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Reconstruction of past atmospheric CO₂ concentrations by ice core analyses

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Abstract: Ice from the central parts of polar ice sheets is the only archive which allows us to reconstruct the atmospheric composition of past climatic epochs. In these central regions ice is formed by the dry sintering of firn. At the transition from firn to ice atmospheric air filling the interconnected pore space is isolated in bubbles. If air from ice samples with a known age is extracted and analysed, it is possible to reconstruct the atmospheric composition at the time of ice formation, assuming that the gas is well preserved in the ice and that no fractionation processes occur during the enclosure or the extraction of the air.

The method of extracting and analysing air from glacial ice was widely applied for CO₂ and it could be shown that the atmospheric CO₂ concentration did increase from 280 ppmv in preindustrial time to 315 ppmv in 1958 when direct and continuous atmospheric measurements started. Absolutely surprising was the result from ice core measurements which showed that the transition from the last glacial epoch to the Holocene was accompanied by an increase of the atmospheric CO₂ concentration from about 200 ppmv to 280 ppmv. These two findings are confirmed by measurements on many different ice cores and can be considered as reliable. However, more detailed measurements showed that there are differences between different ice cores which cannot be explained by local atmospheric concentration differences. Obviously one or several of the assumptions mentioned above are not fulfilled for CO₂.

There is evidence that CO₂ can be produced in cold ice by chemical reactions between impurities in the ice. Detailed analyses along ice cores show that carbonate–acidity reactions as well as the oxidation of organic compounds can produce CO₂. For such investigations results from CO₂ measurements performed with a resolution of 15 mm along short pieces of ice cores are compared with measurements of calcium, formaldehyde, hydrogen peroxide, carbonate and acidity. Because more than one process is able to produce CO₂ in the ice, it will not be possible to select ice samples which are well suited for CO₂ analyses based on a simple chemical analysis, as we were hoping for. Some other criteria to select well suited samples will be discussed in the paper.

For CO₂ analyses air has to be extracted from the ice by a dry extraction technique to avoid CO₂ production during the extraction by a carbonate–acidity reaction. Dry extraction methods have an efficiency of not more than 90 % in ice where air is enclosed in air bubbles and less in ice where air is enclosed in clathrates. No significant fractionation process has

been observed in bubbly ice and none has been observed in ice where all air is enclosed in clathrates. However, in the transition zone where bubbles are transformed to clathrates we observed that the extracted air is depleted in CO₂, especially when short extraction times are applied.

Introduction

The surface temperature in the central regions of Greenland and Antarctica does generally not reach the melting point, not even during summer days. In such regions ice is formed by a dry sintering process. A first metamorphosis of snow crystals in the surface layer into firm grains with simple rounded forms is forced by the surface energy and more important by temperature gradients. This change of the form causes also a certain densification. Further densification occurs mainly by a rearrangement of the firm grains and a growth of larger grains on the expense of smaller ones. A rather close packed system is reached at a depth of 10 m below the surface where the firm has a density of about 550 kg·m⁻³. From here on the sintering process, causing a growth of the contact areas between the grains, becomes the dominant process of further densification. The pore space between grains is filled with atmospheric air, still in contact through tiny channels to the free atmosphere at the surface. With increasing depth more and more of these channels are pinched off and whole clusters of channels become isolated from the surface. At a density of about 840 kg·m⁻³ the permeability decreases to zero [Schwander and Stauffer, 1984] which marks the transition from firm to ice by definition. The clusters of channels are separated into single air bubbles which decrease in size with increasing depth due to the hydrostatic pressure of the

surrounding ice. The simple enclosure process justifies the assumption that the air in the bubbles has the same composition as the atmosphere at the time of ice formation.

In the event of the snow surface reaching the melting temperature, which cannot be excluded, at least not in Greenland, melt water formed at the surface penetrates into the cold firm below and refreezes. Bubbles are formed during this refreezing process from air dissolved in the meltwater. The composition of the air in such bubbles deviates considerably from the atmospheric. Better soluble components are enriched. CO₂ concentrations of up to 2,500 ppmv have been measured in air extracted from melt layers [Neftel *et al.*, 1983]. However, melt layers can easily be recognised by visual inspection at least in the firm and they are rare in ice cores from locations with a mean annual air temperature below -25 °C.

Even if melt layers can be excluded, there are still several mechanisms capable of changing the concentration of components like CO₂ in freshly enclosed air bubbles:

- CO₂ could be enclosed in firm grains, dissolved or as micro bubbles [Stauffer *et al.*, 1984].
- There could be a preferential adsorption of CO₂ at the surface of firm grains [Ocampo and Klinger, 1982]
- Heavier air components could be enriched at the bottom of the firm layer by gravitational separation [Schwander, 1989] [Craig *et al.*, 1988].

- A fractionation of air components by thermal diffusion could be possible during fast climatic changes where we expect a temperature difference between bottom and top of the firn layer [Severinghaus *et al.*, 1998].
- At the bottom of the firn, air is expelled from the still shrinking pore volume through narrow channels which could lead to a fractionation by the flow through capillaries [Bender *et al.*, 1995].

The last three mechanisms are discussed in recent papers, they lead only to minor changes of the CO₂ concentration. Some are used to obtain information about temperature and accumulation rates in the past as discussed by Blunier *et al.* in this volume.

The first two possibilities could have a larger impact. The fact that air extracted from ice formed at a time where direct measurements of the atmospheric CO₂ concentration are already available [Etheridge *et al.*, 1996; Neftel *et al.*, 1985] does only partly exclude the influence of these two effects. CO₂ dissolved in firn grains or adsorbed at the firn grain surfaces would be found in freshly formed ice within the ice lattice and in grain boundaries and would not necessarily be extracted with a dry extraction method. However, with increasing time, due to crystal growth and due to recrystallization, this CO₂ could reach bubbles and lead to an increased CO₂ concentration in older ice.

There is CO₂ in freshly deposited snow and there is a surplus of CO₂ in firn grains at least in the top 10 m as has been measured along a firn profile of North Central (Greenland) [Stauffer, 1981]. A melt extraction method gave about 1.5 µl (STP) air per gram ice, compared with

about 100 µl/g in ice. The CO₂ concentration in this small amount of air decreased from about 5 % by volume to about 2.5 % by volume in 10 m depth. The later value would still correspond to an amount of CO₂ which has the potential to increase the CO₂ concentration in bubbles in the ice by about 250 ppmv. However, these results have been obtained by a melt extraction technique which is not well suited for CO₂ analyses. They have to be repeated with the now available sublimation extraction technique [Güllük *et al.*, 1998] and to be extended to greater depth, where CO₂ is certainly further depleted due to the recrystallization of firn grains. It was estimated that the remaining CO₂ at the firn-ice transition corresponds to a CO₂ concentration increase of about 40 ppmv at Dye 3 (South Greenland) at present and less during the last glaciation when temperatures and accumulation rates were lower [Stauffer *et al.*, 1984]. We estimate that this CO₂ amount at Summit (Greenland) could correspond to a CO₂ concentration increase of 10 ppmv.

The adsorption of CO₂ on firn grain surfaces has been investigated by Ocampo and Klinger [Ocampo and Klinger, 1982]. For an estimate of the amount of CO₂ enclosed at the firn-ice transition based on their values we assumed a firn grain diameter of 0.6 mm at the beginning of the sintering process (at a density of 550 kg·m⁻³). The adsorbed amount of CO₂ at a mean temperature of -32 °C and at an atmospheric CO₂ concentration of 280 ppmv corresponds to an enhancement of the CO₂ concentration in the air, extracted from the ice, by about 2.5 ppmv.

It is assumed that air isolated in bubbles is well preserved for a long time. The surrounding material is relatively pure

frozen water, the temperatures are very low and the diffusion constants, except for Helium and Neon, are small enough to prevent air components from being displaced in the ice over large distances and to escape from ice samples after recovery of ice cores in significant amounts. However, discrepancies between ice cores from different drilling sites show that there is the possibility that:

- CO₂ can be produced in small amounts by chemical reactions between impurities in the ice [Anklin *et al.*, 1997].
- There is a fractionation of gas components between air in bubbles and air in clathrates in the depth interval where bubbles and clathrate coexist. This can lead to a fractionation of extracted gases if the extraction efficiency is below 100 %.

We have investigated both possibilities. A production of CO₂ by chemical reactions between impurities in ice is discussed in detail elsewhere [Tschumi and Stauffer, *in press*] and will only be summarised in this paper. The main focus of this paper is the discussion of the fractionation of air at the transition from bubbles to clathrates. Dry extraction techniques commonly used at present have an extraction efficiency of about 90% for ice with air enclosed in bubbles and much lower ones for ice with air enclosed in clathrates (50–70 %). Neftel *et al.* have already measured the CO₂ concentration in Dye 3 ice from 1616 m depth below surface, where all air is enclosed in clathrates, a few days, a few month and ten month after recovery of the core [Neftel *et al.*, 1983]. Lower CO₂ concentrations have been measured, especially a few days after core recovery if

the extraction time was less than 90 s. With greater extraction times no measurable differences have been observed. We repeated this kind of measurement with an improved analytical technique and with samples specifically from the transition zone between bubbles and clathrates from the North GRIP drilling site as discussed in the chapter about samples extracted two months and seven months after ice recovery.

Discrepancies between CO₂ records from ice cores from different drilling sites

Atmospheric CO₂ has a lifetime of more than 50 – 200 years and a mixing time of about 1 year, so that local concentration differences are rather small [Watson *et al.*, 1990]. The annual mean concentration is at present about 5 ppmv higher in the Northern than in the Southern Hemisphere, it is estimated that it was about 1 ppmv higher in the Southern Hemisphere compared to the Northern during preindustrial times [Siegenthaler and Sarmiento, 1993]. Based on these facts we have to expect CO₂ concentration differences along ice cores from different locations but of less than 5 ppmv if they represent the same time interval. Larger differences are most probably caused by artefacts.

Air is isolated in bubbles at the bottom of a firn layer of 60 – 120 m thickness in dry snow zones of polar glaciers. The CO₂ at the bottom of the firn layer at Summit in central Greenland has a mean age of 12 years and a mean age distribution of 7 years [Schwander *et al.*, 1993]. This implies that short term variations of the atmospheric CO₂ concentration are attenuated. Seasonal

variations would be attenuated by a factor of more than a thousand, variations occurring in a decade still by about a factor of ten and variations with a typical time scale of a century would be practically not attenuated [Schwander, personal communication]. Therefore, variations of the CO₂ concentration along ice cores over short distances, representing less than a decade are caused most probably by artefacts e.g. by chemical reactions between impurities in the ice.

Both, CO₂ concentration differences of more than 5 ppmv between ice cores from Greenland and Antarctica and significant concentration variations within distances of less than an annual layer have been observed.

Barnola et al. [1995] compared CO₂ records from Antarctica and Greenland covering the last 1,000 years. The records from Antarctica are in good agreement with each other despite the fact that the surface temperatures of the drilling sites varied between -24 °C and -51 °C and one of the cores was stored for almost 10 years before the measurements were performed. The CO₂ record from Summit (Greenland) shows a larger scatter of the single measurements and the smoothed record is about 20 ppmv higher at the beginning of the millennium than the record from Antarctica. The difference between Greenland and Antarctica decreases with decreasing age until about 1700 AD. The two smoothed records are in good agreement for the last about 300 years.

The CO₂ record from the Dye 3 (South Greenland) ice core shows in the section representing the time interval from about 40,000 to 25,000 years BP significant concentration variations of the order of 50 ppmv [Stauffer et al., 1984]. The variations

occur in parallel with variations of the δ¹⁸O record, which indicates temperature changes, and parallel with variations of the annual accumulation rates and the concentration of dust and various soluble chemical compounds. Higher CO₂ concentrations correlate with warmer climate and higher annual precipitation rates and are in anticorrelation with the dust concentration and the concentration of various chemical constituents. There was some evidence that these CO₂ variations reflect variations of the atmospheric CO₂ concentration, especially because a check on ice core samples from Camp Century showed very similar variations, despite the fact that this location has a 4 °C lower mean annual air temperature and quite different impurity concentrations in the ice. However, a comparison with measurements from the Byrd (Antarctica) ice core did not confirm the CO₂ variations [Nefel et al., 1988]. There was a controversy whether the variations found in the two Greenland cores were artefacts or whether variations of the atmospheric CO₂ concentration would be missing in Byrd station due to a much lower and possibly more irregular accumulation rate [Oeschger et al., 1988]. Looking for an answer to this important open question was one of the main motivations for the GRIP drilling project at Summit in Central Greenland. With a mean annual air temperature of -32 °C at least an effect due to refrozen melt water can be excluded for this site.

The CO₂ record from this site is shown in Figure 1. The record shows very similar variations of the same order as measured along the Dye3 and the Camp Century record despite the lower surface temperature at Summit (-32 °C). Despite the relatively good agreement between the

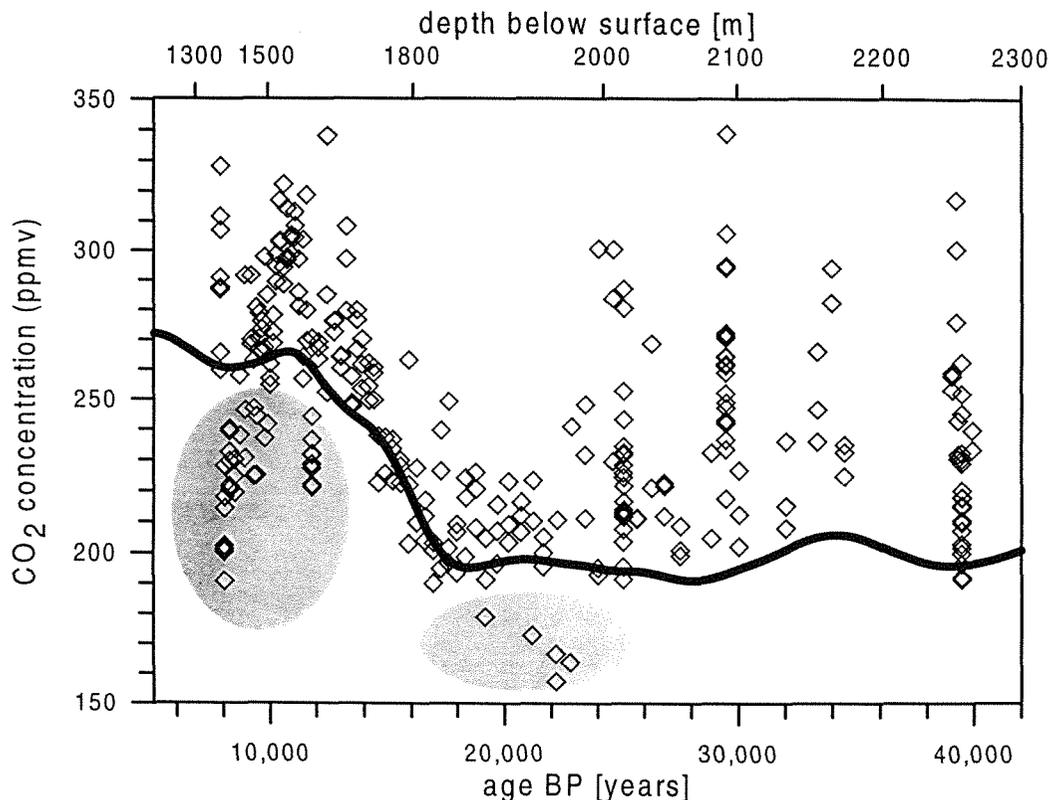


Figure 1: Open diamonds represent single CO₂ measurements versus depth on the GRIP deep ice core [Anklin *et al.*, 1997, with changes]. The solid line gives an estimate of the atmospheric CO₂ concentration based on measurements on ice cores from Byrd Station [Stauffer *et al.*, 1998] and Taylor Dome (Antarctica) [Indermühle *et al.*, submitted]. Two areas with values lower than expected are shaded.

GRIP, the Dye3 and the Camp Century record for the glacial part, it became obvious that the results do not represent a reliable record of the atmospheric CO₂ concentration. The atmospheric record based on measurements along the Byrd core for the glacial part and the Taylor Dome core (Antarctica) for the Holocene part are given in Figure 1 as solid line. If this record is the correct one, then the GRIP record shows most of the time too high values. However, there are also two regions with too low values (shaded areas in Fig. 1). First the values which are higher than expected shall be discussed.

We performed very detailed measurements along short sections of the GRIP core and observed large variations over distances of a few centimetres in sections which show high CO₂ concentrations. One example is shown in Figure 2. As mentioned above, such short term variations cannot reflect variations of the atmospheric CO₂ concentration, it has to be an artefact. Delmas [Delmas, 1993] suggested that the surplus CO₂ is produced by an acid-carbonate reaction in the ice. Another possibility to produce CO₂ would be the oxidation of organic material in the ice.

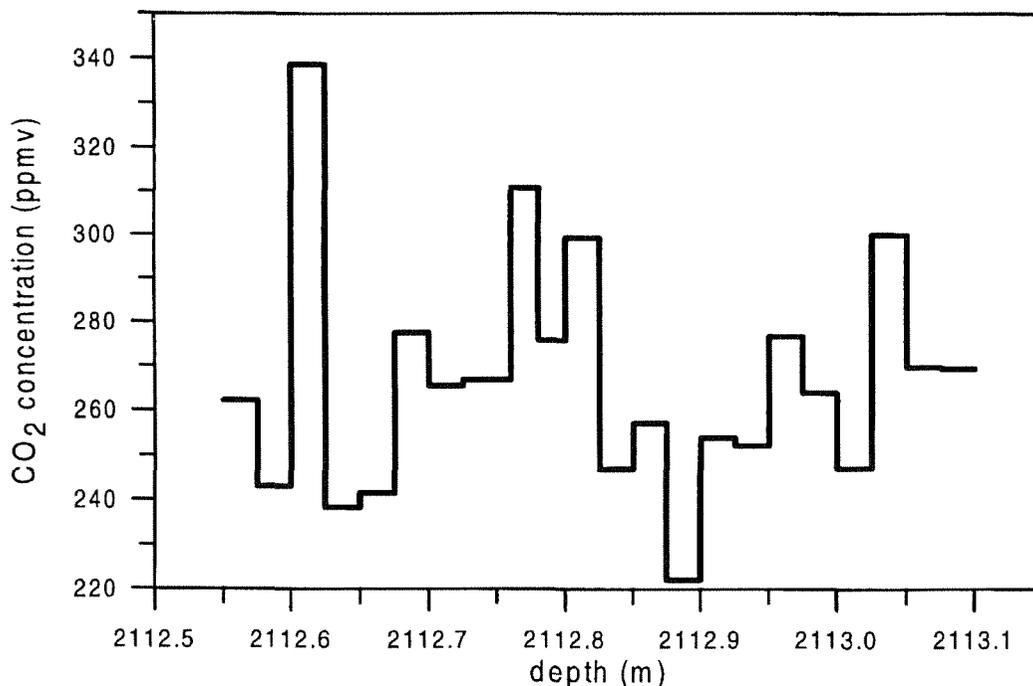


Figure 2: CO₂ measurements performed with the laser absorption spectrometer on a 0.55 m long depth section of the GRIP ice core within a mild phase of a Dansgaard/Oeschger event [Anklin *et al.*, 1997, with changes]. The annual layer thickness at this depth is about 0.02 m.

These two possibilities will be discussed in the next chapter.

Air enclosed in bubbles has a younger age than the surrounding ice, because air becomes enclosed at the firn-ice transition at depths between 60 to 120 m below the surface, where the ice has already an appreciable age. A detailed comparison between the CO₂ and the δ¹⁸O GRIP record shows that a better correlation between higher δ¹⁸O values and higher CO₂ concentrations is obtained if results from the same depth are compared rather than if samples with the same age are compared. This is a further indication that the surplus CO₂ is produced in the ice after the air has already been isolated in bubbles.

The problem with the CO₂ production, especially in Greenland ice cores, makes it

impossible to investigate whether there is a change of the atmospheric CO₂ concentration parallel to Dansgaard/Oeschger events in Greenland ice cores. Recently it became possible to synchronise the age scale of Greenland and Antarctic records with detailed methane records which show fast variations so that a synchronisation of the age scale of two cores is possible with an accuracy of about 200 years. The comparison of the GRIP isotope record from Summit with the CO₂ record from Byrd Station shows finally that the CO₂ variations with amplitudes of 50 ppmv and more, which are observed in Greenland cores, have to be an artefact. The comparison shows on the other hand that smaller variations in the range of 10 to 20 ppmv observed in the Byrd core could go

parallel with the most distinct and long lasting Dansgaard/Oeschger events [Stauffer *et al.*, 1998].

In the depth interval 1,340 m – 1,560 m below surface of the Greenland Summit ice core CO₂ concentrations lower than expected are observed (Fig. 1). Too low values could be caused by a depletion of CO₂ by chemical reactions. However, the main depth interval with too low values corresponds with the one in which air bubbles transform to air clathrates. A longer extraction time did not eliminate but diminished the effect, so that it became obvious that the too low values at this depth interval are mainly caused by fractionation. The question arises whether it is worthwhile to investigate an artefact which seems to be restricted to a relatively short depth interval in an ice core. We decided to perform these investigations because, if there is a fractionation in the clathrate formation zone, then it is very likely that there is a fractionation as well in ice from greater depth which has been stored for a certain time and where only part but not all of the clathrates have been transformed back to bubbles. Investigations in this clathrate transition zone give us the unique opportunity to learn about processes causing such fractionations.

CO₂ production or depletion by chemical reactions between impurities in the ice.

Until recently it was assumed that chemical reactions between impurities in polar ice with temperatures below –20 °C could be excluded. However, Sigg and Neftel showed that H₂O₂ is depleted in deeper layers in the ice and that this is most probably due to chemical reactions [Sigg

and Neftel, 1991]. Delmas suggested that acid–carbonate reactions could occur in Greenland ice cores representing Dansgaard/Oeschger events, where he expected thin acid and alkaline ice layers to be mixed [Delmas, 1993]. CO₂ production is indeed most obvious in ice representing Dansgaard/Oeschger events but is not restricted to such layers and carbonate–acidic reactions are just one possibility; CO₂ could also be produced by the oxidation of organic compounds. Table 1 shows the potential of certain compounds in ice to produce CO₂ by a chemical reaction [Tschumi and Stauffer, *in press*].

There are plenty of compounds present in most ice from the polar ice sheets which could produce CO₂. This is also the reason that air cannot be extracted by melt extraction techniques for measuring the CO₂ concentration in the ice, because compounds would react in the melt water and cause artefacts. What are the conditions that reactions can occur also in the ice at temperatures below –20 °C? – Solid state reactions would be possible but another and more likely possibility are reactions in liquid inclusions in the ice. There is evidence that some of the soluble impurities in the ice are concentrated in veins, formed where three ice crystals meet. Impurities could be concentrated in this narrow veins to a degree that eutectic mixtures could cause these veins to remain liquid to temperatures down to –50 °C [Mulvaney *et al.*, 1988], [Matsuoka *et al.*, 1997]. These veins are not stationary but move through the ice due to crystal growth and recrystallization. If for example, carbonates were present in small dust grains, equally distributed in the ice matrix, and acidity was concentrated in veins, a reaction would only be possible if a dust grain with

Table 1: Estimated mean potential of typical compounds containing carbon or able to react with these compounds to produce CO₂. Both the "Holocene" mean values for the preindustrial epoch and the "Ice age" mean values for the cold periods between 40,000 – 20,000 years BP are given. Adapted from [Tschumi and Stauffer, in press], where references for the individual compounds are also given.

	Greenland		Antarctica	
	Holocene CO ₂ eq. ppmv	Ice Age CO ₂ eq. ppmv	Holocene CO ₂ eq. ppmv	Ice Age CO ₂ eq. ppmv
CO ₂	295	220	275	197
CH ₄	1	<1	1	<1
HCHO	18	50	9	2
CO ₃ ²⁻	25	590	7	75
CH ₃ COO	42	25		
HCOO	55	6		
H ₂ O ₂	440	22	146	7
H ⁺	249			

carbonates would accidentally meet a vein. The oxidation of organic material could be controlled as well by a similar mechanism if either the organic compound or the oxidation reagent are concentrated in veins. Unfortunately we know very little about the distribution of impurities in the ice. Mulvaney et al. showed that sulphate is concentrated in veins and chloride probably not [Mulvaney et al., 1988]. At present no information about the distribution of organic compounds like HCHO or oxidation reagents like H₂O₂ in the ice is available.

We were hoping to get more information about the kind of chemical reactions producing CO₂ by comparing peak values of the CO₂ concentrations with

detailed, high resolution records of possible source compounds. However, we are measuring not compounds which already produced CO₂ but compounds which are still present in the ice and would have the potential to produce more CO₂ in the future. The question arises why there are still compounds available if an exothermic chemical reaction is possible and whether we expect local maxima or local minima parallel to CO₂ peak values in this case. There is no obvious and no simple answer to this question. There are source compounds which show large concentration variations and where only a fraction of their concentration can lead to a significant CO₂ production like carbonates or acidity. In this case we still expect concentration maxima

going parallel with CO₂ maxima. There are other source reagents which show a rather constant and low concentration like H₂O₂ and HCHO. In such cases we expect CO₂ maxima to go parallel with the minima of these compounds [Tschumi and Stauffer, in press].

Figure 3 shows two examples of

detailed records of acidity (based on electrical conductivity measurements), calcium, formaldehyde and hydrogen peroxide concentrations compared with CO₂ concentrations from the GRIP ice core. The two examples show only a CO₂ surplus of up to 30 ppmv, significantly less than maximal surpluses during Dansgaard/

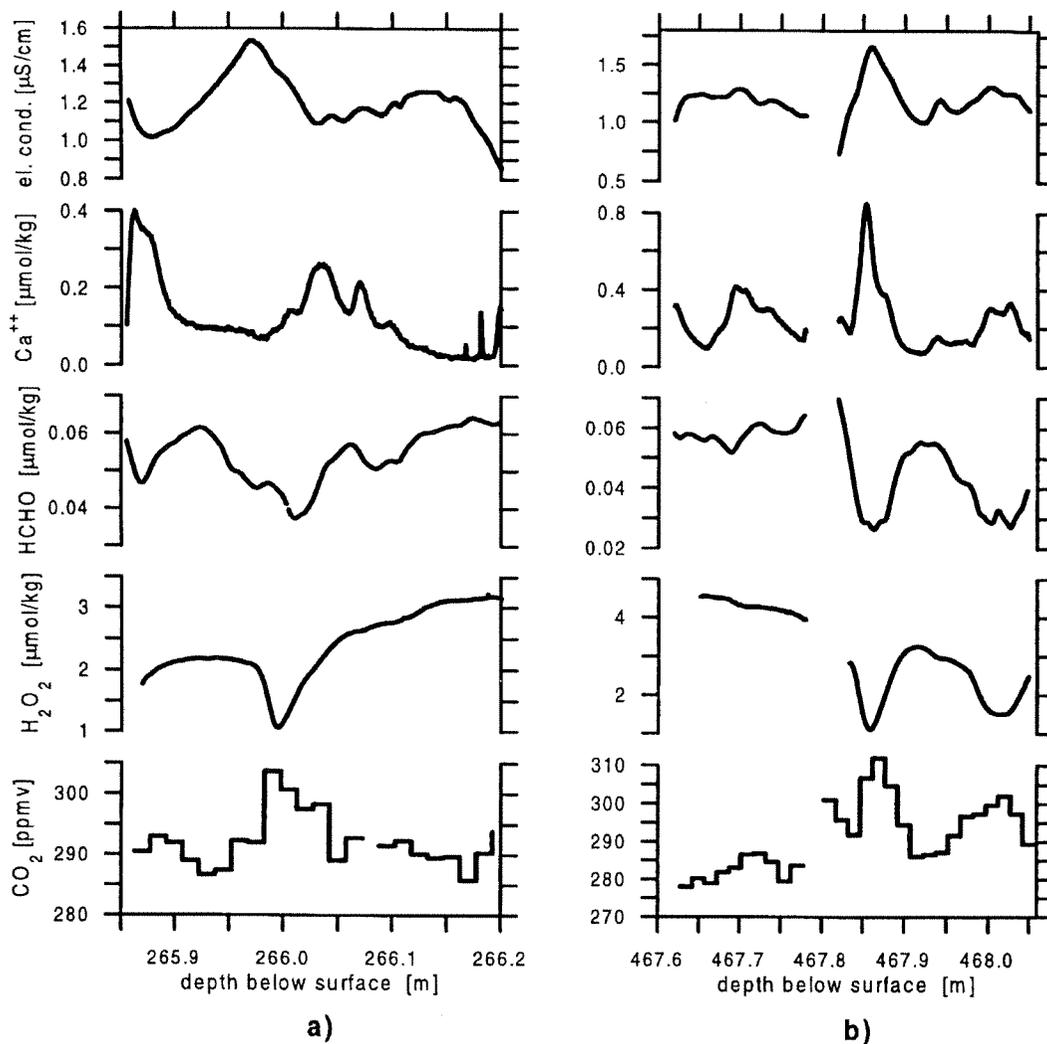


Figure 3: CO₂, H₂O₂, HCHO, Ca⁺⁺ concentrations and electrical conductivity of the meltwater measured along two sections of the GRIP ice core. Concentrations are given in μmol per kilogram of ice. The left record (a) corresponds to a depth interval of about 2 annual layers, the right record (b) of about 3 annual layers [Tschumi and Stauffer, in press].

Oeschger events. We selected the shallow depth core sections, despite the smaller surplus, to avoid problems with clathrates that form in deeper ice as will be discussed in the subsequent chapters.

The mean age of the core section shown in Fig 3a is 1100 years, the section is representing about two annual layers. The CO₂ concentrations are generally higher by about 10 ppmv compared to Antarctic ice cores of the same age, and in addition, between 265.97 and 266.03 m depth there are values elevated by about 20 ppmv above the average value. These elevated values are correlated with higher values in acidity and with depleted values in HCHO and H₂O₂. A Ca⁺⁺ maximum has its highest value 5 cm deeper than the CO₂ its maximum. A shift of the calcium maximum by 5 cm due to the analytical procedure is very unlikely but cannot be excluded. Therefore, the local elevated CO₂ values could be caused by an acid-carbonate reaction as well as due to the oxidation of organic materials. However, it has to be noticed that the drop in the HCHO concentration could be responsible for a CO₂ production corresponding to only about 6 ppmv, but HCHO is just one of several organic species which could become oxidised.

Figure 3b shows a record from a depth interval with a mean age of 2125 years, covering about three annual layers. The lowest CO₂ concentrations measured in this section (280 ppmv) correspond well with the expected value. The elevated concentrations correlate with elevated acidity and Ca⁺⁺ concentrations and with minima of the H₂O₂ and HCHO concentration. The drop of HCHO can only explain a CO₂ production corresponding to

about 7 ppmv so that it can again not be the only reason for the elevated values.

Tschumi and Stauffer [in press] investigated five detailed records and conclude, based on a correlation calculation, that the CO₂ production in Greenland ice is most probably due to different reactions. Oxidation of organic compounds seems to be as important as acid-carbonate reactions. Isotope measurements could help to check whether oxidation of organic material or acid-carbonate reactions are dominant. Organic material has δ¹³C values in the order of -25 ‰, and carbonate at its source region values of about 0 ‰, but it is not known to what degree the isotopic signature of carbonate is changing during transport to Greenland and Antarctica. Until present relatively large samples are needed for isotopic analysis. Measurements on large samples from the South Yamato (Antarctica) ice core representing an epoch during the last glaciation show a remarkable anticorrelation between CO₂ surplus and δ¹³C values [Machida *et al.*, 1996]. The CO₂ surpluses of about 20 ppmv above mean values could represent atmospheric variations, but we consider a production of CO₂ in the ice as a more likely cause. If it is assumed that 205 ppmv would be the atmospheric value at that time and that the δ¹³C value of atmospheric CO₂ was about the same as today, then the CO₂ surplus would have a δ¹³C value of about -22 ‰ which is close to the value of organic material.

CO₂ can also be depleted by chemical reactions. In alkaline ice the reaction



is possible. Smith *et al.* assume that some samples from the GISP-2 ice core representing ice from cold phases of the last

glacial epoch are depleted in CO₂ due to this reaction [Smith *et al.*, 1997]. In the GRIP record the lowest CO₂ values are found in the depth interval 1950 – 2000 m depth. These low values could also be due to a chemical depletion but we have not investigated this depth interval in detail yet.

We conclude that CO₂ can be produced by chemical reactions in the ice and that the oxidation of organic compounds is at least as important as acid–carbonate reactions. A depletion of CO₂ is in principle possible but has not been investigated in detail yet. Antarctic ice cores are generally less affected by acid–carbonate reactions and the oxidation of organic compounds due to the lower impurity concentrations compared to Greenland ice cores [Raynaud *et al.*, 1993]. Best results for the reconstruction of the atmospheric CO₂ concentration are obtained from ice cores with a very low concentration of carbonates and H₂O₂. The best test at present is to make high resolution measurements of the CO₂ concentration along core sections representing only a few annual layers. The scattering of the results should be of the same order of magnitude as the analytical uncertainty.

Problems due to the formation of clathrates

Below the firm–ice transition, but still at relatively shallow depth, most of the air is present as bubbles in the ice. However, there is the question about how much air is trapped in the ice matrix either dissolved or as micro bubbles. As already mentioned, there is some air enriched in CO₂ in micro bubbles in freshly deposited snow, but only a few of these micro bubbles survive

recrystallization in the firm layer. Additional CO₂ adsorbed by firm grains is also present at grain boundaries at the firm–ice transition. We assume that this CO₂ is transported slowly to bubbles after the firm ice transition due to crystal growth and recrystallization. The equilibrium dissolution of CO₂ in ice is rather low. Ice crystals which slowly grow out of water saturated with CO₂ have a CO₂ concentration of less than $8 \cdot 10^{-13}$ mole fractions per Pascal partial pressure [Nefel *et al.*, 1983]. Based on the solubility of He and Ne in ice [Sato *et al.*, 1996], and based on the comparison of the molecular size of CO₂ and the noble gases, Hondoh *et al.* estimated an equilibrium solubility of CO₂ of about $8 \cdot 10^{-15}$ mole fractions per Pascal partial pressure [Hondoh, 1996]. Based on this solubility only about $1.4 \cdot 10^{-5}$ cm³ STP of CO₂ per kg ice would be dissolved at 500 m depth and the rest (99.95 %) would be in the bubbles.

At greater depth, depending mainly on temperature [Miller, 1969], bubbles start to transform into clathrates. The clathrate transition zone is surprisingly large, in Vostok from 500 m to 1250 m which corresponds to a time period of about 60,000 years [Ikeda *et al.*, 1999] (in Byrd Station the depth range is somewhat smaller (800 – 1100 m) and the time interval much smaller (about 4000 years) due to the higher temperature and accumulation rate [Gow and Williamson, 1975]). Generally one bubble is transformed to one clathrate [Kipfstuhl *et al.*, 1997]. The transformation of a specific bubble into a clathrate needs less than hundred years, so that we have in the transition zone mostly bubbles or clathrates and very few objects which are just in the transition phase. Ikeda *et al.* [1999] have observed a fractionation of

oxygen and nitrogen between bubbles and clathrates in the region where both coexist. Oxygen is enriched in clathrates due to a faster diffusion of oxygen from bubbles to clathrates. The diffusion of air from bubbles to clathrates is caused by the higher pressure in the bubbles compared to the clathrate dissociation pressure. For CO₂ with a lower diffusion constant and a lower solubility in ice compared to oxygen and nitrogen we expect a depletion of CO₂ in clathrates due to this fractionation. Below the transition zone, different clathrates have different air compositions due to the effect described above, but with increasing depth the differences will get equilibrated due to molecular diffusion again.

Summarised we have to distinguish in an ice sheet the following depth intervals:

- In the interval just below the firm-ice transition most of the air and most of the CO₂ is in the bubbles. The amount of CO₂ dissolved in the ice is small due to the low partial pressure and the low solubility. In ice crystals we have still micro bubbles in which CO₂ is enriched. In grain boundaries there is CO₂ which was originally adsorbed in the firm at the grain surfaces.
- At greater depth, but still above the zone where clathrates are formed, we expect that most of the CO₂ in micro bubbles and in grain boundaries has reached air bubbles. The amount of CO₂ dissolved in the ice is still very small.
- In the zone where bubbles transform into clathrates we have mainly surviving bubbles, already fully formed clathrates and only a few objects which are half part bubble and half part clathrate. In this transition zone there are higher partial pressures around

bubbles than around clathrates so that there is a transport of molecules from bubbles to clathrates by molecular diffusion. This leads to a fractionation of air components in bubbles and in clathrates due to different diffusion constants.

- Below the clathrate transition zone almost all air is enclosed in clathrates. The amount dissolved in the ice is still very small ($\leq 0.1\%$). The partial pressure of air components in the ice around a clathrate is proportional to the site occupancy in the clathrate.

If ice is recovered from the clathrate zone and stored at ambient pressure, bubbles will form again. The back transformation is a slow process. In the Byrd core it took about 3 years until 40 % of the air was present in bubbles again [Gow and Williamson, 1975], but some clathrates survived until present. During storage we have again bubbles coexisting with clathrates. There is now probably a transport of air molecules from clathrates to bubbles because pressure in the bubbles is lower than the clathrate dissociation pressure. However, if we assume molecular diffusion as the only transport mechanism, then a fractionation between clathrates and bubbles will be small for storage times in the range of a few years.

Measurements on air extracted two months and seven months after core recovery

If air and CO₂ is present in different reservoirs with different mixing ratios and if the extraction efficiency varies for the different reservoirs then the CO₂

concentration in the extracted air can deviate significantly from the atmospheric composition. The effect is expected to be largest in the transition zone where bubbles and clathrates are reservoirs of similar sizes.

The fact that we measured in this depth interval a depletion of the CO₂ concentration depending on the extraction time suggested that we could learn more about the fractionation process by measuring the pressure of extracted air and the CO₂ concentration in function of time after crushing the ice sample. The analyses

of the CO₂ concentration by Laser Absorption Spectroscopy [Zumbrunn *et al.*, 1982] allows measurements on ice samples of only about 6 g size and the measurements are so fast that a detailed record as a function of time can be obtained.

Figure 4 shows schematically our extraction device. For an ordinary measurement about 6 g of ice is placed in the extraction device. The device is evacuated for about 5 minutes (valves 1, 2, 3 and 4 open). Valve 1 and 3 are closed and the ice is crushed in the extraction device (20 strokes in about 10 seconds). Immediately

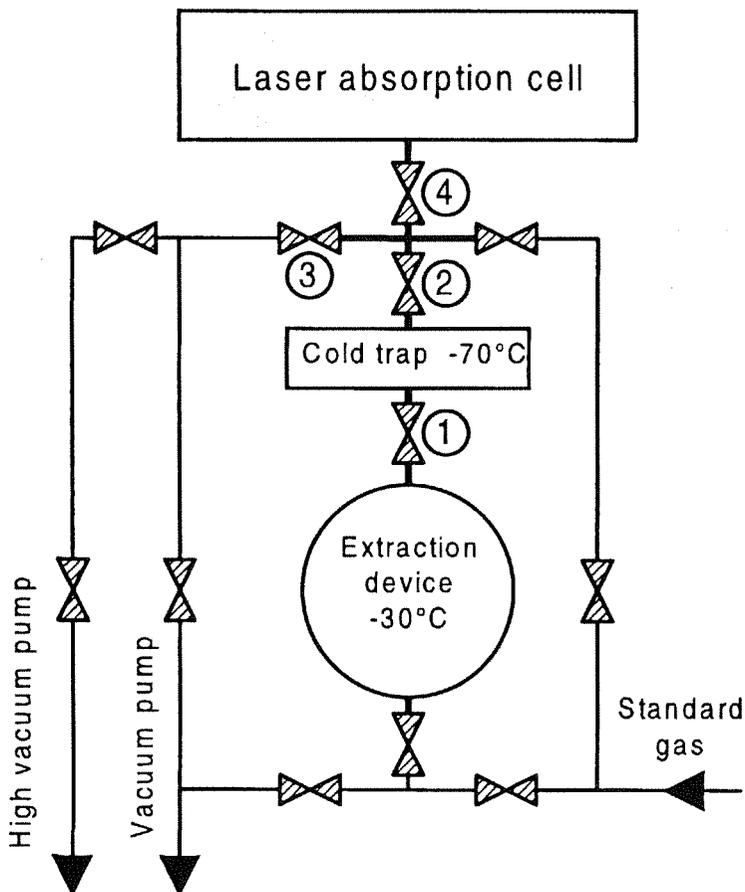


Figure 4: Schematic sketch of extraction system. For the continuous measurements during 11 minutes after crushing valves 1, 2 and 4 are open, all other valves are closed.

after the last stroke valve 1 is opened and the extracted air can expand during a certain time, the extraction time, to the laser absorption cell. After this extraction time valve 4 is closed and the laser absorption measurements are performed. An infrared laser is tuned several times over the absorption line of a vibration-rotation transition of a CO_2 molecule. After measuring an ice sample, a standard gas is measured at the same pressure as the pressure of the sample.

For the measurements of North GRIP samples we modified the extraction procedure. Immediately after opening valve 1 we start with the laser absorption measurements. The analytical equipment was modified to allow one concentration measurement per second, accepting a slightly reduced precision. The CO_2 concentration and the air pressure in the absorption cell are measured during 11 minutes. Afterwards standard gas is measured at the same pressure as the final pressure of the sample.

Figure 5 shows the pressure increase (increase of extraction efficiency respectively) in function of time of the samples from 10 depth levels measured 2 months and 7 months after recovery of the ice core, respectively. All, but the two lowest samples show that the final pressure is reached within a short time of less than 100 s. We assume that the overshooting of the pressure in the first 100 s in the laser absorption cell for some of the samples is due to dynamic effects. The whole system with the crushing device at $-30\text{ }^\circ\text{C}$, the cold trap at $-70\text{ }^\circ\text{C}$ and the laser absorption cell at room temperature needs to reach a kind of equilibrium. The differences of the pressure for the different samples is due to differences of the extraction efficiency. Part

of the varying extraction efficiency is accidental (number of coarser ice pieces surviving the crushing), another part is systematic. Figure 6 shows the estimated extraction efficiency as a function of depth.

At North GRIP bubbles start to be transformed into clathrates at about 960 m depth [Kipfstuhl, personal communication]. For sample *h* (1148 m) less than 25 % of the air, for sample *j* (1261 m) about 50 %, and for sample *k* (1368 m) more than 75 % of the air is trapped in clathrates. Only the two deepest samples show a significant delay of the degassing and a significant decrease of the extraction efficiency even after 11 minutes of extraction time, at least for the samples measured 2 months after recovery of the cores.

There are three different explanations for the delay of ice sample degassing:

1. Air dissolved in ice grains diffuses to the surface of the grains
2. Air from bubbles or clathrates which are not exposed but located close to the surface of one of the grains after crushing permeates to the surface.
3. Clathrates exposed to a grain surface decay rather slowly [Kuhs, discussion contribution during the workshop].

1) *diffusion*: The solubility of air is about $1.4 \cdot 10^{-13}$ mole fractions per Pascal [Hondoh, 1996] (considerably more than in case of CO_2 ($8 \cdot 10^{-15}$ mole fraction/Pa)). At 960 m depth there is a hydrostatic pressure of about $9 \cdot 10^6$ Pa. About 1.4 % of the air would then be dissolved in the ice. Assuming a diffusion constant $D = 1.4 \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ [Hondoh, 1996] and that the crushed ice consists of uniform spherical balls of 0.5 mm radius it would take about $2 \cdot 10^3$ s for at least half of the dissolved air to be extracted from the grains. This is about a factor of ten more than observed by our

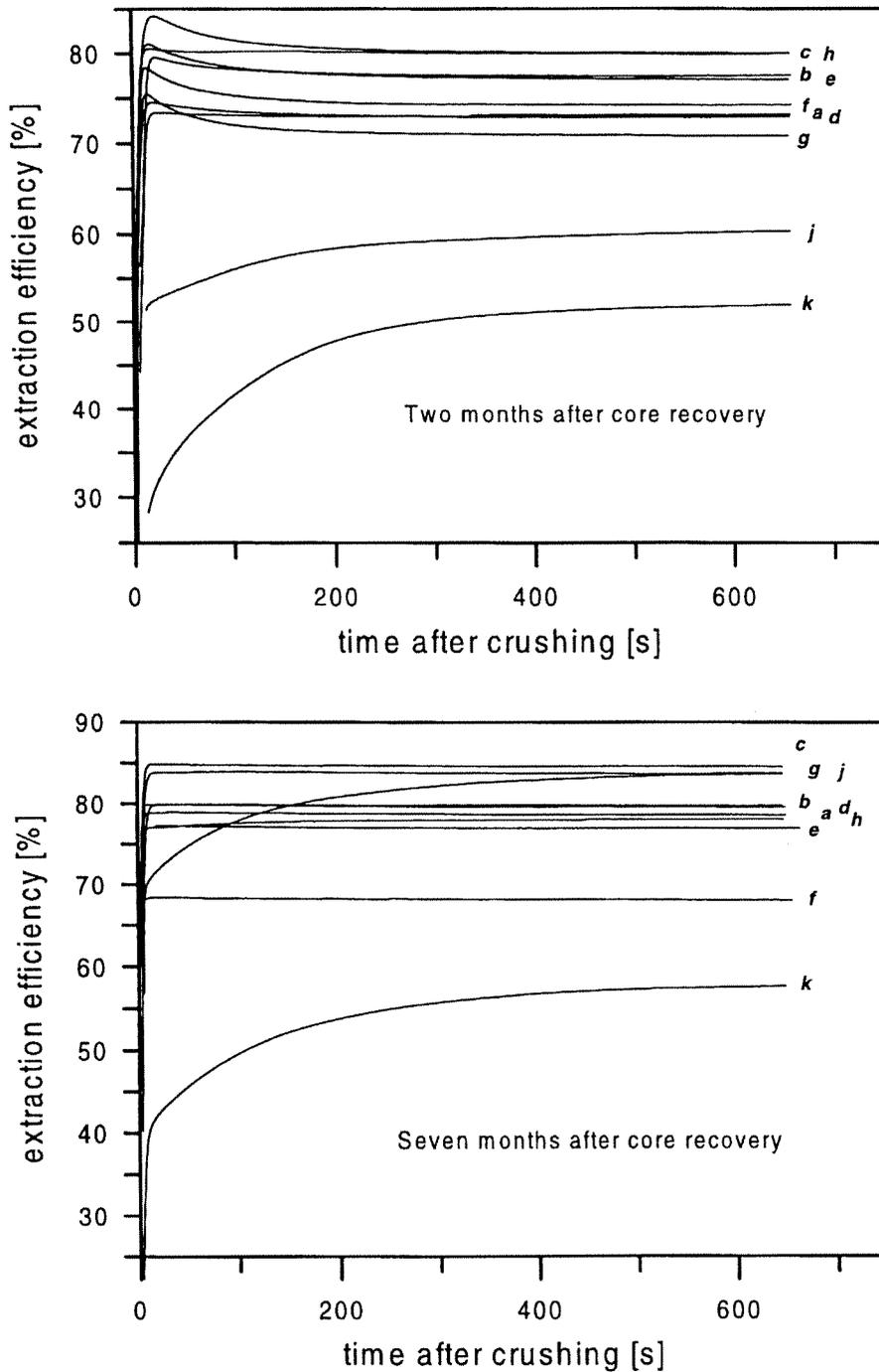


Figure 5: Extraction efficiency as a function of time after crushing. The efficiency is calculated from the pressure measured in the laser absorption cell and the mass of the sample assuming a mean gas content of 0.0865 ml(STP)/g ice [Raynaud *et al.*, 1997]. The letters marking the different lines are identical with the letters in figure 7, where the mean depths and ages of the samples are also given.

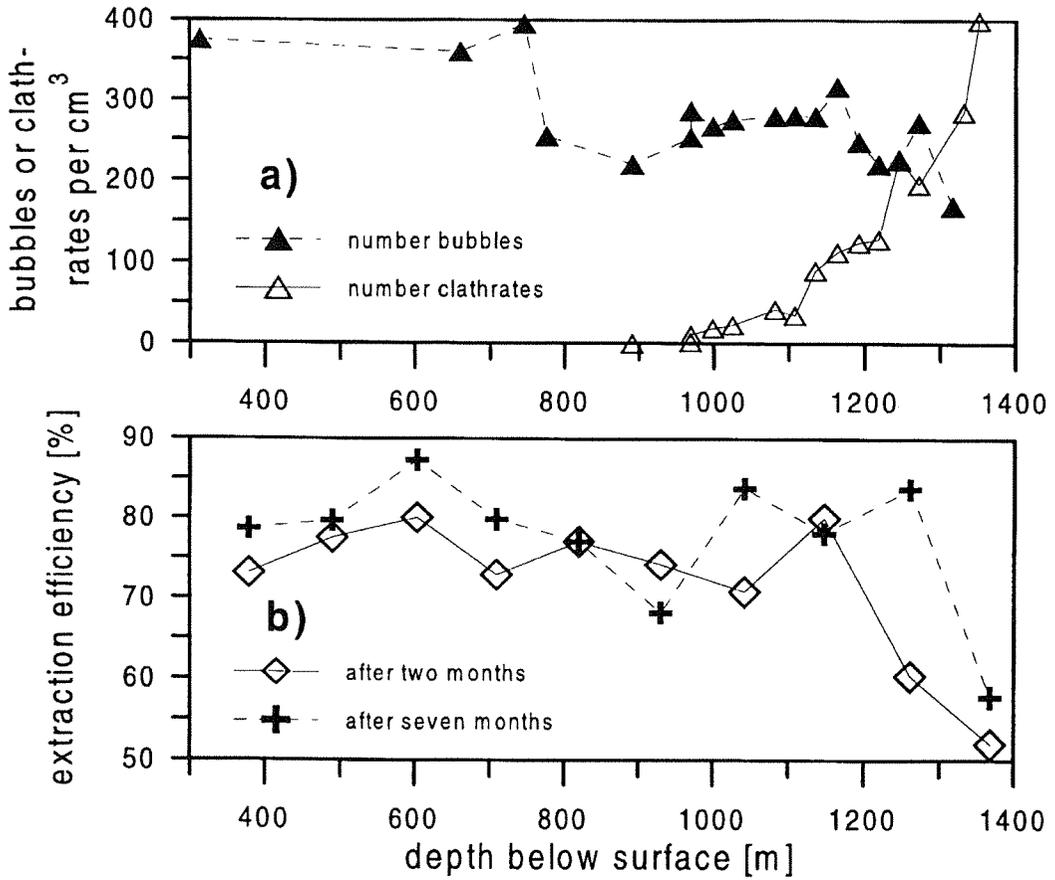


Figure 6: a) Number of bubbles (filled triangles) and clathrates (open triangles) per cm³ of ice [Kipfstuhl *et al.*, in preparation]; b) Extraction efficiency. The values are the ratio of the air extracted after 11 minutes compared to the expected value of 0.0865 ml/g_{ice} [Raynaud *et al.*, 1997].

measurements. However, there are large uncertainties concerning the mean radius of rains after crushing and also about the diffusion constant, so that a pressure increase by dissolved air cannot be excluded based on the time constant. More serious is the discrepancy between the estimated 1.4 % of dissolved air and the observed pressure increase of 30 % with sample *k*. A solubility of 30 % of air dissolved in the ice at this hydrostatic pressure seems to be very unlikely according to theoretical estimates, but there

are observations which claim that on the order of 20 % of air is missing based on estimates of the clathrate volume [Pauer *et al.*, 1999]. The amount of air dissolved depends on bubble pressure and, therefore, increases linearly with depth. Consequently, one would expect a monotonic increase of the delay of degassing with depth, if diffusion of air dissolved in the ice is the cause.

2) *permeation of air from enclosed bubbles and clathrates*: Crushing ice from about 1000 m depth the extraction efficiency is

low because a substantial part of the very small bubbles and clathrates is not exposed to a grain surface. Air from a bubble or clathrate inside a grain can permeate to the surface. Assuming that a bubble (or clathrate) with 90 µm radius is in the centre of a spherical ice grain of 500 µm radius, and assuming a solubility and a diffusion constant according to Hondoh [Hondoh, 1996], it would take about 2 years for half of the air to permeate to the surface. Despite large uncertainties about the assumptions, we can exclude this effect for the observed pressure increase.

3) *decay of clathrates*: Very little is known about the decay of clathrates, freshly exposed to grain surfaces. This explanation has the big advantage that it would affect only samples where air is enclosed already in substantial amounts in clathrates as observed. The amount of air enclosed in clathrates which are exposed to a grain surface during crushing is also in the right order of magnitude but we have no information about the decay of air clathrates of such a small size.

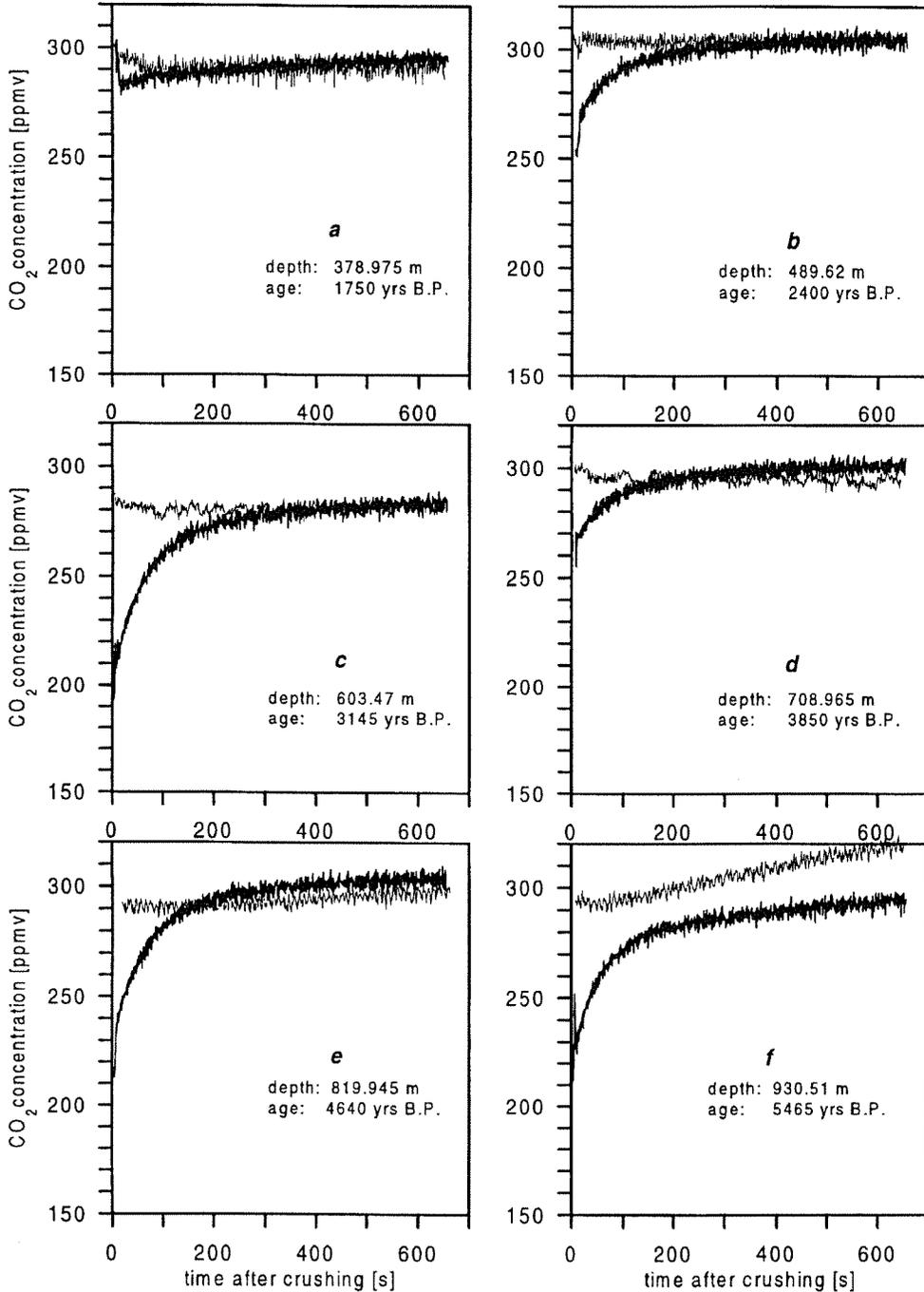
Figure 7 shows the CO₂ concentration of air as a function of extraction time for the ten samples from North GRIP, as previously described in reference to fig. 5. The records make clear that using an extraction time of only 10 seconds (used by Anklin to minimize the uncertainties due to CO₂ desorbing of the walls of the extraction device) [Anklin *et al.*, 1997] leads to much too low CO₂ concentrations. Even after an extraction time of 600 s there is no guarantee that the final concentration is reached. The atmospheric CO₂ concentration between 1750 yrs and 9380 yrs B.P. is between 260 and 280 ppmv according to measurements on ice samples from Taylor Dome (Antarctica) which are considered as

a reliable record of the atmospheric CO₂ concentration due to the low scattering of results from neighbouring samples [Indermühle *et al.*, 1999], so it is obvious that the final CO₂ concentrations of the ten samples do not agree with the atmospheric concentration at the time of ice formation but are enriched or depleted due to chemical reactions. The CO₂ enrichment or depletion can vary over very short distances, as discussed above, so that concentration differences between samples selected from about the same depth for the measurements 2 months and 7 months after core recovery is not surprising. It has to be kept in mind that the first six samples (sample *a* – *f*) are from above the transition zone where bubbles transform into clathrates. However, with the first 7 samples there is only a problem with a too short extraction time for the ice samples measured two months after recovery. Waiting 7 months after recovery, no significant change of the CO₂ concentration with extraction time is observed for samples down to 1042 m depth (only about 80 m below where clathrates start to form). The difference between samples measured 2 months and 7 months after recovery of the ice cores is probably due to the relaxation of the ice. The pressure in bubbles of ice from 960 m depth is about $9 \cdot 10^6$ Pascal at the time of recovery and decreases in 8 months to about $3 \cdot 10^6$ Pascal [Gow, 1971]. This pressure decrease could cause the disappearance of CO₂ hydrates at the bubble walls, as discussed below. Unfortunately we have not found more detailed measurements of the relaxation of an ice core after recovery.

The almost linear increase of the CO₂ concentration in sample *f* measured after 7 months could be an artefact. Water vapour in our extraction system is producing a

small amount of CO₂ by desorption from the walls [Zumbrunn *et al.*, 1982] which corresponds to a concentration increase of between 0.015 and 0.035 ppmv/s. The

observed increase in sample *f* is about 0.034 ppmv/s, the applied correction was 0.019 ppmv/s (based on single crystal measurement on the same day). We



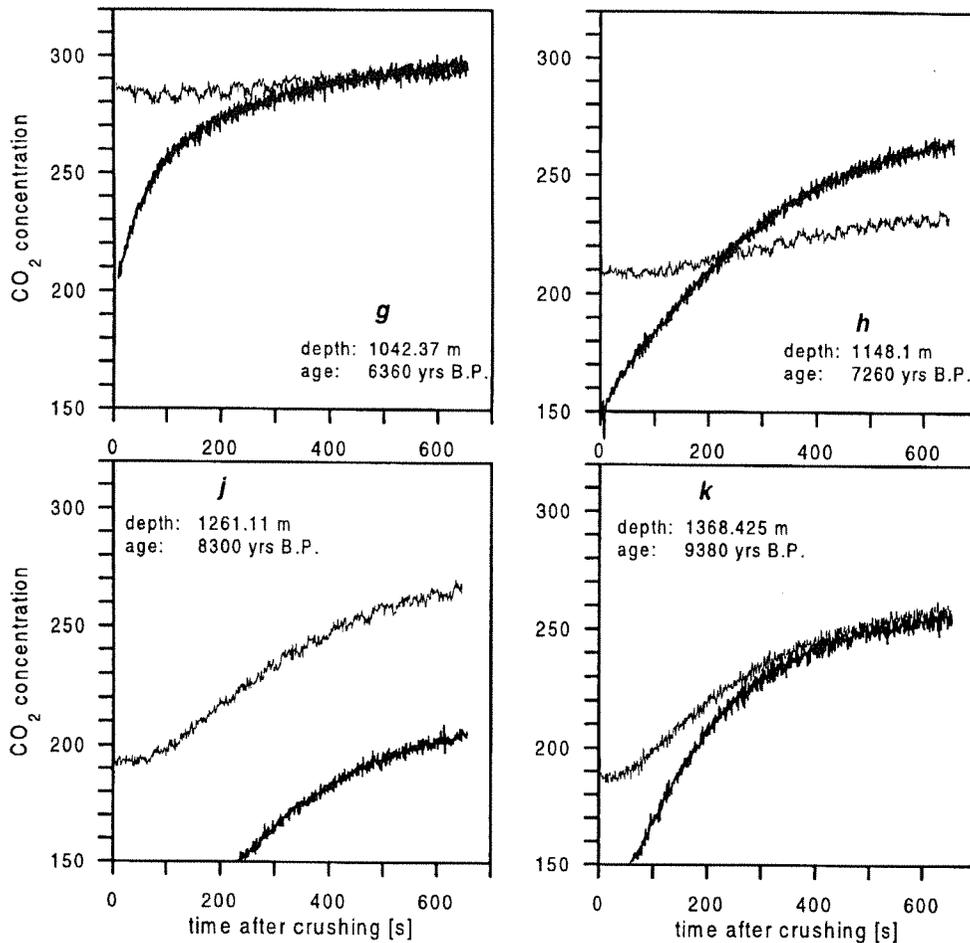


Figure 7: CO₂ concentration of air extracted from samples of different depth from the NorthGRIP ice core. The curves show the CO₂ concentration of the air expanded at that moment it enters the laser absorption cell. Heavy lines: measurements 2 months after recovery of the core, light lines: measurements about 7 months after recovery of the ice core.

neglect this linear increase, which could be due to an underestimate of this correction, from our further discussions.

Explanations for the increase of the CO₂ concentration in the extracted air are at least partly similar to the ones for the pressure increase:

1. CO₂ dissolved in ice grains diffuses to the surface of the grains
2. CO₂ from bubbles or clathrates which are enclosed in a grain after crushing

permeates preferentially to the surface compared to N₂ and O₂.

3. There is a fractionation between the CO₂ concentration in air bubbles and in clathrates, where clathrates have a higher CO₂ concentration. The CO₂ increase would be caused by a delayed decay of the clathrates.
4. Also, above the depth range where bubbles start to be transformed into clathrates, there could be CO₂ hydrates

at the wall of the air bubbles which lead to a delayed extraction of the CO₂ (Kuhs, discussion contribution at the PICR workshop)

1) *diffusion of dissolved CO₂*: At 1000 m depth only about 0.08 % of the total CO₂ is dissolved in ice according to the estimated solubility of CO₂ in ice [Hondoh, 1996]. To explain the concentration increase of sample *g* about 30 % would have to be dissolved in ice, if diffusion of dissolved CO₂ to the grain surface were the explanation. This would indicate a solubility about 400 times larger than expected. Such a large solubility is above the upper limit given by measurements [Nefel *et al.*, 1983] and is, therefore, unlikely. Even if this high solubility was correct, a diffusion constant at least as big as that for N₂ would be needed to explain the observed increases. This is two orders of magnitude larger than the estimate by Hondoh.

2) *permeation of CO₂ from enclosed bubbles and clathrates*: It is even more unlikely that the observed effect can be explained by a preferential permeation of CO₂ from the interior of crushed ice grains with enclosed bubbles or clathrates. Making the same assumptions for the size of the grains and the bubbles as used above to discuss the permeation of air to the surface, and using the diffusion constant and the solubility estimated by Hondoh, it would take about 500 years for half of the CO₂ to permeate from the bubble to the surface of the grain. The observed time for a 50 % increase of the CO₂ concentration is of the order of 100 s, more than 8 orders of magnitude faster.

3) *fractionation between bubbles and clathrates*: Only the three deepest samples show a substantial increase of the CO₂

concentration for samples measured 7 months after core recovery. If decay of the exposed clathrates is delayed, as already mentioned as an explanation for the pressure increase, and if clathrates would be enriched in CO₂ we would expect an increase of the CO₂ concentration to occur parallel with the pressure increase. However, as discussed above, we would expect a depletion of CO₂ in clathrates based on the estimated solubility and diffusion constants. We cannot exclude with certainty that there is not a major error in estimation of the diffusion constant and the solubility of CO₂ in ice and that one of them is substantially larger than those for oxygen and nitrogen, but this is very unlikely. It would be very valuable to get experimental evidence for the diffusion constant and the solubility of CO₂ in ice.

4) *CO₂ hydrates*: It was suggested that the CO₂ concentration increase with extraction time, which is observed in samples above the depth where clathrates are formed, but only after a short storage time of 2 months, could be due to formation of some kind of CO₂ hydrate at the walls of the bubbles [Kuhs, discussion contribution at the PICR workshop]. The hydrates would decay relatively fast after crushing the ice, but a certain delayed release of this CO₂ seems to be possible. The delay does not necessarily need to be in the order of 100 – 200 s as observed in our measurements. A short delay occurring in the crushing device will be registered in the laser absorption cell, further delayed because the surplus of CO₂ has to diffuse from the crushing device to the laser absorption cell. We calculated that it needs about 90 s until 80 % of the new equilibrium concentration is reached after a pulse input of CO₂ in the extraction device. However, a delay of about 10 s of the pulse

input in the extraction device is needed; this corresponds to the time of crushing before opening valve 1. If such hydrates exist at the walls of bubbles with a gas pressure above about $4 \cdot 10^6$ Pascal, they would probably have disappeared within 7 months in ice down to 1000 m depth due to the relaxation of the ice. This would explain why no further concentration increase in CO₂ is observed in samples measured 7 months after core recovery.

Only a few hypotheses can be offered to explain the results of the measurements shown in Figs. 5 and 7. We are still far from being able to decide what mechanisms are responsible for the fractionation of the air components. Especially important for our understanding of the nature of air in polar ice would be the availability of reliable values for the diffusion constant and the solubility of CO₂ in natural ice.

Conclusions

Based on the results shown and discussed in this paper we draw the following conclusions:

- CO₂ can be produced and probably also depleted by chemical reactions occurring between impurities in glacier ice. For the production of CO₂ oxidation reactions are as important as acid carbonate reactions.
- Antarctic ice core records compared to those from Greenland are generally less affected by such chemical reactions, due to the lower impurity concentrations in Antarctic ice.
- The most reliable results concerning reconstruction of ancient atmospheric CO₂ concentrations are obtained with ice samples containing a low con-

centration of carbonates and H₂O₂. Measurements can be considered reliable only if a detailed high resolution record along a few annual layers shows that the scattering of the results is of the order as the analytical uncertainty.

- Measurements on ice where air is enclosed in clathrates show additional difficulties due to a fractionation of air components. This holds especially for the zone in which both air bubbles and clathrates coexist.
- It is very important to develop dry extraction methods which allow for the extraction of gases with an efficiency close to 100 %. The sublimation technique is at present the one which is most promising [Gülliük *et al.*, 1998].

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