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## High precision reconstruction of δ13C-CO2 and major greenhouse gas concentrations (CO2, CH4 and N2O) over marine isotope stage 9 – first application of a novel method

## Content

Ice cores are natural archives preserving valuable information of past atmospheric greenhouse gas concentrations (CO2, CH4, N2O) and the changing climate system. To understand how the complex changes of biogeochemical cycles will respond in the future, we need to decipher the role of changing greenhouse gas concentration and the rearrangement within the major carbon reservoirs (ocean, atmosphere, terrestrial biosphere, and sediment) in the past.

Due to the differences in the carbon isotopic composition of the major carbon reservoirs, respectively the carbon fractionation occurring during exchange processes between the reservoirs,  $\delta$ 13C-CO2 measurements are a useful tool to help disentangle the causes of CO2 variations driven by biogeochemical processes.

Here we present the first application of a novel extraction and analysis system for simultaneous quantification of CO2, CH4, N2O as well as  $\delta$ 13C-CO2 in ice core samples. This is achieved by a semi-continuous laser-induced sublimation extraction technique, developed to liberate 100% of the trapped gases from the ice, followed by the analysis of the extracted air samples by a custom-made Quantum Cascade Laser Absorption Spectrometer (QCLAS), especially designed for small air samples of 1–2 mL STP. While achieving a very high vertical continuous sampling resolution of 1.5 cm of ice, equivalent to a 10–15 g ice core sample, our measurements demonstrate an excellent reproducibility (1 $\sigma$ ) for CO2, CH4, N2O as well as  $\delta$ 13C-CO2 (1 ppm, 4 ppb, 2 ppb and 0.03 ‰). Both methods and instruments were developed to achieve such high vertical resolution and highest precision, imperative, to decipher high-resolution carbon cycle changes in the extremely thinned sections of the future Beyond EPICA – Oldest Ice Core (BE-OIC).

Using the novel method described above, this work will present the first high-resolution  $\delta$ 13C-CO2 record covering the glacial – interglacial termination (TIV) of marine isotope stage (MIS) 9c–10a (332–345 kyr BP). In addition to that, the major greenhouse gases CO2, CH4 and N2O were measured simultaneously. The results of this study will shed light on the mechanisms behind the CO2 overshoot during early MIS 9.

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