

## Progress in clumped isotope measurements of methane in air.

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In an effort to provide information that is useful for tracking global methane cycling and regional methane sources, a number of laboratories have focused on developing ways to extract and analyze methane from air for its clumped isotopologue composition. Two challenges need to be overcome – (1) methane at low (~2-10 ppmv) needs to be separated from a balance of nitrogen and oxygen with appreciable krypton – (2) sufficient methane needs to be isolated and purified for isotopic analysis with some techniques requiring > 1000 liters of air to be processed. We are interested in developing these capabilities because clumped isotope signatures have the potential to provide independent information from traditional isotopes and concentration measurements. We are aware of two publications last year that demonstrate extraction and measurement of clumped isotopes in atmospheric methane (Haghnegahdar et al. 2023; Sivan et al., 2023a). These studies, and collaborative work between the two groups with Greenland Firm air (Sivan et al., 2023b) reveal that prior predictions about clumped isotopologues of methane and their evolution over the last 30 years in air are largely valid, but that further measurements and improvements in techniques will refine the information they provide. The described techniques are also applicable in other cases where a significant balance of nitrogen exists, such as in chamber studies into sampling from confined locations such as sewers and in buildings. The presentation will provide overview and recent progress of our work seeking to reduce the sample size and to explore how uncertainties change as sample sizes decrease.

### References

Haghnegahdar, et al. 2023. Tracing sources of atmospheric methane using clumped isotopes. *Proceedings of the National Academy of Sciences*, 120(47), p.e2305574120.

Sivan, M., et al., 2023a. Extraction, purification, and clumped isotope analysis of methane ( $\Delta 13 \text{ CDH } 3$  and  $\Delta 12 \text{ CD } 2 \text{ H } 2$ ) from sources and the atmosphere. *EGUsphere*, 2023, pp.1-35.

Sivan, M., et al., 2023b, July. Methane from the past: Insights from clumped isotope measurements. In *Goldschmidt 2023 Conference*. GOLDSCHMIDT.