Towards a Novel Continuous Sublimation Extraction/Laser Spectroscopy Method for Greenhouse Gas Measurements in the Deepest Ice

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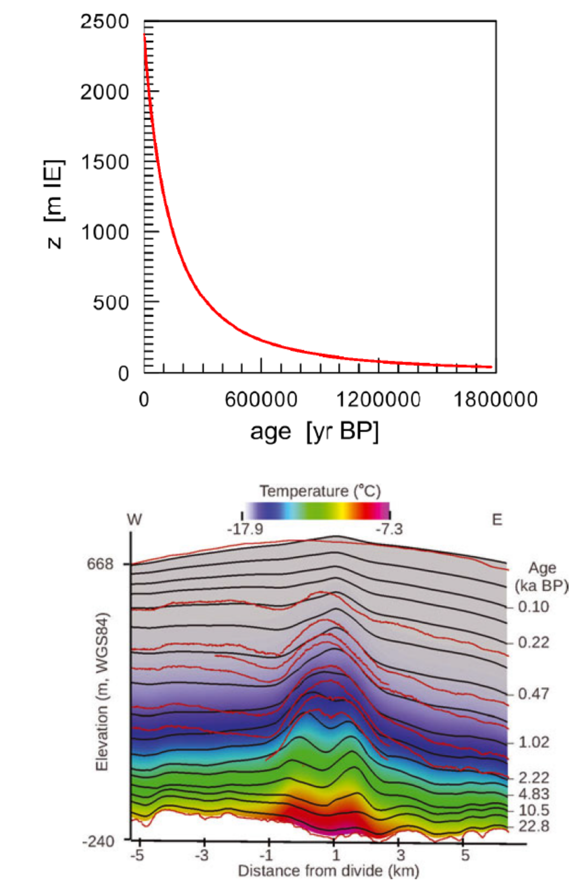
Why We Need a New Method – The Oldest Ice Challenge

In the context of retrieving the oldest stratified ice on Earth (Oldest Ice Challenge), the European “Beyond EPICA” consortium plans to drill an ice core in Antarctica extending over 1.5 million years (Myr), nearly doubling the time span of the existing greenhouse record and covering the time period of the Mid Pleistocene Transition. The ice covering the time interval from 1-1.5 Myr is expected to be close to the bedrock and, due to glacial flow, extremely thinned (up to 100 times more than in any other existing deep ice core record). A resolution of the greenhouse gas record on the order of centuries therefore constrains the vertical sample dimension to about 2 cm (about 15-30 g of ice containing only about 2 mL STP air).

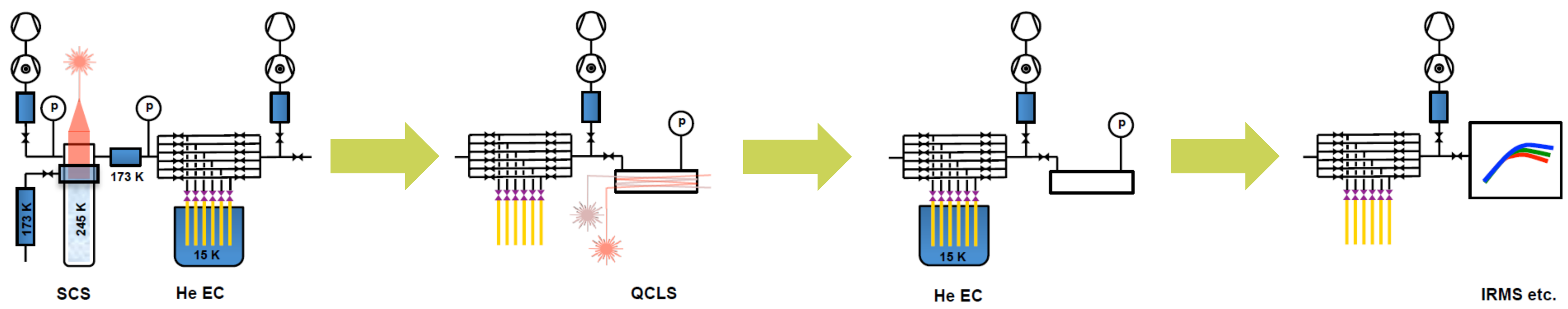
Within the ERC Advanced Grant project deepSLice we aim to unlock this extreme atmospheric archive in extremely thinned ice by developing a novel coupled semi-continuous sublimation extraction/laser spectroscopy system. Sublimation in vacuum with a near infrared (IR) light source is used as extraction method as it allows 100% gas extraction of all gas species from ice without changing the isotopic composition of CO_2 [1]. In order to improve precision and accuracy, to reduce ice consumption and to accelerate sample throughput, we are building a sublimation extraction system that is able to continuously sublimate an ice-core section and subsequently collect discrete full air samples. For the gas analytics, we develop a mid-infrared quantum cascade laser spectrometer (QCL) allowing simultaneous measurement of the CO_2, CH_4 and N_2O concentrations as well as the stable isotope ratio $\delta^{13}C(CO_2)$ on 1-2 mL STP air samples. Due to the non-destructive laser technique, the air sample can be recollected and reused for further analytics.

Thinning in Deep Ice



Strategy for Sample Processing

The continuous sublimation extraction and the QCL spectrometer are coupled via cryo-trapping of the sample in dip tubes. This also allows recollection of the sample air after the non-destructive analytics in the spectrometer and, hence, further analytics on the same sample air.



Continuous Sublimation Extraction

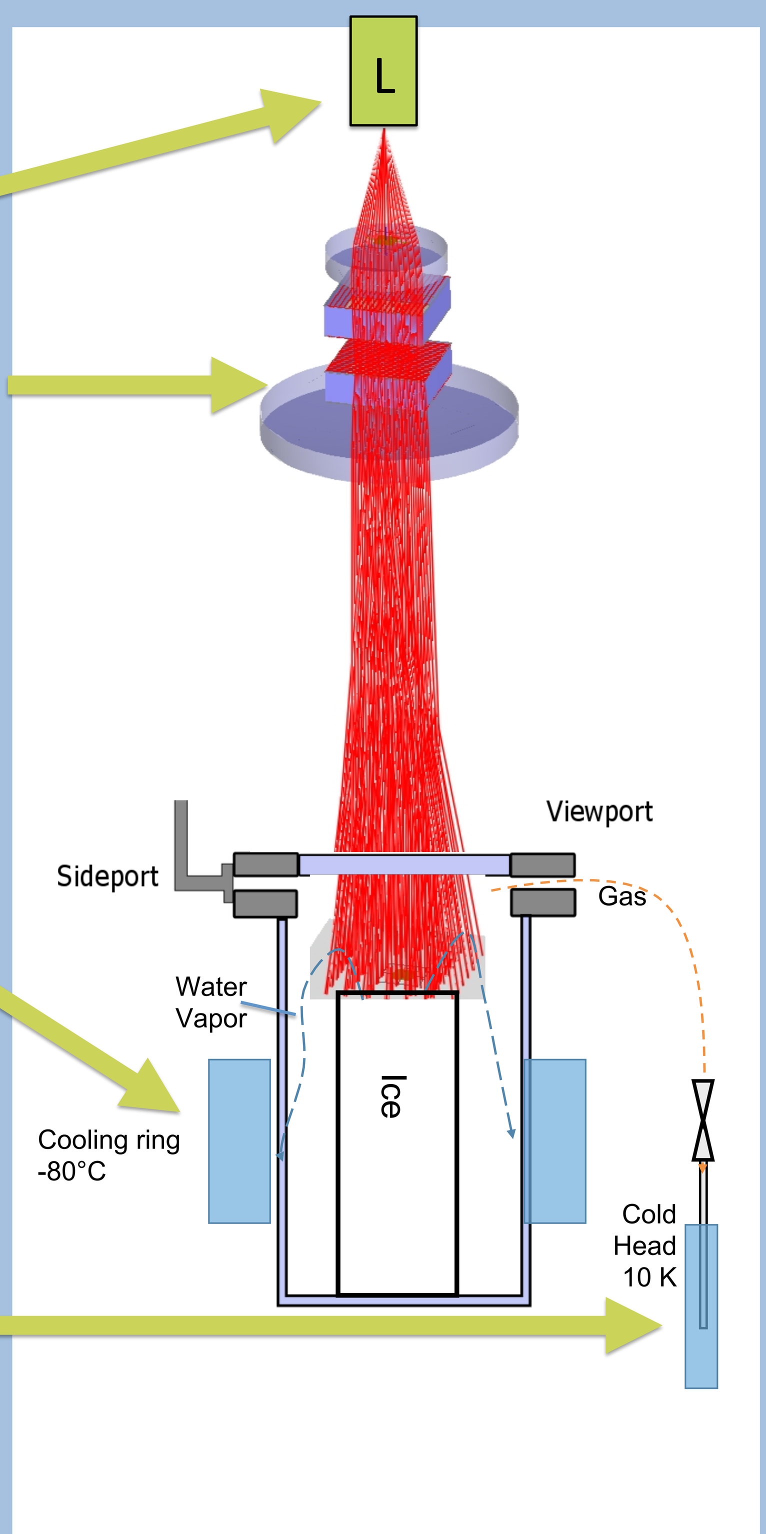
The net rate of sublimation is a function of the ice surface temperature and the vapor pressure above the surface. In our sublimation system these two elements are controlled by warming the surface through NIR light and reducing the vapor pressure by water vapor trapping. To reach a sublimation rate of 2-4 cm/hour the warming of the ice and the vapor removal have to be very efficient

The IR light is provided by a solid state laser with 1520 nm wave length and 150 W power.

An imaging fly’s eye homogenizer optics will be used to project the light homogenously onto the front side of the ice rods. An intensity of 2-3 W/cm² needs to be delivered to compensate for the loss of the latent heat of sublimation at the specified sublimation rate given above.

The glass vessel in which the ice is placed is partially cooled from the outside to -80ºC acting as an efficient vapor trap. The vapor pressure is maintained below 1 mbar to avoid any melting and to keep sublimation rate high.

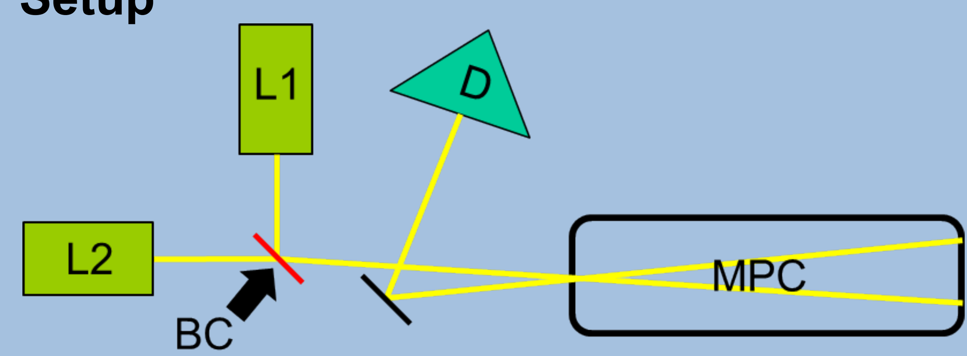
The released gas is then cryo-trapped in a cold finger at 10 K.



Photograph of ice after sublimation. The preliminary set-up with an IR-bulb reached a sublimation rate of 2 cm/hour. In order to maintain a more homogenous sublimation front an NIR-Laser with beam shaping optics will replace the bulb.

Quantum Cascade Laser (QCL) Spectrometer

Concept of Dual Laser Optical Setup



L1: QCL for CO_2 at 4.3 μm

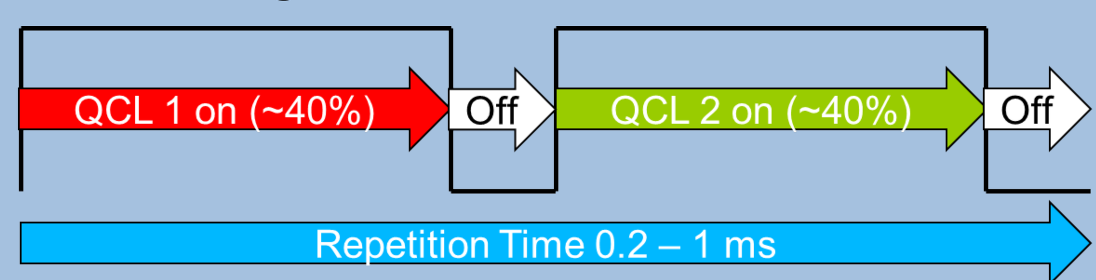
L2: QCL for CH_4 and N_2O at 7.8 μm

BC: Dichroic Beam Combiner

MPC: Astigmatic Herriott Multi Path Cell (36 m path length)

D: IR detector (TEC-MCT)

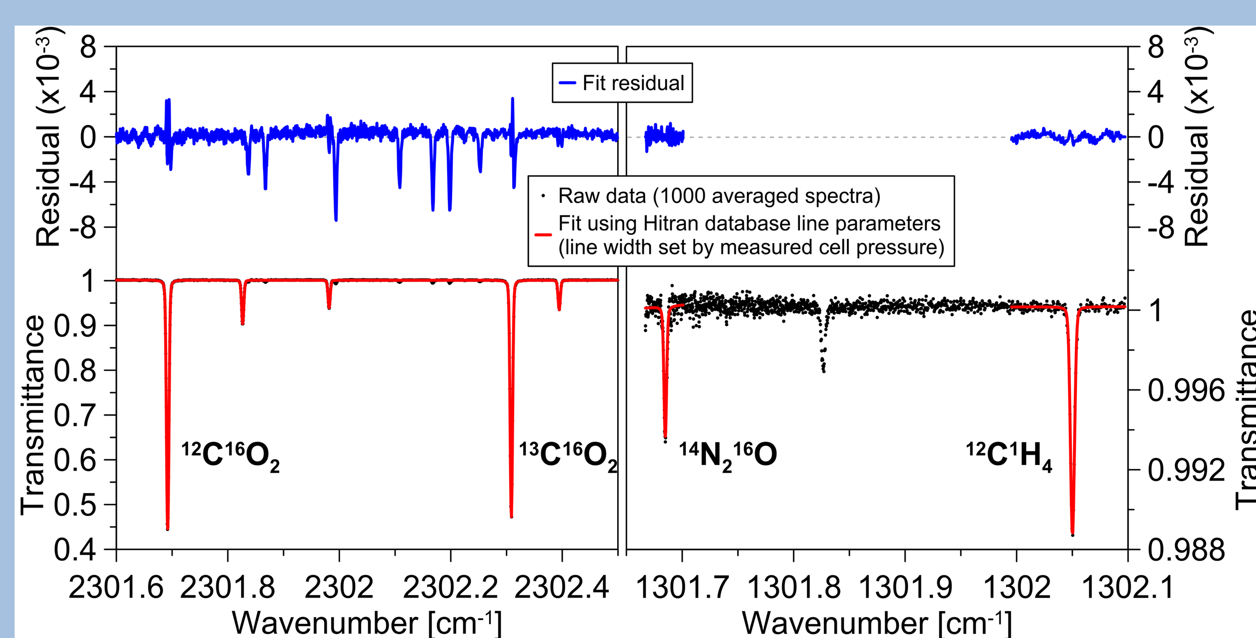
QCL Driving Scheme



The QCLs are driven using the Intermittent Contin-uous Wave (ICW) scheme [2] and are tuned over the target range.

The Analytical Challenge – Line Width

The low amount of gas available from the ice sample leads to very low working pressures in the MPC (~5 mbar). This results in very narrow absorption lines of only ~4e-3 cm⁻¹ full width at half maximum. To reach distortion free resolution of such lines a very high stability of the laser frequency is required, which is achieved by stabilizing the temperature of the QCLs to 1 mK and of the custom-made driving electronics as well as the overall optical module to 10 mK.



Absorption spectrum of a standard gas (352 ppm CO_2; 323 ppb N_2O; 1965 ppb CH_4) obtained with the current QCL spectrometer set-up using a cell pressure of 5 mbar (corresponds to about 1.5 mL STP sample air).

Para-meter	Target Precision
CO_2	0.1 ppm
CH_4	2 ppb
N_2O	2 ppb
$\delta^{13}C(CO_2)$	0.04 ‰

Measured parame-ters and their target precisions. Targets in green have been reached.

References: [1] Schmitt et al., Atmos. Meas. Tech., 4, 1445–1461, doi:10.5194/amt-4-1445-2011, 2011.
[2] Fischer et al., Optics Express, Vol. 22, No. 6, doi:10.1364/OE.22.007014, 2014