

Clumped isotopic composition of atmospheric methane: advancements in measurements and modelling

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The atmospheric methane mole fraction has been increasing since pre-industrial times. As a potent greenhouse gas, this rise poses significant challenges to efforts aimed at mitigating global warming. Atmospheric methane levels are controlled by a complex mix of natural and anthropogenic sources, atmospheric OH levels, and other sink reactions. Understanding the contribution of each of these factors is crucial for a comprehensive understanding of the global methane cycle.

In recent years, the clumped isotopologues of methane (¹³CH₃D and ¹²CH₂D₂) have been developed as an additional tracer to constrain the atmospheric methane sources and sinks. Technical developments towards low-concentration samples facilitate such measurements of methane extracted directly from ambient air. The first measurements of the clumped isotopic composition of atmospheric methane show distinct signatures of about 1 ± 0.3 ‰ for Δ¹³CH₃D and 44 ± 3 ‰ for Δ¹²CH₂D₂, which is much higher for Δ¹²CH₂D₂ than all major source categories [3,4].

These measurements, however, do not agree with existing model predictions [1,2], highlighting knowledge gaps in the known clumped isotopic composition of the sources and kinetic isotopic fractionation associated with the sinks. Although the number of source measurements carried out so far is still limited, it appears unlikely that these discrepancies can be attributed only to undersampled sources. Instead, uncertainties in sink fractionation contribute significantly to the observed differences. However, precise measurements of the sink fractionation are challenging.

To further investigate the discrepancy, To investigate possible changes in the clumped isotope composition of atmospheric methane over time, we established the first historical record of atmospheric Δ¹³CH₃D and Δ¹²CH₂D₂, reconstructed from firn air samples collected in Greenland. The measurement results show an unexpected increase of 10 ‰ in Δ¹²CH₂D₂ from 1993 to 2018. This data is used to constrain a two-box atmospheric model of the five most abundant atmospheric CH₄ isotopologues. Additionally, this optimized model is used to assess the influence of the various sources and sinks on the clumped isotopic composition over time, while also providing predictions for future trajectories. We find that Δ¹²CH₂D₂ is particularly sensitive to changes in the source-sink imbalance, caused by the strong kinetic isotope fractionation in the removal of ¹²CH₂D₂.

References:

- [1] <https://doi.org/10.1029/2020GB006883>
- [2] <https://doi.org/10.1002/2017GB005655>
- [3] <https://doi.org/10.1073/pnas.2305574120>
- [4] <https://doi.org/10.5194/amt-17-2687-2024>