

A sublimation technique for high-precision ¹³C on CO₂ and CO₂ mixing ratio from air trapped in deep ice cores

Glacier ice from polar ice sheets represents the only direct archive to retrieve information about the composition of the paleoatmosphere. From deep Antarctic ice cores like Vostok it is known for more than a decade that the concentration of the greenhouse gas CO₂ periodically varied between glacials and interglacials and its variations are strikingly correlated with temperature. During the glacials the CO₂ concentration was about 90 ppmv lower than during the warm interglacials

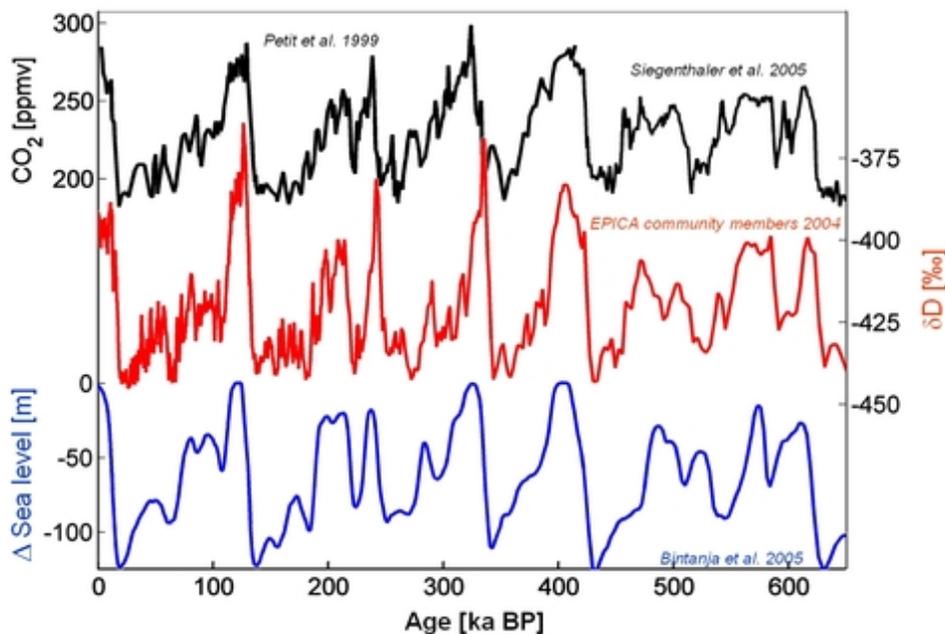
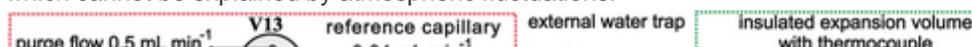


Figure 1: Compilation of Vostok and EPICA Dome C CO₂ concentrations (Petit et al., 1999; Siegenthaler et al., 2005) and δD as a proxy for local air temperature (Petit et al., 1999; EPICA community members 2004) and the changes in global sea level relative to the present level (Bintanja et al., 2005). To a first approximation, sea level changes reflect the volume of ocean water bound in continental ice sheets during the ice ages. CO₂ minima were reached approximately when the sea level was at a minimum, hence, the extent of the continental ice sheets were at a maximum. Vice versa, highest CO₂ levels were found during interglacials during the high stands of the sea level. The evolution of the local temperature (as deduced from δD) follows this overall picture and points to a strong coupling of the climate and the carbon cycle. On a finer time scale leads and lags and a non-linear behavior of the system is clearly visible

With the Dome C ice core drilled within the European Project for Ice Coring in Antarctica (EPICA) the CO₂ concentration record now covers the last 650,000 years. The task to quantitatively understand the processes behind these observed CO₂ changes is of outstanding importance not only for the paleo climate community, but also to predict the CO₂ concentration in the future. One crucial key to unravel the open questions about the coupling of the atmospheric CO₂ concentration with the dynamics of the global carbon cycle is the stable carbon isotope ratio of CO₂ (¹³C). Methodological constraints have, so far, restricted the ¹³C analysis from ice cores to the uppermost core section. Moreover, the available ¹³C data sets are difficult to interpret as accuracy and temporal resolution are insufficient and a large centimeter scale variability of ¹³C was recently measured on the EPICA ice cores, which cannot be explained by atmospheric fluctuations.



Therefore, we developed a new sublimation technique (Figure 2) allowing a quantitative extraction of air from small ice core samples coupled to a high precision gas chromatography-isotope ratio mass spectrometry system (Figure 3) to determine ^{13}C on the released CO_2 . Additionally, this technique precisely determines the CO_2 concentration on the same ice sample. This new technique makes it possible to surmount major analytical limitations and shortcomings encountered during previous studies. Using a unique sublimation technique a nearly complete gas extraction has been achieved which represents a prerequisite for high-precision ^{13}C analysis in deep clathrate ice. As the sublimation technique is equally suitable to analyze bubble and clathrate ice, this new method allows for the first time to measure ^{13}C values and the CO_2 concentration on the entire length of an ice core without adapting the extraction to changing ice conditions.

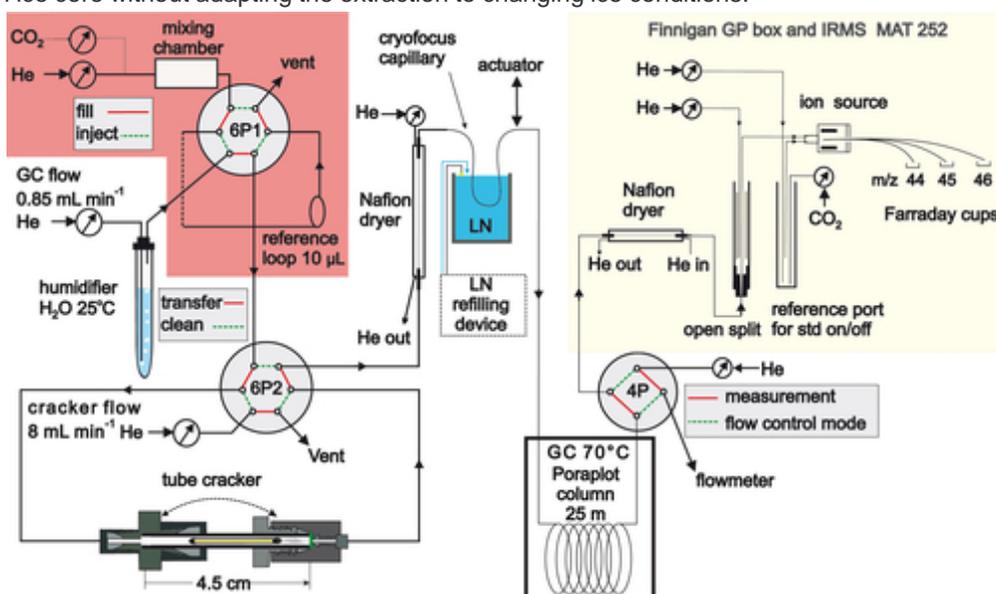


Figure 3: Flow scheme of the continuous flow tube cracker-GC-IRMS line. It consists of a CO_2 reference gas system (red area) to introduce CO_2 pulses onto the tube cracker, followed by a Nafion dryer, cryofocus capillary, GC, where CO_2 is chromatographically separated from N_2O and organic impurities. Via the Valco valve '4P' the system is linked to a commercial Finnigan GP box and MAT 252 (yellow area). The GP box houses the open split and the reference port for standard on/off. The open split capillary directs a fraction of the helium carrier to the ion source of the isotope ratio mass spectrometer (IRMS), where the ion currents of mass 44, 45, and 46 are measured and after integration the ^{13}C values are computed.