Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.20195

Development of measurement strategy to measure methane multiply substituted isotopologue ratios ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) of ambient air within POLYGRAM project.

SARA M DEFRATYKA[1,2], CHRIS RENNICK[2], EDWARD CHUNG[2] AND TIM ARNOLD[1,2]

[1]University of Edinburgh
[2]National Physical Laboratory
Presenting Author: sara.defratyka@ed.ac.uk

Determination of methane (CH_4) source types and strength is crucial for choosing the most efficient climate mitigation policies[1]. In the case of understanding the integrated global CH_4 budget, additional tracers are required to adequately understand the balance of sources and sinks. Bulk isotopic signatures ($\delta^{13}C$-CH_4 and δD-CH_4) have been utilised in multiple studies, however, the global CH_4 system remains significantly underconstrained in terms of adequate observations[2,3].

The multiply substituted (clumped) isotopologues can potentially be used as an additional tracer to improve our understanding. Measurement of CH_4 clumped isotopologue ratios, $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, is more challenging than measurements of bulk isotope ratios and requires more advanced measurement techniques [4–6]. We aim to develop the measurement infrastructure to measure atmospheric air samples to determine clumped isotopologue ratios to study the global source-sink balance. Within the project, pressurised sample cylinders are collected at the world-recognised global monitoring sites at Cape Point, South Africa and station Zeppelin, Svalbard and, after preparation on a custom-built CH_4 preconcentrator, measured using a High Resolution - Isotope Ratio Mass Spectrometer (HR-IRMS).

The home-built preconcentrator is a key step in the measurement chain, as HR-IRMS requires small, high concentrated samples to measure the multiply substituted isotopologue ratios. Our aim is to receive 150 ml sample containing at least 1% of CH_4 in nitrogen from hundreds of litres of ambient air, where the CH_4 mole fraction is less than 2 ppm. We will present the technical and scientific challenges, and progress made in developing this CH_4 sample preparation methodology.

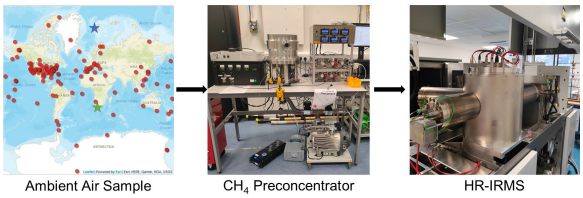

Figure 1. Measurement chain to measure $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$

References:

1. Nisbet *et al. Rev. Geophys.* **58**, (2020), https://doi.org/10.1029/2019RG000675
2. Turner *et al. Proc. Natl. Acad. Sci.* **116**, 2805–2813 (2019), https://doi.org/10.1073/pnas.1814297116
3. Saunois *et al. Earth Syst. Sci. Data* **12**, 1561–1623 (2020), https://doi.org/10.5194/essd-12-1561-2020
4. Douglas *et al. Org. Geochem.* **113**, 262–282 (2017), https://doi.org/10.1016/j.orggeochem.2017.07.016
5. Haghnegahdar *et al. Glob. Biogeochem. Cycles* **31**, 1387–1407 (2017), https://doi.org/10.1002/2017GB005655
6. Chung & Arnold. *Glob. Biogeochem. Cycles* **35**, (2021), https://doi.org/10.1029/2020GB006883