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A sublimation technique for high-precision $\delta^{13}CO_2$ analysis of ice cores

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The challenge to quantitatively identify the processes driving the glacial/interglacial variations in atmospheric pCO_2 of about 100 ppmv is a task of outstanding importance for the paleo climate community.With the EPICA Dome C ice core a continuous pCO_2 data set is available, currently covering 650,000 years. Particularly the last glacial cycle was measured in high temporal resolution and there is good confidence in the accuracy of the measurements due to overlap with other Antarctic cores, e.g. Vostok ice core. In contrast, CO_2's carbon isotopic information, which is controlled by fluxes and equilibrium processes between the global carbon reservoirs, tells a different story. For more than 10 years, several analytical approaches have been set up to provide the needed $\delta^{13}C$ data to better constrain modeled global carbon cycle scenarios [Leuenberger et al., 1992; Francey et al., 1999; Leuenberger et al, 2003; Eyer 2004; Schmitt et al., 2005]. Nevertheless, the $\delta^{13}C$ data set produced until now is still sparse and combining these data sets from different ice cores is not straightforward. The main reason for this situation are the different analytical approaches (dry extraction systems with sample sizes ranging from 1 kg to 10 g, and sublimation extraction with GC separation) with each having its own advantages and drawbacks. Furthermore, the paradigm of $\delta^{13}C$ extracted from ice cores as a pristine global atmospheric signal has faded since Eyer et al., 2004 found hints for a cm-scale heterogeneity in two Antarctic ice cores. To continue to quest, we set up a sublimation system to extract CO_2 from small ice core samples for simultaneous analysis of $\delta^{13}C$, $\delta^{18}O$ and ppmv CO_2. An ice sample of 30 g yields up to 5 sub-samples in individual glass capillaries. The precision of these replicates is 0.05 ‰ for $\delta^{13}C$ and $\sim$2 ppmv for pCO_2. A synthetic air standard with known composition is admitted to the sublimation system in a way that the continuous release of air from the bubbles or clathrates is mimicked as good as possible.

This allows the detection and quantification of systematic fractionation effects. These synthetic air replicates can be analyzed with a precision of 0.05 ‰ for δ^{13}C and $\sim$1 ppmv for pCO_2. With the sublimation approach it is possible to extract enclosed air from an ice volume quantitatively, thus, both bubble and clathrate ice can be analyzed. To overcome problems due to contamination with drill fluid or other organic impurities in the ice, CO_2 is chromatographically separated. Additionally, this allows a δ^{13}C determination without N_2O correction. Since the gas extraction from the ice is by far more time consuming than the actual measurement in the IRMS, the system is split up into a "sublimation extraction" and the "cryofocus-GC device". This allows us to measure several samples within a short time span and, thus, to take benefit of identical measurement conditions at the IRMS for a set of samples. This is crucial as changes in the performance of the IRMS are a well known problem. Here we present the recently modified sublimation system and discuss its performance and potential limitations. First samples were measured on the EPICA Dronning Maud Land ice core within the Holocene on different depth scales to answer questions concerning small scale effects and the possible variance during the younger Holocene.

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