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In situ production of ethane and propane in dust-rich Greenland ice core samples: is methane also affected?

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The analysis of methane and the stable isotopic composition extracted from ice core samples provides a suite of valuable climatic sensitive parameters like CH4 mixing ratios, d13C(CH4), dD(CH4) and the respective interhemispheric differences of these parameters. Their interpretation as palaeoclimatic proxies relies on the assumption that the measured properties represent true atmospheric concentrations after correction for the well-known diffusive processes in the firn column. Up to now, methane is assumed to be unaffected from in situ production with the exception of melt layers and alpine ice cores which show elevated concentrations. In contrast, other trace gases like CO_2 and N2O show in situ production under certain conditions, especially in dust-rich Greenland ice core samples. Also other trace gases which are chemically more related to methane, like the hydrocarbons ethane and propane as well as methyl chloride show pronounced in situ production in some ice cores.

To explore the processes leading to situ production for ethane and propane and a possible link to methane it is helpful to measure these parameters simultaneously on a single ice core sample.

For this task we present a new online preparation line for extraction and measurement of several trace gas species (isotope ratios and/or mixing ratios) of 150-200 g ice samples. The analytical setup comprises continuous flow-isotope ratio mass spectrometry and a custom-built online pre-concentration system with a vacuum extraction part and a continuous He flow GC line. Our setup allows for analysing isotope ratios of CH4(13C) and N2O (d15N, d18O) as well as their mixing ratios and, additionally, the mixing ratios of ethane, propane and methyl chloride.

We measured ice core samples on the NGRIP ice core during, selected time intervals covering DO events, the LGM and, the Bølling/Allerød Younger Dryas. Where possible, we focused on intervals where dust showed its larges variability. In summary, we see a strong in situ production for ethane, propane and methyl chloride related to dust concentrations in Greenland ice. However, methane is likely not affected by this production pathway or the contribution is so small that it is hidden in the atmospheric signal so far. A better sampling strategy focusing with a denser temporal coverage on intervals with variable dust loading could further constrain a possible contribution of methane from in situ production.