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High-resolution δ^{13}C measurements on ancient air extracted from less than 10 cm^3 of ice

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ABSTRACT

A new method for δ^{13}C analysis of very small air amounts of less than 0.5 cm^3 STP was developed. This corresponds to less than 10 g of ice. It is based on the needle-crasher technique, which is routinely used for CO_2 concentration measurements by infrared laser absorption. The extracted air is slowly expanded into a large volume through a water trap held at $-70\,^{\circ}$C where the pressure is measured. This sampled air is then carried by a high helium flux through a preconcentration system to separate CO_2 cryogenically from the air. The small CO_2 amount is then released into a low helium stream which forces the CO_2 via an open split device to a mass spectrometer. The overall precision, based on replicates of standard air without crushing, is significantly better than 0.1‰ for a single analysis, and is further improved by a triplicate measurement of the same sample through a specially designed gas splitter. Performing δ^{13}C measurements on ice air through the whole system, we reach a reproducibility of 0.12‰. Additional information is obtained through amplitude vs. pressure ratio determination, which results in a good control of the CO_2 concentration (1 ppm precision for 1σ). The new method allows us to produce highly resolved records of atmospheric δ^{13}C from air enclosed in ice, which is required to better understand the evolution and the temporal variability of the global carbon cycle.

1. Introduction

The measurements of carbon isotopes is a powerful means to disentangle land biospheric (photosynthesis and respiration) and oceanic (carbon dioxide solubility and carbonate system variations) influences on atmospheric carbon dioxide (Joos et al., 1999; Keeling et al., 1979; Quay et al., 1992). In combination with CO_2 concentration, the O_2/N_2 ratio, sea surface temperature and other proxies, δ^{13}C helps to quantify sources and sinks of atmospheric CO_2. To achieve this task for contemporary records a very demanding measurement accuracy of 0.01‰ is required for δ^{13}C in order to resolve carbon flux variations of about 1×10^{15} g, i.e. similar to the carbon budget uncertainty. For direct atmospheric measurements leading laboratories are approaching this value. However, for paleo records one still has to accept a 5–10 times higher uncertainty. Here, a higher time resolution would help simply due to statistics. Up to present only a few δ^{13}C paleo records are available (Francey et al., 1999; Friedli et al., 1984; Indermühle et al., 1999; Leuenberger et al., 1992; Smith et al., 1999). All of them document only very small variations of a few tens of a permil in δ^{13}C either during the Holocene or during glacial–interglacial conditions. Most of them have a poor time resolution because conventional systems require rather large amounts of ice. In contrast, Indermühle et al. (1999) presented a highly resolved CO_2 concentration record and have shown that carbon dioxide varies significantly even during the Holocene. Explanations for an unexpected CO_2 dip in the early Holocene include oceanic uptake and cumulative biospheric release in combination with sea surface temperature changes. The authors favor the biospheric hypothesis; however, considering the sparse resolution of the carbon isotope

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record, alternative interpretations have been proposed (Broecker et al., 2001). A temporal resolution of the δ^{13}C values which is similar to that of CO_2 would enhance our knowledge considerably, first due to improved reproducibility and second due to the potential of the detection of short-term fluctuations. Conventional carbon isotope analysis is based on the commonly used dual inlet technique in mass spectrometry. This technique requires a minimal air volume of about 50 mL STP, corresponding to 10 μL STP CO_2. This would not allow to match the present resolution for CO_2 concentration measurements. Therefore, we have developed a new measuring system for carbon isotopes based on the well known combined technique of gas chromatography and mass spectrometry (GC-MS).

2. Principle and Layout of the new system

In order to increase the resolution of carbon isotope records, the required amount of ice for such an analysis must be lowered without compromising the reproducibility. Conventional offline techniques require between 200 and 1000 g of ice for a single δ^{13}C data point with a reproducibility of 0.1% (Indermühle et al., 1999). The combined technique of gas chromatography and mass spectrometry allows us to work with a nearly hundred-fold smaller sample amount. This corresponds to 5–10 g of ice containing 0.5–1 mL STP of air or 0.1–0.3 μL of CO_2, which results in a signal amplitude of 2.8 nA in the mass spectrometer (sensitivity-dependent).

The main components of our measuring system are shown in Fig. 1. A stainless-steel needle cracker is combined with a ThermoFinnigan Delta Plus XL mass spectrometer. The ice cracker consists of a stainless steel body with a volume of 52.6 mL in which an array of stainless-steel needles is mounted to crack the ice (Stauffer and Tschumi, 2000; Zumbrunn et al., 1982). While the cracker is being handled, the temperature is held at -30 °C by a closed-cycle cooler filled with silicon oil (SilÖl M60.115.05, Huber). The ice cube ($2.5 \times 2.5 \times 1.5$ cm^3) is cracked under a vacuum of about 10^{-5} mbar. After the cracking process the released gas expands through a water trap (-70 °C) into a stainless-steel container of 700 mL. A 100 mbar Edwards manometer allows us to control the pressure of the expanded gas to a level of 0.001 mbar. The gas is then flushed by a high helium flux of more than 1000 mL min^{-1} (3 bar pressure gradient between helium supply and atmospheric pressure) through a second cooling trap (-115 °C, further cleaning of the gas) and a 12 m glass capillary (1.5 mm diameter) to the Precon system (Fig. 2), which consists of three traps of which only two are used for this application. The first is used to trap the CO_2 from the sampled air. The second allows us to shape the peak through cryo-focussing the CO_2 in a small capillary. The first trap can be switched between the high and the low helium stream, which allows us to inject the sample to the low-flow mass spectrometer circuit. This low gas stream (1 mL min^{-1}) is additionally split into three similar fluxes entering capillaries of different lengths. The three gas portions reach the mass spectrometer roughly every 50 s. A multiport valve handles the flow path such that the three CO_2 peaks enter the capillary leading to the mass spectrometer (Fig. 2). This setup allows us to compare three measurements of a single sample and assess the reproducibility of the mass spectrometer.

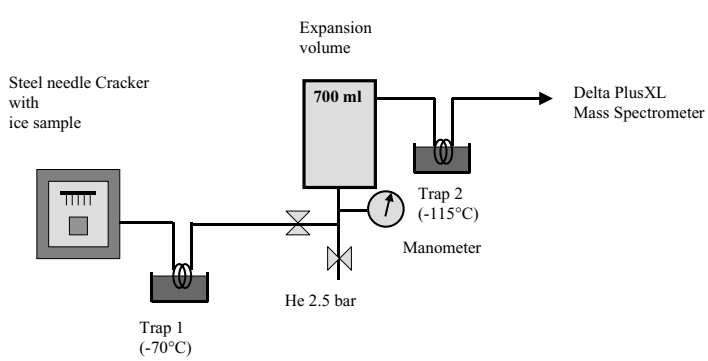

Fig. 1. Main components of the extraction process for online δ^{13}C measurements.

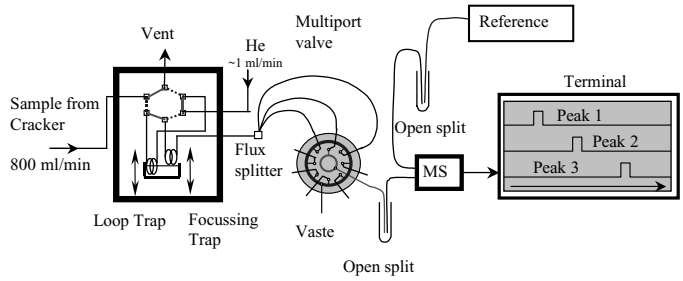

Fig. 2. Layout of CO_2 preconcentration, splitting and detection system. It is based on the Precon-system of Thermo-Finnigan MAT.

3. Reproducibility

To check the reproducibility of the mass spectrometer measurements we performed different series with pure CO_2 gas. This gas is injected into the mass spectrometer in a sequence of 12 peaks by moving the corresponding capillary in and out of the reference open split, which itself is flushed by clean helium. The reproducibility is influenced by several factors: First we assess a dependence of the δ^{13}C determination on the CO_2 amplitude referred to the non-linearity effect of a mass spectrometer. This mainly varies through changes made to the ion source settings. We control the non-linearity effect of our mass spectrometer by step-like signal strength experiments whereby each amplitude level is held constant for a given time interval (>3 min). In these experiments we measure a non-linearity effect of about 0.12–0.15 ‰ nA^{-1} for ion current amplitudes between 1.7 and 6.7 nA (corresponding to voltage amplitudes of ∼0.5 and ∼2 V), and approaches a slope of 0.03 ‰ nA^{-1} for amplitudes larger than 3 V. The non-linearity can be approximated with a polynomial fit of the form $ax^{-1} + bx^2 + cx + d$. The coefficients depend mainly on the ion source settings. For example, the behaviour of the non-linearity at amplitudes larger than 6.7 nA is highly dependent on the sign of the coefficients b and c, accordingly leading to a positive or a negative non-linearity trend. When moving from one amplitude level to another, the system requires a certain time to come into equilibrium again. This transient behaviour to this new equilibrium can be seen in Fig. 3 for 12 consecutive measurements. The slopes of the series in this figure depend on the equilibrium δ^{13}C difference of the two amplitude-levels. The amplitude jumps quickly to its new level while δ^{13}C reaches its new equilibrium value only after several measurements. Hence, for single sample measurements we do not have to take into account this non-linearity effect.

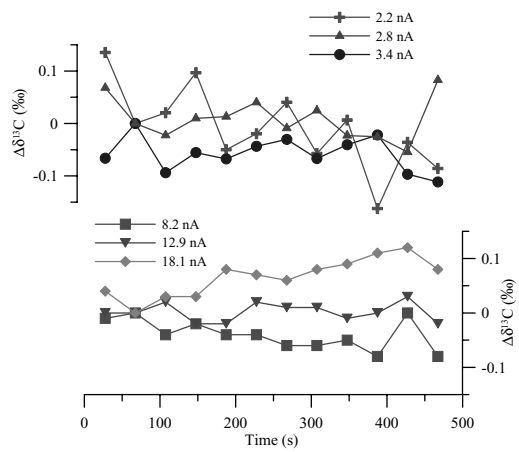

Fig. 3. δ^{13}C reproducibility tests of the mass spectrometer with pure CO_2 show an amplitude-dependent behaviour. This is probably an effect of the transient behaviour from one equilibrium value to another. These different equilibrium values are most possibly associated with amplitude (concentration) dependent adsorption/desorption effects.

Figure 3 illustrates further that, when detrending the series, the scatter of this standard measurements is dependent on the amplitude. This is a statistical effect. The scatter decreases with increasing detection rate in the mass spectrometer proportional to $N^{-1/2}$ (where N is number of counts) according to a Poisson distribution. This behaviour is shown in Fig. 4. Thus the standard deviation of the δ^{13}C values for a standard gas is <0.02‰ for a signal amplitude of >12 nA (∼3.6 V) and <0.05‰ for an amplitude >2.5 nA (∼0.75 V) (Fig. 4). Note that these are values for continuous flow applications, i.e. using helium as a carrier gas. For dual-inlet applications one would expect slightly lower

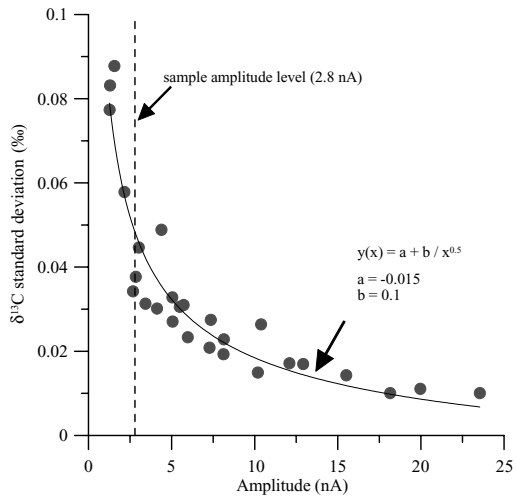

Fig. 4. δ^{13}C measurements of a standard show an amplitude dependent uncertainty, as documented by the one sigma standard deviation of 12 single measurements against the amplitude. This is in accordance with a Poisson distribution of the ion counts. The series of twelve measurements were first detrended according to the trends seen in Fig. 3. Thus the contribution to the standard deviation from the mass spectrometer statistics is lower than 0.05‰ at the amplitude of our samples (∼2.8 nA).

values. The reproducibility for δ^{13}C and δ^{18}O measurements for two different air standards (containing 342 and 244 ppm CO_2, respectively), expanded into the 700 mL STP volume and flushed through the whole system, is slightly lower. We obtained standard deviations (1σ) of 0.06‰ for δ^{13}C and 0.14‰ for δ^{18}O (Fig. 5). These values would be expected for direct atmospheric measurements using our system (note the values correspond to a single measurement, not replicates). The reproducibility of the air standards passing through the whole system, including the crushing process, is again somewhat lower (0.12‰) for δ^{13}C (Table 1). The crushing process is simulated by processing an artificially produced bubble-free ice sample with dimensions identical to the real sample. An aliquot of standard gas is expanded into the evacuated cracker that contains the bubble-free ice sample, before cracking the ice.

Table 1. *Reproducibility of standard and sample gas (1σ)*

Process	Standard (‰)	Sample (‰)
Whole process including cracking	0.12	0.12
Expansion without cracking	0.06	–
Only mass spectrometer for small samples[a]	<0.05	–

[a]See text for a detailed description.

In addition our reproducibility is influenced by fractionation processes potentially occurring during the cracking and expansion process as well as in the open split device [GP (General Purpose) interface–Delta

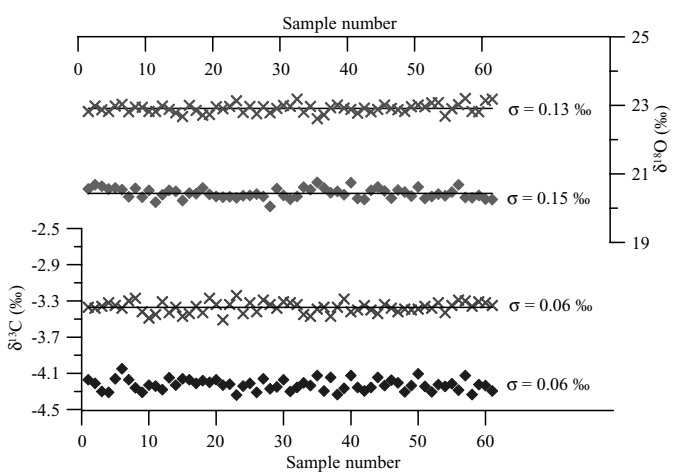

Fig. 5. To check the reproducibility of the mass spectrometer including the Precon system, the stable isotopes ratios δ^{18}O and δ^{13}C of two standard gases were measured by performing a series of 60 data points. For the two standards (standard 1, rhombi and standard 2, crosses) the 1σ standard deviation of the δ^{18}O reproducibility is 0.13–0.15‰ and 0.06‰ for the δ^{13}C, respectively.

Plus XL]. The former is probably an effect of surface absorption in the cracker volume, thereby causing a CO_2 isotope separation. This effect decreases due to the competing influence of adsorption between water vapour and carbon dioxide, since the amount of water vapour increases with the number of samples. It can only be controlled by the standard gas measurements accompanying the sample measurements. The fractionation in the open split device is related to the relative positions of the different capillaries to each other, which does not change within a series, so that this effect simply offsets the isotope values, in our case by about 0.4‰ towards lower values.

Despite these factors influencing our reproducibility, the values obtained with the new system are still comparable with conventional offline systems, in particular for small samples (3 to 10 μL STP CO_2).

4. Background

We have experienced various problems associated with blank measurements, i.e. processing CO_2-free gas (in our case high-purity helium). First of all, the background of the corresponding CO_2 mass/charge ratios 44, 45 and 46 can be influenced by several contaminants, such as N_2O, that can be produced by cold-cathode manometers (Friedli and Siegenthaler, 1988) or, for example, by fragments of isopropyl alcohol (C_3H_8O), which is used for the cold traps. The latter can easily be detected when measuring mass/charge ratios 28, 29 and 30. Indeed, we encountered severe problems with isopropyl alcohol, because it diffused from the contaminated laboratory air through our pressure regulators mounted to the high-pressure cylinder into the helium stream (most probably during pressure cycles). Assuming a δ^{13}C value of -35‰ vs. V-PDB, corresponding to the δ-value of our standard gas, the mass/charge ratio 29/28 should be close to this value without contaminants. However, we measured ratios of 18‰ (δ29/28) and 80‰ (δ30/28), which clearly indicates the contamination and enables us to quantify it. We lowered this problem significantly by operating the closed cycle cooler with silicon oil instead of isopropyl alcohol. Unfortunately, we could not yet fully substitute isopropyl alcohol in our laboratory, so that a small degree of contamination remains. Since isopropyl alcohol has a condensation temperature of -127 °C, it is difficult to separate it cryogenically from CO_2. An improvement of the background was obtained with an additional liquid-nitrogen trapping system close to the helium supply and the relocation of the helium supply cylinder to a non-contaminated room.

Other non-specified contaminations are trapped with a cold trap held at -115 °C. Without cold traps the background level is quite high, and may reach up to 5% of the sample level (0.13 nA/2.67 nA). With all cold traps in operation we reached very low backgrounds, and hardly any traces of mass/charge ratios 44, 45 and 46 were visible (<0.007 nA). The isotopic values ranges between -3‰ and -10‰ V-PDB. This corresponds to <1% of the sample signal and minimizes the contamination shift to less than a few hundreds of permil. We account for this contamination by a simple linear interpolation of similarly influenced neighbouring standard measurements to the sample.

An additional problem became visible recently. When performing ice core samples the cracker system adsorbs CO_2 from the laboratory air while loading ice samples. Flushing–evacuation cycles significantly lower this contamination. Nevertheless, this problem could not be fully solved. This effect is responsible for the lower reproducibility of standard gas for the whole process (see above).

5. First results

To test the system with real ice, we performed a series of single sample measurements on ancient Antarctic ice from the Dome C site, drilled in the framework of the EPICA project. From a depth of 264 m we processed six consecutive ice samples within a depth interval of 9 cm, each of the size $2.5 \times 2.5 \times 1.5$ cm^3. In the pre-cooled needle cracker the ice sample was first evacuated for 5 min. An amount of extracted air of 0.5–0.7 mL STP (0.2 μL CO_2) corresponded to an extraction efficiency of about 70% and led to an amplitude of about 2.8 nA for the mass/charge ratio 44. For calibration purposes, standard gas was processed in exactly the same way between samples. These results are corrected for the gravitational effect, the influence of N_2O and the fractionation offset (discussed above). All these corrections are assumed to be constant. The size of contamination of each sample is estimated by comparing standard air measurements, which are always performed after three sample measurements and at the beginning and end of every series. Differences of the standard measurements from expected values are scaled for the amplitude and then interpolated on the samples, whereby the different interference on the

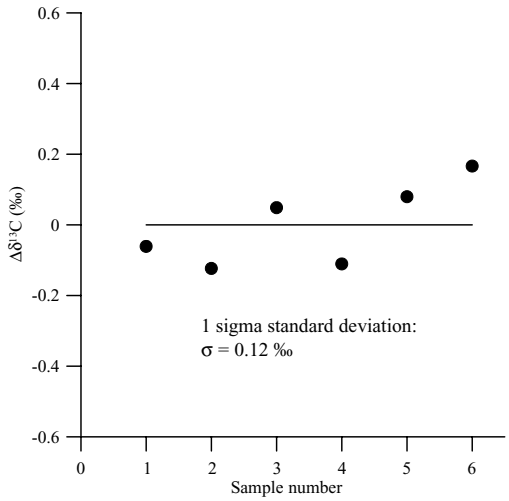

Fig. 6. The reproducibility of the δ^{13}C measurements on air extracted from ice samples processed through the whole system is lower than for standard gas measurements. A series of measurements of adjacent ice samples of ancient Antarctic ice shows a 1σ standard deviation of 0.12‰.

sample due to a different δ^{13}C signature is taken into account. The reproducibility for δ^{13}C after these corrections is given in Fig. 6. The standard deviation of a single measurement through the whole system including the cracking is 0.12‰ (Table 1). This precision can partly be improved through statistics (very dense measurements) when recalling the small sample size. Nevertheless, it still remains a major task to extract the small isotope signals present in the paleo-archive with such precision that it significantly improves our understanding of the carbon cycle.

An important by-product of the isotopic measurement is that our system allows us to quantify the CO_2 concentration simultaneously. This is obtained by calculating the ratio between the major CO_2 amplitude of the mass spectrometer measurement (mass/charge 44) and the pressure reading of the extracted gas expanded into the 700 mL volume. This ratio is compared with the ratio of a standard gas with a well known CO_2 concentration. Tests with two standards of known CO_2 concentrations with rather different concentration levels (322 and 272 ppm) show a small non-linearity effect (the difference is 2 ppm to high). We account for this effect with a second-order polynomial fit through the two standard ratios and the zero-point. Standard reproducibility for the concentration measurement is about 1 ppm (1σ standard deviation) (Fig. 7).

It is noteworthy that the CO_2 concentration measurement is not only an important climate indicator but acts here as a contamination control tool. Additionally, one has to be aware that the amplitude-to-pressure ratio is dependent on the open split setting, like the isotopic composition of the CO_2, and must be checked.

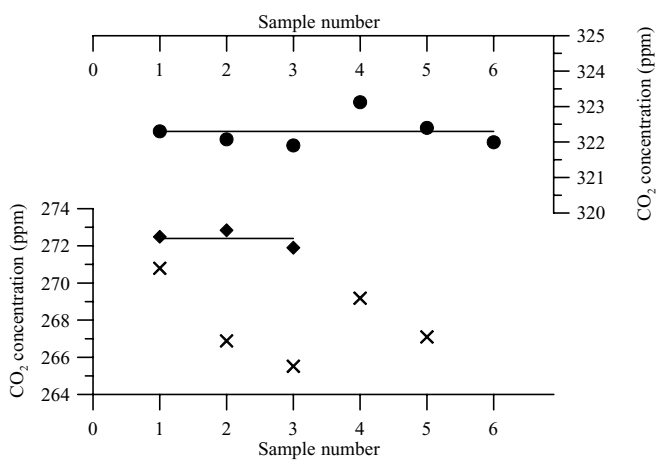

Fig. 7. A series of CO_2 concentration measurements indicates a good reproducibility. Top panel: standard 1, bottom panel: standard 2 and samples (crosses). The standards of different CO_2 concentration levels are reproducible to $\pm$1 ppm. Mean values are given as horizontal lines. The variation of a sample is somewhat larger ($\pm$3 ppm), whereby it is unclear how much of the variability derives from the extraction process and how much could be attributed to real scatter of the air composition in the ice.

6. Conclusions

The presented technique allows us to determine $\delta^{13}C$ on air samples as small as 0.5 mL STP. Regarding ice samples, this corresponds to only 5–10 g of ice, which is comparable to the amount used for state-of-the-art CO_2 concentration measurements with the highest depth or time resolution. The reproducibility is similar to the methods quoted for conventional systems requiring up to 100 times more ice, but there is potential to improve it further. Parallel to the $\delta^{13}C$ measurements we also obtain high-precision results on $\delta^{18}O$ of carbon dioxide as well as the carbon dioxide concentration either volumetrically or with an infrared laser system (IRLS, Indermühle et al., 1999).

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