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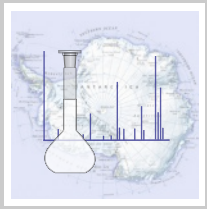

Highlights of Analytical Sciences in Switzerland

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Greenhouse Gas Measurements in Ice Cores: A Novel Instrument Shifts Borders in Analytical Precision and Resolution

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Polar ice sheets serve as the sole direct archive providing information on past fluctuations in atmospheric greenhouse gas concentration by preserving ancient air in bubbles. This unique climate archive extends our understanding of Earth's climate and atmosphere far into the past, with the longest existing, continuous records dating back 800 ka (*kilo annum*).

A new European Commission-funded deep-drilling project in Antarctica, called Beyond EPICA (European Project for Ice Coring in Antarctica) – Oldest Ice Core (BE-OIC), is underway to retrieve a continuous ice core that covers the Mid-Pleistocene Transition (MPT) period from ~1,200 to 800 ka ago. Marine sediment records reveal that the MPT marks a transition in the length and ice volume of ice ages, from glacial cycles with a cyclicity of 40 ka before, to 100 ka after the MPT. The mechanisms driving the transition are not clear and present a major unsolved problem in the field of paleoclimatology. Changing greenhouse gas forcing is at the heart of most hypotheses put forward to explain the MPT and, thus, precise and accurate ice core gas records are essential to resolve this riddle. However, the MPT ice core record will be contained in highly thinned ice at the bottom of the ice sheet, asking for new measurement techniques with higher resolution and precision, and requiring minimal sample volume.

To address this need, a coupled Laser Induced Sublimation Extraction – Quantum Cascade Laser Absorption Spectrometer (LISE-QCLAS) was developed by our laboratories. This allows us to extract and analyse the greenhouse gas composition on ice core air samples of only 1–2 mL, corresponding to 10–15 g of ice or *ca.* 1.5 cm in vertical resolution. The small sample size accounts for a temporal resolution of only a few hundred years in 1.5 Ma old ice. The air is liberated by sublimating the ice under vacuum through irradiation with a near-infrared laser, while avoiding melting by controlled water vapor trapping within the extraction vessel.[1] The QCLAS instrument is based on mid-infrared direct absorption spectroscopy. The dual-laser concept allows us to simultaneously quantify the CO_2 concentration and its stable carbon isotopic ratio ($\delta^{13}C\text{-}CO_2$) as well as CH_4 and N_2O concentrations with precisions of 0.4 ppm in CO_2, 3 ppb in CH_4, 1 ppb in N_2O and 0.04‰ in $\delta^{13}C\text{-}CO_2$.[2]

With the development of the LISE-QCLAS system, we can now perform continuous multispecies greenhouse gas reconstructions from smallest ice core samples with very high precision.

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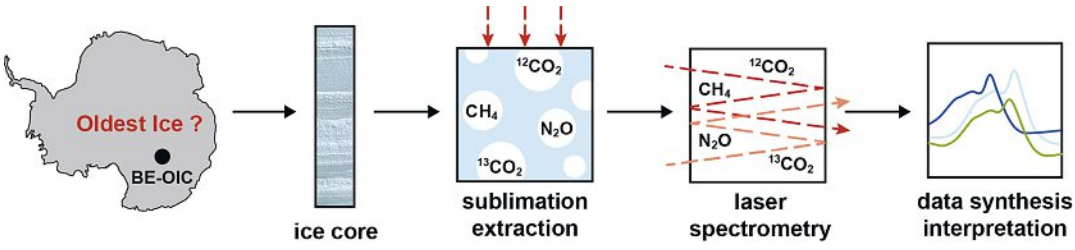

Fig. 1. Schematic illustration, how to decipher past climate and greenhouse gas variations. The air bubbles captured in ice core samples from Antarctica are released through the sublimation extraction step using Laser Induced Sublimation Extraction (LISE). The quantification of greenhouse gases of the air follows, using a dual-Quantum Cascade Laser Absorption Spectrometer (QCLAS). The obtained data are used for synthesis and interpretation.

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