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Scientific paper

Discussion of the reliability of CO₂, CH₄ and N₂O records from polar ice cores

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Abstract: Air in polar ice has about the same composition as atmospheric air at the time of ice formation. This allows to determine the composition, especially the concentration of greenhouse gases, in the past. However, the air composition in the ice can be slightly altered by chemical and biological processes in the ice. The reliability of long term trends can be determined by comparing records from different ice cores. For short duration details and time lags such comparisons are not possible due to uncertainties of the age scales of records from different cores. In this case very detailed records along sections of ice cores show whether the scatter of the results is larger than the theoretical expected one. A larger scatter is assumed to be caused by reactions between impurities in the ice which show generally short term variations. A low scatter of detailed high resolution records is therefore, a prerequisite for reliable records.

key words: greenhouse gases, atmospheric composition, paleoclimatology, CO₂, CH₄, N₂O

1. Introduction

Analyses of ice cores from the central parts of large polar ice sheets are the most direct way to investigate variations of the atmospheric concentration of the important greenhouse gases carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) in the past (Raynaud *et al.*, 1993). Such analyses on different ice cores, with different impurity concentrations and from locations with different surface temperatures gave consistent results concerning the increase of all three greenhouse gases during the past few centuries (since the beginning of industrialisation) and during the transition from the last glacial epoch to the Holocene. Based on this consistency the results are considered as reliable.

More recently, progress in the analytical methods allowed to investigate smaller and more detailed variations. However, the comparison of such details between ice cores from different locations often fails due to the following reasons:

- The dating of the cores is not good enough to synchronise detailed short term variations reliably.
- Certain greenhouse gases can be produced or depleted by chemical reactions between impurities in the ice and possibly by bacteria (Tschumi and Stauffer, 2000; Sowers, 2001).

This paper deals with the question about criteria which shall help to decide which detailed ice core record is more reliable in case of differences between two or several ice

cores and to provide one criteria of reliability if only one core is available. In this paper the criteria will be discussed for each greenhouse gas separately.

2. Carbon dioxide (CO₂)

For CO₂ there was for a long time a dilemma concerning short term variations during the last glacial period. Greenland ice cores show variations of the CO₂ concentrations parallel to Dansgaard/Oeschger events, but an expected time lag is missing. The variations are consistent in ice cores from Dye 3 and Camp Century but in Antarctic ice cores such large variations are missing (Oeschger *et al.*, 1988). It could be shown that the higher CO₂ concentrations found in Greenland ice cores during warm events in the last glacial epoch are artefacts (Anklin *et al.*, 1997; Tschumi and Stauffer, 2000). The surplus CO₂ is most likely produced by chemical reactions in the ice. If CO₂ records cannot be confirmed to be reliable by the comparison with records from ice cores from other locations due to a lack of such records, we postulate that the investigation of high resolution records provides good criteria to characterise the reliability.

The short term variability of the atmospheric CO₂ concentration is limited due to the long residence time of CO₂ in the atmosphere (≈ 100 yr) (IPCC, 2001). Short term variations are further attenuated due to gas diffusion in polar firn as well as to the enclosure process of bubbles in the ice which occurs gradually over a certain depth interval (Spahni *et al.*, 2003). Therefore, we assume that variations of the CO₂ concentration in ice cores over very short depth intervals (in the order of a few annual layers or less) are caused by chemical reactions between impurities and/or possibly by bacterial activity in the ice. On the other hand we cannot conclude that records without fast variations provide necessarily the correct atmospheric composition, but it is an important prerequisite for the reliability of CO₂ records.

In Bern the CO₂ concentration is measured by a combination of an air extraction by cracking the ice at low temperature and the analysis of the extracted air with laser absorption spectroscopy (Zumbrunn *et al.*, 1982). An ice sample of 8 g is placed in a needle cracker at a temperature of -30°C . The closed cracker with the ice sample is then evacuated, the needle cracker activated and the air from the opened bubbles expands over a cold trap ($T = -70^{\circ}\text{C}$) into a laser absorption cell. The CO₂ concentration is measured with an infrared laser absorption spectrometer (based on a tuneable diode laser, wave number range $2335\text{--}2350\text{ cm}^{-1}$) (Monnin *et al.*, 2001). After each measurement of a sample a calibration is done using an air-based standard gas with a CO₂ concentration of 251.7 ppmv. Standard gases with different concentrations (321.06 and 342.03 ppmv) are used to check the linearity of the system.

The extraction procedure is checked with air free single crystal ice. We prepare for this purpose large single crystals from distilled water, further purified by a Millipore filter system. After evacuation of the cracker with the single crystal ice, a certain amount of standard gas, corresponding to the air extracted in average from an 8 g ice sample, and with known CO₂ concentration (251.7 ppmv) is added and then the cracker activated. No significant contamination is observed during such tests. The reproducibility of our measurements is determined by measuring a series of single crystal ice samples with standard gas. The reproducibility is in the order of 1.5 ppmv (1 σ error).

This measuring device can measure ice core samples with a depth resolution of about 15 mm. Figure 1 shows a CO₂ record measured along 0.45 m of an ice core from Kohnen

Station, Antarctica. The age of the air enclosed in the bubbles at 147.4 m depth is about 930 years. The measured mean CO₂ concentration is 281.8 ppmv. This is slightly higher than expected based on measurements on other ice cores representing the same age, but still within the error limits. However, the scattering of the results is significantly larger than our reproducibility. To check if this is extraordinary, and only typical for this depth interval and this drilling site, subsequently two ice core sections from Dome Concordia were measured with the same resolution. The results are shown in Figs. 2 and 3. The age of the enclosed air is about 4270 years BP at 219.2 m depth and about 16500 years BP at 521.7 m depth. The mean values of the CO₂ concentration of 271.7 ppmv at 4270 years BP and of 194.7 ppmv at an age of 16500 years BP are in good agreement with results from other ice cores. The measuring device was checked after each sample by measuring a single crystal ice sample with standard gas added as described above. In Figs. 2 and 3 the results of all these single crystal measurements are shown as well. The corresponding single crystal measurements show a scatter of 1.7 ppmv and 1.9 ppmv, respectively. The scatter of the ice samples of the lower depth interval (2 ppmv) is of the same order, the scatter of the upper depth interval (2.8 ppmv) is significantly higher than for the series of single crystal measurements, but still lower than in the core from Kohnen Station. In these two samples, the younger ice shows a higher absolute scatter than the older ice, which is surprising. All known processes which are discussed to possibly affect the CO₂ concentration in bubbles need a certain recrystallization which needs time. The relative deviations from the mean concentration show in both depth intervals of the Dome Concordia record a mean scatter of 1%, but we have no reasons to assume that the absolute mean deviations should depend on concentration. In relatively shallow ice the size distribution and the form of bubbles change significantly with depth. Our extraction efficiency does not exceed 80%. If there is a fractionation of the CO₂ concentra-

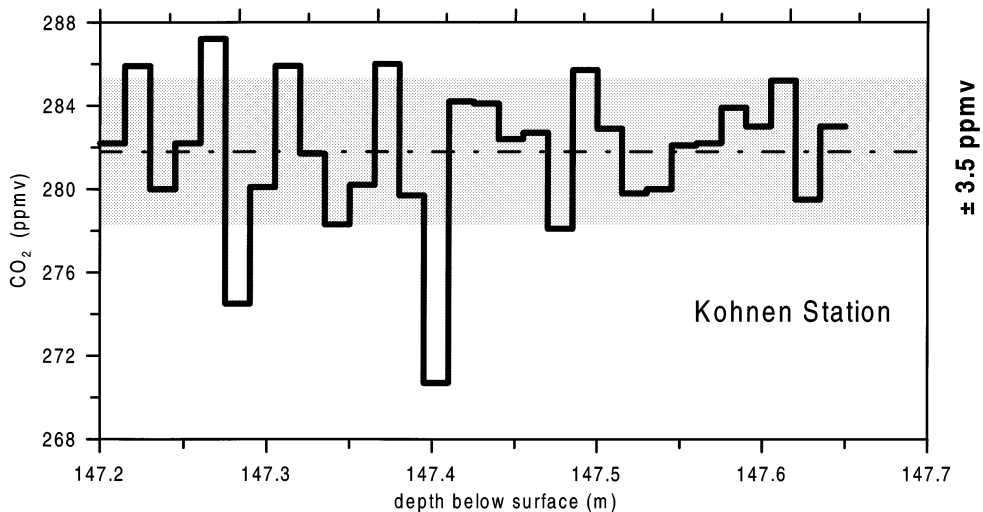


Fig. 1. CO₂ concentration measured along a 0.45 m long core section from Kohnen Station (Antarctica), (75°00.1' S, 0°00.4' E). Altitude of drilling site: 2892 m a.s.l.; mean annual surface temperature: -44.6°C; mean annual accumulation rate during past 180 years: 62 kg · m⁻² · year⁻¹ (Oerter et al., 2000; Sommer et al., 2000). The shaded area characterises the 1 σ scattering (±3.5 ppmv) around the mean value (281.8 ppmv).

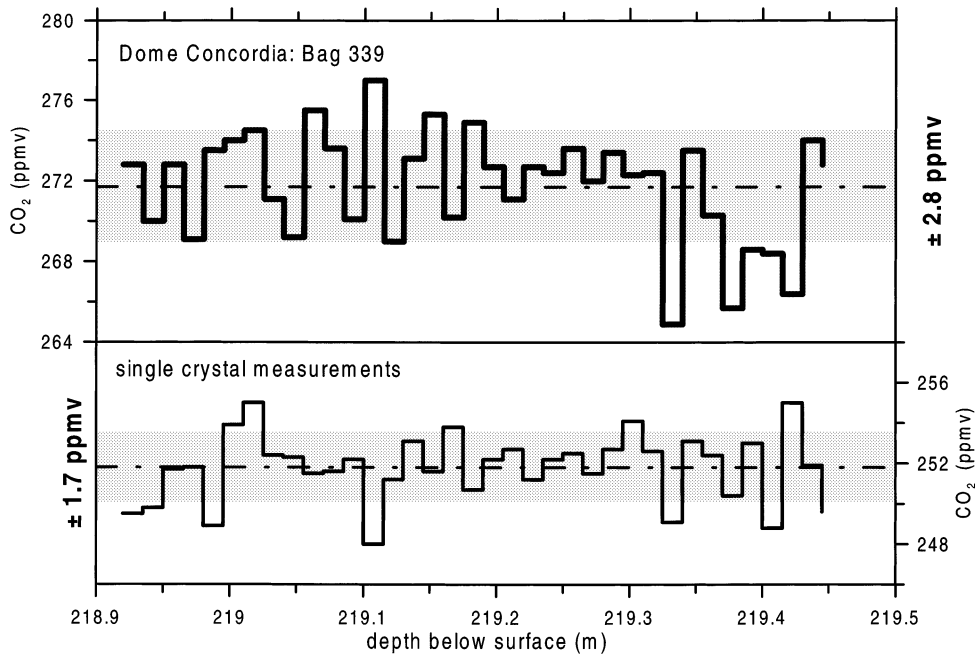


Fig. 2. CO_2 concentration measured along a 0.55 m long core section from Dome Concordia (Antarctica), ($75^{\circ}06.1' \text{ S}$, $123^{\circ}23.7' \text{ E}$), (top). Altitude of drilling site: 3233 m a.s.l.; mean annual surface temperature: -54.5°C ; mean annual accumulation rate: $25 \text{ kg} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$ (Schwander *et al.*, 2001). The shaded area characterises the 1σ scattering ($\pm 2.8 \text{ ppmv}$) around the mean value of 271.7 ppmv. After each measurement a calibration with air free single crystal samples and standard gas was performed. The record at the bottom shows these measurements with a 1σ scatter of 1.7 ppmv (single crystal measurements are plotted in the same depth interval as the previously measured ice sample)

tion between bubbles of different sizes, this could be an explication for the higher scatter at shallower depth. The fractionation could even take place during extraction by diffusion processes.

The deviations of the single crystal measurements follow about a normal distribution, while the deviations of all three ice core records seem to deviate from a normal distribution. It is surprising that there are especially a few very low concentration values which seem to be outside of a stochastic distribution. We have at present no explanation how a depletion of CO_2 could occur within the ice or during our extraction procedure.

We conclude from the three records, shown in Figs. 1, 2 and 3, that there are possibly some small systematic deviations of the measured CO_2 concentration from the atmospheric concentration at the time of ice formation in both Antarctic ice cores. However, the deviations are small. They could be caused by processes in the ice sheet or during the extraction procedure. Due to such deviations our mean error given in previously published records could be slightly optimistic. However, it is unlikely that the mean deviations exceed 1% of the measured concentration in case that larger short term variations can be excluded by measurements of several samples along a short depth interval.

In Fig. 4 the previously published detailed CO_2 record measured on the Dome Concordia ice core (Monnin *et al.*, 2001) is shown, but now with a larger error of 1% of the

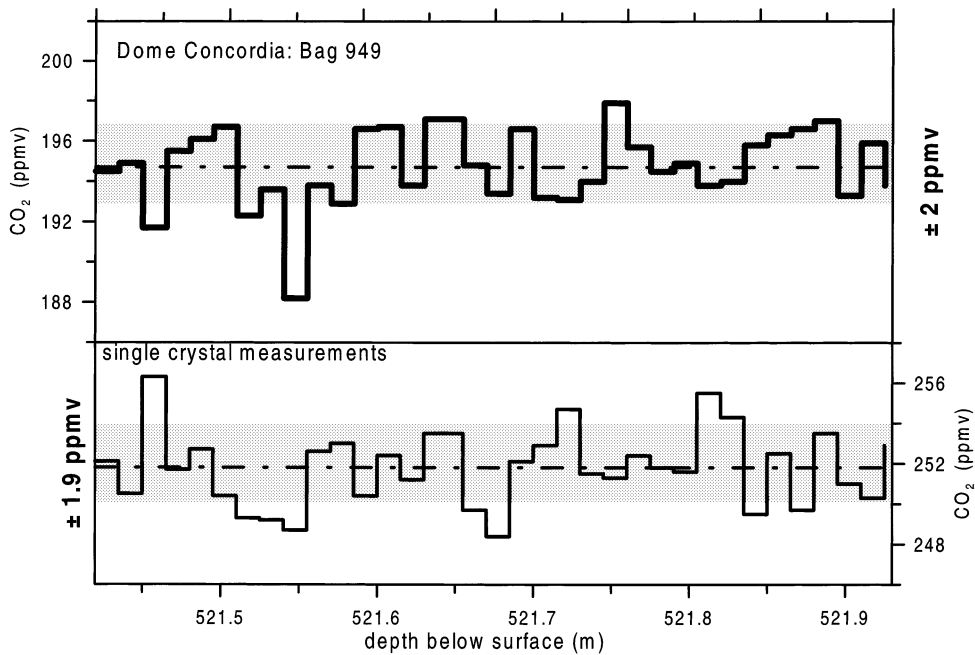


Fig. 3. CO₂ concentration measured along a 0.55 m long core section from Dome Concordia (Antarctica) (top) but at greater depth. The shaded area characterises the 1 σ scattering (± 2.0 ppmv) around the mean value of 194.7 ppmv. After each measurement a calibration with air free single crystal samples and standard gas was performed. The record at the bottom shows these measurements with a 1 σ scatter of 1.9 ppmv.

measured concentration. Each filled circle in Fig. 4 represents the average of 6 measurements along a short depth interval. All conclusions based on the earlier record remain unchanged. It is still possible to distinguish the four different intervals during the transition. Interval I starts at 17000 years BP and is characterised by a synchronous beginning of the CO₂ and CH₄ increase. The start of this increase occurs possibly a few hundred years after the onset of the temperature increase in the Southern Hemisphere. In interval II the increase rate of CO₂ is reduced, the CH₄ concentration does not increase at all. At the transition from interval II to III both CO₂ and CH₄ show a sharp increase. The comparison with Greenland ice cores suggests that these increases occur synchronous with the start of the Bølling/Allerød epoch in the Northern Hemisphere (Dansgaard *et al.*, 1993). Interval III corresponds to this climatic epoch in the North Atlantic region and to the Antarctic Cold Reversal (ACR) (Blunier *et al.*, 1997). The CO₂ concentration is slightly decreasing, and the CH₄ concentration is almost at its early Holocene level. Interval IV corresponds to the Younger Dryas cold period in the North Atlantic region. The CO₂ concentration is increasing at the same rate as in interval I. CH₄ shows a concentration drop of 200 ppbv to a late glacial level before increasing at the end of the interval to its early Holocene value. The general trend of the CO₂ increase follows rather closely the temperature increase in Antarctica, which is assumed to go parallel with the sea surface temperature of the Southern Ocean, and supports, therefore, the idea that the Southern Ocean was an important factor in regulating the CO₂ concentration

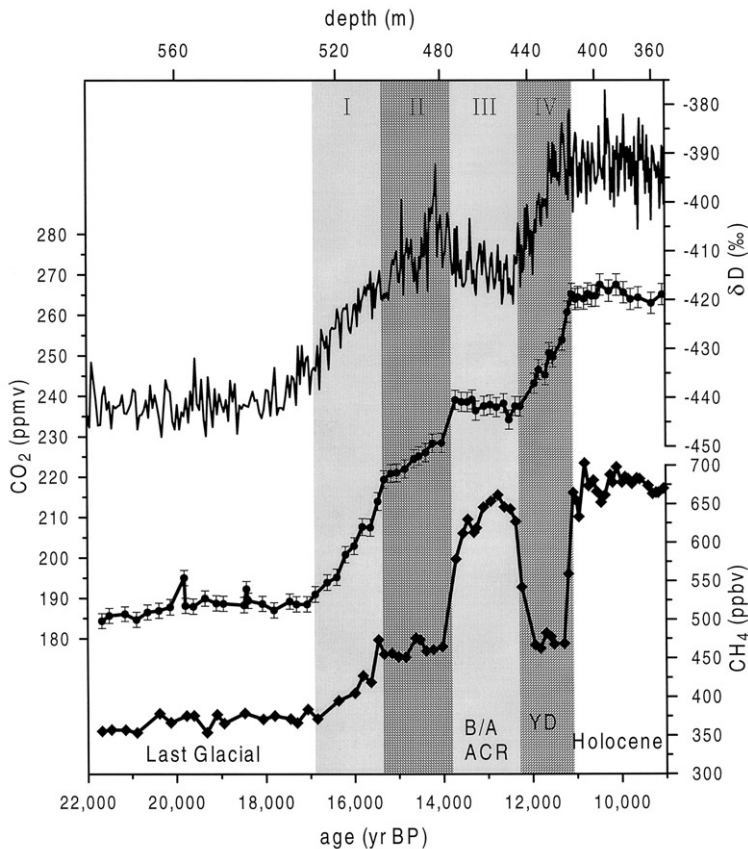


Fig. 4. The top record indicates the Dome Concordia δD values of the ice as a proxy for the local temperature (Jouzel *et al.*, 2001). Solid circles in the middle record indicate CO_2 values measured along the Dome Concordia ice core (Monnin *et al.*, 2001). Each point represents the mean value of 6 measurements. The error bars characterise a 1% error of the measured concentration, taking into account some systematic errors as possibly observed in the high resolution records in Figs. 1–3. The diamonds in the lowest record represent measurements of the CH_4 concentration. The shaded areas characterise four different periods in which the CO_2 and CH_4 increases show typical characteristics.

during the last transition (Petit *et al.*, 1999). However, no causes can be found in Antarctic temperature records for the CO_2 concentration shifts between interval II and III and less pronounced at the end of interval IV, which correspond to the fast CH_4 concentration increases at the beginning of the Bølling-Allerød and at the end of the Younger Dryas periods. These shifts could be caused by effects having their origin in the Northern Hemisphere, possibly through changes in deep water formation (Broecker, 1998; Toggweiler, 1999).

Below a certain depth (depending on temperature and accumulation rate (Miller, 1969)) air gets enclosed in clathrates. CO_2 analyses on such ice samples show additional difficulties because dry extraction methods have lower efficiencies and a fractionation of gas components is more likely (Stauffer and Tschumi, 2000). In general we expect for such ice too low CO_2 concentrations. However, the comparison of recent measurements on the Dome Fuji ice

core with a wet extraction method (Kawamura *et al.*, 2003) with the Vostok record (Petit *et al.*, 1999) show that the deviations do not exceed about 20 ppmv. At present new extraction techniques based on the sublimation of ice and by improving the present cracking technique are developed at the Physics Institute of the University of Bern.

We conclude that the most direct method to exclude artefacts remains the comparison of records from ice cores from different drilling sites with different temperatures, accumulation rates and impurity concentrations. High resolution CO₂ records of a single core cannot replace it, but such high resolution records are a powerful alternative to identify short term variations caused by artefacts, in cases where a comparison of different records is not applicable.

3. Methane (CH₄)

Air for CH₄ measurements is extracted from ice samples by a wet extraction method. An ice sample of about 40 g is melted under vacuum in a glass container sealed with viton and then refrozen from the bottom with an alcohol bath at -30°C to expel gases dissolved in the water. The extraction efficiency is in the order of 99%. The extracted air is expanded into an evacuated sample loop and injected into the gas chromatograph (Varian Star 3400). N₂, O₂, Ar and CH₄ are separated on a Carboxen 1000 column. N₂, O₂ and Ar are detected with a Thermal Conductivity Detector, CH₄ with a Flame Ionisation Detector.

For CH₄ the reproducibility of the concentration measured on polar ice cores is considered to be very good and even allows to determine small interhemispheric concentration differences during past climatic epochs (Chappellaz *et al.*, 1997; Nakazawa *et al.*, 1993; Dällenbach *et al.*, 2000). However, two phenomena are observed which ask for a certain caution: enhanced CH₄ concentrations are observed in polar and mid latitude glaciers close to bedrock and there is evidence for small and short term variations of the CH₄ concentration which do not reflect atmospheric changes, especially in mid latitude glaciers.

In the GRIP ice core CH₄ concentrations increase from less than 500 ppbv, 5 m above bedrock to 6000 ppbv, 0.5 m above bedrock (Souchez *et al.*, 1995). The increase of the concentration goes parallel with an increase of the CO₂, a decrease of the total air content (from 100 ml/kg_{ice} to 40 ml/kg_{ice}) and a decrease of the O₂/N₂ ratio (from 0.32 to 0.08). Such air contents and gas compositions are found in frozen marshy environments. It could be that the ice close to bedrock is a remnant of the beginning of the growth of the Greenland ice sheet (Souchez *et al.*, 1995). Depleted air contents, enriched CO₂ concentrations and depleted O₂/N₂ ratios have also been found in the ice close to bedrock at Dye 3 and Camp Century, but less pronounced. The CH₄ concentration has not been measured in the corresponding parts of these cores. Elevated CH₄ concentrations have also been found in an ice core from Colle Gnifetti (Swiss Alps, 4450 m a.s.l.) close to bedrock (Fig. 5). The question arises whether this could also be an indication that this ice is remnant from the beginning of the growth of this glacier. However, there are substantial differences between the GRIP and the Colle Gnifetti bottom parts. At the bottom of the GRIP ice core the highest values are around 6000 ppbv while at Colle Gnifetti the highest value is 1144 ppbv, a value which could principally still be explained by large melt layers or a contamination with modern air. The other important difference is that at GRIP the concentration increases almost uniformly toward the bedrock while the highest value at Colle Gnifetti is found 15 m above bedrock (at a depth of

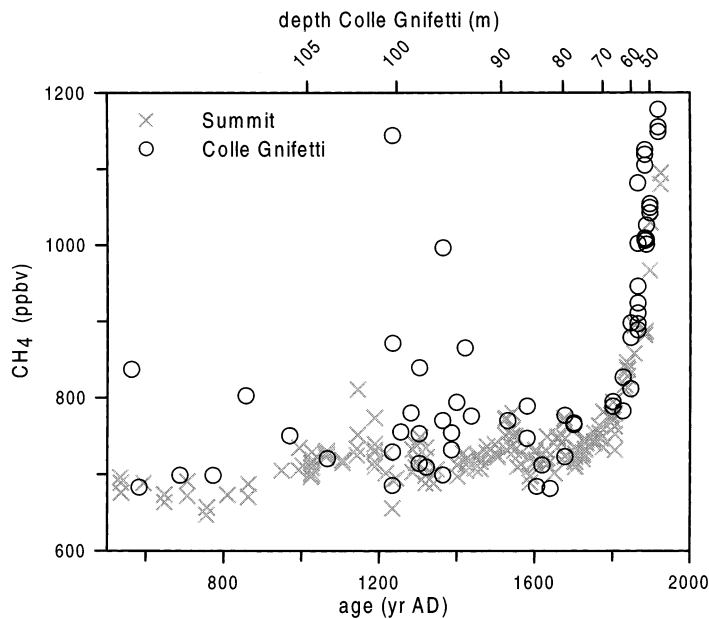


Fig. 5. CH_4 concentration from Colle Gnifetti (open circles) compared with measurements from Summit (Greenland) (grey crosses) along an estimated common time scale (bottom axis). Also indicated is the depth scale of the Colle Gnifetti samples (top axis).

100 m), followed by smaller values further down. We have no explanation for the obviously enhanced CH_4 values close to the bottom in the Colle Gnifetti ice core. However, enhanced values close to bedrock seem to be a common feature of many ice cores but there is no evidence that they are all caused by one distinct phenomenon.

A comparison of the general trend of the CH_4 record from Colle Gnifetti (Fig. 5) down to 90 m depth with the GRIP CH_4 record from Summit has been used to date the Colle Gnifetti ice core (Dällenbach, 2000). The general trend fits quite well but at certain depth levels a high scatter is found in the Alpine core. One example is in ice from 49.5 m depth, where the enclosed air is estimated to represent the atmosphere around 1864 AD. The mean Northern Hemisphere CH_4 concentration at this time was 870 ± 40 ppbv. Just below 49.52 m depth the CH_4 concentration increases from 910 ppbv within 20 mm to 1080 ppbv and subsequently decreases to 900 ppbv within the next 60 mm. The air from these samples have been extracted with a dry extraction method. A core section from a neighbouring core also shows high concentration fluctuations over a short depth interval. The results are shown on a linear depth scale in Fig. 6. Air from these samples have been extracted with our melting refreezing extraction technique. The depth interval represents a time interval of about 2 years. Therefore, the observed variation cannot be of atmospheric origin. The concentration differences of 140 ppbv stand in contrast to the reproducibility of the measurements of about ± 10 ppbv (1σ).

There is an anticorrelation between the CH_4 concentration and the total air content. A reduced air content is generally found in melt layers. Due to different solubility of N_2 compared to CH_4 in water, we expect an enrichment of CH_4 in such melt layers. In an extreme

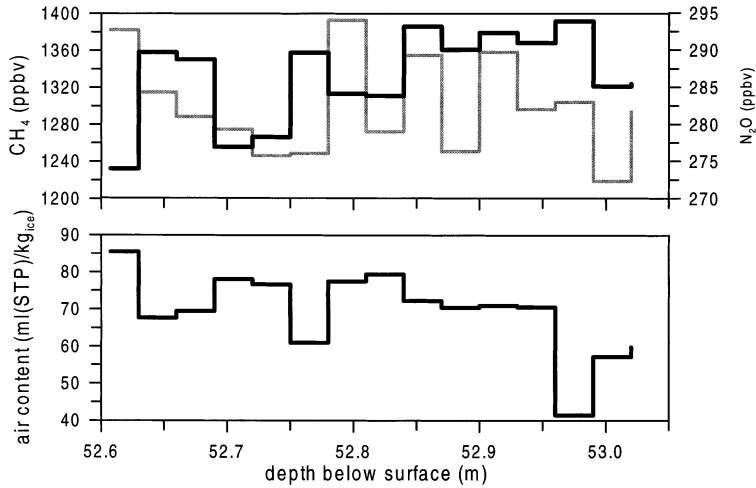


Fig. 6. High resolution CH₄ (black line, left scale) and N₂O (grey line, right scale) record measured along a 0.4 m long ice core from Colle Gnifetti (top) and of the air content of the corresponding samples (bottom).

case, if air saturated water is refrozen so fast that no air can escape, the CH₄ concentration in the enclosed air is about double as high as in atmospheric air in equilibrium with the melt water. A 10% contribution of such a melt layer in a sample can explain a decrease of the total air content by about 7% and an increase of the CH₄ concentration by about 3%. Therefore, a substantial part of the CH₄ variations could be explained principally by melt layer contributions. If the enrichment is caused by a solubility effect O₂ and Ar have to be enriched in the extracted air as well. Unfortunately we do not resolve N₂, O₂ and Ar in our measurements, but we measured parallel the very soluble N₂O which is also shown in Fig. 6. No strong enrichment of N₂O parallel to the suspected CH₄ enrichment is observed. An explanation of the high scatter by melt layers seems therefore, to be unlikely. Another explanation for enhanced CH₄ values could be bacterial activity. However, additional investigations are needed to get insight into a possible CH₄ production due to microbiology.

On the same ice core section high resolution chemical analyses have been performed (Wagenbach, personal communication). A comparison of the records show, that there is an anticorrelation between CH₄ and dust. This would suggest that dust is not producing CH₄ but rather depleting it *e.g.* by an oxidation of CH₄ in the ice or during the wet extraction. To investigate the possibility of a depletion process during the extraction, dust from a large amount of glacier ice was collected. This dust was added to a pure single crystal ice sample and standard gas (408 ppbv) and subsequently the normal extraction procedure (melting and refreezing the ice sample) was performed. Instead of a depletion of CH₄, an enrichment by 3 to 13% was observed. The single experiment is not conclusive, but it seems that the correlation of high dust with low CH₄ concentrations in the short record could be accidental. However, it is not possible with the record of Fig. 6 to decide whether the high or the low values are a better approximation to the atmospheric composition. However, the comparison of the results from Colle Gnifetti and Summit in Fig. 5 indicates that an enrichment of CH₄ is more likely than a depletion. but at present we have no final explanation for the unexpected

high scatter of CH₄ concentrations in ice cores from Colle Gnifetti.

If CH₄ records from mid latitude glaciers shall help to refine the latitudinal distribution of the atmospheric CH₄ concentration and of major CH₄ sources, these records have to be better understood and of the same accuracy and reliability as polar records. Additionally, there is also the possibility that the effects which cause an obvious CH₄ contamination in mid latitude glaciers cause a smaller not obvious contamination in polar ice cores which, for example could lead to wrong inter hemispheric concentration gradients. Therefore, we will investigate in the near future detailed analyses along short core sections concerning the scatter of CH₄ concentrations in polar ice cores from different drilling sites and different climatic epochs.

4. Nitrous oxide (N₂O)

For N₂O analyses the air is extracted in the Bern laboratory by the same melt-refreezing method as for CH₄ (Flückiger *et al.*, 2002). The N₂O concentration of the extracted air is measured with a gas chromatograph using an Electron Capture Detector. Laboratory tests confirmed that the melt-extraction method can be used despite the high solubility of N₂O in water. However, the obtained results have to be corrected by 4–15 ppbv depending on sample size (generally about 40 g of ice). The mean analytical reproducibility of our results is about 3.7 ppbv (1 σ), determined by measuring single crystal ice samples with standard gas and the scattering of three individual analyses of the air extracted from one ice core sample.

Measurements of ice samples from Central Greenland provided a N₂O record over the last millennium which is reproducible and in agreement with previously published records within the error limits (Flückiger *et al.*, 1999; Machida *et al.*, 1995). Measurements on ice samples from GRIP (Greenland) and Byrd (Antarctica) representing part of the last glacial epoch and results from GRIP covering the transition from the last glacial to the Holocene period allowed to reconstruct the atmospheric concentration of N₂O during fast climatic changes during the last glaciation and during the transition (Flückiger *et al.*, 1999). These measurements were in general reproducible and consistent between the two ice cores. In the GRIP core a few elevated values have been observed which cannot be attributed to elevated atmospheric concentrations, due to the fact that the changes occur too fast. Changes of the atmospheric N₂O concentration of 20 ppbv or more within a few years are very unlikely due to the long residence time of N₂O in the atmosphere (estimated to be in the order of 120 yr (IPCC, 2001)), due to the low production rate and due to the slow enclosure of air in bubbles in the ice which attenuates fast variations further. Therefore, these elevated values have to be considered as artefacts. The sporadic high values in the GRIP ice core occur in ice representing the glacial epoch and the transition, but not in the Holocene (Flückiger *et al.*, 2002). They are normally found before or in the first part of Dansgaard/Oeschger events, that means in ice representing stadials. This ice has much higher impurity concentrations than ice representing interstadials or the Holocene. Elevated values could be caused by a chemical or biological production of N₂O within the ice sheet, a contamination of the ice core during drilling or storage or by a chemical production during the analytical procedure. To investigate the last possibility, samples from the same ice core as close as possible from the location with elevated values have been collected and remeasured. All remeasurements showed that the high values are reproducible within a narrow depth range of a fraction of one meter. This

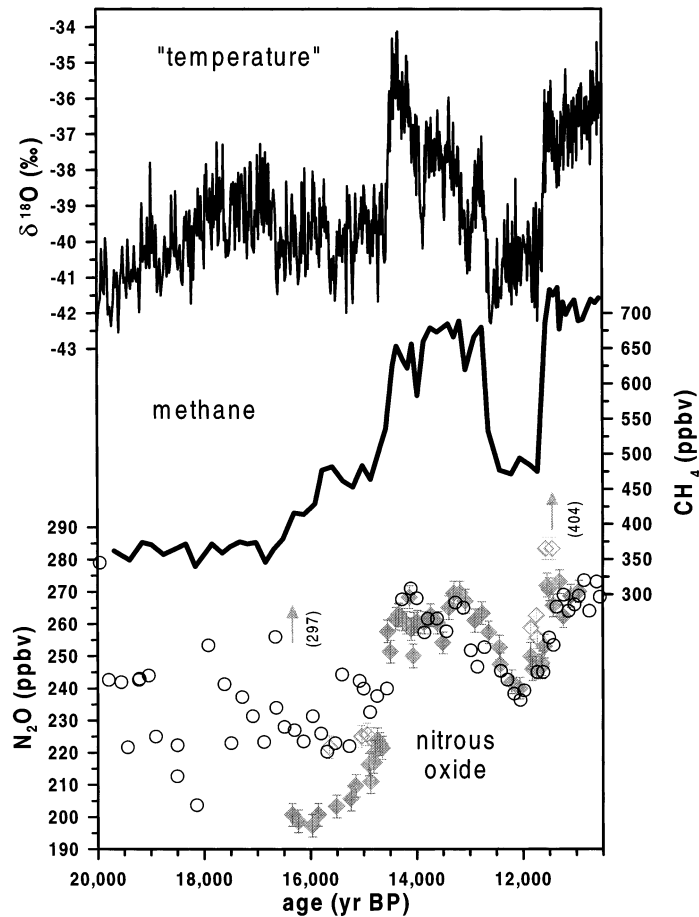


Fig. 7. N₂O measurements from GRIP (solid diamonds assumed to represent atmospheric values, open diamonds assumed to show too high values, and arrows indicate two measurements with very high concentrations which are given in parenthesis) (Flückiger et al., 1999) and from Dome Concordia (open circles) ice core, compared with GRIP CH₄ (middle) and GRIP δ¹⁸O (Dansgaard et al., 1993) (top) record. All values are plotted on the GRIP time scale.

tests exclude an accidental artefact during the analytical procedure. However, a production of N₂O between impurities during the extraction as soon as the ice is melted, cannot be excluded because an enhanced concentration of chemical compounds could be restricted to the narrow depth interval. If the N₂O is produced during the relatively short melting-refreezing extraction, only a chemical reaction could be responsible (a production by bacteria would be too slow). One possible chemical reaction would be between nitrate and ammonium. Both compounds are found in polar ice in the order of 1 μeq/kg_{ice}. A reaction of only 1% of the two compounds would double the N₂O concentration in ice. We formed in the laboratory clean bubble free ice enriched with nitrate and ammonium. The samples were treated like normal single crystal samples (addition of standard gas, afterwards usual extraction). Slightly elevated concentrations have been observed but not in the order we expected, assum-

ing that a substantial amount of the added chemicals would produce N_2O . Another indication against the hypothesis that the N_2O artefacts are only produced during the wet extraction is the fact that artificial high values in glacial ice were also found in a study by Sowers (2001) using a dry extraction technique. Recent measurements on the ice core from Dome Concordia (Antarctica) showed that elevated values are found much more frequently in ice representing the late glacial epoch from this Antarctic ice core than in the GRIP core. A similar high and frequent scattering was found in the Vostok ice core in the time period preceding the penultimate deglaciation (Sowers, 2001). A comparison of the Dome Concordia and the GRIP record is shown in Fig. 7.

N_2O measurements have also been performed on ice samples from cold Alpine glaciers. They show a large range of scattering with especially strongly elevated values. N_2O is even more enriched in melt layers than CH_4 due to its high solubility. In a pure melt layer, formed by fast freezing of air saturated water, a N_2O concentration about a factor of 40 higher than the atmospheric value is expected. In ice with a melt layer contribution of 10% the estimated N_2O concentration is still more than a factor of two higher than in the atmospheric air. Therefore, we conclude that reliable N_2O concentration measurements can only be done on ice cores from drilling sites where any surface melting can be excluded. However, we are convinced that in the alpine ice in addition to melt layers N_2O is produced by chemical reactions and possibly bacteria. An indication for this is that we have not observed a correlation between air content and N_2O concentration on samples from a narrow depth range of the Colle Gnifetti core (Fig. 6).

We conclude that N_2O artefacts are found in ice cores from Greenland and Antarctica. These artefacts are likely produced by chemical reactions or bacteria in the ice. We propose that with today's knowledge the only way to distinguish between artificial and reliable results are high resolution records. However, further investigations have to be done to understand the mechanisms leading to artificial N_2O results.

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References

- Anklin, M., Schwander, J., Stauffer, B., Tschumi, J., Fuchs, A., Barnola, J.M. and Raynaud, D. (1997): CO_2 record between 40 and 8 kyr B.P. from the Greenland Ice Core Project ice core. *J. Geophys. Res.*, **102**, 26539–26546.
- Blunier, T., Schwander, J., Stauffer, B., Stocker, T., Dällenbach, A., Indermühle, A., Tschumi, J., Chappellaz, J., Raynaud, D. and Barnola, J.-M. (1997): Timing of the Antarctic Cold Reversal and the atmospheric CO_2 increase with respect to the Younger Dryas event. *Geophys. Res. Lett.*, **24**, 2683–2686.
- Broecker, W.S. (1998): Paleocean circulation during the last deglaciation: A bipolar seesaw? *Paleoceanography*, **13**, 119–121.
- Chappellaz, J., Blunier, T., Kints, S., Dällenbach, A., Barnola, J.-M., Schwander, J., Raynaud, D. and Stauffer, B. (1997): Changes in the atmospheric CH_4 gradient between Greenland and Antarctica during the Holocene.

- J. Geophys. Res., **102**, 15987–15999.
- Dällenbach, A. (2000): Methan- und Lachgasmessungen aus Arktis, Antarktis und den Alpen. Inauguraldissertation thesis, Universität Bern, Bern.
- Dällenbach, A., Blunier, T., Flückiger, J., Stauffer, B., Chappellaz, J. and Raynaud, D. (2000): Changes in the atmospheric CH₄ gradient between Greenland and Antarctica during the Last Glacial and the transition to the Holocene. Geophys. Res. Lett., **27**, 1005–1008.
- Dansgaard, W., Johnsen, S.J., Clausen, H.B., Dahl-Jensen, D., Gundestrup, N.S., Hammer, C.U., Hvidberg, C.S., Steffensen, J.P., Sveinbjörnsdóttir, A.E., Jouzel, J. and Bond, G. (1993): Evidence for general instability of past climate from a 250-kyr ice-core record. Nature, **364**, 218–220.
- Flückiger, J., Dällenbach, A., Blunier, T., Stauffer, B., Stocker, T., Raynaud, D. and Barnola, J.-M. (1999): Variations of the atmospheric N₂O concentration during abrupt climatic changes. Science, **285**, 227–230.
- Flückiger, J., Monnin, E., Stauffer, B., Schwander, J., Stocker, T., Chappellaz, J., Raynaud, D. and Barnola, J.-M. (2002): High resolution Holocene N₂O ice core record and its relationship with CH₄ and CO₂. Global Biogeochem. Cycles, **16** (1), 10.1029/2001GB001417.
- IPCC (2001): Climate Change 2001: The Scientific Basis, ed. by J.T. Houghton *et al.* Contribution of working group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, Cambridge Univ. Press, 881 p.
- Jouzel, J., Masson, V., Cattani, O., Falourd, S., Stievenard, M., Stenni, B., Longinelli, A., Johnsen, S.J., Steffensen, J.P., Petit, J.R., Schwander, J., Souchez, R. and Barkov, N.I. (2001): A new 27 kyr high resolution East Antarctic climate record. Geophys. Res. Lett., **28**, 3199–3202.
- Kawamura, K., Nakazawa, T., Aoki, S., Sugawara, S., Fujii, Y. and Watanabe, O. (2003): Atmospheric CO₂ variations over the last three glacial-interglacial climatic cycles deduced from the Dome Fuji deep ice core, Antarctica using a wet extraction technique. Tellus, **55B**, 126–137.
- Machida, T., Nakazawa, T., Fujii, Y., Aoki, S. and Watanabe, O. (1995): Increase in the atmospheric nitrous oxide concentration during the last 250 years. Geophys. Res. Lett., **22**, 2921–2924.
- Miller, S.L. (1969): Clathrate hydrates of air in Antarctic ice. Science, **165**, 489–490.
- Monnin, E., Indermühle, A., Dällenbach, A., Flückiger, J., Stauffer, B., Stocker, T., Raynaud, D. and Barnola, J.-M. (2001): Atmospheric CO₂ Concentrations over the Last Glacial Termination. Science, **291**, 112–114.
- Nakazawa, T., Machida, T., Tanaka, M., Fujii, Y., Aoki, S. and Watanabe, O. (1993): Differences of the atmospheric CH₄ concentration between the arctic and antarctic regions in pre-industrial/pre-agricultural era. Geophys. Res. Lett., **20**, 943–946.
- Oerter, H., Wilhelms, F., Jung-Rothenhäusler, F., Göktas, F., Miller, H., Graf, W. and Sommer, S. (2000): Accumulation rates in Dronning Maud Land as revealed by DEP measurements at shallow firn cores. Ann. Glaciol., **30**, 20–26.
- Oeschger, H., Neftel, A., Staffelbach, T. and Stauffer, B. (1988): The dilemma of the rapid variations in CO₂ in Greenland ice cores. Ann. Glaciol., **10**, 215–216.
- Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pépin, L., Ritz, C., Saltzman, E. and Stievenard, M. (1999): Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature, **399**, 429–436.
- Raynaud, D., Jouzel, J., Barnola, J.M., Chappellaz, J., Delmas, R.J. and Lorius, C. (1993): The ice record of greenhouse gases, Science, **259**, 926–933.
- Schwander, J., Jouzel, J., Hammer, C.U., Petit, J.-R., Udisti, R. and Wolff, E. (2001): A tentative chronology for the EPICA Dome Concordia ice core. Geophys. Res. Lett., **28**, 4243–4246.
- Sommer, S., Appenzeller, C., Röthlisberger, R., Stauffer, B., Wagenbach, D., Oerter, H., Wilhelms, F., Miller, H. and Mulvaney, R. (2000): Glacio-chemical study spanning the past 2 kyr on three ice cores from Dronning Maud Land, Antarctica: 1. Annually resolved accumulation rates. J. Geophys. Res., **105**, 29411–29421.
- Souchez, R., Lemmens, M. and Chappellaz, J. (1995): Flow-induced mixing in the GRIP basal ice deduced from the CO₂ and CH₄ records. J. Geophys. Res., **22**, 41–44.
- Sowers, T. (2001): The N₂O record spanning the penultimate deglaciation from the Vostok ice core. J. Geophys. Res., **106**, 31903–31914.
- Spahni, R., Schwander, J., Flückiger, J., Stauffer, B., Chappellaz, J. and Raynaud, D. (2003): The attenuation of fast atmospheric CH₄ variations recorded in polar ice cores. J. Geophys. Res., (in press).
- Stauffer, B. and Tschumi, J. (2000): Reconstruction of past atmospheric CO₂ concentrations by ice core analyses.

- Physics of Ice-Core Records, ed. by T. Hondoh. Sapporo, Hokkaido Univ. Press, 217–241.
- Toggweiler, J.R. (1999): Variation of atmospheric CO₂ by ventilation of the ocean's deepest water. *Paleoceanography*, **14**, 571–588.
- Tschumi, J. and Stauffer, B. (2000): Reconstructing the past atmospheric CO₂ concentration based on ice core analyses: open questions due to the in situ production of CO₂ in the ice. *J. Glaciol.*, **46**, 45–53.
- Zumbrunn, R., Neftel, A. and Oeschger, H. (1982): CO₂ measurements on 1-cm³ ice samples with an IR laser spectrometer (IRLS) combined with a new dry extraction device. *Earth Planet. Sci. Lett.*, **60**, 318–324.

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