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Key Points:
- Analytical bias discovered in the EPICA Dome C CO_2 record
- Bias is confined to 13 ppm and the deepest 200 m (600–800 kyr B.P.)
- Corrected and updated ice core CO_2 compilation is provided

Supporting Information:
- Readme
- Sections S1–S4 and Figure S1
- Data S1

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Revision of the EPICA Dome C CO_2 record from 800 to 600 kyr before present

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Abstract The European Project for Ice Coring in Antarctica Dome ice core from Dome C (EDC) has allowed for the reconstruction of atmospheric CO_2 concentrations for the last 800,000 years. Here we revisit the oldest part of the EDC CO_2 record using different air extraction methods and sections of the core. For our established cracker system, we found an analytical artifact, which increases over the deepest 200 m and reaches 10.1 ± 2.4 ppm in the oldest/deepest part. The governing mechanism is not yet fully understood, but it is related to insufficient gas extraction in combination with ice relaxation during storage and ice structure. The corrected record presented here resolves partly - but not completely - the issue with a different correlation between CO_2 and Antarctic temperatures found in this oldest part of the records. In addition, we provide here an update of 800,000 years atmospheric CO_2 history including recent studies covering the last glacial cycle.

1. Introduction

Our knowledge about the history of atmospheric CO_2 concentrations is based mainly on the analysis of atmospheric air trapped in Antarctic ice cores. So far, the EPICA (European Project for Ice Coring in Antarctica) Dome C (EDC) ice core provides the oldest samples of atmospheric air, allowing the reconstruction of CO_2 concentrations as far back as 800 kyr B.P. (thousand years before present, where present is defined as 1950) [*Lüthi et al.*, 2008]. To date, the EDC CO_2 record is the only record available for the period from 450 to 800 kyr B.P. In more recent periods in time, where overlaps exist between different ice core records, the EDC and other ice core CO_2 records mostly confirm each other within the uncertainty boundaries. In small sections, however, single records show systematic offsets of a few parts per million (ppm) relative to the other records that are beyond calibration issues [*Bereiter et al.*, 2012; *Ahn et al.*, 2012; *Marcott et al.*, 2014]. For the older part of the EDC CO_2 record, the quality of the data could not be independently confirmed yet with measurements on other ice cores. Accordingly, in order to test the integrity of the oldest/deepest part of this record, where lower CO_2 concentrations are found as expected from the CO_2-temperature correlation [*Lüthi et al.*, 2008], we performed extensive remeasurements using two different parts of the core and three different methods to analyze the trapped air.

Accurately measuring atmospheric CO_2 concentrations in ice cores is challenging as the trapped air must be extracted under dry conditions via mechanical destruction or sublimation of the ice. At the University of Bern, three different devices using different dry extraction principles are available: (i) the standard cracker device which was—among others—used for the oldest part of the EDC CO_2 record [*Siegenthaler et al.*, 2005; *Lüthi et al.*, 2008], (ii) a sublimation device primarily built for $\delta^{13}C(CO_2)$ analysis in ice cores [*Schmitt et al.*, 2011], and (iii) a new device called centrifugal ice microtome (CIM) [*Bereiter et al.*, 2013]. Note, that these three different devices have all their own air analytical part, meaning that they are in fact completely independent systems (see Methods for more details).

The key difference between the principle behind these devices is how much of the air that is trapped in the ice sample can be extracted (called extraction efficiency). The deep ice used here belongs to the category of pure clathrate ice, in which the air is exclusively trapped in clathrate hydrates. These inclusions were initially bubbles when they were in the shallower part of the ice sheet and were transformed into clathrates in

the bubble-clathrate hydrate-transition zone (BCTZ; ~600–1200 m depth in the EDC core [*Lüthi et al.*, 2010]) due to the increasing pressure with depth. For pure clathrate ice, the cracker has an extraction efficiency of approximately 50%, the CIM of 90% or more, and the sublimation of 100% [*Bereiter et al.*, 2013]. The generally lower extraction efficiency of the mechanical extraction devices (cracker and CIM) has so far not posed a problem for this type of ice. Overlapping records from pure bubble and pure clathrate ice [*Indermühle et al.*, 2000], as well as sublimation and cracker data from pure clathrate ice (excluding old EDC ice) show no offsets [*Siegenthaler et al.*, 2005; *Lüthi et al.*, 2008; *Schneider et al.*, 2013]. The ice from the BCTZ, however, is problematic for the mechanical devices as they extract air preferentially from the bubbles, which are depleted in CO_2 relative to the neighboring clathrate hydrates [*Lüthi et al.*, 2010; *Schaefer et al.*, 2011].

The two different parts of the EDC core we refer to here are two axially parallel pieces of the original cylindrical ice core, which were cut in the field right after the drilling of the core. The so-called "gas cut" was shipped to Europe shortly after drilling and stored in the laboratory freezer of the University of Bern or Grenoble at -22.5 ± 2.5°C ever since (referred here to as "Bern ice"). The other part is the so-called "archive cut" (or "archive ice"), which was stored near the EDC drilling camp in a subsurface snow cave, and samples from this cut were shipped to Bern just before the analysis for this study. The temperature in the cave is close to the local mean annual temperature of −53.5°C with seasonal variations around ±10°C.

In this study, remeasurements of the CO_2 concentration in the deepest/oldest part of the EDC ice core—performed during the last 4 years—are reported, where the three different methods were used in combination with the two different types of ice mentioned above. The data reveal an extraction bias in previously published records using the Bern cracker system. The offset is smaller than 12.5 ppm and confined to the bottom 200 m of the core, for which we correct in this study. Previous findings based on the uncorrected data are revisited. Furthermore, observations on ice properties are discussed with the aim to offer possible explanations of the mechanism behind our discovery.

2. Results and Offsets

Within this study, we performed 107 remeasurements over the deepest 400 m (442–816 kyr B.P.) of the EDC CO_2 record using the three different extraction devices (cracker, sublimation, and CIM) and the two different parts of the ice core (archive ice and Bern ice) mentioned above (Figure 1). All previously published CO_2 records from this part of the EDC ice core [*Siegenthaler et al.*, 2005; *Lüthi et al.*, 2008] originate from Bern ice. In addition to the new data, six data points from an older sublimation device (see supporting information) are shown here (sublimation 2006 in Figure 1); four of the six data points have been shown already in *Lüthi et al.* [2008]. Due to the weak data basis at that point in time and the difficulties associated with the performance of this older sublimation technique, the remaining two data points were believed to be outliers. We include them here as we now understand why these two data points were offset.

When comparing the records from the different systems, two sources of uncertainty need to be considered. First, the absolute scales of the different systems might be offset in the range of ±2 ppm (see supporting information). Second, the remeasurement samples could not be taken at exactly the same depth as the original samples, which limits the reproducibility of a single data point to about ±3 ppm (gray error bar in Figures 1b–1d). The range is derived from the remeasurements using the original combination of Bern ice and the cracker system (Cracker Bern 2011 in Figure 1c), which should reproduce the original data within their measurement uncertainties. The data, however, shows the larger spread of about ±3 ppm due to the sample displacement. Furthermore, it needs to be taken into account that the sublimation set measured in 2011 [*Schneider*, 2011] could be offset within +2.0/−5.0 ppm (see supporting information). Therefore, interpretation of this set calls for additional caution.

All records that were measured either with a sublimation system or the CIM show significantly higher values relative to the original Bern ice data below 3150 m depth. The same holds true for the data originating from the cracker in combination with (cold) archive ice (Figure 1). Only the combination of Bern ice and cracker shows reproducible low values within this depth range, even 5 years after the original data were obtained (Figure 1c, Cracker Bern 2011). Considering the uncertainties mentioned above, we cannot ascertain a significant offset between the different records above the depth of about 3050 m. Note, however, that both the CIM and the sublimation data tend to have higher values above this depth.

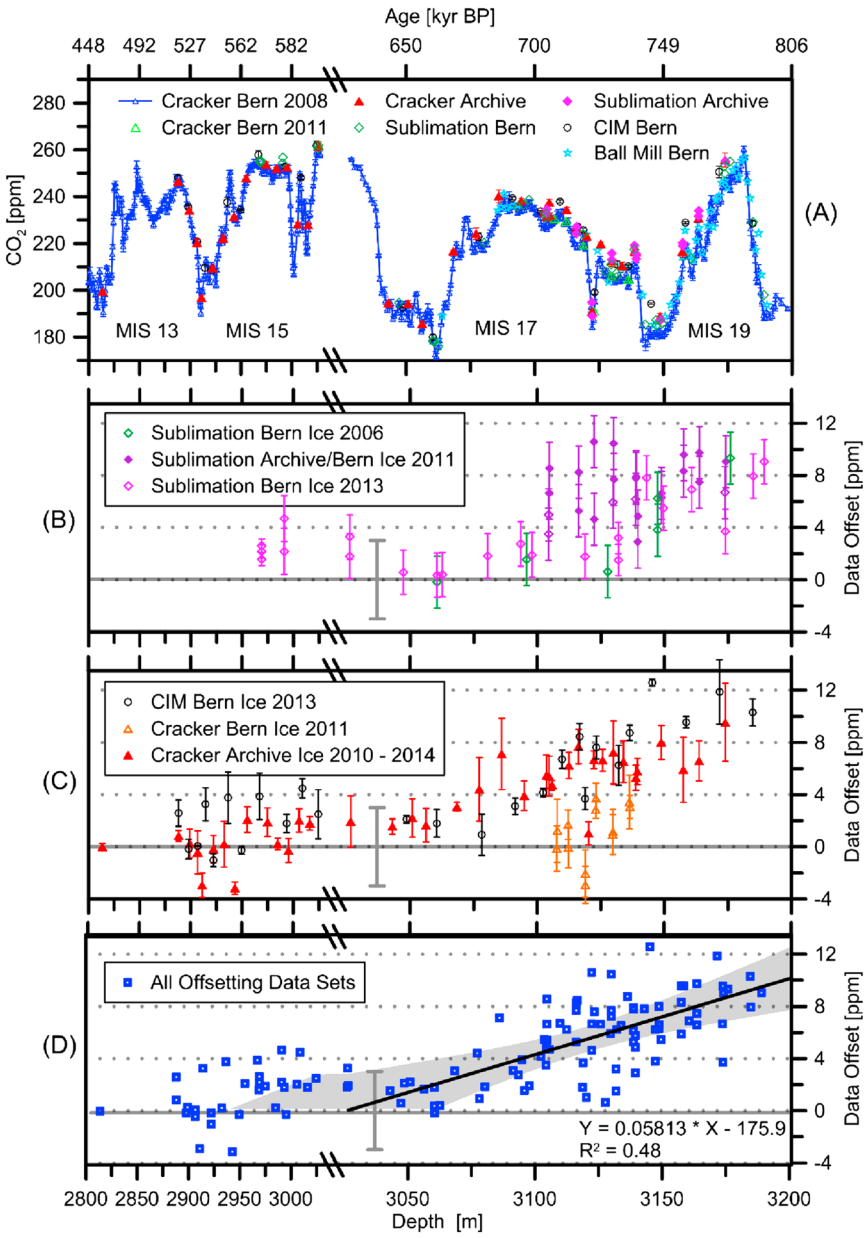

Figure 1. (a) Compilation of EDC CO_2 data between 2800 m and 3200 m depth (442–816 kyr B.P. based on AICC2012 [*Bazin et al.*, 2013]). The original data published by *Siegenthaler et al.* [2005] and *Lüthi et al.* [2008] using the cracker (dark blue triangles), or the ball mill (light blue stars) system, and Bern ice are shown. The cracker data were found to be slightly lower than the ball mill data, which is likely an artifact of the extraction bias found here (see supporting information). The other data are remeasurements of this study and *Schneider* [2011] (Sublimation 2011) using different types of ice and analytical systems according to the following codes: closed symbols: archive ice stored at Dome C at -53.5 ± 10°C, open symbols: ice stored in Bern/Grenoble (Bern ice) at laboratory freezer temperatures (-22.5 ± 2.5°C), triangles: data obtained with the cracker, diamonds: data obtained with the sublimation, and bullets: data obtained with the CIM. Marine oxygen isotope stages (MIS) 13–19 are marked for reference. (b–d) Offsets between original EDC cracker CO_2 records [*Siegenthaler et al.*, 2005; *Lüthi et al.*, 2008] and remeasurements, expressed as current measurements minus previously published cracker values. Depending on the depth of the remeasurement relative to the cracker data, either the nearest or the average of the two neighboring cracker data points is used as reference. The error bar at 3030 m depth represents the estimated range within which a single remeasurement cannot be attributed as being significantly different from the zero line (±3 ppm), since ice samples could not be taken from exactly the same depth. Note that this error does not account for possible systematic uncertainties in the range of ±2 ppm between the different analytical systems. In Figures 1b and 1c, the same symbol coding is used as in Figure 1a with the addition in the legend of the years at which the corresponding data set was obtained. In Figure 1d, the compilation of all remeasurements that indicate an offset (all data from Figures 1b and 1c with the exception of Cracker Bern 2011) is shown, including the best estimate correction curve (black line and linear equation) and its 95% uncertainty range (gray area) (see text for more details). Note the break in the horizontal axes.

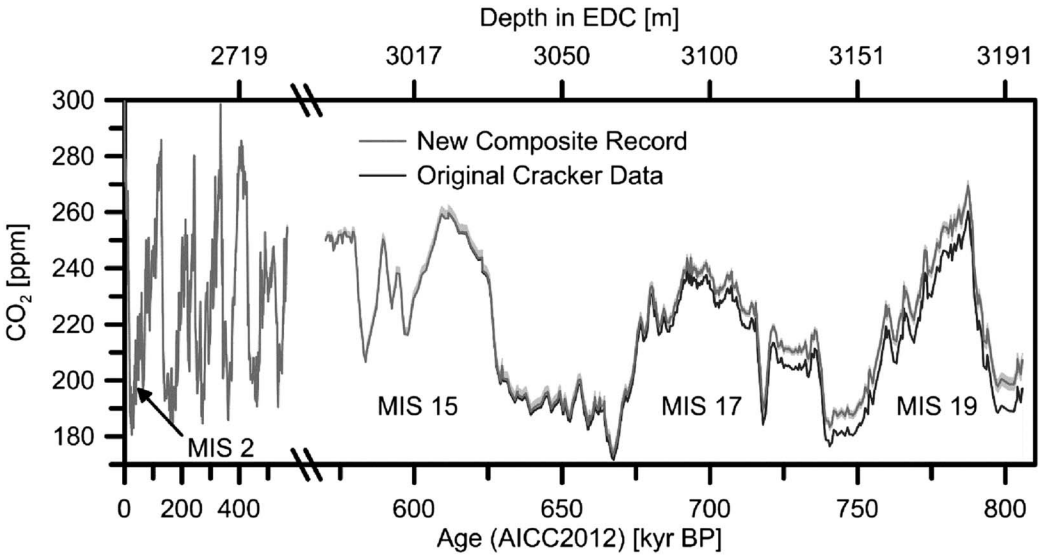

Figure 2. Comparison of the original data (black line) and an updated version of the 800 kyr CO_2 composite (see supporting information) including the corrected data (gray line) and its 95% uncertainty range (light gray area behind). The record low value at 667 kyr B.P. as found by *Lüthi et al.* [2008] remains as such; however, the average value for the period of 650–799 kyr B.P. changes significantly by +5.6 ppm.

The four records that span the affected part of the ice core (Figures 1b and 1c: Sublimation 2006 + 2013, CIM 2013, and Cracker Archive 2010–2014) show an increasing trend of the offset with depth, reaching a maximum offset of about 10 ppm at the lower end of the records. However, the depth at which these records start to diverge significantly is not the same for all data sets. While the cracker and CIM records reach a significant difference at about 3100 m depth, the sublimation record 2013 shows this depth to lie around 3150 m. Sublimation record 2006 is too coarse to shed light on this issue, but the sublimation record 2011—despite its poor accuracy—and the cracker remeasurements at Bern ice support the divergence at 3100 m depth.

In summary, the data indicate that the offset between the different records becomes significant at around 3100 m depth and increases with depth to a maximum of about 10 ppm. All the records that use a highly efficient extraction principle (sublimation and CIM), as well as the record using archive ice in combination with the cracker extraction, show a similar magnitude and trend of the offset relative to the original data.

It appears that the Bern ice has passed through an alteration after the drilling such that the low-efficiency extraction with the cracker results in depleted values relative to the effectively trapped CO_2 concentration in this ice. Hence, we need to correct the original data for this systematic analytical bias. Possible reasons behind this bias are discussed below.

3. Data Correction

Our aim is to provide an objective correction for the original data. In order to achieve this, the following strategy has been applied to derive a best estimate correction curve and its 95% uncertainty range (black line and gray area in Figure 1d): we assume a linear shape for the correction curve since most records indicate a linear change of the offset with depth. Only the sublimation set 2011 [*Schneider*, 2011] does not show such a trend, although its poor accuracy discussed above has to be taken into account. Regardless of the poor accuracy, this data set does not span the entire range and therefore alone cannot provide significant evidence to reject the null hypothesis of a linear shape. Note that we use this linear approach for the sake of simplicity, and we are aware that the real trend could be more complex.

We do not have arguments to favor or reject any record. Furthermore, if we calculate the correction described below based on the individual records, the corresponding correction curves do not differ significantly from each other, meaning that their uncertainty ranges overlap to a large extent. Therefore, all the records that show an offset relative to the original data (all sublimation, the CIM, and the Cracker Archive records in Figure 1) are used

in determining this correction. In a first step, an "affected" depth was derived based on linear regressions through different data windows including all data from the bottom to a certain cutoff depth. We define the depth below 3027 m as affected because for this cutoff depths, the predicted offset reaches almost zero, and for shallower cutoff depths, our correction would create a long tail toward shallower depth. To come up with an uncertainty of our correction curve, we produced 5000 new data sets with randomly changed values within their individual uncertainties (individual analytical uncertainty plus ±3 ppm due to sample displacement) and calculated corresponding linear regressions through the affected data (Monte Carlo method). Based on these regressions, the 95% correction uncertainty is calculated for each point of the original data set. For the depth above 3060 m, this strategy results in negative values for the lower uncertainty bound. However, we assume that the correction is only in positive direction, and hence, we set the lower bound to zero above this depth. Figure 2 shows a comparison of the original data and the corrected data including the correction uncertainty.

4. Discussion

There are two main conclusions of *Lüthi et al.* [2008] that are affected by the correction applied here: First, a record low atmospheric CO_2 concentration value of 171.6 ± 1.4 ppm was found at a depth of 3062 m in the EDC ice core. It is the lowest value ever measured within the last 800 kyr covered by ice cores and defines the lower bound of identified natural atmospheric CO_2 variability within this period. The single remeasurements close to that specific depth are not significantly different from the original value as they lie within the uncertainty of ±3 ppm (gray error bars in Figure 2). However, as we assume a continuous correction, the mean value is corrected to 173.7 ppm (the corresponding correction uncertainty is ±1.9 ppm). This still remains the record low value, and hence, our correction applied here does not change this finding significantly.

Second, the average atmospheric CO_2 concentration of 210.8 ppm over the period of 650–799 kyr B.P. (marine oxygen isotope stage (MIS) 17–19; based on the Antarctic ice core chronology 2012 (AICC2012) [*Bazin et al.*, 2013]) was found to be about 10 ppm lower than expected based on the otherwise strong correlation with Antarctic temperatures [*Lüthi et al.*, 2008]. Based on the corrected data here, the average value lies at 216.4 ppm, 5.6 ppm higher than the previous value. Hence, part of this original finding was caused by the extraction bias that we have identified here. However, the correction we apply here does not fully resolve the anomalous low CO_2 values found in this period. The relationship between CO_2 and Antarctic temperatures is still significantly different for the affected period compared to what is found in earlier times. However, it is not true for all subperiods within the affected period. MIS 19 falls within the "normal" range of CO_2-temperature correlation, while MIS 16 and 17 show "abnormal" correlation (same slope but shifted to lower CO_2 values). In fact, MIS 17 is the only interglacial of the entire record with a peak value below 250 ppm (243.7 ± 3.4 ppm). MIS 18 seems to be a transitional phase (see supporting information for more details). The anomaly of MIS 16 and 17 is robust even if we use the upper bound of our correction curve. Furthermore, regardless of our correction curve, the remeasurements for these periods constrain the correction to less than 5 ppm, which is not enough to change this finding significantly. Nevertheless, this finding could be specific to the available EDC records taking into account that (i) we do not fully understand the mechanism behind the artifact found here, (ii) most current CO_2 records have been obtained with low efficient extraction systems between which slight differences have been identified [e.g., *Marcott et al.*, 2014], and (iii) water isotopes as a proxy for local temperatures are not unambiguous [e.g., *Buizert et al.*, 2014]. Reevaluation of available CO_2 records with highly efficient extraction systems as well as independent proxies for temperature [see *Buizert et al.*, 2014] will provide a better basis.

The cause of the analytical offset found here is still an open question. In the following, we summarize our findings and put them into the context of other observations of air trapped in ice cores:

1. The analytical offset appears only when a method with a low extraction efficiency is combined with the warm-stored Bern ice. Unless the air is dissolved in the ice matrix to a large extent (see supporting information) or bound in another unknown form, this implies that the size of the inclusions matters similar to the situation in the BCTZ (the larger inclusions are depleted in CO_2 relative to the smaller ones nearby) [*Lüthi et al.*, 2010; *Schaefer et al.*, 2011; *Bereiter et al.*, 2013]. Furthermore, it implies that the original CO_2 concentration is conserved in the ice, and hence, that preferential gas loss of the core, which is an issue for O_2/N_2 ratios measured in the warm-stored deep EDC ice [*Landais et al.*, 2012], is not the cause of the offset found here. If so, the offset would be independent of the extraction technique, and we would expect increased CO_2 values in the warm-stored ice relative to the cold-stored ice [*Bereiter et al.*, 2009].

2. The offset occurs only in the very deep ice and increases with depth. This implies that some specific properties of that ice, e.g., grain sizes or in situ temperature, are a prerequisite and that the relevant properties show a similar change with depth as the offset.
3. The offset is not found in the cold-stored archive ice. This implies that the different storage histories of the core sections are relevant and that the faster relaxation of the warm-stored Bern ice likely triggered the offset.
4. The offset has not changed significantly since 2006. This implies that the underlying process was at work mainly prior to this period.

The properties of the ice have not yet been studied to the same extent in the available ice cores. Within the EDC and Dome Fuji ice cores, which have very similar characteristics in terms of core length, depth/age relation, accumulation rate, and borehole temperatures [*Parrenin et al.*, 2007, and references therein], a few relevant studies have been made in the context of this study. In the EDC ice core, the crystallographic structure of the ice changes significantly in the deepest few hundred meters of the ice. Ice grains grow with depth with extraordinary large grains of several centimeters found at the bottom of the core [*Durand et al.*, 2009]. Furthermore, the diffusion length of water molecules reaches up to 40 cm in this deep part [*Pol et al.*, 2010]. A study of the clathrate hydrates in the Dome Fuji ice core revealed that they also grow with depth with a significant increase in growth rate in the lowest 200 m [*Uchida et al.*, 2011]. They reach sizes about 3 times as big as above at the expense of the number density of clathrate hydrates per ice volume. These studies clearly show that in this deep/old ice, both the ice and the trapped gas molecules have been redistributed and, hence, that this deep/old ice is distinct from the shallower/younger ice. Unfortunately, no study has focused yet on the relaxation behavior of such deep/old ice, which is a crucial point here. Note that a recent microscopic look into two deep EDC ice samples stored at the Alfred-Wegener-Institut revealed lots of "glittering" in this ice, which is an indication for ice relaxation.

The EPICA Dronning Maud Land (EDML) core is probably the best studied core in regard to its ice structure and relaxation. Even though the ice is comparatively young in this core and the accumulation rates are larger compared to the EDC core, it is likely that the findings of EDML also apply to some degree to the EDC core. In these studies the relaxation induced air inclusions "plate-like inclusions" (PLI) and "microbubbles" are of particular interest [*Weikusat et al.*, 2012; *Nedelcu et al.*, 2009]. They are both significantly smaller than the regular inclusions ($<200\,\mu m$). While the PLIs are very flat objects (few micrometer thickness) and more common in deep, fully clathrated ice, the microbubbles are spherical objects and more common in the shallower, bubbly ice [*Weikusat et al.*, 2012]. The air within these relaxation features is strongly enriched in O_2 compared to the atmospheric mixture found in the surrounding inclusions [*Weikusat et al.*, 2012; *Nedelcu et al.*, 2009]. Hence, if they are also enriched in CO_2, this could explain the missing CO_2 in the cracker data, similar to the phenomenon observed in the BCTZ.

Both of these relaxation features in the EDML core form preferentially near "microinclusions," which are solid objects (primarily salts) with typical dimensions of up to a few micrometers [*Faria et al.*, 2010]. On a microscopic scale, these microinclusions are homogeneously distributed within the ice grains for the greater part of the ice core. In the lowest 400 m, however, where the ice temperature exceeds −10°C, this distribution starts to change coincident with the beginning of significant changes in the ice morphology (growing of ice grains and disturbance of the ice layering). With increasing depth, microinclusions are increasingly found at grain boundaries and clathrate hydrate surfaces [*Faria et al.*, 2010]. This changing distribution of microinclusions in the deep warm ice and the influence of these microinclusions on the air relaxation features (PLIs and microbubbles) might be the key to the mechanism behind the artifact we have discovered here. If so, we would expect that more air relaxation features, and/or such which are enriched in CO_2, are formed in the environment of non–homogenously distributed microinclusions. This would then have happened to a larger extent in the warm-stored core section (Bern ice) than in the cold-stored section (archive ice).

One of the fundamental assumptions behind our hypothetic explanation above is that the air relaxation features (PLIs and microbubbles) are enriched in CO_2. Direct measurement of the air composition in these small inclusion is only possible for the main air constituents N_2 and O_2 using Raman spectroscopy. Such measurements show an enrichment of O_2 in these features [*Weikusat et al.*, 2012; *Nedelcu et al.*, 2009]. Following the understanding of the BCTZ, this phenomenon could be explained by drawing on the fact that freshly formed relaxation features fill up preferentially with O_2 as it permeates faster through the ice lattice from the neighboring clathrate hydrates. This explanation, however, does not favor a parallel enrichment of CO_2 as the CO_2-hydrate dissociation pressure is roughly 15 times smaller than those of N_2 and O_2 [*Miller*, 1961; *Kuhs*

et al., 2000]. Unless permeation factors overcompensate this dissociation pressure difference, this would mean that CO_2 would be retained in the clathrate hydrates. However, permeation factors are not well constrained [*Bereiter et al.*, 2014], and little is known about the effective structure and behavior of clathrate hydrates in ice.

Regarding time scales, there is only little known about how fast PLIs and microbubbles can form. They can form within hours, but in the EDML core, they were much more abundant after years of storage than in the freshly drilled core [*Weikusat et al.*, 2012]. Relaxation time scales are highly dependent on ice temperatures, in particular when they are close to the melting point. So it could be that they either formed in a steady process while the ice was stored in stable freezer conditions or formed in a short process because of a short period of much warmer temperatures. Unfortunately, the second scenario cannot be ruled out as storage temperatures were not well enough documented during the shipment of the ice to Europe. In any case, the relaxation process was faster than or equal to the time period from ice core retrieval until the first CO_2 measurements were performed on this deep ice, i.e., faster than or equal to 39 months.

After all, we cannot fully explain the mechanism behind our finding here. For this, deeper insight into the nature of air inclusions in ice cores and their relaxation after drilling is required, as well as a more consistent monitoring of the storage conditions.

5. Conclusions

The remeasurements of trapped CO_2 concentrations in the deepest 400 m of the EDC ice core presented here show four robust results: (i) there is a clear analytical difference in the deepest 100 m between the ice stored in Bern at about −22°C (Bern ice) and the ice kept on Dome C at about −53°C (archive ice) when using our standard cracker extraction, (ii) the difference shows an increasing trend with depth from about 3030 m downward, (iii) the difference evolved within about the first 3 years after drilling, and (iv) the difference does not exist for remeasurements using high-extraction efficiency methods, which agree with the values from the archive ice.

We correct the published data by *Lüthi et al.* [2008] and *Siegenthaler et al.* [2005] for this bias and revisit their conclusions. The lowest atmospheric CO_2 concentration ever found in an ice core changes only slightly by 2.1 ± 1.9 ppm to 173.7 ppm and remains the record low value. However, the finding of a phase of low CO_2 concentrations from 650 to 799 kyr B.P. (MIS 16–19) must be redefined based on the corrected data presented here: the periods MIS 16 and 17 remain a phase of low CO_2 concentrations relative to expected values from the strong link to Antarctic temperatures in younger sections of the EDC ice core, whereas MIS 18 and especially MIS 19 are not. The cause of this phase of anomalous CO_2-temperature correlation is still an open question in paleoclimate research, and further studies (specifically using climate models) are required to gain a deeper insight.

The mechanism behind this analytical bias we discovered here is not well understood, but it only occurs when a low-efficiency extraction method is used. Finding (ii) above is a strong indication that it is caused by a gradual change of the ice structure. Several characteristics change in the corresponding depth range: ice crystals and clathrate hydrates grow significantly, and microinclusions accumulate at ice grain boundaries and clathrate hydrate surfaces. We hypothesize that the underlying process has to do with the influence of the microinclusions on the formation of air inclusions during ice core relaxation, combined with a faster relaxation during warm storage. Finding (iii) above indicates that the effect in the Bern ice occurred between core drilling (2002/2003) and the first analysis (2006) and subsequently stopped/slowed down.

This study shows that CO_2 results obtained from extraction systems with incomplete gas extraction should be carefully checked and validated with devices allowing quantitative extraction. Since our current knowledge is insufficient to predict which type of ice or storage conditions may produce extraction artifacts for mechanic devices, such validation measurements should be done more frequently. Further, it points out the need for detailed studies of the ice structure and its relaxation in order to further improve the integrity of the ice core record.

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