Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.28459

Rapid methane clumped isotope analysis using mid-infrared laser spectroscopy: development and first applications

NAIZHONG ZHANG[1], NICO KUETER[2], JAN MEISSNER[2], FRANK KEPPLER[3], JONAS HADELER[3], ADRIANO MAZZINI[4,5], PAUL MAGYAR[1], BÉLA TUZSON[1], LUKAS EMMENEGGER[1], STEFANO M BERNASCONI[6] AND JOACHIM MOHN[1]

[1]Empa
[2]ETH Zurich
[3]Heidelberg University
[4]University of Oslo
[5]Institute for Energy Technology (IFE)
[6]ETH Zürich

Methane clumped isotopes ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$), defined by deviations in the abundances of two doubly substituted isotopologues of CH_4, i.e., $^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, from their stochastic distributions, serve as proxies for CH_4 formation temperatures or the contributions of kinetically controlled processes[1], among other applications. However, their low natural abundance poses analytical challenges: current methods either require ≥20 hours per measurement with HR-IRMS[2] or ≥20 mL STP of sample gas using laser spectroscopy[3].

To address these limitations, we developed a spectroscopic platform using quantum cascade laser absorption spectroscopy (QCLAS), with optimized spectral windows for clumped isotope analysis and a custom-built gas inlet system[4]. This technique allows for reducing sample size down to 3–7 mL CH_4 gas while achieving precision levels comparable to HR-IRMS. Samples larger than 10 mL can be quantified in a single run within 20 minutes.

With this novel approach, we analyze CH_4 from a variety of laboratory experiments and natural settings to explore possible applications. In a comprehensive technical study, we optimized the selection and use of cryogenic adsorbents for CH_4 storage for preservation of both bulk and clumped isotopic signatures. As a geological application, we analyzed thermogenic CH_4 trapped in source rock pore space to assess whether the CH_4 has recorded its formation history. Additionally, clumped isotope signatures of bubble gases collected from mud volcanoes and hybrid systems in Italy and Indonesia provide valuable insights into understanding microbial contributions to the initial thermogenic hydrocarbon sources. We also investigated the clumped isotopic fingerprint of CH_4 formed via iron-oxide-mediated reactions involving methyl radicals, a potential abiotic source of C1 and C2 compounds in nature[5]. Our presentation will showcase the potential of the spectroscopic technique as a highly practical tool for methane clumped isotope analysis.

[1] Young et al. (2017), *Geochim. Cosmochim. Acta. 203, 235-264.*; [2] Eldridge et al. (2019), *ACS Earth Space Chem.* 3(12), 2747-2764; [3] Gonzalez et al. (2019), *Anal. Chem.* 91(23), 14967-14974; [4] Zhang et al. (2025), *Anal. Chem.* 97(2), 1291–1299; [5] Hadeler et al. (2023), *JACS* 145(45), 24590-24602.