

# Processes affecting the CO<sub>2</sub> concentrations measured in Greenland ice

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(Manuscript received 13 December 1993; in final form 26 January 1995)

## ABSTRACT

Detailed CO<sub>2</sub> measurements on ice cores from Greenland and Antarctica show different mean CO<sub>2</sub> concentrations for samples at the same gas age. The deviation between Antarctic and Greenland CO<sub>2</sub> records raises up to 20 ppmv during the last millennium. Based on the present knowledge of the global carbon cycle we can exclude such a high mean interhemispheric difference of the CO<sub>2</sub> concentration between high northern and southern latitudes. Diffusive mixing of the air in the firn smoothes out short term variations of the atmospheric CO<sub>2</sub> concentration. Nevertheless, we observe short term CO<sub>2</sub> variations in Greenland ice in the range of 10–20 ppmv, which cannot represent atmospheric CO<sub>2</sub> variations. Due to the low temperature at Summit, meltlayers can be excluded for most of the ice and they cannot account for the frequent anomalous short term CO<sub>2</sub> variations and the elevated mean CO<sub>2</sub> concentration in the Greenland ice. In this work we give some clues, that in situ production of CO<sub>2</sub> in Greenland ice could build up excess CO<sub>2</sub> after pore close off. Possible chemical reactions are the oxidation of organic carbon and the reaction between acidity and carbonate. We conclude that the carbonate-acidity reaction is the most probable process to explain the excess CO<sub>2</sub> in the bubbles. The reaction could take place in very small liquid-like veins in cold ice, where the mobility of impurities is higher than in the ice lattice. At present, there exists no technique to measure the carbonate concentration in the ice directly. However, a comparison of CO<sub>2</sub> analyses performed with a dry- and a wet-extraction technique allows to estimate the carbonate content of the ice. This estimate indicates a carbonate concentration in Greenland ice of about  $0.4 \pm 0.2 \mu\text{mol/l}$  and a much lower concentration in Antarctic ice.

## 1. Introduction

In polar ice sheets, air is trapped in bubbles below a certain depth (the pore close-off depth). If the temperature is sufficiently low throughout the year (no melting in summer) the trace gas composition in these air bubbles is close to the atmospheric one above the ice sheet. However, CO<sub>2</sub> measurements on ice cores from Greenland and Antarctica do not show exactly the same CO<sub>2</sub> concentration for air of the same age but differ by up to 20 ppmv during the last millennium

(Barnola et al., 1995). This difference between Greenland and Antarctic CO<sub>2</sub> records is too large to reflect an atmospheric CO<sub>2</sub> difference between the two hemispheres. Therefore the air composition in ice cores from at least one location, Greenland or Antarctica, must deviate from the atmospheric CO<sub>2</sub> concentration at the time of the pore close off.

At the close off depth air is enclosed in bubbles with a diameter generally in the order of 1 mm. The pressure of the ice increases with depth and the bubbles get more and more compressed. Below a depth of several hundred metres the occluded air begins to form clathrates (Miller, 1969), e.g., below roughly 700 m at Summit (Greenland). The for-

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mation and destruction of the clathrates and their possible influence on the trace gas composition are presently not fully understood. However, the results discussed in this work are obtained from ice where the air is occluded in bubbles and not in clathrates.

Delmas (1993) has shown, that during the last glaciation the interaction between acidity and alkaline impurities could lead to a production of excess CO<sub>2</sub> in Greenland ice. The aim of this work is to discuss processes, which can explain the difference between Antarctic and Greenland CO<sub>2</sub> records and the relatively high CO<sub>2</sub> variability observed in Greenland ice during the last millennium and, thus, to estimate the upper limit of in situ CO<sub>2</sub> production for ice obtained from different locations.

## 2. CO<sub>2</sub> measurements in Greenland and Antarctic ice cores

Due to the molecular diffusion of air in the firn, the seasonal atmospheric CO<sub>2</sub> variations are smoothed out completely below the close off depth (Schwander, 1989). Nevertheless, ice cores from Summit show CO<sub>2</sub> variations in the order of 15–50 ppmv, which are measured within only one or two annual ice layers (Figs. 1, 2). The accuracy of a single CO<sub>2</sub> measurement is  $\pm 3$  ppmv and therefore the observed variations cannot be explained by analytical uncertainties. Because these variations in CO<sub>2</sub> concentration cannot a priori reflect an atmospheric signal they must be caused by a post-deposition process in the ice. Any CO<sub>2</sub>, which is produced during the firnification process, is likely to escape to the atmosphere. Thus, the short term CO<sub>2</sub> variations in Greenland ice cores must be due to processes that produce CO<sub>2</sub> mainly below the firn-ice transition. This hypothesis is corroborated by the small dispersion of the peaks (Fig. 1).

Fig. 1 shows a layer with an elevated CO<sub>2</sub> concentration at 253.95 m depth in the GRIP (Greenland Icecore Project) core from Summit. According to the time scale of Johnsen et al. (1992) the analyzed gas has an age of 873 years BP (corresponding to 1117 years AD). This core has been measured in parallel samples with a high reproducibility of the CO<sub>2</sub> peak. There is a 50 ppmv CO<sub>2</sub> increase within an only 25 mm

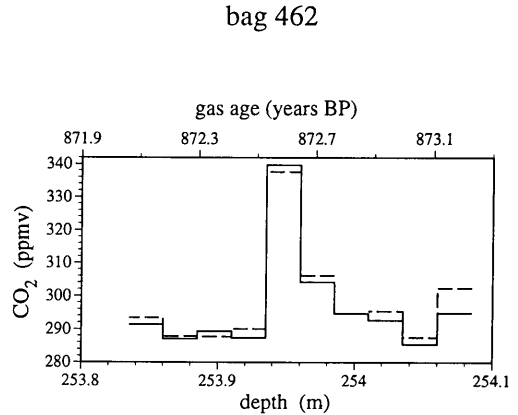


Fig. 1. The CO<sub>2</sub> peak in a depth of 253.95 m of the GRIP ice core has been measured twice with good agreement between these two data sets. This depth corresponds to a gas age of about 873 years BP (1117 AD).

broad depth layer, which is a clear indication of an in-situ CO<sub>2</sub> production.

Staffelbach et al. (1991b) measured in the Crête Site A core (Greenland) an elevated CO<sub>2</sub> value, which was 60 ppmv higher than the mean CO<sub>2</sub> concentration measured in that core section. They explained this CO<sub>2</sub> peak as an effect of melt layers or an effect, which occurs when the temperature of the snow or the ice gets close to the melting point. The results shown in Fig. 2 exclude a temperature effect as cause of the CO<sub>2</sub> variations in the GRIP core. There are two local CO<sub>2</sub> maxima, one at 575.42 m and one at 575.64 m depth (2570 years BP). Using the  $\delta^{18}\text{O}$  value as a proxy for the temperature of the precipitation (Johnsen et al., 1989) we find that the first CO<sub>2</sub> maximum (304 ppmv) occurs in summer ice layers (high  $\delta^{18}\text{O}$  values) whereas the second CO<sub>2</sub> maximum (314 ppmv) occurs in a winter layer (low  $\delta^{18}\text{O}$  values) with most likely no surface melting ( $\delta^{18}\text{O}$  data from Johnsen et al., 1992). Also, the visual stratigraphy indicates no sign of percolation of melt-water from the overlaying summer precipitation. Furthermore, Fig. 2 shows that there is neither a clear correlation between the CO<sub>2</sub> and the H<sup>+</sup> record nor between the CO<sub>2</sub> and the Ca<sup>2+</sup> record. The H<sup>+</sup> concentration is used to estimate the acidity of the ice and the Ca<sup>2+</sup> concentration is used to estimate the order of magnitude of the carbonate content of the ice. The dashed line in Fig. 2 will be discussed in Section 4.

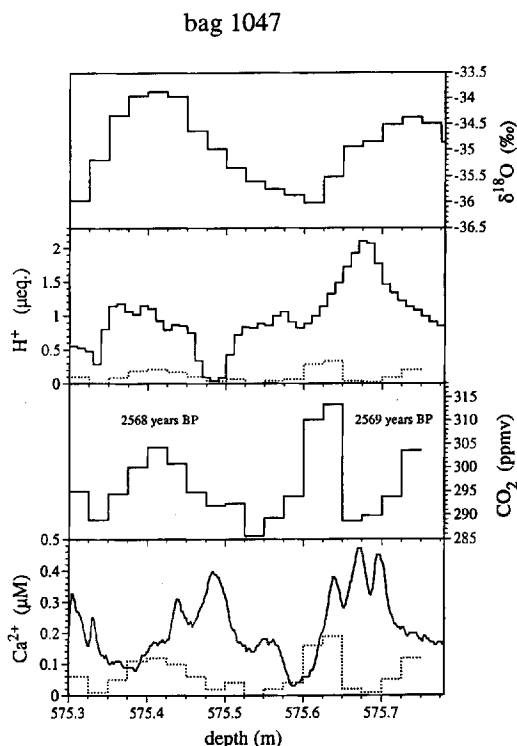


Fig. 2. Short-term CO<sub>2</sub> variations of about 10 ppmv within only two annual ice layers have been obtained in the GRIP ice core. The gas age of this ice layer corresponds to about 2568–2569 years BP (before AD 1990). The δ<sup>18</sup>O values plotted in this figure are proxy data of the temperature at the time of the precipitation. High δ<sup>18</sup>O values correspond to summer- and low values to winter-ice-layers. The H<sup>+</sup> concentration is calculated by electrical-conductivity-measurements and indicates the amount of acidity in the ice. The Ca<sup>2+</sup> concentration is used as a proxy for the carbonate concentration in the ice. The dashed lines indicate the amount of H<sup>+</sup> and carbonate needed to build up these CO<sub>2</sub> variations, assuming the carbonate-acidity-reaction to be the main cause of the observed variations, and assuming a CO<sub>2</sub> base level of 286 ppmv for this core section (see text).

Fig. 3 shows that mean CO<sub>2</sub> concentrations measured in Greenland ice are generally higher than those measured in Antarctic ice. Between 1300 to 1920 years AD CO<sub>2</sub> records from Greenland and Antarctica deviate up to 10 ppmv from each other. The older part of the records (1000 to 1300 years AD) indicates differences of about 20 ppmv. To investigate more carefully the CO<sub>2</sub> difference between Greenland and Antarctic ice younger than 700 years, we analyzed sections of

two ice cores from Byrd (Antarctica) and Summit (Greenland) under similar laboratory conditions. The two ice cores have been measured on the same day to eliminate any analytical bias in the CO<sub>2</sub> concentration. From both sites, ice of roughly the same gas age has been analyzed. Three different age levels have been investigated: 1400, 1500, and 1600 years AD. The standard deviations of the CO<sub>2</sub> measurements are 2.2 to 3.2 ppmv for the Antarctic ice sections and 6.1 to 10.6 ppmv for the Greenland ice sections. The average CO<sub>2</sub> concentrations in the Greenland ice sections are 11, 6 and 8 ppmv higher than in the corresponding sections of the Antarctic ice. These results confirm the overall trend shown in Fig. 3.

### 3. Possible processes changing the CO<sub>2</sub> composition in the air bubbles

There are several processes, which can lead to a modification of the initial composition of the air in the bubbles above the depth of clathrate formation. (1) Physisorption and chemisorption, which play most probably a minor role for the composition of inert gases and CO<sub>2</sub> in the bubbles (Schwander, 1989; Adamson and Jones, 1971; Ocampo and Klinger, 1982). (2) In meltlayers, which are due to surface melting, the CO<sub>2</sub> concentration in the occluded air bubbles is strongly enriched as shown by Neftel et al. (1983). (3) Micro-bubbles in snow flakes can be strongly enriched in CO<sub>2</sub> (Schwander, 1980), but most of this trapped gas is released during the firnification process in the upper meters of the firn. Therefore micro-bubbles can increase the CO<sub>2</sub> concentration in the bubbles of the ice by less than 0.3 ppmv (Stauffer et al., 1981). (4) The gravitational separation of heavier molecules towards the base of the firn can lead to a CO<sub>2</sub> enrichment in the air bubbles of about 2 ppmv, depending on the close off depth (Craig et al., 1988; Schwander, 1989; Sowers et al., 1989). For the drill sites Summit (Greenland), D47 and D57 (Antarctica) the close off roughly takes place in the same depth and therefore the CO<sub>2</sub> enrichment due to gravity is about the same for all these three sites. (5) Since chemical reactions in the ice cannot be excluded, as indicated by the quantitative decay of H<sub>2</sub>O<sub>2</sub> in the ice during the Holocene (Sigg and Neftel, 1991; Fuhrer et al., 1993), CO<sub>2</sub> could also be

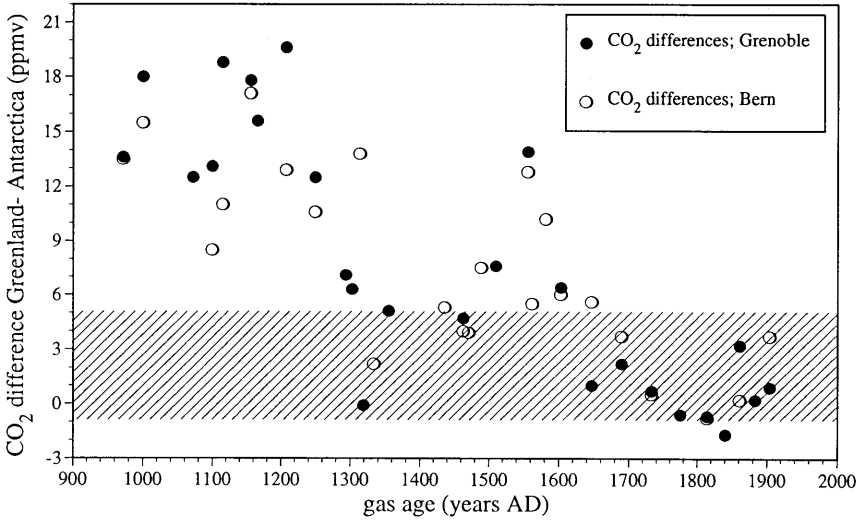


Fig. 3. Differences between CO<sub>2</sub> results obtained from Greenland (Eurocore, GRIP) and Antarctic ice cores (South Pole, D47, D57). The hatched area (CO<sub>2</sub> differences between -1 and 5 ppmv) indicates the range of CO<sub>2</sub> differences, which can be explained by the inter-hemispheric gradient.

produced by interaction between acidity and carbonate in the ice, according to the aqueous system (Zurmühle, 1991; Delmas, 1993) or by oxidation of organic material, e.g., formaldehyde or organic acids. In solid ice, such chemical reactions are certainly much slower than in the aqueous system or in the atmosphere, if they occur at all. In order to compare the importance of chemical reactions possibly leading to excess CO<sub>2</sub> in the air bubbles, we list the carbon components and their concentrations measured in polar ice (Table 1). The total potential for in situ produced CO<sub>2</sub> is for Greenland ice roughly one order of magnitude higher than for Antarctic ice.

As shown in Table 1 carbonate, organic acids and formaldehyde are the most important candidates for a chemical CO<sub>2</sub> production in the ice and they have a capacity to raise the CO<sub>2</sub> concentration in the air bubbles by several ppmv. The carbonate concentration is estimated from the Ca<sup>2+</sup> concentration in the ice. Organic acids can be oxidized in the atmosphere to CO<sub>2</sub> through several steps (Logan et al., 1981). Since the concentration of formaldehyde is rather stable during the Holocene and there is no indication for a decay during this period (Staffelbach et al., 1991a; Fuhrer et al., 1993) we do not expect any chemical reaction with formaldehyde. Methane

can be oxidized to CO<sub>2</sub>, but the capacity of methane to form CO<sub>2</sub> is below 1 ppmv and plays only a minor role. Also a production of CO<sub>2</sub> by in-soluble particles like black carbon is negligible, because these particles are most likely chemically inert. Carbonates can react with H<sup>+</sup> to CO<sub>2</sub> and water. We consider the chemical reaction of carbonate with acidity as one of the most probable process producing CO<sub>2</sub> and we will concentrate the discussion on this reaction. However, we cannot yet judge whether this is the main contribution to the 20 ppmv difference observed between the CO<sub>2</sub> ice records of the two hemispheres, or if oxidation of organic acids can also play a significant role.

#### 4. Chemical reaction between carbonate and acidity in the ice

Carbonate is transported in the atmosphere as Ca-, Na- or MgCO<sub>3</sub> aerosol and partially neutralized (forming CaSO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>) before it is deposited on the ice sheet. Rain water is naturally acidic on a global scale (Charlson and Rodhe, 1982) and, especially, polar precipitation is weakly acidic in present climatic conditions (Neftel et al., 1985a; Hammer et al., 1985; Legrand et al., 1988a).

Table 1. Carbon is present in Greenland ice in different forms

		Greenland concentration in ice/air bubbles	CO <sub>2</sub> equivalent	Ref.	Antarctica concentration in ice/air bubbles	CO <sub>2</sub> equivalent	Ref.
carbon dioxide	CO <sub>2</sub>	280 ppmv		12 1	280 ppmv		9
(calcium) carbonate	(Ca <sup>2+</sup> ) CO <sub>3</sub> <sup>2-</sup>	0.1–1 μmol/l estimated from Ca <sup>2+</sup>	?15–150 ppmv	5	0.04 μmol estimated from Ca <sup>2+</sup>	?6 ppmv	7
organic acids		0.7 μmol/l	100 ppmv	6	0.05 μmol/l	7 ppmv	8
acetate	CH <sub>3</sub> COO <sup>-</sup>						
formate	HCOO <sup>-</sup>						
methanesulfonate	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>						
oxalate	C <sub>2</sub> O <sub>4</sub> <sup>-</sup>						
formaldehyde	HCHO	0.1 μmol/l	15 ppmv	5	0.035 μmol/l	5 ppmv	10
methane	CH <sub>4</sub>	700 ppbv	0.7 ppmv	2	650 ppbv	0.65 ppmv	11
black carbon		1.5 μg/kg	10 ppmv	3	0.5 μg/kg	3 ppmv	4

The main species containing carbon are listed in this Table. Since there are no data available about the CO<sub>3</sub><sup>2-</sup> concentration in the ice, we estimated the CO<sub>3</sub><sup>2-</sup> concentration from the Ca<sup>2+</sup> concentration assuming that Ca<sup>2+</sup> indicates the CO<sub>3</sub><sup>2-</sup> level which is a first-order guess.

References. 1. Barnola et al. (1995). 2. Blunier et al. (1993). 3. Chylek et al. (1992a). 4. Chylek et al. (1992b). 5. Fuhrer et al. (1993). 6. Legrand et al. (1992). 7. Legrand and Delmas (1988b). 8. Legrand and Saigne (1991). 9. Neftel et al. (1985b). 10. Staffelbach et al. (1991a). 11. Stauffer et al. (1988). 12. Wahlen et al. (1991).

Therefore the longer the transport path in the atmosphere of the aerosol is, the more carbonate can be neutralized during this transport. For the carbonate-acidity reaction to take place in the ice it is required that carbonate and acidity are deposited with the snow and have not yet completely neutralized during the transport (Delmas, 1993). Assuming the carbonate-acidity reaction to be the reason for the elevated Greenland CO<sub>2</sub> values, then the step like change of the deviation between Greenland and Antarctic CO<sub>2</sub> records around 1200 years AD (Fig. 3) could thus be due to either a change in acidity or carbonate content in the ice or may be due to the thinning of the annual ice layers with increasing depth, which could accelerate the reaction between carbonate and acidity by bringing acid and alkaline sites of the ice closer together (Delmas, 1993).

In analogy to the aqueous system the sum of the carbonate-acidity reactions in the ice can be written as 2H<sup>+</sup> + CO<sub>3</sub><sup>2-</sup> ⇌ CO<sub>2</sub> + H<sub>2</sub>O. Stoichiometrically, 0.1 μeq. of acidity produces 0.05 μmol of CO<sub>2</sub>. This would raise the CO<sub>2</sub> concentration in the bubbles by about 8 ppmv. The reaction is

limited either by the available acidity or by the available carbonate.

The acidity in the ice is calculated from electrical-conductivity-measurement (ECM) (Hammer, 1980). For Summit ice the corresponding H<sup>+</sup> concentrations are roughly between 0.5 and 1.5 μeq. during the Holocene (unpublished data, personal communication H. B. Clausen). Stoichiometrically this amount of H<sup>+</sup> could raise the CO<sub>2</sub> concentration in the air bubbles by 40–120 ppmv. Since such high excesses of the mean CO<sub>2</sub> concentration have never been measured in Holocene ice it seems that the carbonate-acidity reaction is rather limited by the carbonate content.

Unfortunately, there are no direct methods to measure the carbonate concentration in the ice and only different estimates about the level of the carbonate concentration can be made. The acidity/alkalinity titration method developed by Legrand et al. (1982) provides an estimation of the acidity and carbonate content of the melt-water. This is confirmed by the ion balance of soluble melt-water impurities discussed by Legrand (1987) and Delmas and Legrand (1989). It has thus been

shown that Antarctic ice melt-water contains no carbonate (Legrand, 1987). However, the titration provides a budget between alkaline and acidic species of melt-water and consequently does not reflect necessarily the initial carbonate content of the ice. Calcium can be used as an indicator of the original aerosol carbonate content, but in-cloud reactions neutralizing calcium carbonate during the transport make this element unqualified to estimate the exact carbonate content of the ice. To get additional information about the carbonate concentration in the ice we compare here  $\text{CO}_2$  results from dry extraction methods with those from the melting-refreezing method for Antarctic and Greenland ice. The latter is used for methane measurements but usually  $\text{CO}_2$  is also measured simultaneously although these results can often not directly be interpreted as an atmospheric concentration. In acidic ice most of the carbonate will react in the melt-water and form gaseous  $\text{CO}_2$ . Similar  $\text{CO}_2$  values from both, dry and wet extraction methods indicate therefore a low carbonate content (in acidic melt-water), whereas an enhanced  $\text{CO}_2$  concentration obtained with the melting-refreezing method points to carbonate that has not yet reacted in the ice. The quantitative evaluation of these results is however limited, because other processes exist that can change the amount of  $\text{CO}_2$  when using a melting method, e.g., adsorption and desorption in the extraction vessel. Fig. 4 shows the  $\text{CO}_2$  results from both, the dry and the melting-refreezing extraction method for a Greenland (Eurocore) and an Antarctic (D47) ice core. In the Eurocore record the  $\text{CO}_2$  values obtained by melting-refreezing extraction are systematically higher than the values obtained by dry extraction (about  $60 \pm 30$  ppmv), whereas, in the D47 record, there seems to be no systematic shift between the two extraction methods. If, in the Eurocore, the  $60 \pm 30$  ppmv difference between the two extraction methods is due to a carbonate-acidity reaction producing  $\text{CO}_2$  in the melting-refreezing extraction vessel, then this would indicate a carbonate concentration of  $0.4 \pm 0.2$   $\mu\text{mol/l}$  in this Greenland ice. Since there is no systematic shift in the D47 record between the two extraction methods we can assume that the carbonate concentration is generally much lower in the Antarctic ice from D47 than in the Greenland Eurocore. This is in good agreement with the fact that the transport path of aerosols

through the atmosphere is longer for Antarctica than for Greenland, as mentioned above.

A reaction of acidity with carbonate, leading to a  $\text{CO}_2$  excess in the air bubbles, would consume  $\text{H}^+$  ions, which should manifest itself by a lower ECM signal. In Fig. 2 the dashed lines indicate the calculated amount of  $\text{H}^+$  and carbonate needed to build up these  $\text{CO}_2$  variations assuming a  $\text{CO}_2$  base level of 286 ppmv according to the concentrations measured in this ice section. The needed amount of  $\text{H}^+$  (dashed line) is calculated assuming that there is enough carbonate available in the ice and, on the other hand, the needed amount of carbonate is calculated under the assumption that acidity is not limited for the carbonate-acidity reaction. However, the lowest concentrations of this Greenland ice section may already be affected by chemical reactions increasing the  $\text{CO}_2$  concentration in the air bubbles. Since the pre-industrial atmospheric  $\text{CO}_2$  concentration may fluctuate by about 10 ppmv ( $280 \pm 5$  ppmv) during the Holocene as discussed by Barnola et al. (1995) the  $\text{CO}_2$  value of the lower limit in Fig. 2 may be wrong by about 10 ppmv, which could shift the dashed line in Fig. 2 upwards by  $0.06$   $\mu\text{M}$  for the carbonate and by  $0.12$   $\mu\text{mol/l}$  for the  $\text{H}^+$  content. Taking into account the uncertainty of the base level of the  $\text{CO}_2$  concentration in Fig. 2 then a carbonate-acidity reaction has not necessarily to show up as a clear and pronounced drop in the  $\text{H}^+$  signal because the amount of  $\text{H}^+$  needed to build up this  $\text{CO}_2$  excess (dashed line) is in the range of the noise of the ECM-signal and is anyway much smaller than the seasonal variations (about  $1.5$   $\mu\text{eq. H}^+/\text{year}$ ). The needed amount of carbonate to produce the excess  $\text{CO}_2$  in Fig. 2 (dashed line plus an uncertainty of about  $0.06$   $\mu\text{M}$ ) is in the same order of magnitude as the  $\text{Ca}^{2+}$  concentrations. Therefore, the carbonate content of the ice may be limiting this reaction in most cases.

There are different authors proposing a liquid-like layer or a liquid-like film along grain boundaries of cold polar ice. Since the mobility of impurities is higher in a liquid-like phase than in the ice lattice chemical reactions could most likely take place in such a liquid-like phase.

A liquid-like layer has been proposed along the grain boundaries with a thickness of one to several hundred molecular layers due to asymmetrical environment of the water molecules at the grain

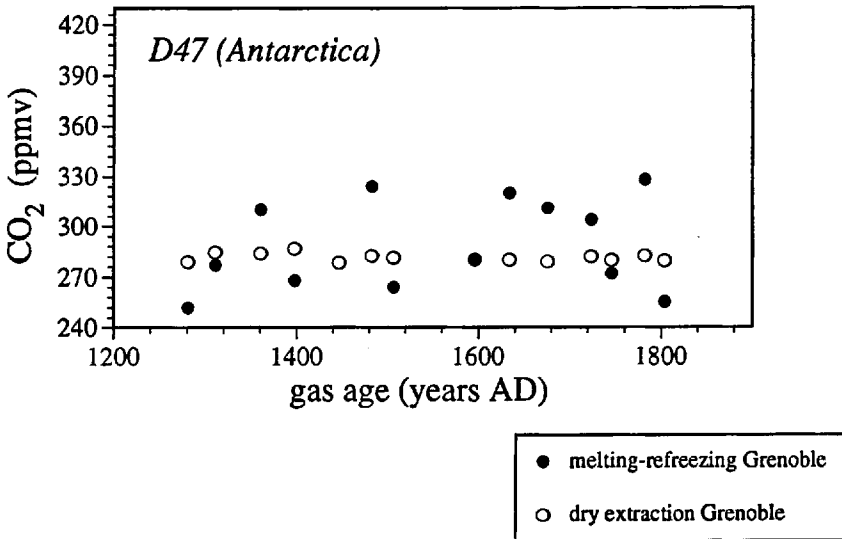
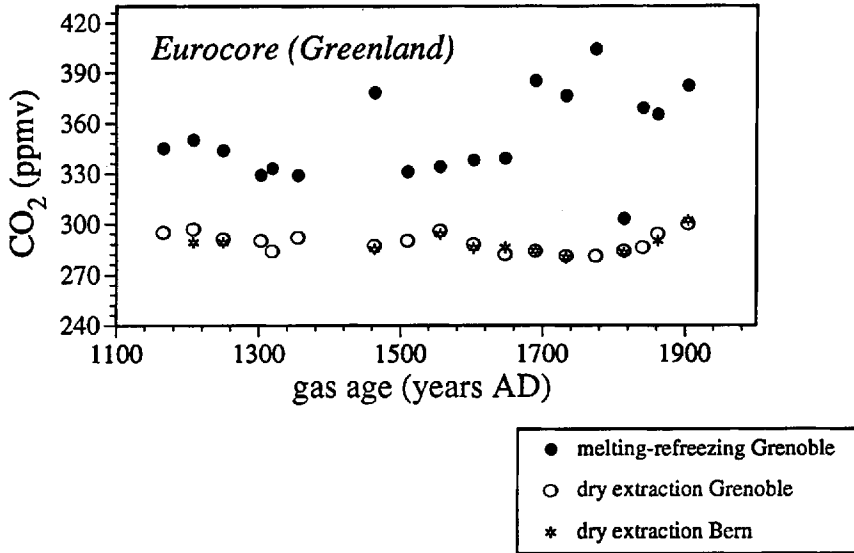


Fig. 4. CO<sub>2</sub> results obtained with a dry extraction system and the melting-refreezing system used for methane measurements. The comparison of these two data sets can be used as a rough indicator of carbonate in the ice (see text).

surface (Hobbs, 1974). This liquid-like layer may only be stable above a temperature of  $-15^{\circ}\text{C}$  and is therefore negligible at sites with ice temperatures below  $-15^{\circ}\text{C}$ . Conklin and Bales (1993) calculated a liquid-like film with a thickness ranging from 3–30 nm at  $-60^{\circ}\text{C}$  to 500–3000 nm at  $-1^{\circ}\text{C}$  around the grains of the firn, which is due to impurities that are assumed to be located mostly at grain boundaries. Mulvaney et al. (1988) found that sulfuric acid present in the analyzed Antarctic ice is enriched at junctions where three grains meet and that, therefore, most of the sulfuric acid is excluded from the ice matrix. While small ions can be partly incorporated into the ice lattice, larger ions seem to be kept out of the ice matrix and will therefore remain along the grain boundaries possibly leading to liquid-like veins (Moore et al., 1992). Within these liquid-like veins chemical reaction can produce excess  $\text{CO}_2$  increasing the  $\text{CO}_2$  concentration in the occluded air whenever these veins are in contact with a bubble. An uptake of gaseous  $\text{CO}_2$  into the liquid-like film is negligible since the Holocene ice is acidic (based on unpublished ECM data from Summit, personal communication H. B. Clausen) and for acidic water the equilibrium of the reaction  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  is strongly on the  $\text{CO}_2$  side and therefore the solubility of  $\text{CO}_2$  is low.

## 5. Conclusions

Greenland  $\text{CO}_2$  records are up to 20 ppmv higher than Antarctic records during the last millennium. Beside this elevated mean values, Greenland ice sections show short term  $\text{CO}_2$  variation in the order of 10–20 ppmv, which cannot represent atmospheric variations. We consider chemical productions of  $\text{CO}_2$  below the close off depth as the most probable process for the elevated  $\text{CO}_2$  concentration in air bubbles of Greenland ice. An interaction between carbonate and acidity is the most probable process leading to the deviation

between Greenland and Antarctic  $\text{CO}_2$  measurements. We cannot totally exclude that also  $\text{CO}_2$  records from Antarctica are affected by chemical reactions in the ice, but since the measured concentrations of impurities, especially the estimated concentration of carbonate, are about one order of magnitude lower in Antarctica than in Greenland ice, the concentration of excess  $\text{CO}_2$  for Antarctic ice would be in the range of the error of a single  $\text{CO}_2$  measurement ( $\pm 3$  ppmv) or less.

To receive more information about the carbonate-acidity reaction in the ice, detailed carbonate measurements on ice cores are needed. In this work, we have mainly discussed the carbonate-acidity reaction as the most probable process for an in site  $\text{CO}_2$  production. A  $\text{CO}_2$  production by oxidation of formaldehyde, black carbon and methane can be neglected. However, a substantial contribution by the oxidation of organic acids cannot be excluded at present. This possibility needs further investigations.

## 6. Acknowledgments

We want to give a special thank to R. Delmas and M. Legrand for their fruitful discussions during the preparations of the manuscript. The ice samples have been obtained in the frame of Eurocore and the Greenland ice core project (GRIP) co-coordinated and supported by the European Science Foundation. We thank the national funding agencies and organizations in Belgium, Denmark, France, Germany, Iceland, Italy, Switzerland and the United Kingdom together with the XII Directorate of CEC final support. The laboratory analyzes are supported by the Swiss National Science Foundation and the Bundesamt für Energiewesen in Switzerland and, in France, by the Programme Nationale d'Etudes de la Dynamique du Climat and the EEC EPOCH program.

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