Clumped methane isotope analysis using HR-IRMS

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Goal

This application note 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 $^{12}CH_2D_2$. We highlight the scientific added value of combined classical and clumped methane analyses, to constrain methane sources and differentiate formation mechanisms.

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. 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.
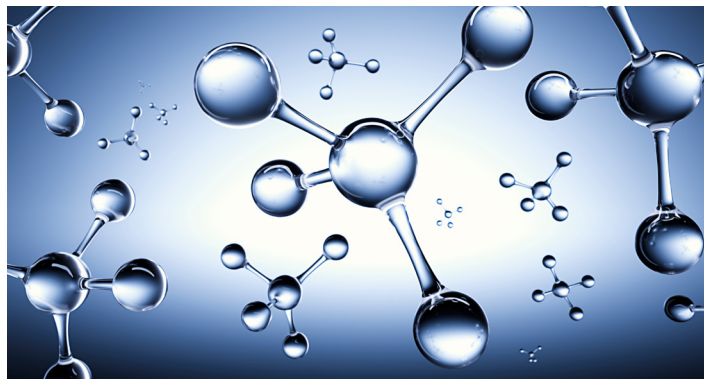
The importance and versatility of methane fuels the development of methods to decipher its origins, sources and sinks, formation conditions, and transport paths. The isotopic composition of methane is a valuable tool to address these questions. The commonly measured isotope compositions, $\delta^{13}C$ and δD, are determinable by combining chemical transformations (via combustion/pyrolysis to CO_2 or H_2, respectively) with classical low resolution IRMS. Such measurements can aid in identification of methane's origins but are often ambiguous with respect to provenance and formation conditions because multiple formation pathways can lead to broadly similar bulk isotope contents. The 'clumped isotope' signatures, $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, add additional independent compositional dimensions, which improve forensic identification, recognition of methane's formation mechanisms, and have the potential to record the absolute formation temperature of methane in cases where the natural gas formed in internal thermodynamic equilibrium.

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Both bulk and clumped isotope signatures can be directly determined with exceptional precision using the Ultra HR-IRMS.

Instrumentation

The Ultra HR-IRMS is a double-focusing, multi-collector gas source isotope ratio mass spectrometer (Figure 1). The system employs ion counters and is optimized, both in detector sensitivity and analyzer abundance sensitivity, for the detection of exceptionally rare isotope species, such as clumped isotopologues. Mass resolving powers beyond 30,000 (5%, 95% edge definition; reaching up to 50,000 for some applications) enable the separation of isobaric interferences arising from ionization adducts, contaminants, fragments, and isotopologues of the analyte that share the same cardinal mass. This is key to analyzing interference-free signals of all singly and doubly substituted methane isotopologues at natural abundance levels, to derive both the classical isotope signatures ($\delta^{13}C$ and δD), and the clumped signatures ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$).

Peak separation with high resolution

With HR-IRMS using the Ultra, all isotopologues of methane and its fragments and adducts are fully resolvable from each other and from potential adducts, fragments, and contaminants.

Full peak separation of methane isotopologues and respective adducts at mass 17 (Figure 2a) and mass 18 (Figure 2b) is routinely obtained in high resolution mode at mass resolving powers beyond 30,000. This is achieved by narrowing the ion beam, removing edge-effect related aberrations, and finally focusing the beam through a narrow collector slit. Further improvement is possible by engaging the aperture lens. Fine adjustment of the ion beam ('resolution tuning') is performed by adjusting two sets of focus quadrupoles along the beam path, to optimize the energy profile and trajectory of the ion beam. Users typically achieve MRP >40,000 up to 50,000.
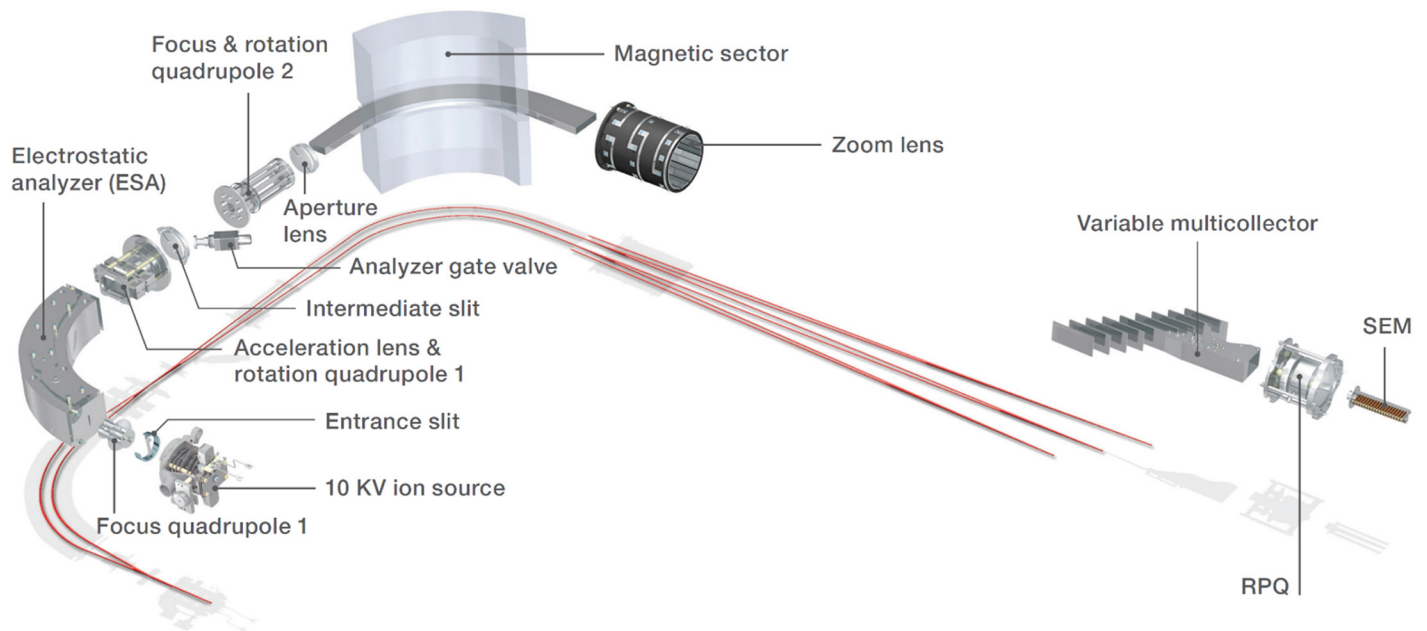

Figure 1. Ultra HR-IRMS ion beam path. The electrostatic analyzer is followed by the magnetic sector in the double-focusing Nier-Johnson type mass analyzer, and a multicollector equipped with 9 movable Faraday cups and 3 ion counters.

In addition to the focus, the conditions within the ion source ('source tuning') are of crucial importance for the successful measurement of clumped methane isotopologues. Ion source parameters, such as the extraction potential, determine residence time of analyte molecules proximal to the electron beam, thereby controlling the formation and fragmentation rates in the sample gas. These parameters are balanced to maximize the intensity of the analyte ion beam while minimizing the formation of adducts.
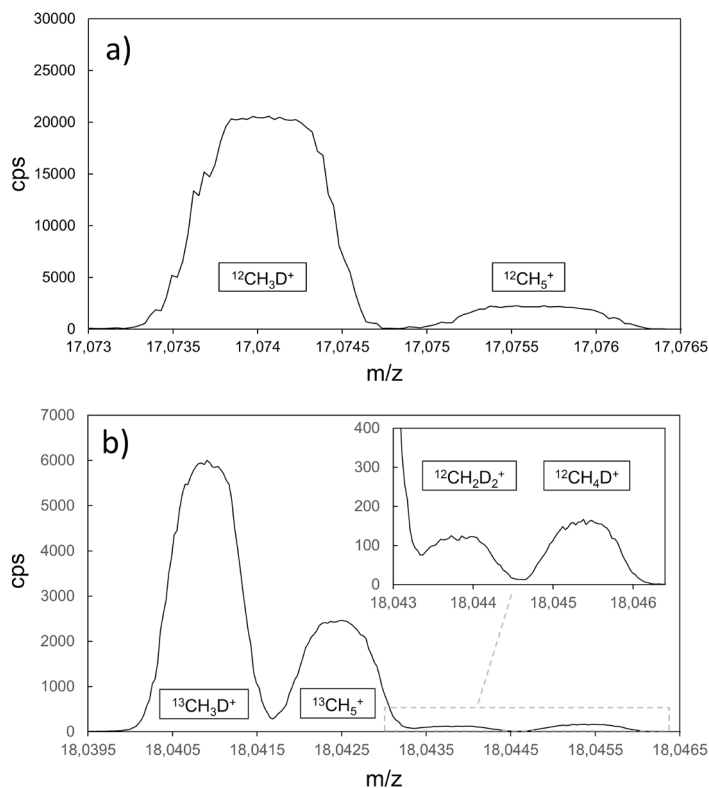

Figure 2. (a) Full peak separation for methane at mass 17 in high resolution mode. Isotopologue and adduct are fully resolved. (b) Full peak separation for methane at mass 18 in high resolution mode. Isotopologues and adducts are fully resolved. Mass resolving power ~45,000 (5%, 95% edge definition), statistically flat plateaus of about 0.0004 *m/z*. Instrument mass stability is specified to 10 ppm, corresponding to ~0.0002 *m/z*.

Limitations of conventional stable isotope systematics of methane ($\delta^{13}C$ and δD)

The molecule-average (or 'bulk') stable isotope characteristics of methane, $\delta^{13}C$ and δD, are utilized to distinguish between (1) thermogenic methane (formed by thermal degradation of buried organic matter), (2) biogenic methane (formed by microbial metabolism), and (3) abiotic methane (formed inorganically, typically by water-rock reaction). Thermogenic, microbial, and abiotic mechanisms can potentially be distinguished by measurements of $\delta^{13}C$ and δD because these processes draw on isotopically distinct substrates, and because isotopic fractionations associated with these processes differ from one another. However, large variations are observed in the resulting isotopic signatures of each process due to variations in substrate isotopic content and in the progress or conditions of reactions. As a result, the three major methane types occupy overlapping fields in a plot of $\delta^{13}C$ vs. δD (Figure 2), impeding an unambiguous distinction in many cases. Moreover, the bulk isotopic signature does not directly record other information of potential interest, such as formation temperature.
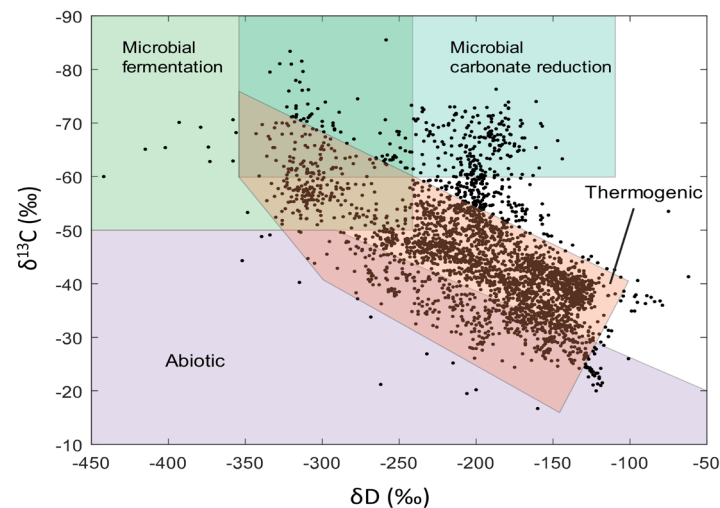

Figure 3. Values of $\delta^{13}C$ vs. δD for methane from diverse sources. Note that natural variations can be associated with ranges characteristic of several formation processes, but data for each type spans ranges that partly overlap fields for one or more others. Modified based on Douglas et al. (2017), Etiope (2015), Etiope & Sherwood Lollar (2013), Milkov and Etiope 2018, Schoell (1980), Sherwood et al. (2017), Thiagarajan et al. (2020).

The scientific benefit of clumped isotope systematics of methane ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$)

The doubly substituted (or 'clumped') isotopologues of methane, $^{13}CH_3D$ and $^{12}CH_2D_2$, provide two new independent constraints that can resolve ambiguities in its provenance and add fresh tools for understanding the environments and chemical mechanisms of natural methane formation.

The potential of clumped isotope measurements to illuminate the origins of methane are illustrated in Figure 3, which plots the excesses, relative to a stochastic distribution of all isotopes among all possible methane isotopologues, of the two doubly substituted species (i.e., the $\Delta^{12}CH_2D_2$ value vs. the $\Delta^{13}CH_3D$ value, see Eiler (2007) and Eldridge et al. (2019) for a general explanation and further details regarding the Δi nomenclature). A sample that plots at the origin of this figure possesses concentrations of $^{13}CH_3D$ and $^{12}CH_2D_2$ exactly equal to what would be expected if all ^{13}C and D in that sample were randomly distributed among all possible isotopic forms of methane. The upward-concave curve represents the set of compositions that would be observed in methanes that have obtained a distribution of isotopes among isotopologues consistent with isotope exchange equilibrium at the indicated temperatures. Simple kinetically controlled processes, such as gas phase diffusion, also lead to distinctive enrichments and depletions in the multiply substituted species (dashed arrows). Finally, more complex kinetically controlled methane formation mechanisms, such as pyrolysis of aliphatic hydrocarbons (red arrow), biological hydrogenotrophic CO_2 reduction (green curved field) and abiotic CO_2 reduction (purple rectangle), are associated with distinctive fractionations that also depart from the equilibrium curve.
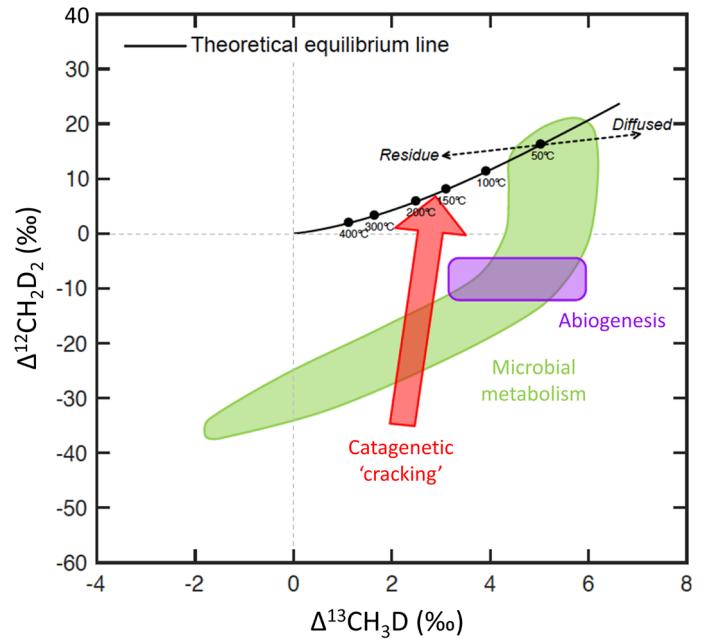

Figure 4: Schematic illustration of the clumped isotope signatures associated with mutual thermodynamic equilibrium among all methane isotopologues (solid black curve, marked with corresponding temperatures of equilibrium), gas phase diffusion (dashed line), catagenetic 'cracking' of aliphatic precursors (red arrow, pointing from low to high thermal maturity), microbial production by CO_2 reduction (green curved field) and abiotic formation on metal catalysts (purple rectangle).

Our understanding of how different mechanisms affect clumped isotopologue abundance and distribution (Figure 3) suggest three ways in which they can be used to study the origins of methane:

- **Improved forensic discrimination** between the major methane types, because a four-dimensional composition space ($\delta^{13}C$ vs. δD vs. $\Delta^{12}CH_2D_2$ vs. $\Delta^{13}CH_3D$) offers better separation between compositional types than two dimensions alone

- **Recognition of specific chemical mechanisms** of methanogenesis, through matching of sample data to known trends

- **Quantitative geothermometry**, based on the specific location of an equilibrated sample along the equilibrium curve

In-depth examples of these three approaches are described in Whitepaper WP30767.

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References

1. Thermo Scientific White Paper WP30767 "Clumped isotope analysis of methane using HR-IRMS" (2020)

2. Douglas, P.M., Stolper, D.A., Eiler, J.M., Sessions, A.L., Lawson, M., Shuai, Y., and Niemann, M. (2017). Methane clumped isotopes: progress and potential for a new isotopic tracer. Organic Geochemistry, 113, 262-282.

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

4. Eldridge, D.L., Korol, R., Lloyd, M.K., Turner, A.C., Webb, M.A., Miller, T.F., Stolper, D.A. (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 and Space Chemistry, 3, 2747–2764.

5. Etiope, G., Sherwood Lollar, B. (2013) Abiotic methane on Earth. Reviews of Geophysics, 51, 276–299.

6. Etiope, G. (2015) Natural Gas Seepage: The Earth's Hydrocarbon Degassing. Springer, Cham, Switzerland.

7. Milkov, A. V., and Etiope, G. (2018). Revised genetic diagrams for natural gases based on a global dataset of> 20,000 samples. Organic Geochemistry, 125, 109-120.

8. Schoell, M. (1980) The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochimica et Cosmochimica Acta 44, 649–661.

9. Sherwood, O. A., Schwietzke, S., Arling, V. A., and Etiope, G.: Global Inventory of Gas Geochemistry Data from Fossil Fuel, Microbial and Burning Sources, version 2017, Earth Syst. Sci. Data, 9, 639–656, https://doi.org/10.5194/essd-9-639-2017, 2017.

10. Thiagarajan, N., Kitchen, N., Xie, H., Ponton, C., Lawson, M., Formolo, M. and Eiler, J. (2020b) Identifying thermogenic and microbial methane in deep water Gulf of Mexico Reservoirs. Geochimica et Cosmochimica Acta 275, 188–208.

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