Earth and Planetary Science Letters 297 (2010) 226–233

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

CO_2 and O_2/N_2 variations in and just below the bubble–clathrate transformation zone of Antarctic ice cores

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ARTICLE INFO

Article history:
Received 5 November 2009
Received in revised form 10 June 2010
Accepted 11 June 2010
Available online 24 July 2010

Editor: P. DeMenocal

Keywords:
CO_2
O_2/N_2 ratio
ice core
fractionation process
EPICA
bubble–clathrate transformation

ABSTRACT

CO_2 measurements on the EPICA (European Project for Ice Coring in Antarctica) DML ice core in depth levels just below the bubble ice–clathrate ice transformation zone (1230–2240 m depth) were performed. In the youngest part (1230–1600 m), they reveal variations of up to 25 ppmv around the mean atmospheric concentration within centimetres, corresponding to a snow deposition interval of a few years. Similar results are found at corresponding depth regions of the Dome C and the Talos Dome ice cores. Since we can exclude all hitherto known processes altering the concentration of CO_2 in ice cores, we present a hypothesis about spatial fractionation of air components related to episodically increasing clathrate formation followed by diffusion processes from bubbles to clathrates. This hypothesis is supported by optical line-scan observations and by O_2/N_2 measurements at the same depth where strong CO_2 variations are detected. Below the clathrate formation zone, this small-scale fractionation process is slowly smoothed out, most likely by diffusion, regaining the initial mean atmospheric concentration. Although this process compromises the representativeness of a single CO_2 measurement on small ice samples in the clathrate formation zone of an ice core, it does not affect the mean atmospheric CO_2 concentration if CO_2 values are averaged over a sufficiently long depth scale (>10 cm in case of the EPICA DML ice core).

1. Introduction

Air inclusions in polar ice cores represent the only direct archive to reconstruct atmospheric records of CO_2 and other greenhouse gas concentrations over the last up to 800 000 yr (Loulergue et al., 2008; Lüthi et al., 2008; Schilt et al., 2010). However, on the way from the surface to the bottom of the ice (down to 3600 m depth), the air is exposed to numerous processes, such as convection in the upper few meters (Colbeck, 1989), diffusion in the firn down to the bubble close-off depth of about 70 to 100 m (Sowers et al., 1989), and transformation of bubbles to clathrates. The latter occurs over a depth range of several hundred meters somewhere between 500 and 1700 m depending on the temperature and the accumulation rate at the specific site (Miller, 1969; Shoji and Langway, 1982). During these processes the main air components can be affected by a number of natural effects, i.e. a fractionation of the O_2/N_2 ratio at bubble close-off (Huber et al., 2005; Severinghaus and Battle, 2006), a production of additional CO_2 by chemical reactions in Greenland ice cores (Anklin et al., 1995; Smith et al., 1997; Tschumi and Stauffer, 2000), a potential change of the entrapped atmospheric information due to meltlayers (Neftel et al., 1983; Ahn et al., 2008), biological production (Campen et al., 2003; Souchez et al., 2006), or stratigraphic disturbances near the bedrock (Landais et al., 2004; Raynaud et al., 2005; Jouzel et al., 2007). Changes in the ice and the entrapped air may also occur during ice core recovery and storage (Bender et al., 1995; Ikeda-Fukazawa et al., 2005; Suwa and Bender, 2008; Bereiter et al., 2009).

In case of CO_2, however, it has been demonstrated by a large number of independent and overlapping studies from different Antarctic ice cores and firn gas sampling programs that the atmospheric CO_2 concentration is hardly affected by most of these processes in Antarctic ice (Battle et al., 1996; Petit et al., 1999; Indermühle et al., 2000; Monnin et al., 2001; Kawamura et al., 2003; Siegenthaler et al., 2005b; Meure et al., 2006; Ahn and Brook, 2008; Lüthi et al., 2008). Exceptions are meltlayers (Neftel et al., 1983; Ahn

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doi:10.1016/j.epsl.2010.06.023

et al., 2008) and the out-gassing during storage (Bereiter et al., 2009), the latter affecting only the outer millimetres of the ice core. The first effect is easily detected due to unrealistically high concentrations in meltlayers, the second can either be avoided by storing the ice at temperatures below −50 °C or be excluded by removing the outermost millimetres of the core during sample preparation (Bereiter et al., 2009). Here we present new CO_2 measurements on ice from the bubble–clathrate transformation zone (BCTZ) of the EPICA Dome C ice core (EDC, mean annual surface temperature: −54.5 °C, mean annual accumulation rate: 25 kg/m^2 yr) (EPICA Community Members, 2004) and on the shallowest part of the pure clathrate ice of the EPICA ice core from Dronning Maud Land (EDML, −44.6 °C, 64 kg/m^2 yr) (EPICA Community Members, 2006), which show a previously unrecognized process causing additional centimetre-scale scatter in the CO_2 concentration in ice cores around the mean atmospheric composition.

2. Methods

2.1. CO_2: Dry extraction with steel needle crusher

An ice sample of 7–8 g is cut with a bandsaw in a cold room at −16 °C. The sample is placed in the sample vessel (−33 °C) while the inner surfaces are flushed by N_2 to avoid air intrusion. The vessel is evacuated for several minutes. Immediately after the ice is crushed by a magnetically coupled steel needle stamp, the vessel is connected to a cold trap for 5 min for releasing the air from the inclusions. Afterwards, the air is expanded to a measuring cell and analyzed by laser absorption spectroscopy. The size of the sample allows two independent CO_2 measurements at the same depth. Thereby, the maximum depth resolution is limited to 2.5 cm. The analytical precision of the dry extraction system is 1.5 ppmv (1 standard deviation).

2.2. CO_2: Sublimation

A cylindrical ice sample with 4 cm in diameter and 4.5 cm length (about 40 g) is placed in a glass vessel and evacuated for 60 min. The ice sample is irradiated by a 68 W CO_2 laser (wave length: 10.6 μm) for 30 min. Thereby, the middle 2.5 cm of the depth interval of the ice sample is sublimated (about one fourth of the ice sample). The water vapour is continuously trapped by two cold traps (−70 °C and −115 °C). The extracted air is frozen in a steel cold finger on a cold head. After several hours of resting, the defrosted air is expanded and analyzed by laser absorption spectroscopy. The analytical precision of the sublimation extraction system is 2.2 ppmv (1 standard deviation).

2.3. O_2/N_2: Continuous melting technique

An ice bar of 40–45 cm in length with a square area of 2×2 cm is continuously melted on a melting device (3 cm/min). The produced water–air-mixture is permanently drained off by a pump and the water is degassed with a gas permeable hydrophobic membrane. Water vapour and CO_2 are removed from the gaseous phase using a Nafion drying column and a liquid nitrogen cold trap before the sample is injected via an open split into an isotope ratio mass spectrometer (IRMS). The elemental and isotopic ratios of the major air components are measured simultaneously by 8 Faraday cups (m/z = 28, 29, 32, 33, 34, 36, 40 and 44) (Huber et al., 2005). The following corrections are applied to the data: Background correction, signal intensity imbalance effect, chemical slope correction and drift correction. The analytical precision of the O_2/N_2 ratios is on the order of 12‰ in bubble–clathrate ice for 1 cm averages but less than 8‰ for 15 cm averages (Huber and Leuenberger, 2004). Note, that this analytical scatter cannot explain the systematic variations seen in Fig. 2.

2.4. O_2/N_2: Melt–refreeze technique

The ice sample is prepared in a cold room at −25 °C. 5 mm are removed from the surface with a band saw. The sample is then placed in a glass vessel immersed in a −20 °C ethanol bath and connected to an extraction line via a gold covered copper o-ring. After evacuation of the ambient air for 40 min, the vessel is isolated and the ethanol bath removed. Once the melting is completed, the ice is slowly refrozen with liquid nitrogen and the air is trapped in a stainless steel tube immersed in liquid He at −270 °C. The sample in the dip tube is allowed to homogenize at room temperature for 40 min before mass spectrometric analysis (see Landais et al. (2003) for details on the analytical procedure). Isotopic and elemental ratios are measured on a dual inlet Delta V mass spectrometer (Thermo) which permits simultaneous measurements of masses 32 and 28. Results are reported with respect to atmospheric air after corrections for pressure imbalance and chemical interferences of CO_2 and $\delta O_2/N_2$ (Landais et al., 2003; Severinghaus et al., 2001).

3. Measurements

3.1. CO_2 measurements in the bubble–clathrate transformation zone

Measurements on Vostok ice in the bubble–clathrate transformation zone (BCTZ: Interval of an ice core between the depth levels where the first clathrate and the last original bubble, respectively, are detected in microscopic investigations; Vostok: 500–1250 m corresponding to the time interval between ~20 to ~85 kyr BP) on gas extracted at the Laboratoire de Glaciologie et Géophysique de l'Environnement in Grenoble with a ball crusher on much larger samples than used in our dry extraction described above (sample weight: 40 g) show CO_2 concentrations in the range of 190 to 240 ppmv (Petit et al., 1999). These variations are fairly in line with CO_2 concentrations observed in Taylor Dome (pure bubble ice) (Indermühle et al., 2000) and Byrd ice (originally pure clathrate ice) (Ahn and Brook, 2007; Ahn et al., 2008). Investigations in the BCTZ of the EDC ice core at the University of Bern showed instead strongly depleted concentrations (up to 70 ppmv) using the routine dry extraction technique (black diamonds in Fig. 1; measurement procedure is described in paragraph 2.1). Stauffer and Tschumi (2000) explain these observations with a combination of an enrichment of CO_2 in clathrates due to diffusion processes during the transformation from bubbles to clathrates connected with a lower probability of extracting air from clathrates compared to bubbles using the routine extraction technique at Bern (extraction efficiency of pure clathrate ice: ~50%; pure bubble ice: ~70%).

In order to investigate the hypothesis of Stauffer and Tschumi (2000) in more detail, we measured a sequence in the BCTZ of the EDC ice core (800–900 m corresponding to 43–50 kyr BP) using the sublimation technique. In contrast to the routine dry extraction technique, this provided significantly higher values. But, although the sublimation device is assumed to have an extraction efficiency of 100% for both pure bubble and pure clathrate ice, the CO_2 variations found in the Taylor Dome (Indermühle et al., 2000) or Byrd (Ahn and Brook, 2008) ice cores could not be reproduced (inset in Fig. 1). Measurements of neighbouring samples (Δdepth = 4.5 cm) in the depth interval between 847.0 and 847.3 m revealed concentration differences of up to 35 ppmv (Fig. 2a) with deviations from the Byrd record to both lower and higher values.

3.2. CO_2 measurements just below the BCTZ

Measurements using the routine cracking technique on the shallowest part of the pure clathrate zone of the EDML ice core (1230–1780 m) covering the period between 30 and 65 kyr BP are shown in Fig. 1. In comparison to previous results from Taylor Dome

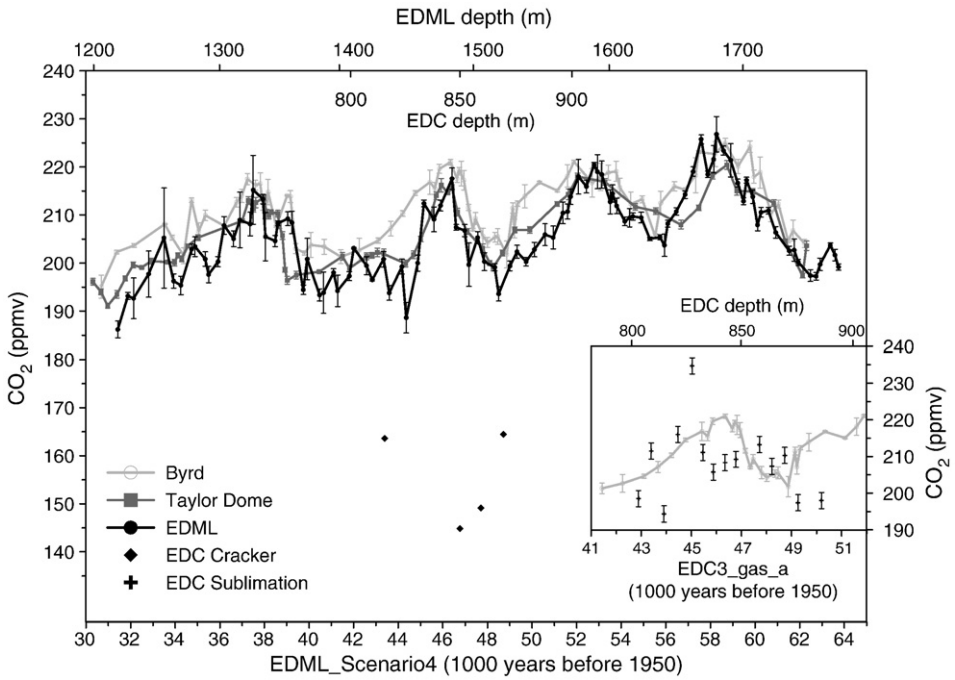

Fig. 1. New EDML and EDC CO_2 measurements: CO_2 concentrations measured on EDML ice using dry extraction (black full circles: Mean value of 4–24 independent measurements on neighbouring samples) compared with CO_2 concentrations measured on the Taylor Dome (dark grey squares; Indermühle et al., 2000) and Byrd ice cores (light grey circles; Ahn and Brook, 2008). The Byrd and Taylor Dome age scale are synchronized on the EDML_Scenario4 timescale (Loulergue et al., 2007) with the help of the CH_4 data. The error bars indicate 1σ of the mean. Black diamonds are dry extraction measurements on samples from the bubble–clathrate transformation zone (BCTZ) of the EDC ice core. The inset shows CO_2 concentration on samples from the BCTZ of the EDC ice core obtained by sublimation (black crosses; σ = 2.2 ppmv and corresponds to the standard deviation of single crystal test measurements) compared to the Byrd CO_2 record (light grey circles; Ahn and Brook, 2007). EDC results are plotted on the EDC3_gas_a age scale (Loulergue et al., 2007), Byrd results on the EDML_Scenario4 age scale. Both gas age scales agree with each other within ±100 yr for this time interval.

(Indermühle et al., 2000) and Byrd (Ahn and Brook, 2007; Ahn and Brook, 2008), they reproduce the peak-to-peak variations of 15 to 20 ppmv related to the larger Antarctic Isotope Maxima (EPICA Community Members, 2006), but indicate additional short-term CO_2 variations of about 5–10 ppmv in the younger part of the record (especially between 40 and 45 kyr BP; Fig. 1).

These apparently fast CO_2 changes are the result of concentration differences between neighbouring samples (Δdepth = 2.5 cm corresponding to ~1 yr) of up to 25 ppmv with deviations from the expected CO_2 concentration to lower and higher values (Fig. 2b–f). This is three orders of magnitude higher than the maximum possible rate of change in low accumulation ice cores (Schwander, 1989) and well above the measurement uncertainty of ±1.5 ppmv. Similar observations are made in the upper part of the pure clathrate sections of the EDC and the Talos Dome (mean annual surface temperature: −41 °C, mean annual accumulation rate: 80 kg/m^2 a) ice cores. These variations on a centimetre scale are found to decrease with depth, approaching the analytical uncertainty around 1600 m in the EPICA cores (corresponding gas age: EDC: ~120 kyr BP; EDML: ~53 kyr BP) and around 1100 m in Talos Dome (~42 kyr BP), respectively (Fig. 3).

4. Possible explanation of the centimetre-scale CO_2 variations

4.1. Artefacts

There are several processes which may alter the CO_2 concentration measured in ice cores: Chemical reactions, selective degassing during storage and laboratory artefacts. The first can be excluded for two reasons: First, the variations are detected in three different ice cores with different amounts of impurities, and second, CO_2 alteration in Antarctic ice cores related to chemical reactions are estimated to be only on the order of several ppmv in worst case scenarios (Anklin et al., 1995). These authors estimated a maximum possible CO_2 production of i) about 7 and 5 ppmv by oxidation of organic material and formaldehyde, respectively, based on the amount of organic acids and formaldehyde found in Antarctic ice cores, and ii) about 6 ppmv related to acid–carbonate reactions estimated from the amount of Ca^{2+} available as a first order estimate for the carbonate concentration in Antarctic ice cores. In total, chemical reactions in ice cores are not able to produce CO_2 variations of up to 30 ppmv on centimetre scale in Antarctic ice cores (Fig. 2a). In fact, no such variations are found in bubble ice from the Holocene or the LGM for Antarctic ice cores (Monnin et al., 2001; Siegenthaler et al., 2005a).

Previous CO_2 measurement series by Siegenthaler et al. (2005b) and Lüthi et al. (2008) on EDC ice from the depth interval between 2700 and 3200 m do not show any CO_2 differences between neighbouring samples exceeding the analytical uncertainty (±1.5 ppmv) although the ice has been stored under conditions identical to the present study. Furthermore, recently performed CO_2 measurements on the Byrd ice core (Ahn and Brook, 2007; Ahn and Brook, 2008), which has been stored for more than 37 yr at −25 °C, reproduce concentration variations found in ice cores drilled more recently (Taylor Dome and EDML) within the measurement uncertainties. Accordingly, we exclude alteration of the CO_2 concentration by selective degassing during storage as a reason for the short-term variations.

Finally, the samples have been measured in random order. If the CO_2 variations on centimetre scale were the result of accidental deviations from the measurement protocol, different concentrations also in samples from identical depths would be expected. Since two samples from identical depths are in agreement within the measurement uncertainty in 95% of the cases, we can exclude systematic errors related to the analysis as the origin of the observed CO_2 changes in our CO_2 data records.

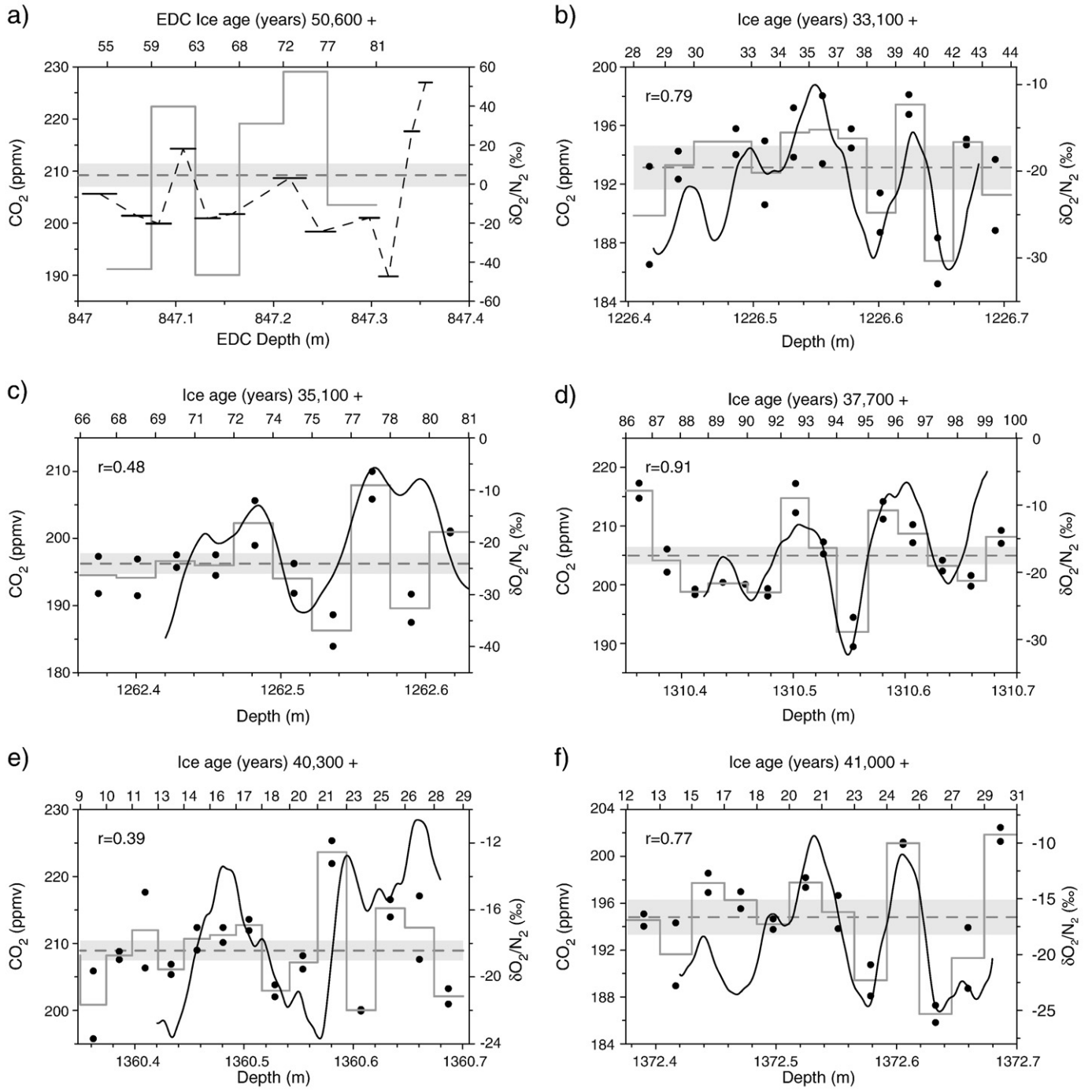

Fig. 2. Comparison between O_2/N_2 and CO_2: a): CO_2 sublimation results (grey step line) and O_2/N_2 measurements (black horizontal bars connected by the dashed black line; discrete melt extraction, LSCE) on EDC ice in the BCTZ. The grey dashed line shows the mean CO_2 concentration of all measurements over the ~0.3 m depth interval and the grey area indicates the analytical uncertainty of the sublimation device ($\sigma = 2.2$ ppmv). Deviations of the O_2/N_2 ratios are given as per mille deviations of the ratio of present atmospheric air. b–f): Comparison of CO_2 dry extraction measurements (grey step line) and O_2/N_2 measurements (black continuous line; continuous melting system, University of Bern) on EDML ice just below the BCTZ. The black dots are individual CO_2 measurements. The grey step line represents the mean values of two samples from the same depth. The grey dashed line shows the mean CO_2 concentration of all measurements over the ~0.3 m depth interval and the grey area indicates the analytical uncertainty ($\sigma = 1.5$ ppmv). Deviations of the O_2/N_2 ratios are given as per mille deviations of the ratio of present atmospheric air.

4.2. Possible mechanism associated with the clathrate formation

Since CO_2 measurements on ice from above the BCTZ (pure bubble ice) show excellent results for Taylor Dome (Indermühle et al., 2000), EDC (Monnin et al., 2001) and for EDML (Siegenthaler et al., 2005a), a possible explanation for the observed CO_2 variations on centimetre scale must be found in the transformation of bubbles to clathrates. Bubbles are observed to transform to clathrates within a depth interval of several hundred meters. The transformation starts at depths where the pressure within bubbles (to first order corresponding to the hydrostatic pressure) exceeds the dissociation pressure of the entrapped air components (Miller, 1969; Shoji and Langway, 1982). During this transformation, some gas molecules are preferentially taken up in the clathrate phase. Kobashi et al. (2008) showed that Ar/N_2 was uniformly enriched within the BCTZ, because of preferential gas loss during core recovery from the bubble phase in

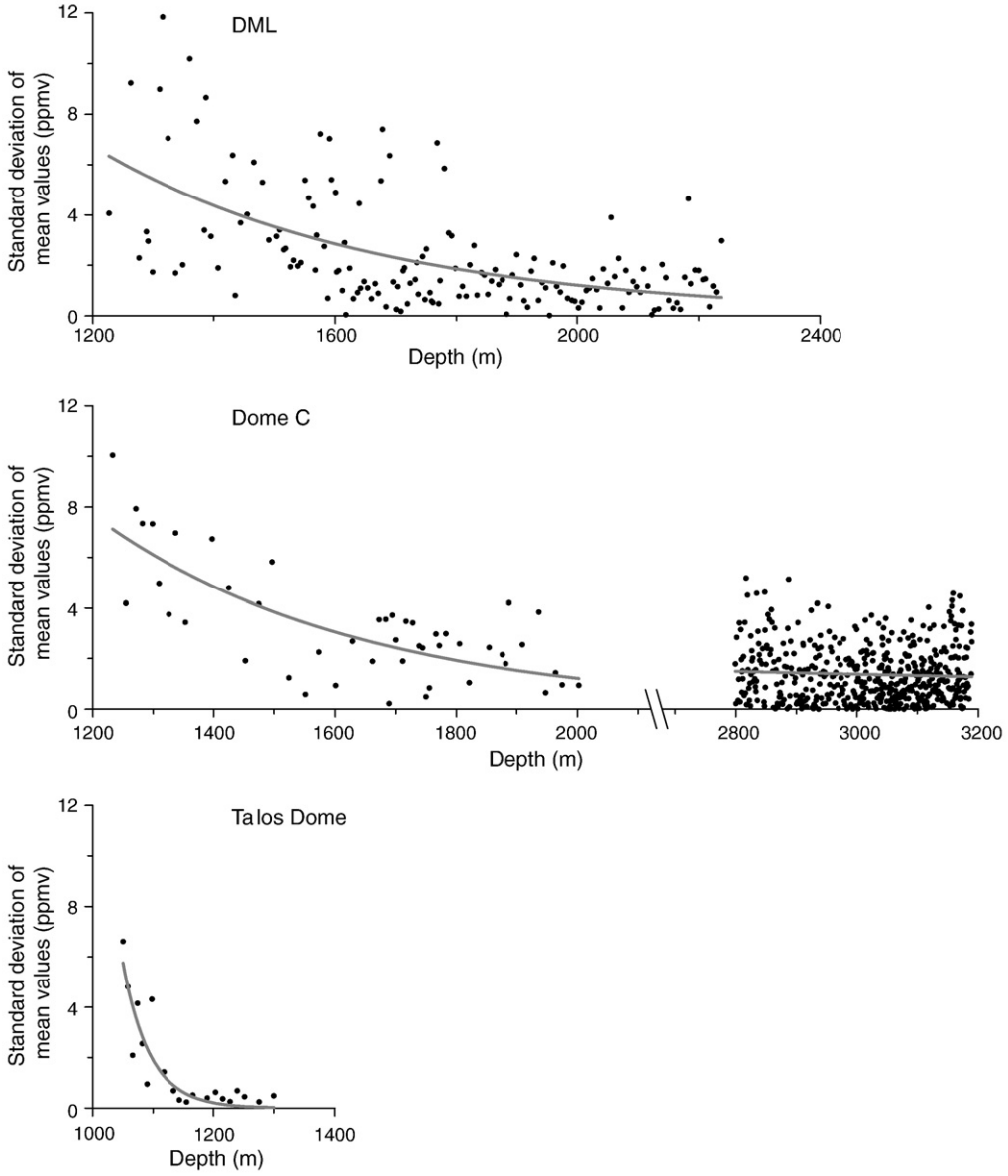

Fig. 3. CO_2 variations on centimetre scale decreasing with depth: Standard deviation of the mean values of the two samples from identical depth as a representation for the short-term variations within neighbouring samples from the shallowest part of the pure clathrate ice zone of EDML, EDC and Talos Dome compared with the standard deviations of the mean values of the two samples from identical depths of the long-term EDC CO_2 records of Lüthi et al. (2008) and Siegenthaler et al. (2005b). Grey lines indicate exponential fits.

combination with a preferential uptake of Ar in the clathrate phase. Ikeda et al. (1999) and Ikeda-Fukazawa et al. (2001) have measured the O_2/N_2 ratios within the two forms of inclusions over the BCTZ of the Vostok and the Dome Fuji ice core. In case of bubbles, they have detected a trend from atmospheric values at the top (~600 m) to strongly depleted ratios at the bottom of the transformation zone (~1200 m). In case of clathrates, they have found maximum O_2/N_2 ratios around 700 m decreasing with depth. The atmospheric ratio is reached at the end of the BCTZ. Thereby, they assumed diffusion of air from bubbles to clathrates and a fractionation of the air composition within the two forms of inclusions due to different permeation coefficients and dissociation pressures of O_2 compared to N_2 through the ice matrix.

There is still insufficient quantitative knowledge about the permeation coefficients and the dissociation pressures of O_2, N_2 and CO_2 in the ice. The results for the permeation coefficients are based on different approaches (molecular dynamic modelling in pure mono-crystalline ice versus empirical fitting of a gas permeation model to observed O_2/N_2 ratios in the Vostok ice core) and differ over several orders of magnitudes (Ikeda-Fukazawa et al., 2001; Salamatin et al., 2001; Ikeda-Fukazawa et al., 2005). Nevertheless, we adopt the concept of different permeation coefficients used as an explanation of the O_2/N_2 fractionation and extend it to a fractionation of CO_2. To explain our observation of the strong CO_2 variations on a centimetre scale, we postulate that the ratio between clathrates and bubbles is not steadily increasing, but shows a millimetre- to centimetre-scale layering, leading to a flux of CO_2 from layers with lower to layers with higher clathrate-to-bubble ratios. Such a bubble–clathrate layering may be related to small-scale variations in the grain size or in the amount of chemical and particulate components in the ice and can be directly observed under the microscope (see below). The data of chemical compounds and the observations of grain sizes, however, are not conclusive. This leaves space for speculations and hence, more specific investigations are needed to shed light on the reasons for the bubble-to-clathrate conversion.

With increasing depth, the formation of clathrates becomes completed resulting in layers of several millimetres to centimetres thickness with different CO_2 concentrations and O_2/N_2 ratios. Subsequently,

we assume that diffusion through the ice with a much longer time scale, driven by the different gas compositions within clathrates, becomes dominant. When it has reached equilibrium at a depth of several hundred meters below the BCTZ, the air entrapped in the ice represents the initial but slightly smoothed atmospheric information. This process is enhanced by the slow downward movement of ice layers in the core which causes a continuous thinning of the layers, increasing the gradient driving the diffusion.

5. Supporting evidence

A first argument in support of our hypothesis lies in the strong variations of the O_2/N_2 ratios found in the BCTZ of the Vostok, GISP2 and GRIP ice cores (Bender et al., 1995; Huber and Leuenberger, 2004; Suwa and Bender, 2008), which are to be expected if such a stratified clathrate formation process occurs. To further explore this effect we have measured the O_2/N_2 ratios in very high resolution on EDC ice in the depth interval around 847 m (BCTZ, Fig. 2a) and on five 30 cm depth intervals just below the BCTZ of the EDML ice core, where we expected variations from parallel CO_2 samples (Fig. 2b–f). Changes, which significantly exceed maximum centimetre-scale variations found in the pure bubble ice zone (<20‰; Huber and Leuenberger, 2004), are indeed observed (up to 100‰), but are only partly in phase with CO_2. In EDML ice we have found a relation between the two parameters ranging from a weak correlation ($r=0.48$ and $r=0.39$) for intervals around 1262 m and 1360 m, to a good correlation for 1226, 1310 and 1372 m ($r=0.79$, 0.91 and 0.77, respectively).

Our hypothesis is also qualitatively in agreement with optical line-scan analyses detecting a layering of the ratio between bubbles and clathrates on EDML ice on a millimetre to centimetre scale (Faria et al., 2010). Fig. 4 shows line scans from two 45 cm depth intervals on the BCTZ of the EDML ice core (~1023.5 and ~1046.5 m). The line-scanner images between 1000 and 1200 m were taken around July 22 in 2003, so roughly 7 months after drilling. Both pictures, the light and the dark, are the same line scans but differently modified by image processing to depict grey bands and bubbles (black dots) as clearly as possible. The grey bands, generally called cloudy bands, originate from a combination of micro-inclusions and an increased density of grain boundaries caused by a drastically reduced grain size within the bands. They are clearly visible in the dark pictures. The bright black and white pictures have been filtered with a grey value threshold such that the cloudy bands are mostly eliminated while the black bubbles are retained. These pictures are used to estimate the bubble-to-clathrate ratios. The percentage of the black area is a rough estimate of the fraction of bubble volume. Since clathrates are not visible on line-scan pictures, the ratio between bubbles and clathrates can only be estimated by bubble counting. The estimated bubble volume fraction is hence a best guess of the bubble-to-clathrate ratio.

The depth resolution in CO_2 measurements in the BCTZ is limited to 4.5 cm (sublimation technique). A direct comparison between the CO_2 variations and the estimate of the bubble-to-clathrate ratio cannot be drawn. Since a correlation between CO_2 and O_2/N_2 in and below the BCTZ is observed, a continuous O_2/N_2 record is used for comparison with the line scans.

O_2/N_2 measurements on these depth intervals reveal variations of up to 90‰ within 25 mm (Fig. 4). The comparison with the line scans shows that the most prominent peaks in O_2/N_2 ratio occur at depths where local minima in bubble number density are observed and hence, where maxima of clathrates are assumed (marked by black triangles in Fig. 4). The estimate of the relative bubble density in the line scans, however, is strongly influenced by the grey bands, the quality of the line scans and the graphical modification. Accordingly, a more quantitative statistical analysis cannot be performed based on data currently available. Nevertheless, we consider the concurrence of 10 out of 12 major O_2/N_2 peaks with local minima in bubble density as support for our hypothesis.

A more circumstantial argument for our hypothesis comes from the modelling of the smoothing of the CO_2 concentration differences below the BCTZ. We changed one basic point in the model of Bereiter et al. (2009) to be able to simulate this smoothing by gas diffusion. The radial symmetric diffusion equation was changed into a one-dimensional linear equation to be able to calculate the gas exchange in vertical direction. Furthermore, the boundary layer was removed, since we focus here on the vertical in situ exchange of gases in the clathrate zone of the ice sheet. The way in which the equilibrium between the enclosed gases in the clathrates and the dissolved part in the ice was calculated remains unchanged.

With these adaptations, the model was started with a CO_2 concentration distribution as it is found in the interval between 1360.54 and 1360.64 m (Figs. 2e, 5) of the DML ice core and the CO_2

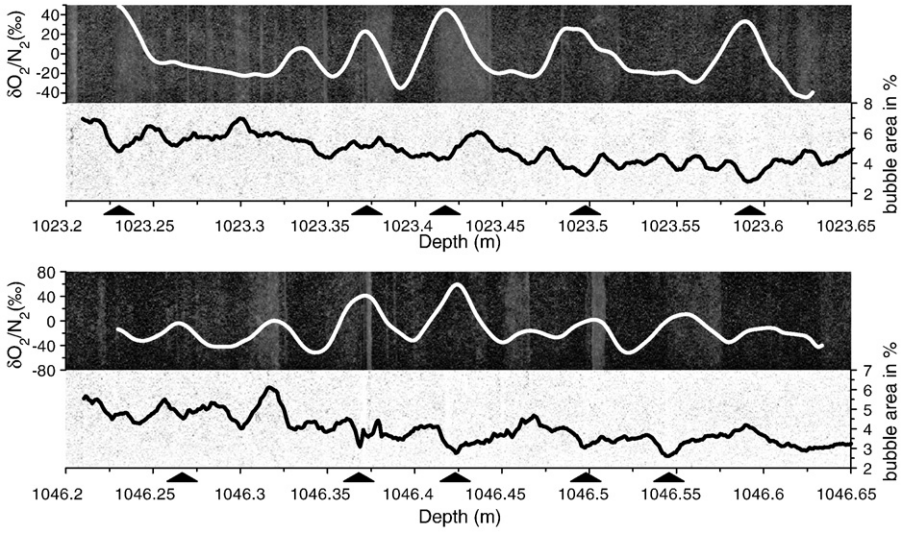

Fig. 4. Comparison of O_2/N_2 with bubble-to-clathrate ratio: O_2/N_2 measurements on ice from the BCTZ of the EDML ice core using a continuous melting system (white line; depth uncertainty is ±10 mm; measured at the University of Bern) compared with the percentage of the black area of filtered line-scan pictures, which is considered as rough estimate of the bubble-to-clathrate ratio (black line; running mean over a depth interval of 10 mm of the percentage of the black area measured in 1 mm depth intervals). Brightness and contrast of the original line scans have been modified by image processing to enhance grey bands (dark pictures) or bubbles (black dots in bright pictures). See main text for details. Black triangles indicate depths where strong O_2/N_2 peaks are accompanied by local minima in the bubble number density corresponding to maxima in the clathrate-to-bubble ratios. Deviations of the O_2/N_2 ratios are given as per mille deviations of the ratio of present atmospheric air.

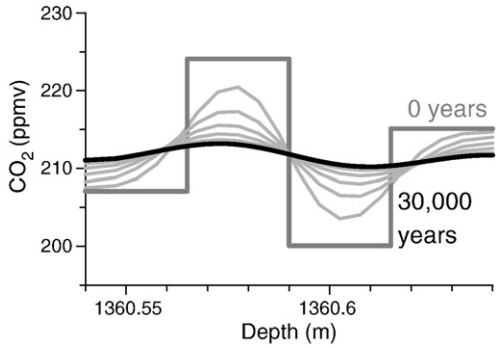

Fig. 5. Homogenization model results: Homogenization of CO_2 variations detected in EDML in a depth of about 1360 m calculated with a modified one-dimensional diffusion model (Bereiter et al., 2009; see description in the main text) after 5000, 10000.. and 30000 yr using the solubility and diffusion constants obtained by Ahn et al. (2008) for CO_2. The interval of 10 cm has been divided in boxes of 5 mm. Each box can interact with its neighbouring boxes. The 10 cm interval is closed, so that the first and the last box can only interact with one neighbouring box.

permeation coefficient empirically derived by Ahn et al. (2008). The diffusive exchange was then calculated forward in time at local temperature conditions in the DML ice sheet of −33 °C (Fig. 5). About 30000 yr are needed to reduce the CO_2 difference between neighbouring samples to below the measurement uncertainty. This time span is on the order of the observations (Fig. 3), which indicate a homogenization length of about 400 m below the BCTZ corresponding to about 23000 yr. In comparison to this, it takes considerably longer at EDC (~40000 yr) and significantly less at Talos Dome (~10000 yr) until the short-term variations are smoothed out. This is in line with our diffusion hypothesis, since EDC (Talos Dome) is about more than 10 °C colder (less than 5 °C warmer) compared to EDML and thus diffusion processes are slower (faster).

6. Conclusion

The spatial fractionation process of CO_2 and O_2/N_2 proposed here is mass conserving. It is limited to the BCTZ and the shallowest hundreds of meters of the pure clathrate zone and mostly occurs in layers of millimetres to centimetres thickness. This and the fact that the short-term variations decrease with depth and approach the measurement uncertainty around 1600 m for the EPICA cores and 1100 m for Talos Dome, respectively, shows that the disturbance is slowly removed and that a slightly smoothed atmospheric signal is recovered below this depth. Furthermore, estimates from the five 30 cm intervals mentioned above (Fig. 2b–f), allow us to derive reliable CO_2 concentrations even in the affected part of the core, if an average over a depth interval of at least 10 cm is taken.

The routine measurement protocol at the University of Bern, with at least four independent neighbouring samples, of which pairs are taken from identical depths, reduces the risk of laboratory, melting or diffusion artefacts. The first would be detected by different concentrations in samples from identical depth, the second by significantly enhanced CO_2 values (Neftel et al., 1983; Ahn et al., 2008) and the third by concentration differences between two neighbouring depth levels exceeding the measurement uncertainty (±1.5 ppmv). Therefore, we conclude that the long-term records of Lüthi et al. (2008) and Siegenthaler et al. (2005b) which cover the interval between 800 and 390 kyr BP provide true records of atmospheric CO_2 concentrations in the past, which are unaffected by the process described here.

Besides those depth intervals of EDML, EDC and Talos Dome ice discussed here, we recommend cautious interpretation of CO_2 results from the Vostok ice core in the interval between 20 and 110 kyr (Petit et al., 1999). This period corresponds to the depth interval between 500 and 1600 m and, hence, is probably also affected by the bubble–clathrate transformation effect. The extent of the alteration in the Vostok record, however, is expected to be lower compared to the EPICA and Talos Dome results, because larger ice samples were used (Δdepth = 6 cm), reducing the mean deviation from the expected mean value to 2.3 ppmv based on estimates on the five 30 cm EDML data sets (Fig. 2b–f). The general 10 ppmv difference between values measured on Vostok and the data obtained on Byrd (Ahn and Brook, 2008), Taylor Dome (Indermühle et al., 2000) and EDML throughout this period, however, reflects a systematic offset, potentially related to a different gas extraction efficiency for bubbles and clathrates in the BTCZ. For CO_2 results on Dome Fuji ice obtained by a wet extraction method, no influence of the BCTZ fractionation effect is expected, because of a 100% extraction efficiency combined with the use of large enough ice samples to overcome short-scale CO_2 variations (Kawamura et al., 2003; Kawamura et al., 2007). Note, however, that wet extraction of CO_2 is more likely to be subject to in situ artefacts in CO_2 concentrations such as carbonate acid reactions in the melt water.

In summary, small-scale CO_2 and O_2/N_2 variations in the BCTZ and the shallowest hundreds of meters of the pure clathrate zone of Antarctic ice cores are likely caused by a layering in the clathrate formation, followed by selective gas diffusion from bubbles to clathrates. However, based on results from three different ice cores, we conclude that this process is mass conserving and therefore does not affect air compositions entrapped in ice several hundred meters below the BCTZ, or samples large enough within the BCTZ.

Acknowledgements

This work is a contribution to the "European Project for Ice Coring in Antarctica" (EPICA), a joint ESF (European Science Foundation)/EC scientific program, funded by the European Commission and by national contributions from Belgium, Denmark, France, Germany, Italy, The Netherlands, Norway, Sweden, Switzerland and the United Kingdom. The main logistic support was provided by IPEV and PNRA (at Dome C). We thank the technical team in the field and at the three labs. We acknowledge financial support by the Swiss NSF, the University of Bern, and the Prince Albert II of Monaco Foundation. The presented data is available on: http://www.ncdc.noaa.gov/paleo/icecore/antarctica/maud/maud_data.html. This is EPICA publication no. 269.

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