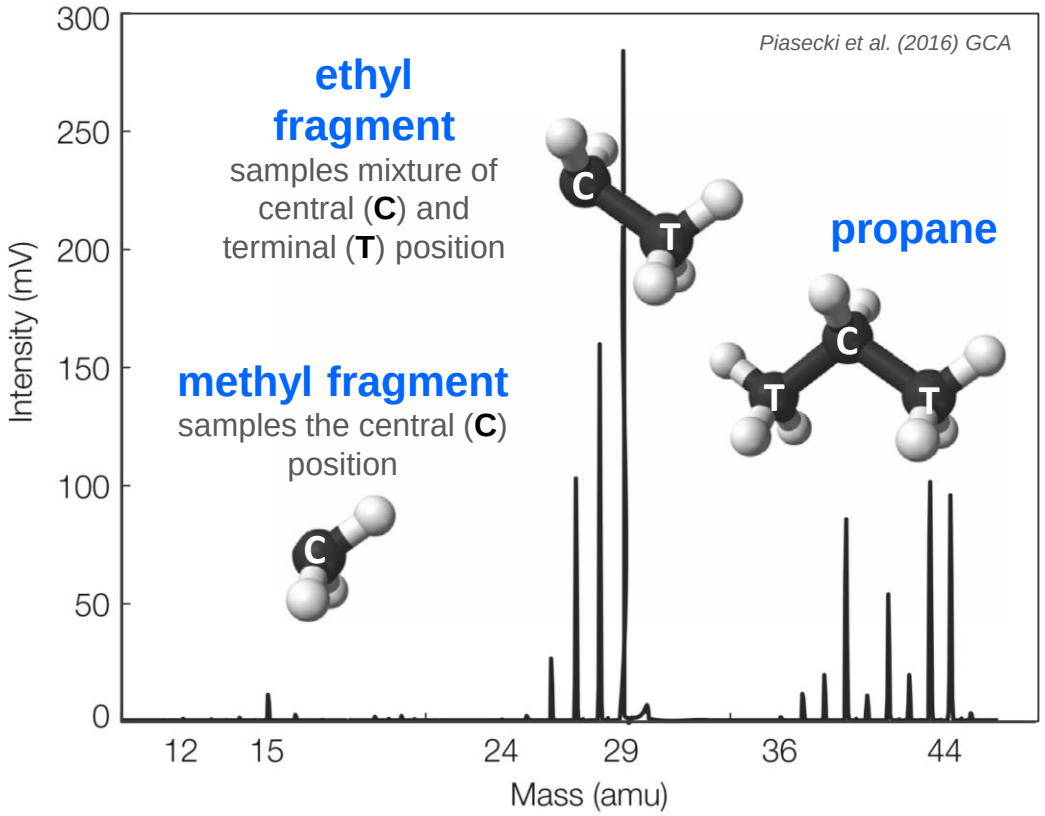
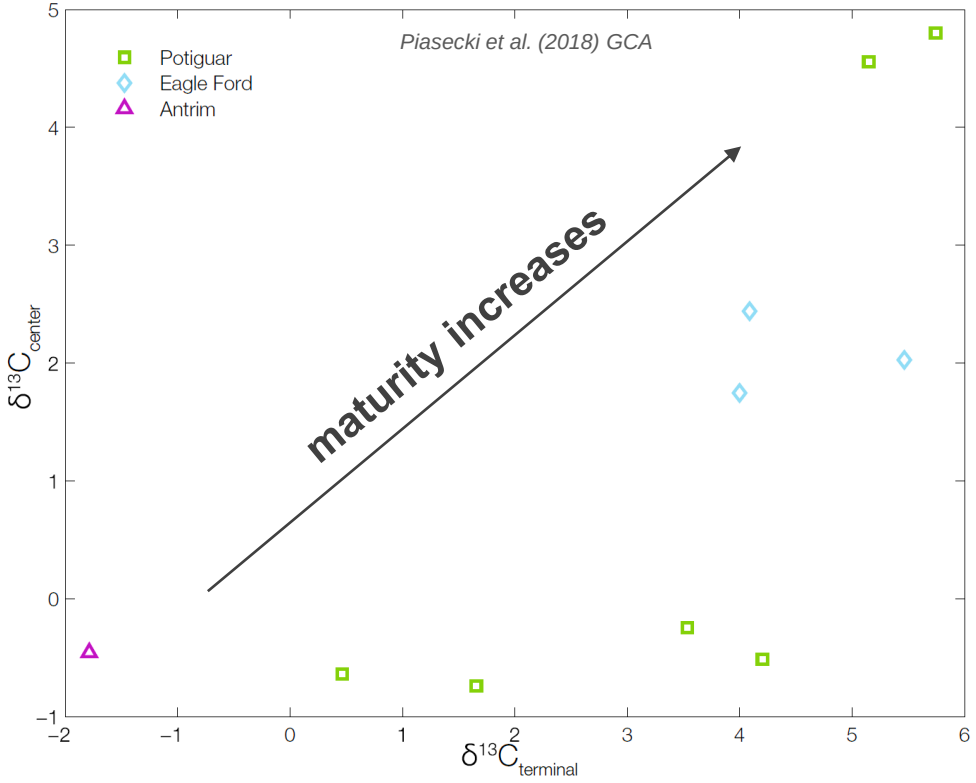
Propane: Position-Specific Isotope Analysis





The variation in the site-specific carbon isotope structure of propane is correlated with thermal maturity

Piasecki et al. (2016) GCA, http://dx.doi.org/10.1016/j.gca.2016.04.048

Piasecki et al. (2018) GCA, https://doi.org/10.1016/j.gca.2017.09.042

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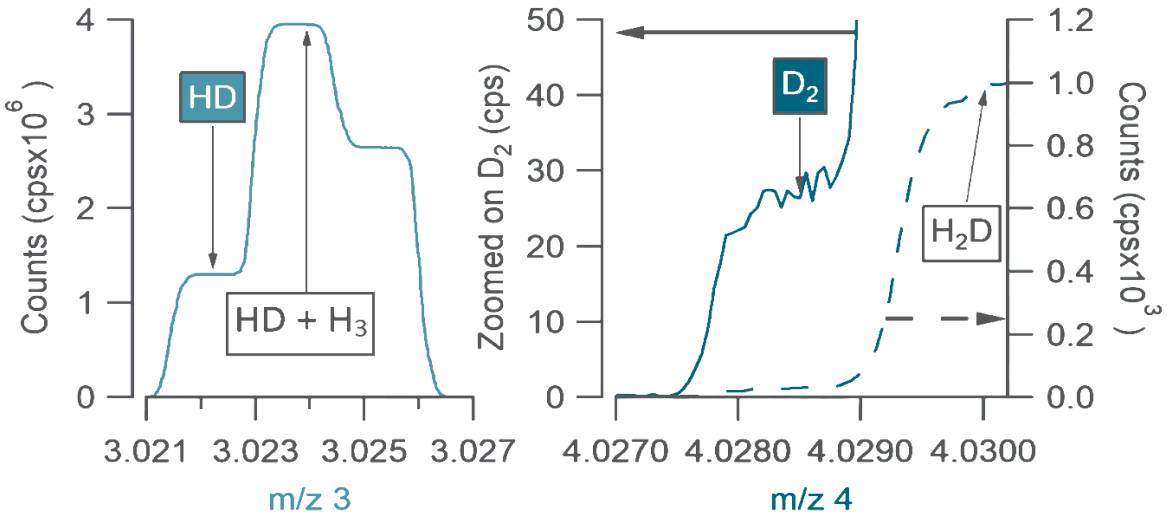
Hydrogen: Clumped Isotopes ΔDD

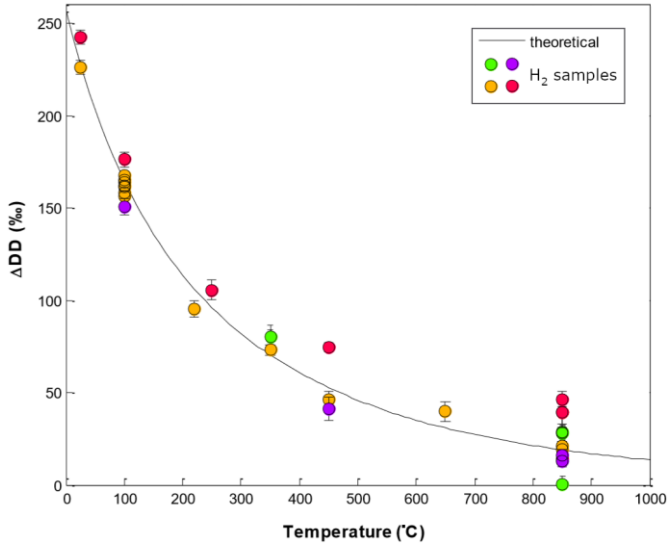
Geothermometry

In hydrogen that has formed in thermodynamic equilibrium, the clumped isotope anomaly provides a direct and absolute estimate of the temperature of gas formation in geologic samples, such as emission from H_2-bearing seeps, volcanoes, and natural gas reservoirs.

In hydrogen samples where the clumped isotopic composition is not in thermodynamic equilibrium, one can deduce the contribution of kinetic processes (or mixing with non-equilibrated gas sources). Such kinetic processes could be possibly related to microbial activity, as likewise observed for methane.



Popa et al. (2019) RCMS



Popa et al. (2019) RCMS, https://doi.org/10.1002/rcm.8323

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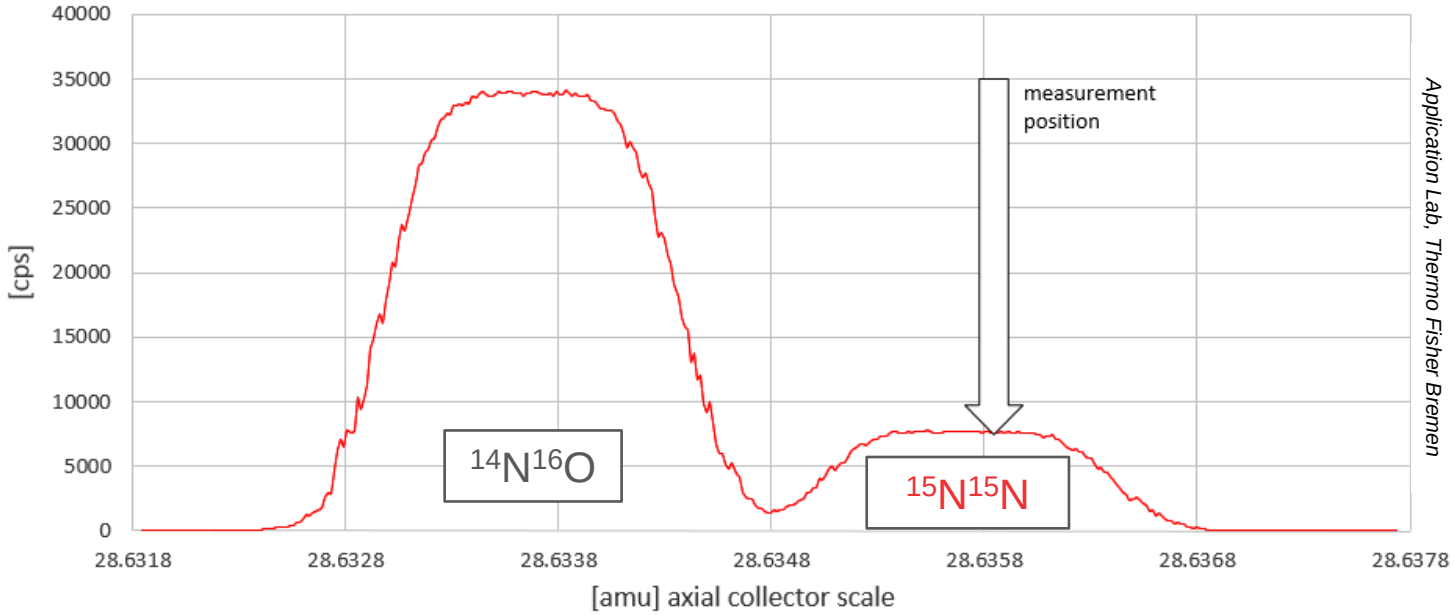
Nitrogen: Clumped Isotopes $\Delta^{30}N_2$

Full peak separation at resolving power >40,000



An additional constraint on the origin of natural gasses?

The clumped nitrogen composition could be utilized as a measure of denitrification rates. In combination with classical $\delta^{15}N$ it could enable a more accurate linking of the nitrogen sources of geological N_2 gas reservoirs / outgassing.

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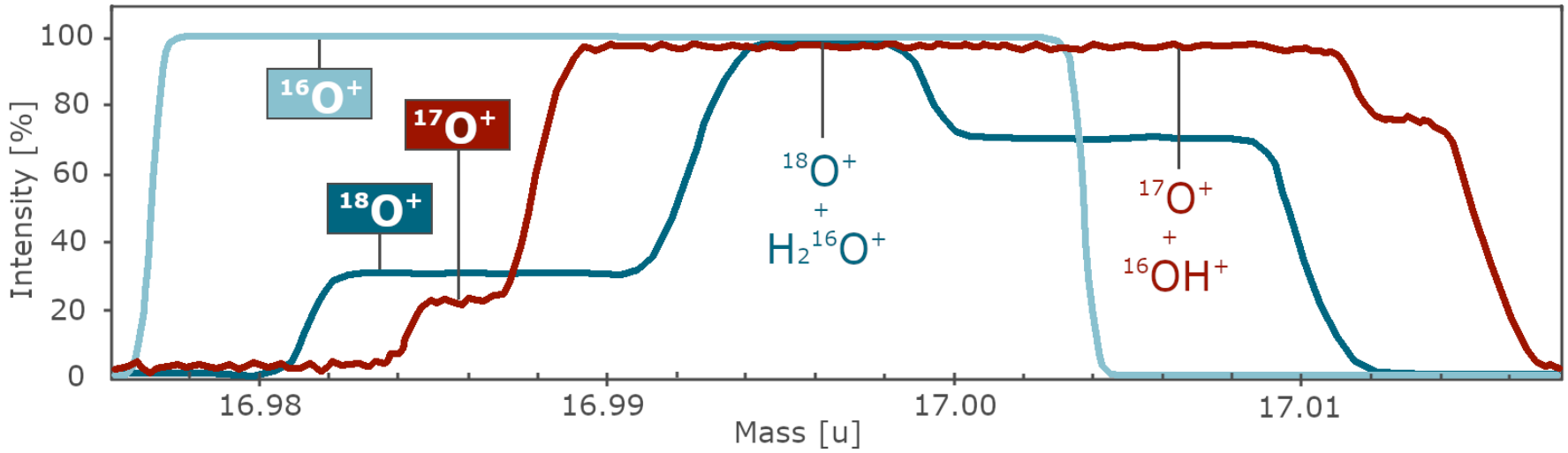
Carbon Dioxide: Fragment Method – $\delta^{18}O$, $\delta^{17}O$, $\delta^{13}C$

How do we get $\delta^{18}O$, $\delta^{17}O$, and $\delta^{13}C$ directly from CO_2?



Partial peak separation at resolving power ~16,000

Getachew et al. (2019) RCMS, https://doi.org/10.1002.rcm.8478

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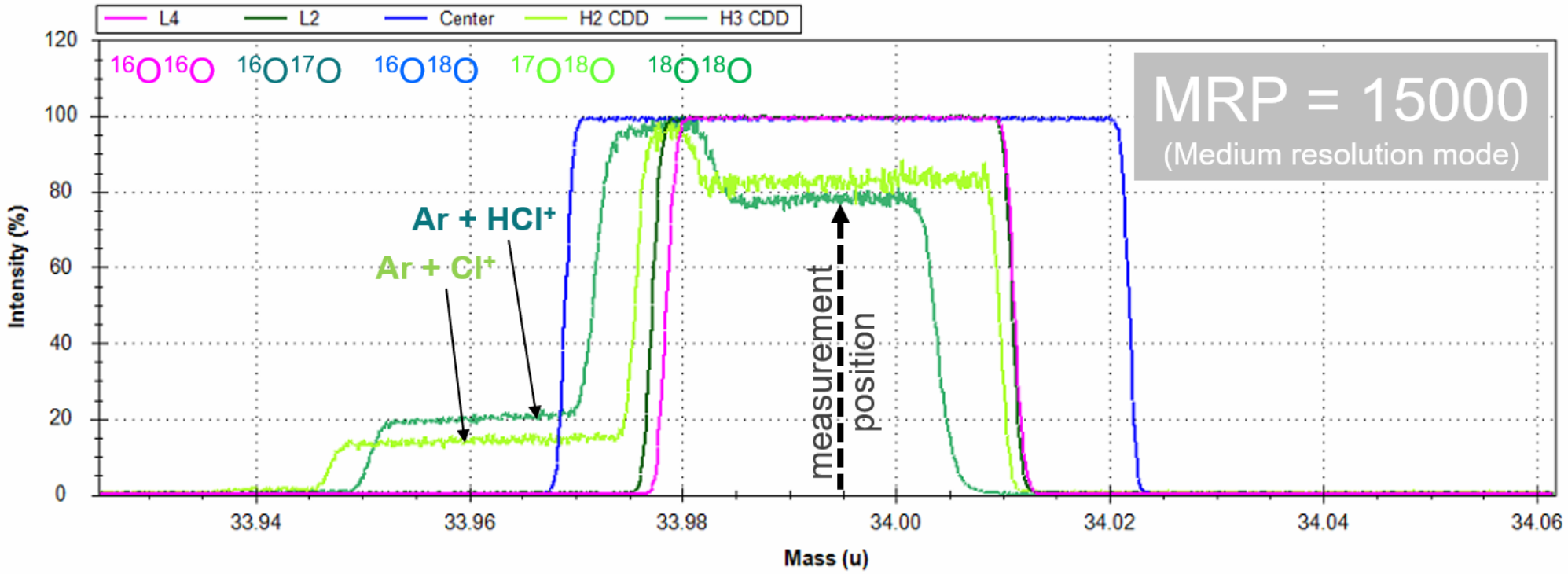
Interference-free measurement of $^{17}O^{18}O$ and $^{18}O^{18}O$



Laskar et al. (2019) RCMS, doi: 10.1002/rcm.8434

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Further Reading

A fundamental introduction to Clumped Isotopes:

Eiler (2007) “Clumped-isotope” geochemistry – The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters 262*, 309–327.

A review on Clumped Isotopes in methane:

Douglas et al. (2017) Methane clumped isotopes: progress and potential for a new isotopic tracer. *Organic Geochemistry 113*, 262–282.

A detailed description of a methane measurement setup:

Eldridge et al. (2019) Comparison of Experimental vs Theoretical Abundances of $^{13}CH_3D$ and $^{12}CH_2D_2$ for Isotopically Equilibrated Systems from 1 to 500°C. *ACS Earth Space Chem 3*, 2747-2764.

A detailed description of the Ultra™ HR-IRMS:

Eiler et al. (2013) A high-resolution gas-source isotope ratio mass spectrometer. *International Journal of Mass Spectrometry*, *335*, 45-56.

COMING SOON: Clumped Methane Application Note (Ultra™ HR-IRMS Homepage)

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