A new system for stable isotope measurements of CO_2 developed in view of obtaining the first CO_2 ice core record from Greenland.

CENTRE FOR
ICE AND CLIMATE

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Background

In 2007 the Centre for Ice and Climate (CIC) was launched. One focus of the CIC is to obtain a first CO_2 record from Greenland (i.e. NEEM). A new research group for the analysis of atmospheric trace gases was formed. In the past two years, the necessary laboratory facilities were established. This included designing and building of a new dry extraction systems for analysis of $\delta^{13}CO_2$ on gases entrapped in the ice.

Motivation

Air bubbles entrapped in ice represent the only direct archive of the past atmospheric composition. To better understand the dynamics and mechanisms of the climate system palaeo-records from both, the Northern and Southern Hemisphere are needed. For greenhouse gases such as CO_2, valuable information about climate related processes and exchange fluxes between sources and sinks can be gained from the isotopic signature of the gases (i.e. $\delta^{13}C$). So far, extended concentration records of CO_2 are available from Antarctic ice cores only (i.e. the Southern Hemisphere) and to date no reliable record of $\delta^{13}CO_2$ exists for neither of the Hemispheres.

In central Greenland, 1000-1500 m of Holocene ice is available in each core. Compared to Antarctic sites, higher accumulation rates (~0.2 m ice per year) allow to obtain gas records with a higher temporal resolution (around 20 years), additionally the offset between the age of the gas and the surrounding ice can be constrained more accurately. However, due to the occurrence of CO_2 in-situ formation observed in ice cores from Greenland (see box below) their examination has not been fully exploited yet.

"The dilemma of rapid CO_2 variations in Greenland[1]"

First studies of CO_2 in Greenland ice cores revealed unexpected variations and ominous peaks of high concentrations which can not be related to changes in the atmosphere (e.g. Oeschger, 1988; Anklin et al., 1997) (Fig. 1). A higher impurity content in ice from Greenland compared to ice from Antarctica causing in-situ formation of CO_2 seems to be responsible for these anomalies. However, not much is known about the exact processes so far. Some studies suggest reactions such as the acidification of carbonates to be the reason for the observed additional CO_2 but disagree with others which point to a contamination derived from chemical reactions of organic matter (Francey et al., 1997; Guzmàn et al., 2007) (Fig. 2).
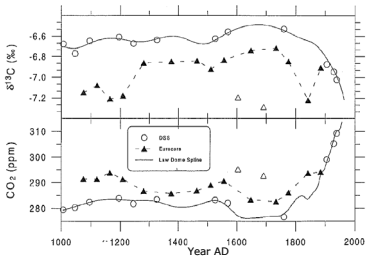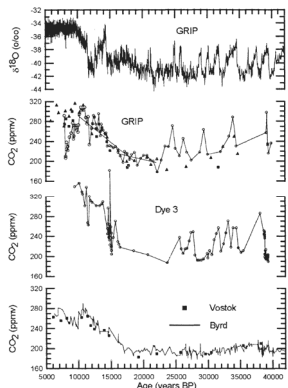

Fig. 1:
The $\delta^{18}O$ record from the GRIP ice core versus ice age is shown together with CO_2 records from Greenland (GRIP, Dye 3) and Antarctica (Byrd, Vostok) versus gas age. High CO_2 variations with elevated concentrations can be observed in the Greenland records during mild events. Figure from Anklin et al., 1997.

Fig. 2:
Differences in CO_2 concentrations and $\delta^{13}C$ values from Law Dome (Antarctica) and Eurocore (Greenland) are generally too large to represent atmospheric spatial variations between the sites. A uniform contamination from organic matter can be assumed according to the more depleted values in $\delta^{13}C$. Figure from Francey et al., 1997.

Towards a first clean CO_2 record from Greenland

The isotopic composition of the possible contaminants causing the elevated CO_2 concentrations in Greenland ice core records and the atmospheric $\delta^{13}CO_2$ are significantly different from each other (around 0‰, -25‰ and -7‰ for carbonates, organic matter and atmosphere, respectively). Therefore, $\delta^{13}C$ can not only give deeper insight in the climatic processes but also is a promising tool to obtain a first clean Greenland CO_2 record.

We intend to focus on the warm periods (Holocene and the Eemian) in the first place. For the Holocene, previous studies (e.g. Anklin et al., 1995) indicated that the peaks of high CO_2 concentrations are restricted to relatively small and well defined layers of a few cm only. Based on their characteristic chemical properties, i.e. their content of chemical impurities (Fig.3) we have selected 21 samples (bags à 55cm) from three different sites (Dye-3, GRIP, NGRIP) with parallel sections of different age. This summer, these samples have been measured for a variety of parameters (e.g. TOC, Ca^{2+}, dust, pH) using the NEEM CFA system. Comparing the obtained results to the data from the parallel highly resolved $\delta^{13}CO_2$ (to be done) we aim to (i) identify 'contaminated layers' and (ii) quantify the sources of CO_2 in-situ production by applying a simple model based on mass balance equations. From that we intend to find a method to identify the unbiased sections of the NEEM samples to finally obtain a first clean CO_2 record from Greenland.
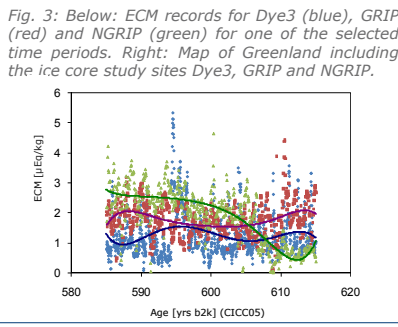
Fig. 3: Below: ECM records for Dye3 (blue), GRIP (red) and NGRIP (green) for one of the selected time periods. Right: Map of Greenland including the ice core study sites Dye3, GRIP and NGRIP.

The CIC CO_2 dry extraction system

The CIC dry extraction system to analyze concentration and isotopic composition of CO_2 ($\delta^{13}C$) in ice was designed for high resolution analysis, i.e. small sample sizes resulting in amounts of approx. 0.5 µl of CO_2 (Fig. 4). With an improved design we aimed to achieve a higher sample throughput and better conditions during analysis compared to existing systems based on the same principle. Major changes include (i) a new approach allowing fast introduction of the ice sample, i.e. to open and seal the vacuum chamber, (ii) a low temperature (-55°C) during the extraction of the entrapped gas which reduces the in-situ production of CO_2 during this process (e.g. carbonate reaction in H_2O) due to a low content of water vapor and (iii) using Helium as carrier gas to flush the gas out of the extraction unit for the subsequent analysis.
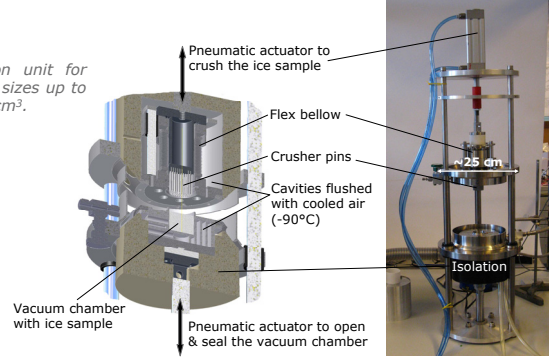
Fig. 4:
Dry extraction unit for small sample sizes up to $2.0x2.5x2.5$ cm^3.

Pneumatic actuator to crush the ice sample
Flex bellow
Crusher pins
Cavities flushed with cooled air (-90°C)
~25 cm
Isolation
Vacuum chamber with ice sample
Pneumatic actuator to open & seal the vacuum chamber

Analysis of CO_2 stable isotopes at the Centre for Ice and Climate

The approach of our set-up (see photo) is to use a continuous helium flow as a carrier for continuous, coupled GC-IRMS analysis.

First, the ice extracted gas sample is flushed out of the extraction unit before CO_2 is separated from the rest of the gases by chromatography. Sequentially, both the air and CO_2 content is quantified in a GC equipped with a pulsed discharge detector (PDD) and a thermal conductivity detector (TCD) to determine the CO_2 concentration. After passing the PDD, the sample is split into three aliquots of equal size for final analysis of $\delta^{13}C$ by IRMS (Fig. 5).
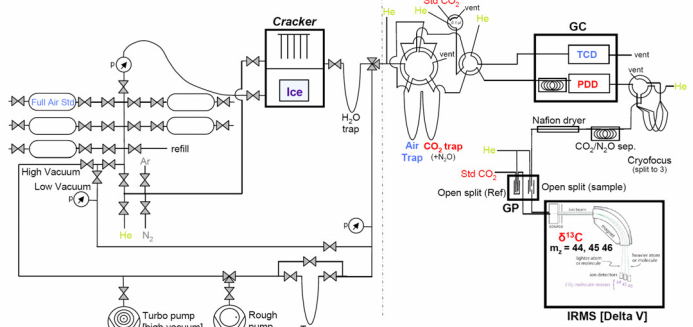

Fig. 5: Scheme of the coupling between extraction unit, GC and IRMS. The analytical side of the system is fully automated (right of the dashed line).

Preliminary results

We intend to combine results of at least 3 replicates for 'real' ice samples. For CO_2 concentrations, our current precision for measurements of standard gas (NOAA full-air) over bubble free ice (blank ice) is in the range of around ±4 ppm (1σ, n=3) with a good potential for improvement. For $\delta^{13}C$ the precision for similar samples is currently around 0.09‰ (1σ, n=3).

References

[1]Oeschger (1988), Annals of Glaciology, 10, 215-216.
Anklin et al. (1995), Tellus, 47B, 461-470.
Anklin et al. (1997), JGR, 102, C12, 26'539-26'545.
Francey et al. (1997), 5th International Carbon Dioxide Conference, AB0170.
Guzmàn et al. (2007), JGR, 112, D10123.

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