

## Clumped isotope measurements reveal aerobic oxidation of CH<sub>4</sub> below the Greenland ice sheet

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Clumped isotopes of methane (CH<sub>4</sub>), specifically  $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$ , provide additional information to constrain its sources and sink processes. These isotopes complement interpretations of CH<sub>4</sub> provenance based on bulk isotopes. However, interpreting the origin of CH<sub>4</sub> using isotopes becomes challenging when the isotopic signature is altered by post-generation processes. In this study, we measured, for the first time, the bulk and clumped isotopic composition of sub-glacial CH<sub>4</sub> samples. These samples were collected from the air-filled headspace of the glacier portal (ice cave) at the edge of the Isunnguata Sermia glacier (ISG), located at the western margin of the Greenland ice sheet (GrIS). Our goal was to identify the processes underlying the sub-glacial production and potential processing of CH<sub>4</sub>. The  $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$  values of the samples measured in this study are  $3.7 \pm 0.3$  ‰ and  $39.7 \pm 2.0$  ‰, respectively (95 % confidence interval). The  $\Delta^{12}\text{CH}_2\text{D}_2$  values are close to those of atmospheric CH<sub>4</sub>. The elevated  $\Delta^{12}\text{CH}_2\text{D}_2$  values can be attributed to the alteration of the source's isotope signal by aerobic oxidation. This conclusion is supported by previous studies at this site, which reported the presence of methanotrophic bacteria and dissolved oxygen close to saturation in the meltwater. Our results confirm that the correlation between  $\Delta^{13}\text{CH}_3\text{D}$  and  $\Delta^{12}\text{CH}_2\text{D}_2$  is a useful tool for deciphering oxidation pathways. Our results support the inference that aerobic CH<sub>4</sub> oxidation can strongly modify the  $\Delta^{12}\text{CH}_2\text{D}_2$  isotope signal, which must be considered when determining the source signatures of environmental samples.