On the suitability of partially clathrated ice for analysis of concentration and $\delta^{13}C$ of palaeo-atmospheric CO_2

Hinrich Schaefer [a,*], Anna Lourantou [a,1], Jérôme Chappellaz [a], Dieter Lüthi [b,c], Bernhard Bereiter [b,c], Jean-Marc Barnola [a,†]

[a] Laboratoire de Glaciologie et Géophysique de l'Environnement, Centre National de la Recherche Scientifique and University of Grenoble I, 54 Rue Molière, St. Martin d'Hères, France
[b] Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland
[c] Oeschger Centre for Climate Change Research, University of Bern, Switzerland

ABSTRACT

The stable carbon isotopic signature of carbon dioxide ($\delta^{13}CO_2$) measured in the air occlusions of polar ice provides important constraints on the carbon cycle in past climates. In order to exploit this information for previous glacial periods, one must use deep, clathrated ice, where the occluded air is preserved not in bubbles but in the form of air hydrates. Therefore, it must be established whether the original atmospheric $\delta^{13}CO_2$ signature can be reconstructed from clathrated ice. We present a comparative study using coeval bubbly ice from Berkner Island and ice from the bubble–clathrate transformation zone (BCTZ) of EPICA Dome C (EDC). In the EDC samples the gas is partitioned into clathrates and remaining bubbles as shown by erroneously low and scattered CO_2 concentration values, presenting a worst-case test for $\delta^{13}CO_2$ reconstructions. Even so, the reconstructed atmospheric $\delta^{13}CO_2$ values show only slightly larger scatter. The difference to data from coeval bubbly ice is statistically significant. However, the 0.16‰ magnitude of the offset is small for practical purposes, especially in light of uncertainty from non-uniform corrections for diffusion related fractionation that could contribute to the discrepancy. Our results are promising for palaeo-atmospheric studies of $\delta^{13}CO_2$ using a ball mill dry extraction technique below the BCTZ of ice cores, where gas is not subject to fractionation into microfractures and between clathrate and bubble reservoirs.

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1. Introduction

Measurements of the stable carbon isotope ratio $^{13}C/^{12}C$ of carbon dioxide ($\delta^{13}CO_2$) extracted from ice cores provide important constraints on the controlling mechanisms of the atmospheric mixing ratio of carbon dioxide [CO_2] during different periods. Studies have characterised $\delta^{13}CO_2$ for the period of industrialisation (starting around 1850 A.D.) (Francey et al., 1999; Trudinger et al., 1999), the Holocene (Elsig et al., 2009), the last glacial termination (~20 to 10 kiloyears before present; ka BP) (Lourantou et al., 2010a; Smith et al., 1999) and the penultimate glacial termination (~145 to 125 ka BP, Lourantou et al., 2010b). Except for the work by Lourantou et al. (2010b), these studies used ice where the enclosed air is preserved in bubbles. In contrast, the deeper sections of long ice cores, which provide ice from previous glacial cycles, are typically clathrated; that is, due to the high hydrostatic pressure, bubbles disappear and the enclosed gases are incorporated in clathrate structures. Gas

extraction using mechanical crushing has proved suitable for analysis of [CO_2] from fully clathrated ice (e.g., Lüthi et al., 2008), but so far it remained untested whether crushing would liberate CO_2 without fractionating the stable carbon isotopes or other artefacts that interfere with $\delta^{13}CO_2$ reconstructions. Our study tests the suitability of an analytical method comprising dry extraction using a ball mill, sample transfer, and isotope ratio mass spectrometry for $\delta^{13}CO_2$ measurements on partially clathrated ice. Comparison of two sample sets of Antarctic ice covering the same time period (42–48 ka BP) provides a definitive test; one sample consists of bubbly ice and the other of ice from the bubble–clathrate transformation zone (BCTZ). The BCTZ ice used here is analytically more challenging than fully clathrated samples because the ice is typically brittle and may contain microfractures. More importantly, in the BCTZ CO_2 gets partitioned between bubbles and clathrates (Anklin et al., 1997; Bereiter et al., 2009; Lüthi et al., 2010). If this partitioning is associated with an isotope effect, the CO_2 reservoir in bubbles will be isotopically distinct from the reservoir in clathrates. Consequently, different yields from each CO_2 reservoir during gas extraction would lead to a bias in the measured $\delta^{13}CO_2$. In principle, this concern does not apply to fully clathrated ice, so our study is a conservative test if fully clathrated ice may be subject to natural or experimental artefacts. Successful analysis of $\delta^{13}CO_2$ in clathrated ice will enable reconstructions of this parameter for previous glacial cycles, providing important constraints for the history of

* Corresponding author at: National Institute of Water and Atmospheric Research Ltd, 301 Evans Bay Parade, Wellington 6021, New Zealand. Tel.: +64 4 386 0316; fax: +64 4 386 0574.
E-mail address: h.schaefer@niwa.co.nz (H. Schaefer).
[1] Now at Laboratoire d'Océanographie et du Climat: Expérimentation et Approches Numériques (LOCEAN), Institut Pierre Simon Laplace, Université Pierre et Marie Curie (UPMC), Paris, France.
[†] Deceased in September 2009.

the carbon cycle and allowing for comparison to current, anthropogenically influenced trends.

2. Materials and methods

We used ice from the EDC core (75°06′S, 123°21′E; 3233 m.a.s.l.; EPICA Community Members, 2004) with depths from ~800 to 861 m below surface, which is in the BCTZ. For comparison, we measured bubbly ice (~725 to 758 m) from the Berkner Island core (BIC; 79°33′S, 45°41′W; 890 m.a.s.l.; Mulvaney et al., 1997). All measurements were performed at the Laboratoire de Glaciologie et Geophysique de l'Environnement (LGGE, Grenoble, France) using the method described by Lourantou (2008) and Lourantou et al. (2010a,b). In short, a ~40 g piece of ice is cut and ~3 mm trimmed off all surfaces (in order to avoid possible fractionation at the ice/atmosphere interface; Bereiter et al., 2009). The sample is then evacuated in a stainless steel ball mill flask sealed with indium wire for 60 min while kept in an ethanol bath at ~−75 °C (Barnola et al., 1983). The flask is taken into a cold room (−20 °C) and the ice crushed for a total of 1.5 min or 2.5 min using a shaker set-up. The flask is immediately placed in the cold bath again and reconnected to the line, which is then pumped out for 20 min. The liberated gas is expanded into a sample loop and from there flushed through a high-flow system, for quantitative transfer, and low-flow system, for peak focusing; meanwhile the CO_2 is frozen at liquid nitrogen temperature in a glass trap (high-flow) and capillary tubing (low-flow). After gas chromatographic separation, $\delta^{13}CO_2$ is measured on a MAT 252 (Thermo Finnigan, Bremen) isotope ratio mass spectrometer (IRMS). We report $\delta^{13}CO_2$ in the standard δ-notation relative to V-PDB standard. All measurements are corrected against injections of a standard gas ($[CO_2] = 260$ ppmv; $\delta^{13}CO_2 = -6.40‰$, provided by CSIRO). $[CO_2]$ is calculated from the peak height of the $m/z = 44$ trace and calibrated against the standard. Three consecutive expansions from each processed sample were transferred to the IRMS to provide multiple analyses. In addition, we analysed either two or three ice samples for each depth. This amounts to a total of 146 IRMS runs on 49 samples from 22 depth levels. From these, 18 IRMS runs were discarded because of handling errors, as well as when gas sample pressure, $[CO_2]$, or the $m/z = 45$ trace indicated contamination of the analysis. This leaves 128 analyses on 44 samples from the 22 depth levels, with 3 depth levels represented by only one ice sample because the duplicate measurement is disregarded. We report for each age horizon the mean of all expansions of replicate samples, resulting in records with average age resolution of 440 years for EDC and 650 years for BIC.

All results are reported on the EDC3_gas_a age scale (Loulergue et al., 2007), with BIC synchronised using methane concentration changes. All data have been corrected for the effects of gravitational and thermal fractionation of gases and isotopes that take place during diffusion through the snow pack (although thermal fractionation is negligible in Antarctic ice; Goujon et al., 2003). BIC data were corrected using $\delta^{15}N$ of N_2 data by Mani et al., (in prep.) from the same core. These closely approximate the fractionation of carbon isotopes, as they are subject to the same gravitational (and potential thermal) diffusion (Severinghaus and Battle, 2006). This approach ignores differences of negligible magnitude from thermal diffusion coefficients (Severinghaus et al., 2001) and kinetic behaviour in potential wind-induced convective zones (Severinghaus et al., 2010). For EDC no $\delta^{15}N$ data are available for the measured time period, instead we use an empirical relationship between $\delta^{15}N$ and the ratios of Deuterium to ^1H in the ice matrix (δD) (Dreyfus, 2008) to derive the correction factors:

$$\delta^{15}N = 0.0020032 \times \delta D + 1.2969 \qquad (1)$$

The correction amounts on average to $0.21 \pm 0.01‰$ on BIC results and to $0.44 \pm 0.01‰$ for the EDC results. We note that, although concentration gradients in the firn can also lead to isotopic fractionation (Trudinger et al., 1997), the rate of $[CO_2]$ change is too small during the studied period to generate an effect high enough to necessitate separate corrections.

In order to test whether the results from EDC differ significantly from the BIC data we had to account for the variations in sampling of the two cores, i.e. the fact that discrete ages do not match between the two data sets. To this end, we created synthetic datasets with the same uncertainty envelopes as their respective parents. A cubic spline fit was applied through the EDC time series. The uncertainties were calculated using a Monte Carlo technique. 10,000 perturbations of the spline were generated such that the mean and standard deviation of each set of replicates of measured EDC samples was met. The total of splines was then sub-sampled at the ages of BIC data points. The mean and standard deviation of the synthetic BIC data reflect those of the 10,000 perturbations to the cubic spline fit. The process was then reversed, i.e. spline fits through BIC were sampled at EDC ages, in order to rule out artefacts from the synthetic data construction.

Two 2-way analyses of variance (ANOVA) were used to test the effects of ice core and gas age on the $\delta^{13}C$ of CO_2 for the measured (BIC and EDC) and synthetic (BIC_{spline} and EDC_{spline}) data sets, where core (BIC vs. EDC_{spline}; and EDC vs. BIC_{spline}) was treated as a categorical variable and gas age was treated as a continuous variable. Levene's tests were used to assess heteroscedascity among categorical factors (cores). Residual plots were used to detect heteroscedascity in continuous predictor variables (gas age). All data met the assumptions of the ANOVA. To gain insight to which gas ages drove significant differences in the cores' $\delta^{13}CO_2$ records, gas age was treated a categorical factor so that the 'gas age x core' interaction term could be evaluated by post hoc testing using a Fisher's LSD test. A t-test was used to determine the effect of core (EDC vs. BIC) on the pooled $\delta^{13}CO_2$. All values are reported as mean ± 1 standard deviation.

3. Results

3.1. Gas preservation in the Berkner Island Core

Measurements on BIC ice, where air is stored in bubbles, have a pooled standard deviation of 1.5 ppmv for $[CO_2]$ ($n = 57$). $[CO_2]$ shows a peak of ~15 ppmv magnitude centred around 46.0 ka BP over a baseline of ~200 ppmv (Fig. 1). This is the atmospheric response to the coeval Antarctic Isotope Maximum 12 (AIM12) warming event (EPICA Community Members, 2006) and has been previously reported, e.g., from the Byrd ice core by Ahn and Brook (2008), who refer to the episode as Antarctic Event 2. Due to the well-mixed nature of atmospheric CO_2 the peak in concentration as recorded in different ice cores is a truly coeval signal. This is irrespective of uncertainties and inconsistencies between the assigned age scales of individual cores. An attempt to unify the age scales of all the presented and cited ice records is beyond the scope of this study. It will be shown that age scale discrepancies have no bearing on the main findings. After accounting for a lead of ~1.1 ka of the BIC relative to Byrd, our data are consistently ~6 ppmv lower than the measurements by Ahn and Brook (2008) at Oregon State University (OSU). Earlier $[CO_2]$ measurements on Byrd ice (Neftel et al., 1988) show several inexplicably low values during AIM12 but in general agree within 2 to 3 ppmv with our data (Fig. 1). Also, $[CO_2]$ results from the EPICA Dronning Maud Land (EDML) core (Lüthi et al., 2010; Fig. 2) compare well with our data, as do measurements from Taylor Dome (Indermühle et al., 2000); uncertainties in the different age scales notwithstanding. The discrepancy between BIC and the Ahn and Brook (2008) data exceeds the combined uncertainty of the two data sets (± 1.5 ppm for either study). Tracing the respective calibrations back to the WMO scale via standards may possibly explain some of the offset because our reference gas is provided by CSIRO, whereas OSU uses a WMO reference gas. However, such standard propagations typically result in differences of <1 ppmv, unless strong drift occurred in one tank. This was not observed in either lab. In contrast to BIC, Ahn and Brook (2008) did not correct for gravitational fractionation of gases. Doing so improves the fit between the two records, but only marginally, as the magnitude of the correction is <0.8 ppmv (based on $\delta^{15}N$ values in Byrd ice reported by
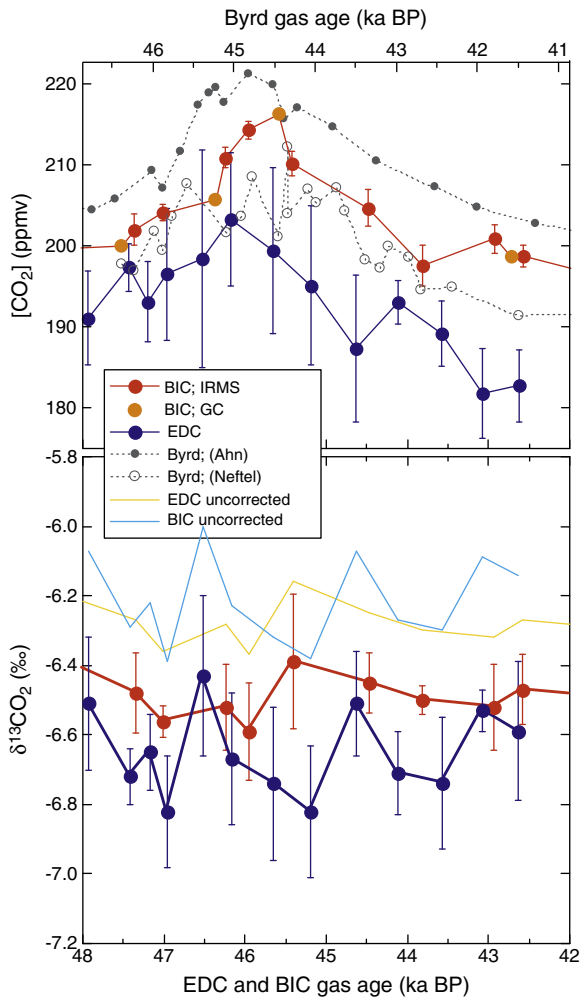
Fig. 1. Records of carbon dioxide concentration and its stable carbon isotopic signature measured in bubbly and partially clathrated ice. Upper panel: [CO_2] data from the BCTZ of EDC display large scatter and lower values due to preferential release of CO_2-depleted air compared to bubbly BIC ice. [CO_2] data from the Byrd ice core (Ahn and Brook, 2008; Neftel et al., 1988) are shown for comparison on their own age scales (top axis). Lower panel: $\delta^{13}CO_2$ records from EDC and BIC before and after correction for fractionation in the firn layers. Error bars are added for corrected values.

Sowers et al., 1992). Given that the Ahn and Brook (2008) Byrd data also exceed other OSU measurements from the same time period on the Siple Dome core (Ahn, personal communication) as well as coeval data from the same core measured by Neftel et al. (1988), the discrepancy to the BIC record may not reflect on the LGGE procedures. Apart from the discussed offset, the magnitude of the [CO_2] variability agrees well between BIC and the two Byrd records, although uncertainties in the respective age scales make a direct comparison difficult. There is no apparent trend in $\delta^{13}CO_2$ measured in BIC (Fig. 1): values stay consistently around −6.49‰ with measurement uncertainties for the individual data points between 0.04 and 0.19‰. Pooled standard deviation is 0.12‰ (n = 43). A detailed analysis of this dataset will be given elsewhere (Schaefer et al., in prep).

3.2. Gas preservation in ice from the bubble–clathrate transformation zone

3.2.1. Carbon dioxide concentration

The [CO_2] data from EDC showcase the problems of CO_2 analysis in partially clathrated ice. Although the general evolution of [CO_2] (Fig. 1) is similar to the trends seen in BIC, values are consistently lower by ~11 ppmv and show very strong scatter (pooled σ = 6.8 ppm). A solid

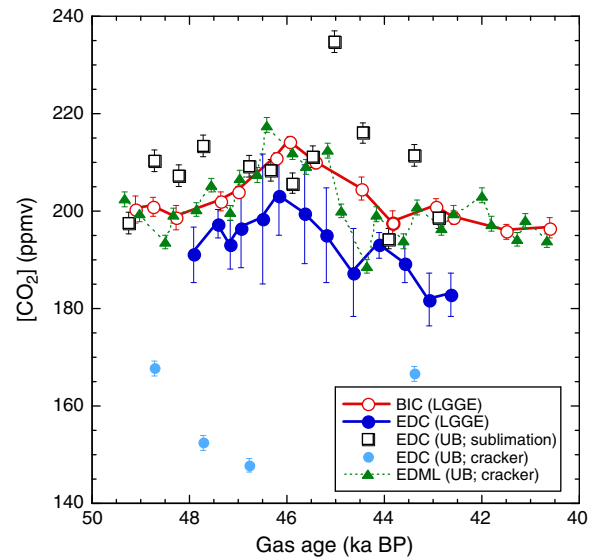**Fig. 2.** Comparison of [CO_2] analysed in bubbly, clathrated, and BCTZ ice with various extraction methods. When using dry extraction techniques, [CO_2] measured in bubbly ice (BIC; red circles) yields higher values than analyses in BCTZ ice (EDC; dark blue circles for LGGE, light blue circles for UBern) due to the respective extraction efficiencies for bubbles and clathrates. Sublimation measurements from the BCTZ (EDC, white squares, UBern), and from the uppermost clathrate zone (EDML, green triangles, UBern) show scatter beyond analytical precision due to clathrate layers (Lüthi et al., 2010).

treatment of these phenomena and their causes has recently been presented by Bereiter et al. (2009) and Lüthi et al. (2010). Here we discuss the issue only to provide a background for the potentially equivalent isotope dynamics investigated in Section 3.2.3 and following.

The depletion of the relative abundance of a gas in the BCTZ has been observed by Ikeda et al. (1999), who reported that O_2 in air bubbles of the transformation zone gets strongly depleted relative to N_2. Salamatin et al. (2001) propose that this depletion results from gas-dependent mass transfer during the transformation from bubble to clathrate. According to their model, O_2 permeates faster between the transforming enclosures than N_2 and consequently becomes enriched in clathrates. The crucial parameter in their model for this diffusion induced fractionation is the permeation coefficient (diffusivity x solubility) of the different gases. By fitting their model to O_2/N_2 ratio measurements in the transition zone, they estimated permeation coefficients of O_2 and N_2. A similar estimation is done by Ikeda-Fukazawa et al. (2001) resulting in comparable values. The permeation coefficient for CO_2 was empirically determined by Ahn et al. (2008) to be larger than the coefficients for O_2 and N_2, from which an enrichment of CO_2 in clathrates would follow. However, estimates for O_2 and N_2 permeation using simulation of molecular dynamics (Ikeda-Fukazawa et al., 2004, 2005) are 1–2 orders of magnitude faster, indicating very similar permeation rates for N_2 and CO_2 that are about three times smaller than for O_2 (Bereiter et al. (2009). From these permeation coefficients alone, one would expect higher than atmospheric [CO_2] in bubbles due to preferential loss of O_2. However, as proposed by Bereiter et al. (2009), the dissolved amount of gas around a clathrate scales with the clathrate dissociation pressure of the single gases. This assumes that the dissociation is controlled by ambient pressure and not the partial pressure of the specific clathrate forming gas. The assumption is supported by the findings of Miller (1961) for O_2 and N_2. If the assumption holds, it would indicate that the concentration gradient between bubbles and clathrates is steeper for dissolved CO_2 than for O_2 and N_2, since the dissociation pressure for CO_2 is about one order of magnitude lower compared to both O_2 and N_2 (calculated for T = −40 °C; Bereiter et al., 2009). For completeness, we

note that CO_2 in bubbles has the potential to dissolve into the quasi-liquid layer at ice grain boundaries and form carbonic acid. We are not aware of any physical explanation how this process would speed up CO_2 permeation. In contrast, Benziher (2004) reports that presence of carbonic acid slows the rate of CO_2 clathrate formation. Consequently, the CO_2-carbonic acid equilibrium is unlikely to have bearings on our findings.

Aside from the theoretical background, enrichment of CO_2 over N_2 during clathrate formation with corresponding CO_2 depletion in the vapour phase has been observed in a variety of experiments. The most pertinent example is the work by Seo and Lee (2004) for mole fractions of CO_2 as low as 1% and in both structure I and II clathrates. The enrichment is predicted by models of clathrate stability and becomes more pronounced with decreasing temperatures, such as they are observed in ice sheets (Yoon et al., 2006). It must be acknowledged that the magnitudes of diffusion and solubility coefficients for the various gases in ice are subject to considerable uncertainty, as accurate direct measurements cannot or have not been performed. If current knowledge, as reviewed above, correctly captures the relative magnitudes of the relevant parameters, it would explain the partitioning of CO_2 with depletion in the remaining bubbles and enrichment in clathrates. Furthermore, Stauffer and Tschumi (2000) and Lüthi et al. (2010) demonstrate experimentally that gas partitioning occurs between bubbles and clathrates in the transition zone and that CO_2 gets depleted in the bubbles. In summary, theory, experimental evidence and direct observation all indicate that where clathrate structures and air bubbles coexist in ice sheets, CO_2 is enriched in the former and depleted in the latter. Because the mechanical crushing of the ice works more efficiently on air bubbles (62% released) than on clathrates (52%, Lourantou et al., 2010b), it liberates disproportionate amounts of the CO_2-depleted air. This finding is consistent with the test results of Stauffer and Tschumi (2000), who showed that CO_2 depletion from BCTZ ice varies with percentage of clathrate formation, pressure equilibration during core storage and extraction times. Comparison with $[CO_2]$ data from the same ice extracted with a needle cracker and analysed at the University of Bern (UBern) (Lüthi et al., 2010) further supports this hypothesis. The needle cracker has a greater difference in extraction efficiencies than the LGGE ball mill: 70% for bubbles and 50% for clathrates (Lüthi et al., 2010). Consequently, the dry extraction data from UBern are even more depleted in CO_2 than those from LGGE, with values of up to 40 ppmv below BIC (Fig. 2). The large difference in $[CO_2]$ yield between LGGE and UBern for BCTZ ice seems to exceed the corresponding efficiencies for clathrated and bubbly ice. This may be explained by the fact that UBern's needle cracker crushes the whole sample to comparatively coarse grains of fairly uniform size. In contrast, the LGGE ball mill produces a much finer powder but leaves single, larger pieces of ice intact. The LGGE extraction efficiencies for clathrated and bubbly ice may be more similar than quoted above if the large residual pieces were not included. Furthermore, the extraction efficiency of the UBern system can vary by 10% from sample to sample.

Lüthi et al. (2010) analysed the BCTZ of EDC and the upper horizons of pure clathrate ice from the EDML ice core with the needle cracker as well as with a sublimation technique. Independently of the technique used, they found $[CO_2]$ variability on a scale of a few centimetres between neighbouring samples that exceeds both possible natural variations and analytical precision (Fig. 2). The authors attribute this to preferential clathrate formation in centimetre-scale layers that enrich CO_2. This process is mass conservative and over time the effect is reversed by diffusion in the clathrate zone. Within the BCTZ, however, the effect could contribute to the large scatter in our $[CO_2]$ data because our replicate measurements were conducted on adjacent depths. The distance between them is short enough to rule out true atmospheric variation between them, but they could be subject to centimetre-scale clathrate enrichment. By comparing the average standard deviations between repeat measure-

ments of one extracted sample (4.7 ppmv, n = 23) and of duplicate analyses (6.7 ppmv, n = 10), we show that the layering may contribute to the larger scatter of $[CO_2]$ in the BCTZ but does not explain it by itself. It is noteworthy that, despite the poorer precision and lower values, the LGGE $[CO_2]$ analyses of EDC reproduce the general shape of the AIM12 peak, while this is not the case for needle cracker and sublimation results from UBern. The latter represent depth intervals of 2.5 and 4.5 cm, respectively. Although individual LGGE samples are only 4.5 cm long, Fig. 2 shows the average of two replicate measurements. Effectively, the LGGE $[CO_2]$ data therefore represent 9 cm depth intervals, which seem sufficient to integrate over clathrate enriched and depleted layers. This is close to the estimate of >10 cm for homogenisation of Lüthi et al. (2010).

3.2.2. Dissociation tests

We observed increasing CO_2 yields from subsequent expansions of the same extracted EDC sample that could indicate additional CO_2 clathrate dissociation during the ~1.5 h between first and last expansion (Fig. 3). On average the second expansions (~30 min after the first) were elevated by 4.3 ± 3.2 ppmv over the first, and the third expansions (~60 min after the second) were elevated by a further 4.7 ± 3.6 ppmv over the second (Fig. 3). This is consistent with the result of Stauffer and Tschumi (2000) that air yield and $[CO_2]$ from BCTZ ice increase with extraction time; although in their system, with the flask kept at a higher temperature (−30 °C) and smaller sample size (6 g), equilibrium was already reached within 300–600 s. In contrast to the EDC ice, differences between expansions of BIC samples are statistically not significant, attesting that they record the same gas content throughout the ~1.5 h interval between the first and last expansion. In order to test whether the observed increase in EDC samples results from clathrate dissociation, we tried to facilitate this process by adding a 20-min period after the milling when the sample warmed to −20 °C instead of returning to the −70 °C cold bath. Contrary to our expectations, the resulting $[CO_2]$ was rather lower than measured with the standard procedure in coeval ice, although the difference (−1 to −8 ppmv) is within the general range of scatter for BCTZ ice in two cases and comparable to the results of the standard method for the third case. Also, in the standard extractions the observed increasing trend in $[CO_2]$ between the expansions shows no correlation with the temperature of the cold bath ($r^2 = 0.04$ for a temperature range of −55 to −78 °C) or the warming of the bath throughout the expansions ($r^2 = 0.002$ for differences from 6 to 15 K). The above observations are consistent with the finding of Circone et al. (2003) that during warming 80% of CO_2 clathrates remain stable up to temperatures of −3 °C. The additional warming of the flask to −20 °C is therefore ineffective. Any substantial release would occur too close to the melting point of the ice in the flask as to be practical, due to the risk of initiating chemical reactions modifying the CO_2 content in the ice. We note that the higher dissociation pressure of N_2 and O_2 clathrates can lead to their preferential dissociation during the warming, while CO_2 clathrates remain stable, which would explain the observed CO_2 depletion in the dissociation tests. However, we cannot rule out that the lower $[CO_2]$ relative to normally processed duplicates may be a coincidental choice of ice with clathrate-enriched layers. With only three tests conducted, this is not improbable.

3.2.3. Stable carbon isotope values

In contrast to $[CO_2]$, the $\delta^{13}CO_2$ values measured in the BCTZ of EDC are quite stable around −6.65‰. Standard deviations for the samples vary between 0.06‰ and 0.23‰; pooled standard deviation is 0.16‰ (n = 69). Precision compared to BIC is significantly lower at the 95% confidence interval and also exceeds EDC σ-values derived from bubbly ice (σ = 0.1‰; n = 63) and from fully clathrated ice (σ = 0.1‰, n = 39) (Lourantou et al., 2010b). It is not clear whether the larger scatter could be related to the partitioning between bubbles and clathrate. Another possible explanation is poor ice quality
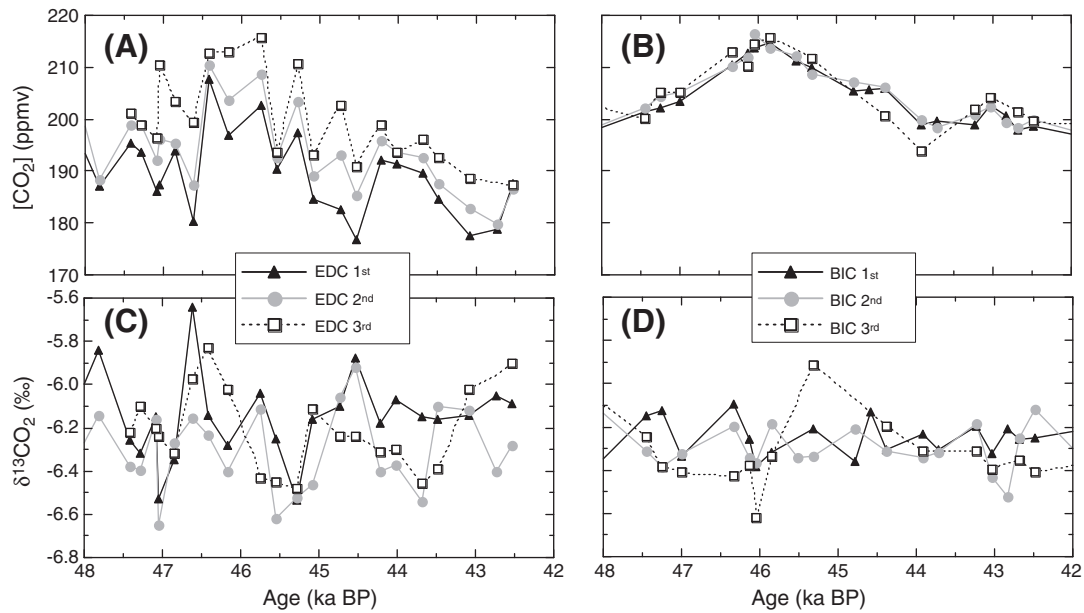
Fig. 3. Comparison of [CO_2] and $\delta^{13}CO_2$ for subsequent expansions from the same ice sample. Second and third expansions are measured ~30 min and ~90 min, respectively, after the first one. (A) EDC samples from the BCTZ show increasing [CO_2] values with subsequent expansions, probably as a result of gas equilibration between clathrates and head space after milling. (B) Clathrate-free BIC ice shows no trend in [CO_2] over the expansions. (C) and (D) Neither of the cores shows a trend over the extraction sequence for $\delta^{13}CO_2$. Plotted ages are not accurate but have been adjusted by −0.1 ka for the first one of each replicate sample of same age and by +0.1 ka for its duplicate(s) so that they can be visually distinguished from each other.

(microfractures). The actual $\delta^{13}CO_2$ values from EDC show an offset of ~0.16‰ to BIC but the two data sets compare well concerning the absence of discernible trends or step changes. Importantly, there are no significant trends in $\delta^{13}CO_2$ over successive expansions from the same sample (Fig. 3) or in the dissociation tests. The fact that successive extraction from clathrate influences [CO_2] but not $\delta^{13}CO_2$ suggests that isotope fractionation between gas and clathrate phase is unlikely to affect $\delta^{13}CO_2$ analysis.

4. Discussion

In the following we assume that the values measured in BIC contain no artefacts introduced by extraction and analytical procedure and represent the true palaeo-atmospheric signal. This assumption is supported by the fact that measurements on bubbly ice conducted with our set-up agree well with independently published data for the same time period (e.g., Fig. 2), and with analyses from other laboratories (Lourantou et al., 2010a; Lüthi et al., 2010; Schaefer et al., 2008).

The statistical tests using two-way ANOVAs for the effect of core and gas age reveal that the $\delta^{13}CO_2$ did not change significantly over time in either core ($p > 0.05$, for both tests of BIC vs. EDC$_{spline}$ and EDC vs. BIC$_{spline}$). However, the $\delta^{13}CO_2$ signatures differ significantly between the cores ($p > 0.001$, for both tests). Box plots and post-hoc testing of the 'gas age × core' interaction term for the comparison BIC-EDC$_{spline}$ suggest that the significant effect of core was driven by three out of nine gas ages in EDC$_{spline}$ (Fig. 4). Visual inspection does not suggest that these values are outliers. This is supported by the Fisher's LSD test where only two out of three points show significant differences to only two other spline points (the same ones in each case). As gas age was not a significant predictor of $\delta^{13}CO_2$ in either core, we can discount this parameter to evaluate the statistical difference between the two cores using the measured instead of synthetic data. We pooled the $\delta^{13}CO_2$ values from all ages and directly compared the cores (EDC vs. BIC) using a t-test, revealing a significant difference among cores ($p > 0.001$). Mean $\delta^{13}CO_2$ values of EDC and BIC were −6.65 ± 0.16 (1 σ) and −6.49 ± 0.12, respectively.

In comparison, the −0.16 ± 0.20‰ difference between $\delta^{13}CO_2$ measured in EDC and in BIC is very small, given the magnitude of

[CO_2] depletion in the BCTZ and the general sensitivity of isotopes for fractionation. One would expect $^{13}CO_2$ to have higher solubility in ice than $^{12}CO_2$ but lower diffusivity, thereby producing similar permeation coefficients for the isotopologues. Although this would be consistent with our data, it remains speculative without available quantifications of the relevant coefficients. The same applies to possible differences in the dissociation pressures of $^{13}CO_2$ and $^{12}CO_2$ clathrates, which have the potential to lead to isotopic fractionation between the bubble and clathrate gas reservoirs.
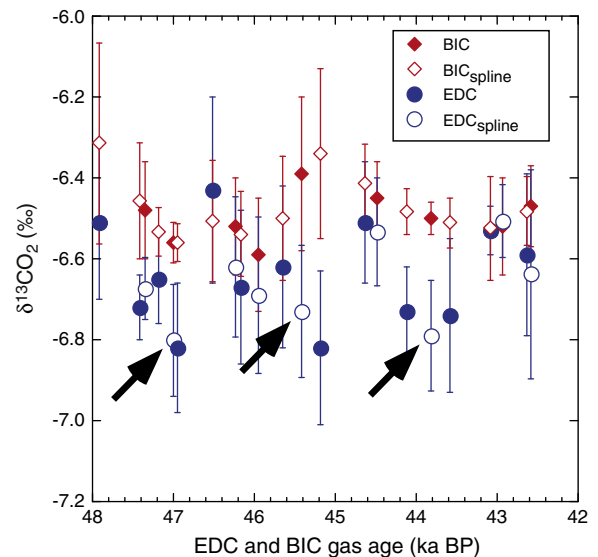

Fig. 4. Measured and synthetic $\delta^{13}CO_2$ data. Synthetic data (EDC$_{spline}$ and BIC$_{spline}$) have been generated by sampling spline fits through the records at the gas ages of the other core. Error bars indicate ± 1 σ and have been derived using a Monte Carlo technique for the synthetic data. Three data points in EDC$_{spline}$ marked by arrows cause the significance in difference to BIC.

Analyses of EDC and BIC ice using the exact same technique were interspersed. We can therefore rule out that the slight offset between BCTZ and bubbly ice is introduced by analytical procedure, intercalibration, instrument shift, etc. The consistency in $\delta^{13}CO_2$ values over consecutive expansions, which contrasts with the associated $[CO_2]$ enrichment, could indicate that fractionation between bubbles and clathrates is not the cause of the BIC-EDC offset. Ice quality may be a factor because ice from the BCTZ is brittle and the analysed EDC core sections were often broken. Despite careful choice of the analysed piece, we cannot rule out that EDC samples contained microfractures. Studies have shown that fractured ice produces erroneous stable isotope values for $\delta^{13}C$ (Behrens et al., 2008; Craig et al., 1988; Schaefer and Whiticar, 2007) and δD (Sowers, 2010) of enclosed methane. However, in those studies the effect was either large scatter (Schaefer and Whiticar, 2007; Sowers, 2010) or enrichment of the heavy isotope (Craig et al., 1988). In contrast, EDC $\delta^{13}CO_2$ values are only marginally less reproducible than BIC and slightly depleted in the heavy isotope. Consequently, there is no clear evidence that fracturing introduces a bias in $\delta^{13}CO_2$ analysis, possibly because EDC ice quality is sufficient or because the relative mass difference between the CO_2 isotopologues is smaller than for methane. It is possible that microfractures contribute to the larger scatter in the EDC data set. In contrast, potential centimetre-scale inhomogeneities in the bubble/clathrate ratios of the ice, as observed by Lüthi et al. (2010), do not seem to affect the $\delta^{13}CO_2$ scatter. This follows from the fact that the average standard deviation between replicate ice samples (0.11‰, n = 10) is significantly better (at the 99% confidence interval) than the one for multiple analyses of an extracted air volume from one piece of ice (0.16‰, n = 23).

Other than the presence or absence of clathrates in the ice (i.e., the tested parameter), the only potential bias in the results is the gravitational correction for fractionation in the firn layer (Fig.1). The fractionation depends on temperature and accumulation rates at the deposition site. The strongly differing environmental conditions at the inland site of EDC and the coastal location of BIC are expected to alter the atmospheric isotopic signature differently in each core. The correction factors for diffusion in the firn directly affect the reconstructed atmospheric $\delta^{13}CO_2$. Theoretically, false correction factors could skew the results and create a false impression of agreement or disagreement between the two data sets. However, $\delta^{15}N$ is a robust quantitative indicator of the relevant fractionation processes. Some uncertainty is introduced by the fact that for EDC no direct measurements of $\delta^{15}N$ are available for the relevant period. Instead, the correction factors were derived using an empirical relationship between δD in the ice and $\delta^{15}N$. The correlation between the two parameters is robust and consistent for the last three glacial terminations and is consequently expected to be valid for glacial as well as interglacial conditions (Dreyfus, 2008). We note that the raw $\delta^{13}CO_2$ data of the two cores differ by only 0.05 ± 0.20‰ (averages for BIC and EDC are −6.28‰ and −6.23‰ respectively). The close match is expected to worsen after correction, because gravitational fractionation is higher in cold, low-accumulation, inland sites like EDC than at coastal locations with higher temperatures and snowfall as is the case for BIC. For modern conditions, Landais et al. (2006) report a difference in $\delta^{15}N$ between EDC and BIC of ~0.26‰ for the present and of ~0.12‰ for the Last Glacial Maximum. The difference between our correction factor averages is 0.23‰ and therefore closer to an interglacial value. In the range of values found by Landais et al. (2006), the real difference between EDC and BIC $\delta^{13}CO_2$ data could be no more than 0.03‰ higher than our best estimate. However, if the diffusive environment at the two coring sites between 42 and 48 ka BP is closer to glacial than interglacial conditions, as could be argued, then at least part of our observed EDC-BIC discrepancy would be caused by the choice of correction factors.

Finally, we note that although statistically $\delta^{13}CO_2$ in EDC is significantly different from BIC, the actual offset is small and does not surpass the pooled standard deviation of EDC. Ice from the BCTZ with its brittleness, potential for microfracturing and fractionation of gases between clathrates and bubbles provides a worst case for $\delta^{13}CO_2$ analysis. The fact that the results are nevertheless very close to those from bubbly ice is encouraging for palaeo-atmospheric reconstructions using deep, fully clathrated ice. The latter is not subject to the structural problems that occur in the BCTZ. Any effects on $\delta^{13}CO_2$ analysis are likely to be smaller than reported here, suggesting that they would be negligible.

5. Conclusions

We measured the concentration and stable carbon isotope ratio of CO_2 in ice samples from the transformation zone between bubbly and clathrated ice with an age of ~42 to ~48 ka BP. These results were compared with analyses of coeval bubbly ice in order to establish whether clathrated ice can be used for reconstructions of past atmospheric $\delta^{13}CO_2$. We find that in BCTZ ice the LGGE ball mill produces $[CO_2]$ results that are depleted and strongly variable. This is due to a known shortcoming of mechanical crushing for gas extraction, namely, the technique liberates more air from bubbles and less from clathrate structures where CO_2 is enriched. Accommodating clathrate dissociation by raising the extraction temperature proved ineffective in tests and will be impractical because CO_2 clathrates dissociate quantitatively almost at the melting point of water ice. The difference between our $\delta^{13}CO_2$ records derived from partially clathrated ice and coeval bubbly ice is statistically significant, although the offset is very small. Correction factors for isotopic fractionation in the firn that are derived by different methods for the two cores introduce some uncertainty, but are more likely to contribute to the observed offset rather than disguise a larger true discrepancy. Our study shows that partially clathrated ice yields slightly decreased precision and close to the true palaeo-atmospheric $\delta^{13}CO_2$ when using a ball mill dry extraction technique. For practical purposes, we consider the adverse effects of BCTZ ice on the $\delta^{13}CO_2$ signal marginal. We expect this finding to translate into truly negligible effects for fully clathrated ice, which lacks microfracturing and gas fractionation between two reservoirs and therefore the main potential causes for erroneous isotope analysis. If that indication holds true, deep clathrated ice cores can be used to reconstruct variations in atmospheric $\delta^{13}CO_2$ over previous glacial cycles and constrain CO_2 fluxes between various reservoirs.

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