Development of a setup for the analysis of $\delta^{13}C$ in CO_2 at the Centre for Ice and Climate

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Motivation

In 2007 the Centre for Ice and Climate (CIC) was launched. One of the goals is to obtain a first CO_2 record from Greenland. For this purpose a gas group was formed, representing a new research topic at the Niels Bohr Institute (Copenhagen University, DK). In the first year, a laboratory for measurements of atmospheric trace gases was established and a new dry extraction system to analyze stable isotopes in CO_2 (i.e. $\delta^{13}C$) on small ice core samples was designed and built.

CO_2 records from ice cores

Air bubbles entrapped in ice represent the only direct palaeo-atmospheric archive. To understand the dynamics of our climate system, results both from the Northern and Southern Hemisphere are important. So far, extended CO_2 records are available from Antarctic ice cores (i.e. the Southern Hemisphere) only. The examination of Greenland ice cores has not been fully exploited yet; this is due to the occurrence of CO_2 in-situ formation found there (see box below).

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 of around 20 years. In Greenland, the offset between the age of the gas and the surrounding ice can be constrained within 30 years. This is important because the age offset determines how well CO_2 variations can be assigned to climate variations as archived in stable water and aerosol records.

A Greenland CO_2 record would give first time insight into CO_2 sources and sinks of the Northern Hemisphere and into the global CO_2 concentration gradient (i.e. N-S gradient). Together with the achievable high resolution and extraordinary age control of such a record, contribution to an improved understanding of the global carbon cycle could be gained.

How to tackle "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 (e.g. Oeschger, 1988; Anklin et al., 1997) (Fig. 1). A higher impurity content in the Greenland ice (especially during the last glacial period) compared to Antarctica is most likely the reason for these anomalies, causing in-situ formation of CO_2. Not much is known about the processes so far. Some studies suggest the reason to be additional CO_2 from the acidification of carbonate but disagree with other works rather pointing to a contamination from organic matter (Francey, Guzmàn et al., 2007) (Fig. 2).

The CO_2 isotopic signature (i.e. $\delta^{13}C$) contains valuable information about processes and exchange fluxes in the global carbon cycle. $\delta^{13}C$ seems also to be a promising tool to obtain a first clean Greenland CO_2 record based on the fact that the isotopic composition of the possible contaminants and the atmospheric CO_2 significantly differ from each other (around 0‰, -25‰ and -7‰ for carbonates, organic matter and atmosphere, respectively). A combination of highly resolved $\delta^{13}C$ with parallel chemical impurity measurements should thus allow to identify and correct for the CO_2 in-situ contribution. A new design of the dry extraction unit will additionally allow to test for effects on CO_2 concentration and $\delta^{13}CO_2$ due to changes in crushing degree and temperature during the gas extraction process.

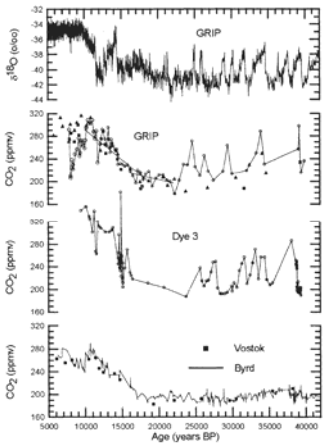

Figure 1:
$\delta^{18}O$ record from the GRIP ice core versus ice age and CO_2 records from Greenland (GRIP, Dye 3) and Antarctica (Byrd, Vostok) versus gas age are shown. High CO_2 variations with elevated concentrations during mild events can be observed in the Greenland records. Figure from Anklin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

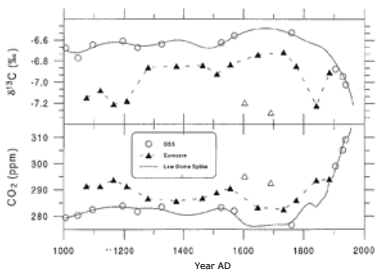

Figure 2:
Differences in CO_2 concentrations and $\delta^{13}C$ values from Law Dome (Antarctica) and Eurocore (Greenland) are generally too large to represent atmospheric spatial variations between the sites. A uniform contamination from organic matter can be assumed according to the more depleted values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

The first steps

A laboratory for measurements of atmospheric trace gases was established and a dry extraction unit for CO_2 measurements on small ice samples has been designed and built (Fig. 3.). The system will allow analysis of sample sizes up to 2.5x2.5x2.5 cm^3. We came up with a new design with the main advantages compared to other system being: a) fast sealing of the vacuum chamber (no screws), b) the use of a compressible below and a pneumatic activated cylinder to reduce heat production due to friction during ice cracking inside the sample chamber and related to that, c) a cooling allowing for lower temperatures with small gradients inside the chamber.

A compressible, welded bellow builds the hart of the design allowing to crush the ice by axial movement. Both, the bellow compression mechanism and the opening/closing of the unit to introduce the ice sample in the vacuum chamber are pneumatic actuated to assure for a fast operation. We are using Indium wire for the vacuum seal. To reach the operational temperature, a fast cooling of the system is achieved by using liquid nitrogen in the first place. In the following the temperature is kept constant by using a stream of cold air.

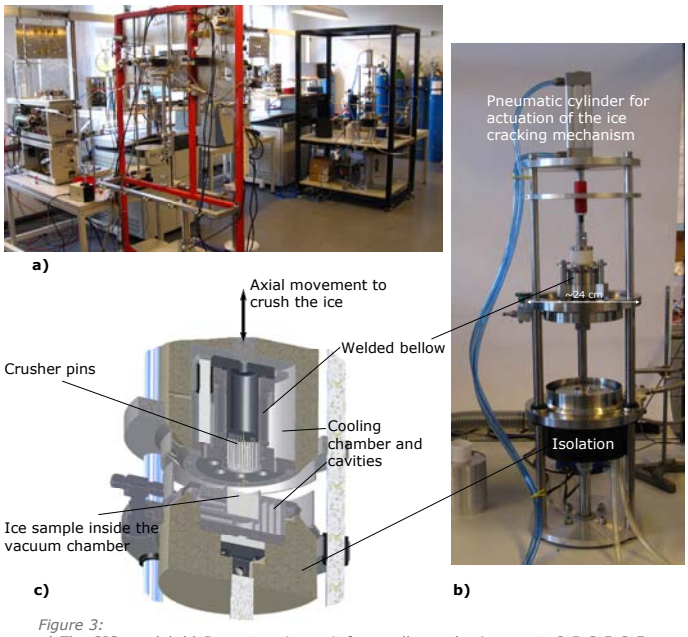

Figure 3:
a) The CIC gas-lab b) Dry extraction unit for small sample sizes up to 2.5x2.5x2.5 cm^3. c) Enlarged cross section. The inside volume varies between ~35 - 84 cm^3 dependent whether the inbuilt welded bellow is in its compressed or extended state. The system can be cooled down to a temperature of around -45°C and can be evacuated to a pressure of around 10^{-6} bar.

The overall set-up of the extraction line to analyze $\delta^{13}CO_2$, i.e. the coupling between the extraction unit, gas chromatograph (GC, ThermoScientific, Trace GC Ultra) and isotope ratio mass spectrometers (IRMS, ThermoScientific, Delta plus V) is under development. In Fig. 4, the aimed setup for the analysis of CO_2 and $\delta^{13}C$ is presented. Basically, released air from the ice bubbles will be flushed with Helium from the extraction unit to the IRMS.

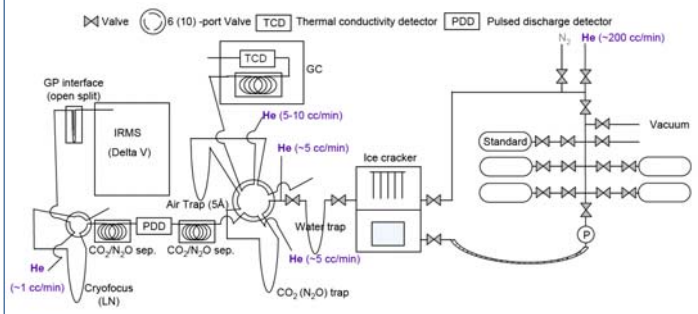

Figure 4:
Scheme for a possible coupling between the extraction unit, GC and IRMS to allow for fully automated CO_2 and $\delta^{13}C$ analysis.

References

[1]Oeschger (1988), Annals of Glaciology, 10, 215-216.
Anklin et al. (1997), JGR, 102, C12, 26'539-26'545.
Francey et al. (1997), 5th International Carbon Dioxide Conference, AB0170.
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