A sublimation technique for high-precision δ[13]C and CO_2 analysis for bubble and clathrate ice

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Overview

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 Dome C ice core a continuous pCO_2 data set is available currently covering the last 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 an overlap with other Antarctic cores, e.g. the Vostok ice core. In contrast, the carbon isotopic information of CO_2, which is controlled by fluxes and equilibrium processes between the global carbon reservoirs, tells a different story. For more than 20 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; Smith 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. Furthermore, the paradigm of $\delta^{13}C$ extracted from ice cores as a pristine global atmospheric signal was challenged since Eyer et al. (2004) found hints for a cm-scale heterogeneity of up to 0.15‰ in the EDML core. It is clear that these large fluctuations are not atmospheric signals. Instead, unidentified processes, e.g. isotopic fractionation during pore close-off of the firn, might be responsible. Since neither a sound theory nor an empiric relation to physical or chemical parameters of the firn/ice was established, the interpretation of $\delta^{13}C$ on CO_2 from ice cores as a pure atmospheric signal was somehow questioned. With the new developed sublimation technique, allowing to analyze both bubble and clathrate ice samples, we found no sign for this small scale $\delta^{13}C$ variance within the EDML core.

Results

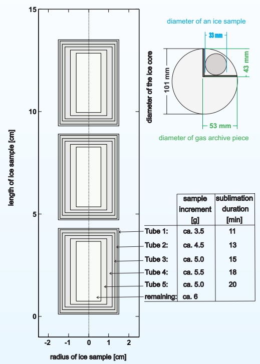
Analytical precision:

- Reproducibility of the cracker-GC-IRMS system: 0.04‰ (pure CO_2)
- Reproducibility of the entire system (sublimation apparatus + cracker-GC-IRMS): 0.06‰ (~0.5 mL STP air standard)

Ice core results:

- Reproducibility among three adjoining ice samples = 'cm-scale heterogeneity': 0.06‰
- Systematic effects among the five tube numbers during the sublimation extraction and purification: 0.2‰

Ice core sampling

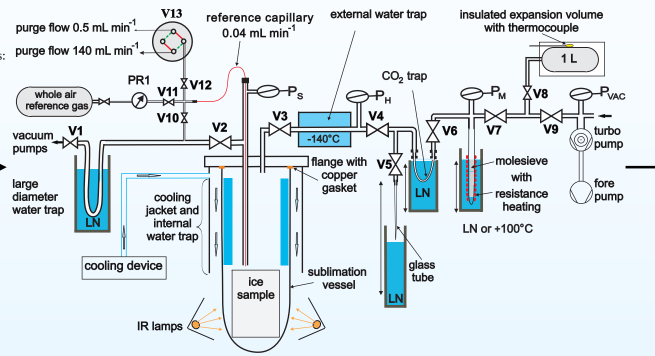


	sample increment [g]	sublimation duration [min]
Tube 1:	ca. 3.5	11
Tube 2:	ca. 4.5	13
Tube 3:	ca. 5.0	15
Tube 4:	ca. 5.5	18
Tube 5:	ca. 5.0	20
remaining:	ca. 6	

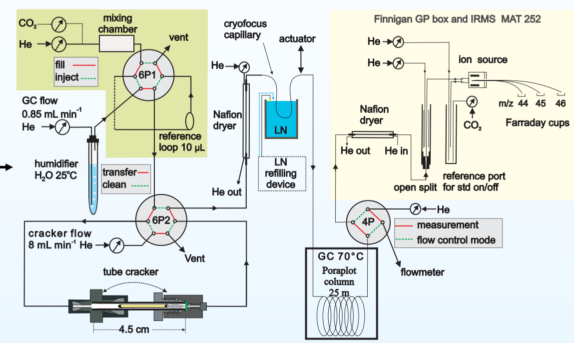
measured EDML depths:

151 m
253 m
420 m
1056 m

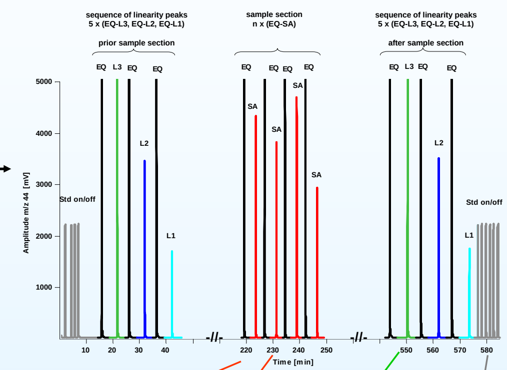
Sublimation and CO_2 collection



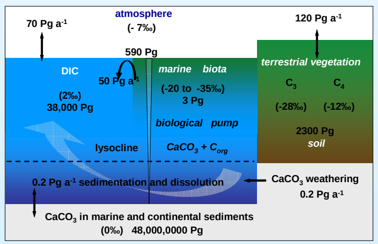
GC-cryofocus-IRMS measurement



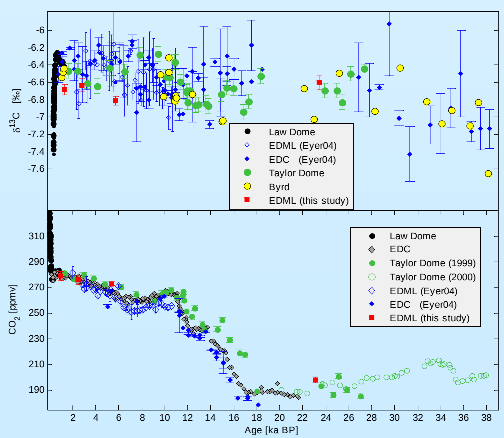
Measurement scheme



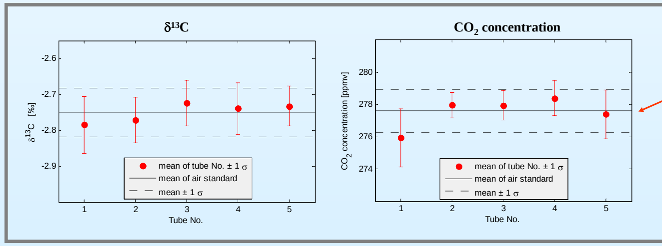
Global Carbon Cycle



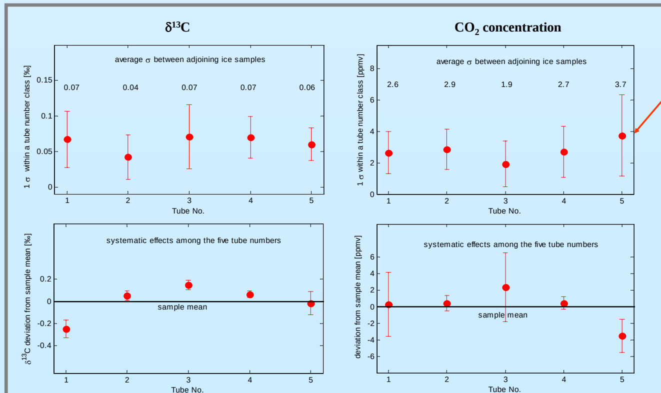
Comparison with previous studies



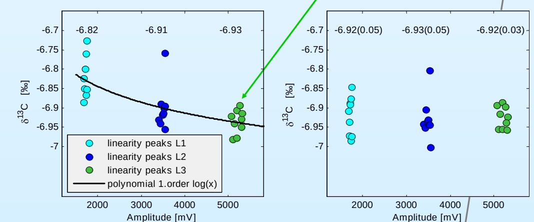
Reproducibility of air standards



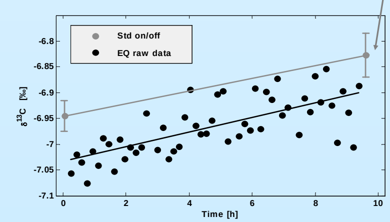
Reproducibility of ice core samples



Correction for the sample size effect ('linearity')



Correction for instrument drift with time



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