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Methane from the past: Insights from clumped isotope measurements

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Atmospheric methane (CH_4) is the second most important anthropogenic greenhouse gas after CO_2. Global scale measurements of CH_4 mole fractions show an increasing trend since the 1800s as a consequence of anthropogenic emissions, overlayed by significant multi-annual variability. Understanding the evolution of CH_4 in the past is important to predict the change in future. Various studies have attempted to attribute the temporal changes in atmospheric CH_4 to changes in the contribution of different CH_4 sources, or variations in the atmospheric OH concentration and CH_4 sink reactions.

Previously, CH_4 mole fractions and bulk isotopic composition ($\delta^{13}CH_4$ and $\delta^{12}CH_3D$) from air trapped in firn or ice [1] were investigated to understand the possible causes of past CH_4 variability. However, these existing measurements and models couldn't converge on the same conclusion.

Measurements of the clumped isotopic composition ($\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$) and incorporating them in the global CH_4 budget model can serve as an additional tool to constrain the sources or sinks of CH_4 [2]. Recent developments towards low-concentration samples facilitate such measurements of CH_4 extracted from atmospheric air.

In this study, we present the first measurements of CH_4 clumped isotopes of air from the past. We analyzed 14 firn air samples collected at EGRIP (Greenland) in high-pressure cylinders, from different layers of firn down to a depth of 70 metres, dating back to the 1980s. We observe a change of 10 ± 2 ‰ for $\Delta^{12}CH_2D_2$ over the last 30 years (from 1990 to 2018) while $\Delta^{13}CH_3D$ remains constant within the measurement uncertainty. We use a box model to test possible sources and sink evolution scenarios for compatibility with our experimental data.

References:

[1] Sapart, C. J. et al., 2013: https://doi.org/10.5194/acp-13-6993-2013

[2]Chung, E & Arnold, T 2021: https://doi.org/10.1029/2020GB006883