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Do glaciers tell a true atmospheric CO_2 story?

Z. Jaworowski[a,*], T.V. Segalstad[b] and N. Ono[c]

[a]*Norwegian Polar Research Institute, P.O. Box 158, N-1330 Oslo, Norway*
[b]*Mineralogical-Geological Museum, University of Oslo, Sars' Gate 1, N-0562 Oslo, Norway*
[c]*Arctic Environment Research Center, National Institute of Polar Research, 9-10, Kaga 1-Chome, Itabashi-ku, Tokyo 173, Japan*

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ABSTRACT

Until 1985 most studies of CO_2 in gas inclusions in pre-industrial ice indicated that CO_2 concentrations (up to 2450 ppm) were higher than the current atmospheric level. After 1985, lower pre-industrial CO_2 values were reported, and used as evidence for a recent man-made CO_2 increase. The errors in these revised values, however, are of a similar magnitude to the apparent increase in atmospheric CO_2 level. The assumptions used in estimating lower CO_2 values in past atmospheres have been: no liquid phase in polar ice; younger age of air than of ice due to free gas exchange between deep firn and the atmosphere; and no change in composition of air inclusions. These assumptions are shown to be invalid. Liquid saline water exists in ice at low temperatures, even below −70°C; airtight ice layers are ubiquitous in Antarctic firn; and more than 20 physico-chemical processes operating in situ and in ice cores contribute to the alteration of the chemical composition of air inclusions. The permeable ice sheet with its capillary liquid network acts as a sieve which redistributes elements, isotopes, and micro-particles. Thirty-six to 100% of air recovered from old ice is contaminated by recent atmospheric air during field and laboratory operations. The value of ~290 ppm, widely accepted from glacier studies for the pre-industrial atmospheric CO_2 level, apparently results from: invalid assumptions; processes in ice sheets; artifacts in ice cores; and arbitrary rejection of high readings. To date, glaciological studies are not able to provide a reliable reconstruction of either the CO_2 level in pre-industrial and ancient atmospheres or paleoclimates. Instead these studies have led to a widely accepted false dogma of man-made climatic warming. This dogma may have enormous negative impact on our common future.

Key words: CO_2; isotopes; glaciers; greenhouse warming

INTRODUCTION

More than 50 years ago, Callendar (1938) revived the hypothesis of greenhouse warming due to man's activity, proposed by Arrhenius (1896)

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[*] Present address: Institute of Physics, University of Oslo, P.O. Box 1048, Blindern, N-0316 Oslo, Norway.

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four decades earlier. Callendar's was a pioneering paper posing questions which have now become the subject of intense discussion. Among these questions are those related to changes in global temperature, the natural carbon cycle, and man's contribution to both. Callendar may truly be regarded as the father of the current paradigm on man-induced global warming.

In support of this hypothesis, Callendar (1938, 1940, 1958) used his estimate of an increase in atmospheric CO_2 from a 19th century level of 292 ppm to about 325 ppm by 1956. He claimed that both this increase and a 0.33°C rise in global surface temperature between 1880 and 1935 were caused by fossil fuel burning. A set of 19th century data compiled by Fonselius et al. (1956) indicated that CO_2 concentrations ranged from about 250 to 550 ppm (Fig. 1). Callendar accepted an average concentration of 292 ppm for the 19th century data by application of a selection method questioned by Slocum (1955), who demonstrated that without such selection these data average 335 ppm.

Slocum (1955) pointed out that, from a set of twenty-six 19th century averages, Callendar rejected 16 that were higher than the global average of 292 ppm, and only two that were lower. On the other hand, from the 20th century set Callendar rejected three averages that were lower than his global average of 317 ppm, and none that was higher. This shows a bias in the selection method.

Five decades later the Callendar CO_2 estimates are still used and their reliability discussed (see, e.g., Stanhill, 1982; Waterman, 1983; Wigley, 1983).

It is interesting to note that a tendency to select low values for the CO_2

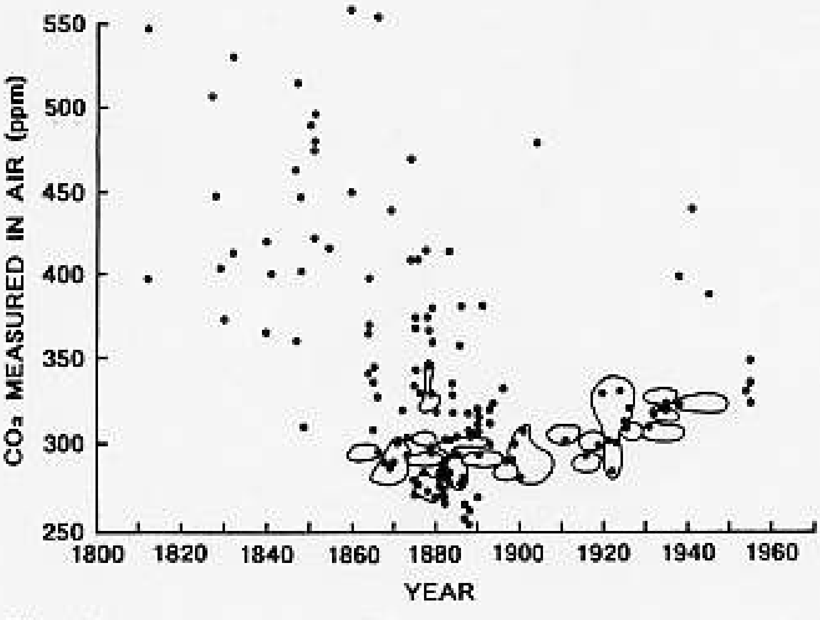

Fig. 1. Average atmospheric CO_2 concentrations measured in the 19th and 20th century. Encircled are the values used by Callendar. Redrawn after Fonselius et al. (1956).

concentration in the 19th century atmosphere still exists. This is because the carbon cycle model simulations, which are based on an assumption that the increase in atmospheric CO_2 is due only to man's activity, require starting concentrations even lower than 290 ppm to agree with current CO_2 observations at Mauna Loa (Keeling et al., 1976; Wigley, 1983; Siegenthaler and Oeschger, 1987), an active and strongly CO_2 emitting volcano (Jaworowski et al., 1990a).

Wigley (1983) claimed that 'the most compelling support for a (low) 270 ppm pre-industrial CO_2 level comes from direct measurements of CO_2 in the ice cores', and cited Neftel et al. (1982) in support of this statement. But no such evidence was presented by Neftel et al. (1982). Their data indicate rather a decreasing trend during the last 2000 years. They found that CO_2 concentrations in air bubbles from 150-year-old ice ranged from 300 to 2350 ppm.

Ironically, those who found CO_2 concentrations of between 270 and 390 ppm in 180-year-old ice also preferred values close to the lower end of the range, because these were 'within the range of the estimated (by Callendar) pre-industrial atmospheric content of 290 ppm' (Berner et al., 1978; for similar statements see also Raynaud and Barnola, 1985, and Pearman et al., 1986).

Because of uncertainties in 19th century air measurements, studies of CO_2 in glacier ice became a cornerstone of the current greenhouse warming edifice, and a basis for studies of the global carbon cycle (e.g., Broecker et al., 1985; Bolin et al., 1989). It is astonishing that these studies have been so credulously accepted (e.g., IPCC, 1990), and were never critically evaluated, except by Jaworowski et al. (1990a). Thorough validation of these studies is much required in view of the enormous cost which may unduly be imposed on society by incorrect interpretation of their results. In this paper we present a more detailed discussion of the reliability of these determinations.

Glaciers are often thought of as the cleanest parts of the Earth's surface, providing a unique chemical record of past atmospheric environments. Falling snow flakes collect atmospheric aerosols containing particulate and gaseous components of the atmosphere. Deposited on the surface of glaciers, they are covered each year by consecutive layers of snow, and form an annual ice stratification. The air is trapped within snow crystals, in liquids at their surfaces, and in the voids of the porous firn structure. The pores close, and after transition of firn into ice, form completely occluded air bubbles. But before this stage, the air in the firn is isolated from the atmosphere by dense layers of ice. Such ice layers, sandwiching the firn into airtight pockets, are ubiquitous both in temperate glaciers and in polar ice sheets.

These characteristics of glaciers enable us to study changes in atmospheric composition during the past hundreds and thousands of years, provided that the concentrations of chemical species recovered from the snow or ice samples are directly proportional to their original atmospheric concentrations. Atmospheric components associated with insoluble particulates usually meet this condition, but gases may not.

The validity of current reconstructions of pre-industrial and ancient atmospheres, based on CO_2 analyses in polar ice, depends on three speculative assumptions:

(1) that the age of the gases in the air bubbles is much lower than the age of the ice in which they are entrapped (e.g., Oeschger et al., 1985);

(2) that 'the entrapment of air in ice is essentially a mechanical process of collection of air samples, which occurs with no differentiation of gas components' (Oeschger et al., 1985); and

(3) that the original air composition in the gas inclusions is preserved indefinitely.

The main argument in support of the last two assumptions is another assumption that no liquid phase occurs in the polar ice at a mean annual temperature of -24°C or less (Berner et al., 1977; Raynaud and Barnola, 1985; Friedli et al., 1986). This is why, after initial research in the 1950s and 1960s, CO_2 glacier studies were conducted exclusively on the Greenland and Antarctic ice sheets where such low temperatures exist. Over time the sampling sites were transferred to increasingly cooler regions.

As will be seen in the discussion below, all these assumptions are invalid in view of the following: (1) the ubiquitous presence of ice layers in Antarctic snow, making the age of the entrapped air similar to the age of the ice; (2) the presence of liquid water in polar ice even at the lowest Antarctic temperatures; and (3) the occurrence of physical and chemical phenomena in glacier ice. Due to these phenomena, entrapment of air in ice is not just a mechanical process, but one that leads to substantial chemical and isotopic changes (Segalstad and Jaworowski, in prep.) in the composition of gas inclusions.

EARLY STUDIES

Determinations of CO_2 in snow and ice were initiated at a small glacier in Norway (Coachman et al., 1956, 1958a,b), and then the studies were continued in Greenland and Antarctica (Table 1). In the first Antarctic study of Matsuo and Miyake (1966) an elegant method of ^{13}C isotopic dilution was used for CO_2 determinations. The precision of these determinations, with an analytical error of ± 0.002%, was never matched in later studies, which reported errors usually ranging between ± 0.2 and 3%.

Two important observations were made in these early studies. It was found that the CO_2 content of the air trapped in pre-industrial and ancient ice is rather high, and has a very wide concentration range of about 100–7400 ppm

TABLE 1

Concentrations of CO_2 in glacier ice (ppm by volume)

Age of ice	Locality	Concentration	Reference
PI[a]	Storbreen (Norway)	~200–2900	Coachman et al. (1956, 1958a,b)
	Greenland		
PI	11 localities	80–2500	Scholander et al. (1961)
2700	Tuto tunnel	~100–800	Scholander et al. (1961)
PI	Antarctica	280–2900	Matsuo and Miyake (1966)
PI	Antarctica	80–320	Lorius et al. (1968)
Present		155	
Holocene	Greenland and Wisconsin	1700–7400	Raynaud and Delmas (1977)
	Antarctica		Raynaud and Delmas (1977)
>100	Byrd station	900–1800	
Present	Pionerskaya[c]	160	
Present	Vostok[c]	240	
180	Greenland	270–390	Berner et al. (1978)
PI	Antarctica		
	Whole ice[d]	210–740	Delmas et al. (1980)
	Air bubbles[e]	160–335	
PI up to 40 000	Greenland	200–800	Berner et al. (1980)
	Antarctica	230–400	
5000–30 000	Greenland		
	Camp Century	200–700	Stauffer et al. (1981)
180	Camp Century	250–1000	Stauffer et al. (1981)
180	Camp Century[e]	300–550	Stauffer et al. (1981)
410–640	North Central	300–500	Stauffer et al. (1981)
1000?–30 000	Antarctica	200–520	Stauffer et al. (1981)
	Greenland		
>100	Dye 3[e]	300–2350	Neftel et al. (1982)
600–40 000	Camp Century[e]	140–470	Neftel et al. (1982)
680	North Central[e,f]	271	Neftel et al. (1982)
	Antarctica		
600–40 000	Byrd Station[e]	190–500	Neftel et al. (1982)

TABLE 1 (*Continued*)

Concentrations of CO_2 in glacier ice (ppm by volume)

Age of ice	Locality	Concentration	Reference
3230	Greenland		
	Dye 3[e]	283–773	Neftel et al. (1983)
	Greenland		
PI	Dye 3[e]	135–275	Stauffer et al. (1984)
Present	Dye 3	28 000	Stauffer et al. (1985)
185[g]	Dye 3[e]	290–2450	Stauffer et al. (1985)
7000[g]	Dye 3[e]	290–490	Stauffer et al. (1985)
700–9000	Six sites in Greenland and Antarctica[e]	258–283	Stauffer and Oeschger (1985)
	Antarctica		
> ~ 300	D57[e]	247–295	Raynaud and Barnola (1985)
	Antarctica		
1663–1891[b]	Siple[e]	279–328	Neftel et al. (1985)
110–820	South Pole[e]	278–281	Neftel et al. (1985)
	Antarctica		
1530–1900[b]	Law Dome[e]	268–326	Pearman et al. (1986)
4050–163 670	Antarctica		
	Vostok[e]	191–296	Barnola et al. (1987)
5000–50 000	Antarctica		
	Byrd[e]	180–280	Neftel et al. (1988)

[a] PI = pre-industrial, exact age not given.
[b] years A.D.
[c] Interstitial air from frozen firn.
[d] Samples washed in water or alcohol.
[e] In gas inclusions after dry extraction, otherwise in melted ice.
[f] In one 11 cm thick layer at 103 m depth.
[g] After Reeh et al. (1985).
Numeric age of ice is given as years before present if not stated otherwise (footnote b).

(Table 1). Even more important was the finding that several physical and chemical processes (such as melting, the presence of liquid brines in the capillary-like interstitial voids, the presence of carbonates, over-pressure in the air bubbles, and solid deposition of super-cooled fog, combined with large differences in the solubility of different gases in cold water, and mobility of CO_2 in ice) lead to differentiation of the original atmospheric ratios of N_2, O_2, Ar, and CO_2, and to depletion or enrichment of CO_2 in the ice (Coachman et al., 1958; Hemmingsen, 1959; Scholander et al., 1961; Matsuo and Miyake, 1966; Raynaud and Delmas, 1977).

In these early studies it was recognized that the liquid water in glaciers may be the most important factor in this differentiation, because the composition of atmospheric air (78.08% nitrogen, 20.95% oxygen, 0.93% argon, and approximately 350 ppm, by volume, carbon dioxide) is different from the composition of air dissolved in cold water. It was known at that time that, in such air, at 0°C and ambient pressure, the concentration of oxygen is 67% higher than in the atmosphere (Scholander et al., 1961; Hodgman et al., 1962). This is because the solubility of oxygen in cold water is 2.1-times higher than that of nitrogen. Argon has 2.4-times higher solubility than nitrogen, and CO_2 73.5-times higher (Weast et al., 1989). This explains why the air extracted from melt layers in polar firn has extremely high concentrations of about 12 000 ppm CO_2 (Stauffer et al., 1985). This is also why the air bubbles contain much lower concentrations of CO_2 than the ice which encompasses them.

Three different methods of gas extraction were used, and they produced different results. This is illustrated in Fig. 2. It can be seen that in air from the same section of a pre- industrial ice core, after 7 h 'wet' extraction of melted ice, the CO_2 concentration was up to about 1000 ppm, and it was 1.5–4.5-times higher than after 15 min 'wet' extraction. The 'dry' extraction, consisting in crushing or shaving the ice samples at about −20°C, produced results similar to the 15 min 'wet' extraction. The short 'wet' and 'dry' extractions recovered about a half or less of the total CO_2 present in the ice.

Later papers showing the recent increase in CO_2 atmospheric level ignored or played down these early findings. It was tacitly assumed in these papers that no exchange exists between the ice matrix rich in CO_2 and the gas occluded in the air bubbles.

THE PERIOD OF HIGH CO_2 READINGS

After 1980 most of the studies of CO_2 in glaciers were carried out on Greenland and Antarctic ice by Swiss and French research groups; one core was studied in an Australian laboratory. A striking feature of the data published until about 1985 is the high concentrations of CO_2 in air extracted from both pre-industrial and ancient ice, often much higher than in the contemporary atmosphere (Table 1).

For example, in 11 samples of about 185-year-old ice from Dye 3 (Greenland) an average CO_2 concentration of 660 ppm was measured in the

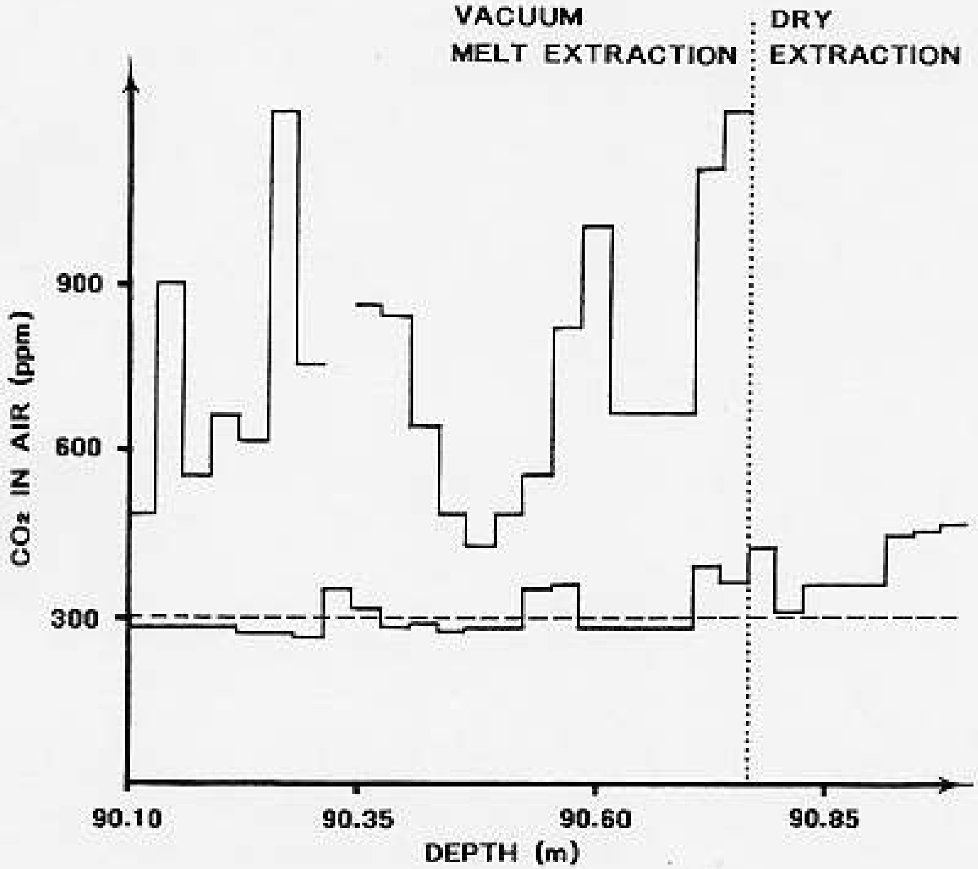

Fig. 2. Concentration of CO_2 in a 90 cm long section of a Camp Century (Greenland) ice core. The lower curve represents 15 min 'wet' extraction from melted ice and 'dry' extraction; the upper curve 7 h 'wet' extraction. Redrawn after Stauffer et al. (1981).

air bubbles (using the 'dry' extraction method), with a range of 290–2450 ppm (Stauffer et al., 1985). In a deep ice core from Camp Century (Greenland), covering the last 40 000 years, Neftel et al. (1982) found CO_2 concentrations in the air bubbles ranging between 273 and 436 ppm (average, 327 ppm). They also found that in an ice core of similar age from Byrd Station (Antarctica) these concentrations ranged between 257 and 417 ppm. Both these deep cores were heavily fractured and contaminated with drilling fluid. Neftel et al. (1982) arbitrarily assumed that 'the lowest CO_2 values best represent the CO_2 concentrations of the originally trapped air'.

Using the same dry extraction method, in the same segment of an ice core from a depth of 1616.21 m in Dye 3 (Greenland), Neftel et al. (1983) found a CO_2 concentration of 773 ppm in the air bubbles. Two years later, Stauffer et al. (1985) reported only about half of this concentration (410 ppm).

It appears from Table 1 that the change from high to low CO_2 values reported for polar ice occurred in the middle of 1985.

THE PERIOD OF LOW CO_2 READINGS

Since 1985, low concentrations, near a value of 290 ppm or below, started to dominate the records. They were interpreted as indicating 'the CO_2 increase during the last 150 years' and 'overlapping or adjacent to results from direct measurements on Mauna Loa started in 1958' (Stauffer and Oeschger, 1985).

Except for a cursory description of a few measurements in Greenland and Antarctica (Stauffer and Oeschger, 1985), there were six cores analyzed for CO_2, all from Antarctica, and in all of them much lower values of CO_2 were reported for pre-industrial and ancient ice than during the previous Antarctic studies (Table 1). In all these cores the CO_2 contents were determined only in gas extracted by the 'dry' method from primary air bubbles or secondary air cavities, a few months to 19 years after drilling. No information was given on the total CO_2 contents of the ice itself.

A striking feature of these studies is that the sampling was started deep below the surface, and no data were presented on the recent concentration of CO_2 in firn and ice deposited in the twentieth century. The results from these younger strata are essential for estimates of temporal changes of CO_2 levels, because they could demonstrate whether the air trapped in the firn contains the original atmospheric concentrations of CO_2.

The only study in which frozen firn samples were sealed in airtight containers before analysis demonstrated that this is not the case (Raynaud and Delmas, 1977). In the top 0–1 m layers of firn from Vostok Station (mean annual temperature about –57°C) and Pionierskaya (mean annual temperature –37.6°C), which represent contemporary precipitation, the authors found a CO_2 concentration in the interstitial air of 240 and 160 ppm, respectively (Table 1). This is much lower than in the present atmosphere, and similar to concentrations in air recovered from Antarctic ice of pre-industrial and ancient age. These low CO_2 concentrations are due to various processes in the ice sheet (discussed below) or in the firn samples.

A serious flaw of the Antarctic studies discussed here is a scanty description of the cores, and the disregard of the methodological details which bear on the interpretation of the analytical results. We do not learn whether the cores were drilled thermally or mechanically (Neftel et al., 1985, 1988; Raynaud and Barnola, 1985; Barnola et al., 1987). Even the diameters of the cores are not indicated. This diameter is changing with time; first it increases due to relaxation of the load pressure, and then shrinks due to sublimation of the core during the long time that elapses between its collection and analysis. Up to 30% shrinking of the volume was reported for an ice core stored for 16 years at a temperature of –20°C (Ng and Patterson, 1981). Information on the structure, texture and history of the cores is not presented. Outstanding in this respect is a paper by Neftel et al. (1985) in which no information at all is given on the collection of a South Pole core. Some such flaws are discussed below.

Important information on the temperature changes during collection of the cores, their transportation from Greenland, Antarctica, or storage facilities in the United States, to laboratories in Europe or Australia, and during their long storage, are not given at all. That such temperature changes occur may be inferred from Pearman et al. (1986), who found that parts of the Law Dome core exhibited 'post-coring melting'. The Law Dome samples exposed to melting yielded significantly lower CO_2 concentrations in air extracted by the 'dry' method from the air bubbles. This indicates that a proportion of the CO_2, from air bubbles was dissolved in meltwater, and by subsequent refreezing (at –80°C) of this water, was eliminated from the bubbles.

According to Etheridge et al. (1988) the Siple core drilled during the Antarctic summer of 1983/84 and used by Neftel et al. (1985) was exposed to melting, but the latter authors did not mention this in their paper. Other cores from Siple also 'melted partially during shipment' (Alley and Bentley, 1988). Increasing the temperature of polar ice cores during transportation and handling to near the melting point is probably not a rare phenomenon and was often reported (e.g., Ng and Patterson, 1981; Boutron and Patterson, 1983, Legrand et al., 1988), but not by CO_2 students, except Etheridge et al. (1988).

Two types of Antarctic cores were analyzed in the 'low readings period': three shallow cores representing pre-industrial ice, and two deep cores reaching the ice layers deposited about 160 000 (Vostok core) and 50 000 years (Byrd core) ago. (We do not discuss three 2-cm long sections of the South Pole core.) Most of these cores were drilled many years before analysis, and all were exposed to ambient atmosphere and physical and chemical changes during drilling and storage. The results of these five studies have been used as proof of the recent increase in atmospheric CO_2 and for reconstruction of its long-term variations (e.g., IPCC, 1990). They deserve closer examination.

Shallow cores

Samples from three approximately 108–473 m long cores of pre-industrial ice were analyzed by Neftel et al. (1985), Friedli et al. (1986), Raynaud and Barnola (1985), Pearman et al. (1986) and Etheridge et al. (1988). The samples were collected at the Siple Station (average annual temperature –24°C), D-57 (average temperature –32°C) and Law Dome-5 (average temperature –22°C), from various depths starting at 68, 89 and 72 m, respectively, below the surface of the ice sheet (Table 2).

TABLE 2

Concentrations of CO_2 in air bubbles from three Antarctic ice cores at the starting depth

Site	Starting depth (m)	Age of ice[a] (A.D.)	CO_2 (ppm)	Reference
Siple	68	1890	328	Neftel et al. (1985)
D-57	89	1680	288	Raynaud and Barnola (1985)
Law Dome-5	72	1896	325	Pearman et al. (1986)

[a] Based on precipitation rate (Siple); Tambora 1815 volcanic explosion (D-57); oxygen isotope stratigraphy (Law Dome-5).

From the precipitation rate, Neftel et al. (1985) estimated the age of the ice in the Siple core at 68 m to be 1890 A.D., but they assumed that the air was trapped in this ice during 1962–1983 (i.e. the air was about 90 years younger). In the D-57 core, Raynaud and Barnola (1985) found, at a depth of about 50 m, sulfur deposition from the Tambora (Indonesia) volcanic explosion in 1815. The corresponding precipitation rate was calculated to be 18 cm of ice equivalent. Therefore, the age of the ice at 89 m depth was about 1680 A.D., but the authors assumed that the air in this ice was trapped in 1940 A.D. (i.e. it was 260 years younger than the ice). For the Law Dome-5 core, Pearman et al. (1986) and Etheridge et al. (1988) gave neither the depth at which ice samples were collected nor the age of the ice. According to a private communication by Etheridge (1990) the youngest ice was collected at ~72 m depth, and it was deposited about 1896 A.D. But they assumed that the age of air in this ice was 70 years younger (i.e. it was trapped in 1966 A.D.). The validity of these assumptions is discussed below.

The CO_2 concentrations recovered from these three cores at the starting depths were 328, 288 and 325 ppm, respectively (Table 2), and they were more or less systematically decreasing with increasing depth and pressure in the ice. This is most clearly seen from the data for the Siple core (Fig. 3) and for the Law Dome-5 core (Etheridge et al., 1988). Only one explanation for these observations was offered: fossil fuel burning, although the ice samples were not from the twentieth century.

The results were interpreted as indicating 'a rapid increase in atmospheric CO_2 ... during the second half of the nineteenth century or early twentieth century' (Pearman et al., 1986), 'the increase in atmospheric CO_2 due to burning of fossil fuels and probably due to the anthropogenic influence on the biosphere over the nineteenth and twentieth century' (Raynaud and Barnola, 1985), and that 'atmospheric CO_2 concentration around 1750 was 280

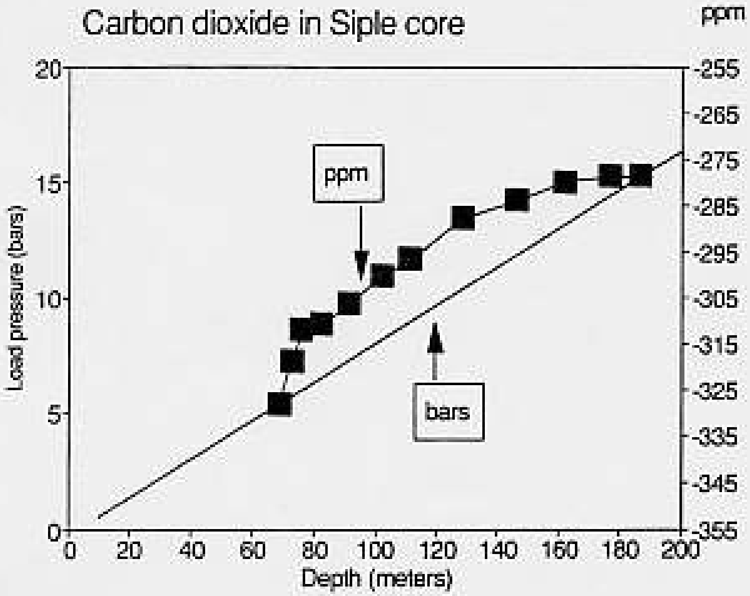

Fig. 3. Concentration of CO_2 in the ice core from Siple (Antarctica) decreasing as a function of depth and load pressure. Note that the right axis' scale is negative. This core was inadvertently partially melted prior to analysis. The reported analytical uncertainty is ± 3 ppm or larger, i.e. larger than the size of the data points. Adapted from Neftel et al. (1985).

ppmv and had increased since, essentially because of human factors, by 22.5% to 345 ppmv in 1984' (Neftel et al., 1985).

Another explanation for the concentration gradient decreasing with depth is considered more plausible. As may be seen in Fig. 3, the CO_2 concentration in gas recovered from air bubbles in the Siple core, between a depth of 68 and 187 m, decreased sympathetically with increasing load pressure in the ice. At this depth interval the CO_2 decrease in the Siple core was about 14%, and 6% between 111 and 187 m depth, where the age of the ice was 173 and 322 years B.P., respectively. At a similar depth interval of 126 to 250 m in the Vostok core (age of ice 4050 and 9320 years B.P.) a similar decrease in CO_2 concentration of about 8% occurred.

The decrease in the CO_2 content of ice of completely different age but exposed to similar changes in load pressure is due to three factors: differential diffusion and solubility, clathrate formation of air components in the ice sheet, and micro-fracturing of ice cores with increasing depth (see below).

Different diffusion rates of CO_2 into the ice lattice and liquid veins versus other air components is related to the lower molecular volume and lower gas viscosity of CO_2 than for N_2, O_2 and Ar. Differential diffusion occurs both in the ice sheet and in the ice cores in which the post-drilling structure disturbances are related to the depth from which the cores were recovered.

The pressure in air bubbles in cores recovered from below about 100 m depth is less than the load pressure in the ice sheet (see section Structural

Changes and Physico-chemical Processes). The total gas contents in these cores were about ≥ 25% lower than in those from shallower depths. This is due to gas release from air bubbles via micro-cracks developed in ice cores recovered from below 100 m depth. Below 100 m the frequency of cracks increases with depth. CO_2 may escape through these micro-cracks at a different rate than other gases. Disturbances in the ice structure are associated with redistribution of the liquid phase and of the gases, which leads to differentiation of the gas composition of the air bubbles.

The solubility of CO_2 in cold water increases with decreasing temperature, and at a faster rate than the solubilities of N_2 and O_2 increase. At higher pressure more CO_2 than other air components dissolves in the intercrystalline liquid (Enns et al., 1965). Siegenthaler et al. (1988) found that the oxygen in CO_2 gas inclusions of ice from three Antarctic stations had exchanged isotopes and was close to isotopic equilibrium with the ice. They calculated that a 10-molecular-layers thick shell of H_2O around each gas inclusion permits rapid equilibration between CO_2 and H_2O. This mechanism is also valid for the firn and ice strata discussed here.

In the region of load pressure between 5 and 9 bars the CO_2 concentration decreases more rapidly than at greater depths, i.e. between 9 and ~ 15 bars. The first steep decrease is probably due to the formation of CO_2 clathrate (solid-state hydrate: $CO_2 \cdot 5.75H_2O$), which at temperatures below -15°C is expected to form at a pressure of 5 bars or lower (Takenouchi and Kennedy, 1965). We assume that the location of CO_2 clathrate is related to the presence of liquid water and vapor in the ice structure, because free water molecules are needed for its formation. N_2 and O_2 need much higher pressures than CO_2 (above 70 and 100 bars, respectively) to enter the clathrate phase at low temperatures (Miller, 1969). When the pressure increases above 5 bars, CO_2 starts to enter the clathrate form, long before N_2 and O_2. Thus differential diffusion, solubility, clathrate formation, and cracking of ice makes depletion of CO_2 from the air bubbles in shallow ice cores roughly proportional to increasing pressure.

As mentioned before, the core samples studied by Pearman et al. (1986) were exposed to post-coring melting, and then to a temperature of -80°C. This certainly changed the composition of the gas inclusions, making determinations unreliable for estimates of past atmospheric CO_2 levels.

Raynaud and Barnola (1985) and Neftel et al. (1985) observed totally different concentrations of CO_2 in air bubbles from ice at the starting depths, i.e. lower and higher, respectively, than in the present atmosphere. However, both groups reached the same conclusion: that their results demonstrate an anthropogenic increase in atmospheric CO_2. This suggests that there is bias in the interpretation of analytical results.

Jaworowski et al. (1990a) compared the range of analytical uncertainties with the temporal differences in CO_2 concentrations in ice used in support of claims discussed above that the level of this gas has increased in the atmosphere due to man's activity. This 'CO_2 glacier signal' was in the case of Raynaud and Barnola (1985) 17 ppm, in the case of Neftel et al. (1985) 49 ppm, and in the case of Pearman et al. (1986) 13 ppm (Fig. 4). According to Oeschger et al. (1985) the 'errors' (at assumed 68% probability) of single measurements of CO_2 in air trapped in ice cores from Greenland and Antarctica range between 11 and 24 ppm. At an assumed 95% probability, the 'errors' of measurements reach about 47 ppm (Fig. 4). Thus the claimed signals of man-made CO_2 increase are of the same magnitude as the range of uncertainty of measurements.

In air bubbles from neighboring 1.5-cm thick slices of an Antarctic ice core, representing 6 months precipitation, the CO_2 concentrations differed by 32 ppm and by 25 ppm in the same slice (Barnola et al., 1983) (see discussion below).

It is clear from this comparison that the claims of a recent increase in atmospheric CO_2 content, based on glacier studies, are not justified by the available data.

Deep cores

Carbon dioxide concentrations were studied in two deep cores from Antarctica collected at the Vostok Station (126.4–2077.5 m below the surface) (Barnola et al., 1987) and at the Byrd Station (~600 to ~1900 m below the surface) (Neftel et al., 1988). The assigned age of the ice in these cores spanned from 4050 to 159 690 years B.P. The same assumptions as for shallow

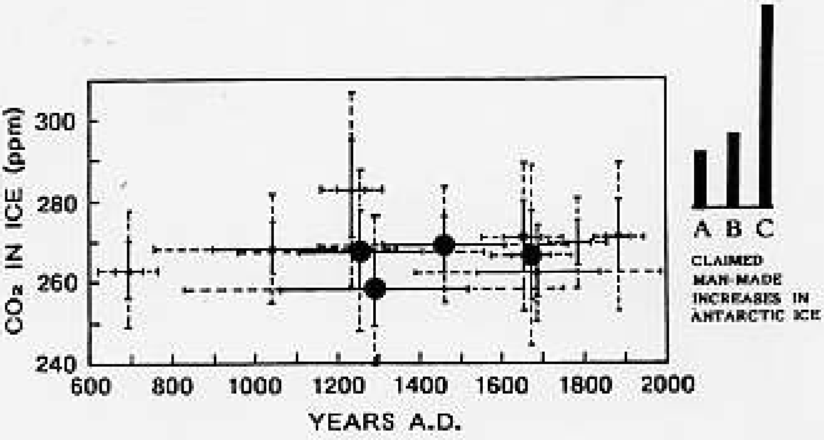

Fig. 4. Errors of measurement of CO_2 in air bubbles of ice cores from Greenland and Antarctica (Oeschger et al., 1985) and claimed man-made increases of CO_2 level in recent Antarctic ice samples due to fossil fuel burning (A, Pearman et al., 1986; B, Raynaud and Barnola, 1985; C, Neftel et al., 1985). Solid lines indicate ± 1 S.D.; broken lines indicate ± 2 S.D.

cores with respect to the stability of the gas composition and air age were accepted in these studies. The conclusions in these papers were based on an unverified assumption that the CO_2 variations observed in the cores reflect the real changes in composition of the ancient atmosphere.

We challenge this assumption because new evidence indicates that the ice in the polar sheets is not a single, solid-state phase with bubbles in which the air composition is preserved indefinitely, and because the elemental and isotopic composition of air in the gas inclusions is changed by many physicochemical processes in the ice sheets and in the ice cores.

For the Vostok core, Barnola et al. (1987) provided no information as to how it was decontaminated from the drilling fluid, how deep this fluid and meltwater penetrated the core, what was the vertical and radial distribution of the micro- and macro-cracks and how the authors countered this problem, which might seriously influence their CO_2 determinations. Instead, a general statement on 'the good core quality' is offered. This statement is in disagreement with the reports of De Angelis et al. (1987) and Petit et al. (1990) on the poor quality of this core.

There is also a lack of important information on the time elapsed between the collection of the Vostok core and the CO_2 analysis. No information is provided on the post-drilling history of the core samples, how they were preserved, how their temperature changed during transportation, storage and analysis, and how much their volume decreased due to sublimation and evaporation. The diameters of the sections of the Vostok core analyzed by Boutron et al. (1988) of 9.1 and 10.5 cm were different than the original diameters reported for various core depths by Kudryashov et al. (1984a) of 8.8 and 11.1 cm. Sublimation leads to an important loss of mass of the cores stored for longer times at about –20°C. This loss is neither controlled nor recorded, but is easily seen in the form of hoar covering the surface of the cores and deposited inside their envelopes. Sublimation will seriously influence the isotopic composition of the ice (Segalstad and Jaworowski, in preparation).

There is neither information on the disappearance of air bubbles in the ice sheet, reported at Vostok to occur below 800 m depth (Korotkevich et al., 1978), nor on their re-appearance as secondary cavities in the bubble-free part of the core after its collection and decompression (see discussion below). This, among other effects, led to mixing of the gas from primary air bubbles with much larger amounts of CO_2 enclosed in the ice itself. There is no evidence for the expectation that the gas entering the secondary cavities may have the same composition as the gas in the primary bubbles, or the original ancient atmospheric composition. Most of this criticism is valid for descriptions of other cores studied in Antarctica since 1985.

For the Byrd core, Neftel et al. (1988) presented neither information on, nor a reference to, the analytical methods used, preparation of samples, and the effects of storage of the unsealed core sections for 19 years 'at different places' (Friedli et al., 1984). The data of Neftel et al. (1988) show a maximum value for the CO_2 concentration in air recovered from this core of about 290 ppm. In a previous paper, much higher concentrations were reported for the same core (Neftel et al., 1982). The high readings recorded by Neftel et al. (1982) in the upper part of the Byrd core of 417 and 325 ppm are omitted in the Neftel et al. (1988) paper. Figure 5 demonstrates this selection of the results.

A criterion for such data selection was the high CO_2 concentration, and its discussion by Neftel et al. (1982, 1988) is rather fuzzy. They stated that 'in the larger samples (300 g) contamination [with drilling fluid] is almost inevitable and the measured CO_2 concentrations tend to be higher than the air [sic!] originally included in the ice'. However, they did not measure CO_2

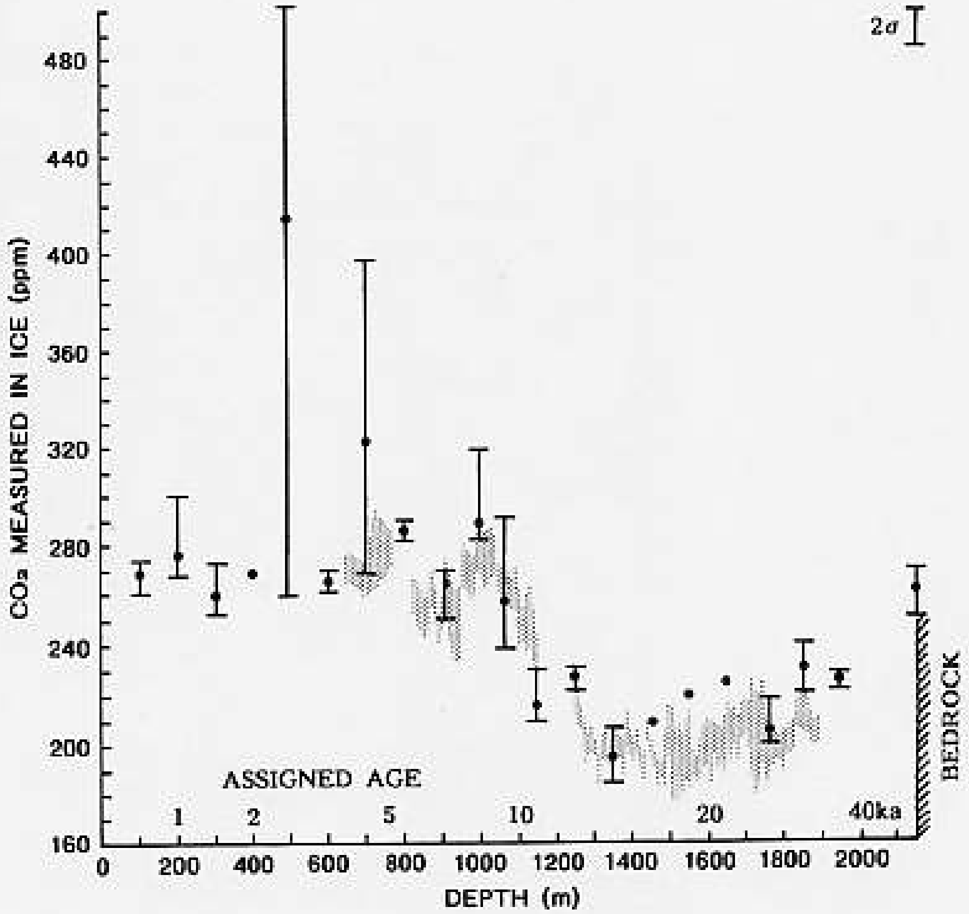

Fig. 5. Two sets of CO_2 concentrations in gas recovered from the Byrd ice core (Antarctica); redrawn from Neftel et al. (1982) (dots and bars for median and range) and Neftel et al. (1988) (shadowed areas represent the reported 1σ errors). Because the data have very wide variations Neftel et al. (1982) have shown the median values. Note that wide variations high readings from both upper and lower parts of the core recorded in 1982 were not presented in 1988.

in the air bubbles and secondary gas cavities from such larger samples, but only from 1 g samples. These small samples were used to 'avoid samples with visible internal cracks'. They stated that, in the case of small (~ 1 g) samples, their 'small size meant that [they were] probably uncontaminated and we conclude that the lowest CO_2 values best represent the CO_2 concentrations of the originally trapped air'. But they recorded both the high and the low CO_2 concentrations in 1 g samples, so their conclusion is neither based on analytical evidence nor logical arguments.

As discussed below, 1 g ice core samples may contain about 5 healed macro-cracks. Visual inspection is not sufficient to distinguish contaminated samples from uncontaminated ones, because invisible micro-cracks containing drilling fluid are present in the inner parts of the cores where no visible cracks were observed (Gow and Williamson, 1975; see also the section Macro- and Micro-cracks). It is not possible to distinguish between contaminated and uncontaminated samples on the basis of their size.

Neftel et al. (1988) claimed that their data revealed 30% lower CO_2 values during glacial periods than during interglacial periods. However, the lower values are from parts of the core where many melt layers and important ice structure changes occurred (Gow, 1970). The decrease in CO_2 concentrations started at 1200 m depth, where all original air bubbles disappear in the ice sheet. Here the number of secondary cavities, an artifact appearing in the relaxed ice cores, reached its maximum. It is from these secondary cavities and not from the original air bubbles that the gas samples with the lowest CO_2 content were collected by Neftel et al. (1988).

Neftel et al. (1988) stated that, in the core, 'no melt features were observed', quoting Gow (1968a) in support. But Gow (1970) found many 'layers of variable thickness of refrozen meltwater up to 10 mm thick' in this core. Apart from this, a distinctive ice crust layering (up to about 10 layers per meter) was observed in the firn strata, and below down to a depth of 240 m. The formation of ice crusts involved local radiational melting (Gow, 1970).

The Byrd core was contaminated with a drilling liquid composed of a mixture of trichloroethylene and diesel oil (Gow, 1971) and with meltwater from thermal drilling. Neftel et al. (1982, 1988) did not mention any attempt to decontaminate the core. This drilling liquid contaminated the core even more than the Vostok liquid (Boutron et al., 1987). Pollutants enter deep into the core through the micro-fractures, even in parts at the depth at which no visible cracks were reported (Boutron et al., 1987).

Several papers provide evidence for serious contamination of deep Antarctic cores with metals and major ions (see below). The factors that caused this contamination also influenced the gas composition of the cores. The contamination occurred along the natural capillary network of liquid veins, and along a network of micro- and macro-cracks.

MACRO- AND MICRO-CRACKS

The cracks in the ice are first formed by sheeting in the bottom of 'dry' and 'wet' boreholes due to partial release of the load pressure; then due to vibration or thermal shock during drilling and later due to pressure relaxation of the cores. Macro- and micro-cracks occur in ice cores from all depths below about 100 m. The volume of micro-cracks in deep ice cores reaches about 10% of the volume of gas inclusions (Gow, 1971). It was reported that large parts of the Vostok core were 'badly fractured' (De Angelis et al., 1987), and that 'the upper part of the core (above 1000 m) shows many cracks ... which may have been contaminated by drilling fluid' (Petit et al., 1990). Between 125 and 700 m depth the core was extremely fractured (Legrand et al., 1988). This is the region where dramatic decreases in CO_2 concentrations, and changes in stable isotope ratios, were observed. In the classical papers on CO_2 and stable isotopes in the Vostok core the possibility that this decrease and these changes may be related to post-drilling effects were not considered. To prevent the breaking of ice due to fracturing, the temperature of the Vostok core sections was increased in the laboratory to −3°C for 24 h before analysis (Legrand et al., 1991). Such treatment of the cores must lead to redistribution of their chemical components due to thermal gradients (Jaworowski et al., 1990b) and the increase in volume of the liquid phase.

Deep drilling in ice sheets involves extremely brutal treatment of the ice samples. This procedure leads to dramatic changes in the recovered cores. We will describe here such changes using the Vostok core as an example, and the technical data on thermal drilling from Kudryashov et al. (1984a,b,c) and Zotikov (1986).

The thermal drills at the Vostok station operated at working temperatures of −60 to +120°C. The power flux per unit area of the heaters was about 20 W/cm^2, and the power consumption was 4.5–6 kW per heater. The body of the heaters was made of copper and aluminum. The speed of drilling was about 8.5 cm/min, and during 1 min about 700 ml of ice was melted. The meltwater was mixed with a rapid stream of a hydrophobic drilling fluid. The fluid was forced by a special device through the openings in the heater to the bottom of the borehole, and pumped out via heated tubes operated at 350 W of power per running meter length, i.e. a total of 600 kW for the 2000 m borehole, to avoid refreezing of the meltwater.

Due to these operational conditions, with the heater at a temperature close to the boiling point of water, the hot mixture of meltwater with the highly contaminated drilling fluid penetrated the core via macro- and micro-cracks. This penetration occurred at the moment of passing the heater through the bottom ice, and then in the 'inner tube' of the drill, filled with the drilling fluid. Some of its components (e.g., ethylene glycol monoethyl ether) are excellent solvents for metals, and dissolve aluminum and copper from the heaters during operation at high temperatures.

The total amount of drilling fluid in the 2000-m deep Vostok borehole was about 28 metric tons. The drilling fluid was used to counter the load pressure on the borehole. This, however, was never achieved completely, because the fluid level was maintained 200–300 m below the surface of the ice sheet. The difference between the cryostatic pressure and the drilling fluid pressure in the Vostok borehole, at any depth below 200 or 300 m, can be calculated from the densities of firn and ice between the surface and a depth of 300 m (given by Barkov et al., 1975; and Korotkevich et al., 1978), and from the average density, 0.925 g/cm^3, of the drilling fluid (Kudryashov et al., 1984a). At a drilling fluid level of 200–300 m depth this pressure difference will be between about 15 and 24 bars, respectively.

Such a pressure difference is sufficient to cause horizontal sheeting of the ice in the bottom of the borehole, before drilling a new portion of the core. Thus the drilling head penetrates ice which is already fractured or preconditioned for fracturing. Cracking is also likely to be induced by thermal shock, caused by a rapidly formed steep thermal gradient, which may reach about 150°C across the 1.5-cm thick ice between the surface of the heater and the ice core interior ahead of the drill (Zotikov, 1986).

Sheeting is a well known phenomenon in geology, and usually designates horizontal fracturing due to stress-releases within a rock mass. The fractures occur approximately perpendicular to the volume extension. Sheeting is caused by elastic relaxation of compression, which proceeds rapidly in ice. After just a few minutes, this accounts for about a 0.2% volume increase of ice cores (Gow, 1971). Volume changes of the order of tenths of a percent may form such stratified sheeting cracks (Hobbs et al., 1976). Sheeting also occurs in relaxed ice cores (Jones and Johari, 1977), in which the volume increase may reach 0.6%, and the ice density decreases by 2–9.5 kg/m^3 (Nakawo, 1986) or more. Typical horizontal sheeting 'stratifications' were observed in cores, starting at a depth just below 100 m, where the pressure relaxation was about 8 bars.

Narita (1978) presented photographic evidence of dense horizontal stratification comprised of thin layers in ice cores from the Mizuho Station (East Antarctica) drilled thermally without a hole-retaining fluid. These layers appeared below a depth of 108.25 m and were observed down to the bottom of the core at 145.35 m. A similar 'stratification' due to cracks was observed by Nakawo and Narita (1985) in samples from a 413.5-m deep Mizuho core, 1–2 days after core recovery. After 2 days storage the cracks were partly healed. Micro-cracks were revealed by the microscope in a thin piece of specimen taken from in between two macro-cracks. This fracturing is presented schematically in Fig. 6.

Nakawo and Narita (1985) found that, below a depth of 110 m, where the

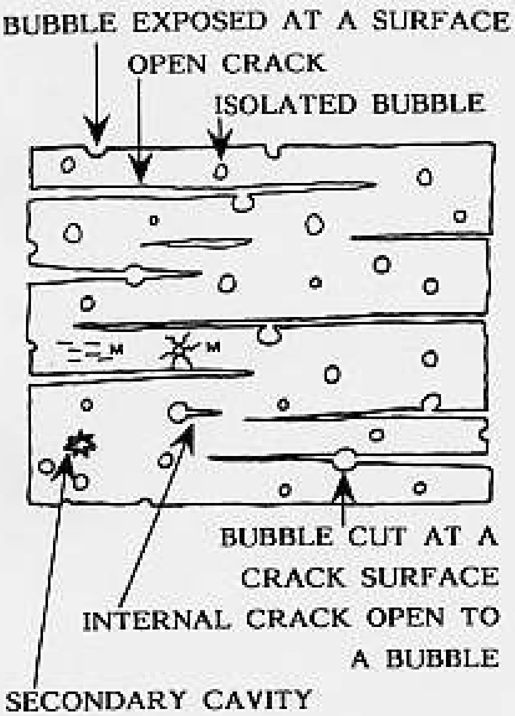

Fig. 6. Schematic illustration of fractures in a block sample from a deep ice core (not to scale). M, micro-cracks formed around a pressurized air bubble and between macro-cracks. Note the dense system of fractures penetrating throughout the core and opening some of the bubbles. Modified after Nakawo and Narita (1985).

samples were rich in cracks, the bubble pressure was much lower than the load pressure. This difference was due to gas release through the cracks. A similar pressure reduction was recorded in ice cores from various sites (Langway, 1958; Gow, 1968b; Gow and Wiliamson, 1975). In the Mizuho core the cracks were associated with up to an ~40% decrease in the gas content of the ice (Nakawo and Narita, 1985). For the same Mizuho core, Narita and Nakawo (1985) reported pressure-cracked bubbles, with 'brims' which might be caused by thermal shock and pressure release. Similar crack rings, and a fissure-like distortion of the ice structure, were observed in and around relaxed air bubbles by Shoji and Langway (1983).

Narita and Nakawo (1985) observed a substantial difference in the ice structure of cores examined within 1 month, and 1 year after recovery. The most important textural change was in the crystal size, increasing with time, due to recrystallization. They found that this effect was quite large, even in shallow cores from a depth of < 100 m. An important implication of this finding is that the observations on crystal size in ice cores stored for several years before analysis represent post-drilling processes rather than the temporal distribution of crystal size in the ice sheets, which was interpreted as being related to climatic changes (Duval and Lorius, 1980; Petit et al., 1987).

One of us (Z.J.) observed horizontal stratification in Mizuho cores from

105.97, 356.03 and 657.69 m depth, but not at a depth of 79.39 m. The observation was carried out 7–19 years after collection of the cores, which were stored at −20°C. The horizontal strata were densely distributed throughout the whole length of the cores. The cores revealed no macroscopic cracks when inspected on a light-table. The strata appeared at about 2–5 mm intervals and were associated with delicate horizontal corrugation of the surface. The rugae reached a depth of 0.5–1 mm. The tint of the striations was different from that of the enclosing ice. When successive concentric 1-cm thick veneers of ice were removed from each of these cores, the deformations produced at the surface were evident throughout the whole cross- section of the cores (Fig. 7). This horizontal stratification is a remnant of old cracks, completely healed by regelation. Such cracks, before they were healed, are shown

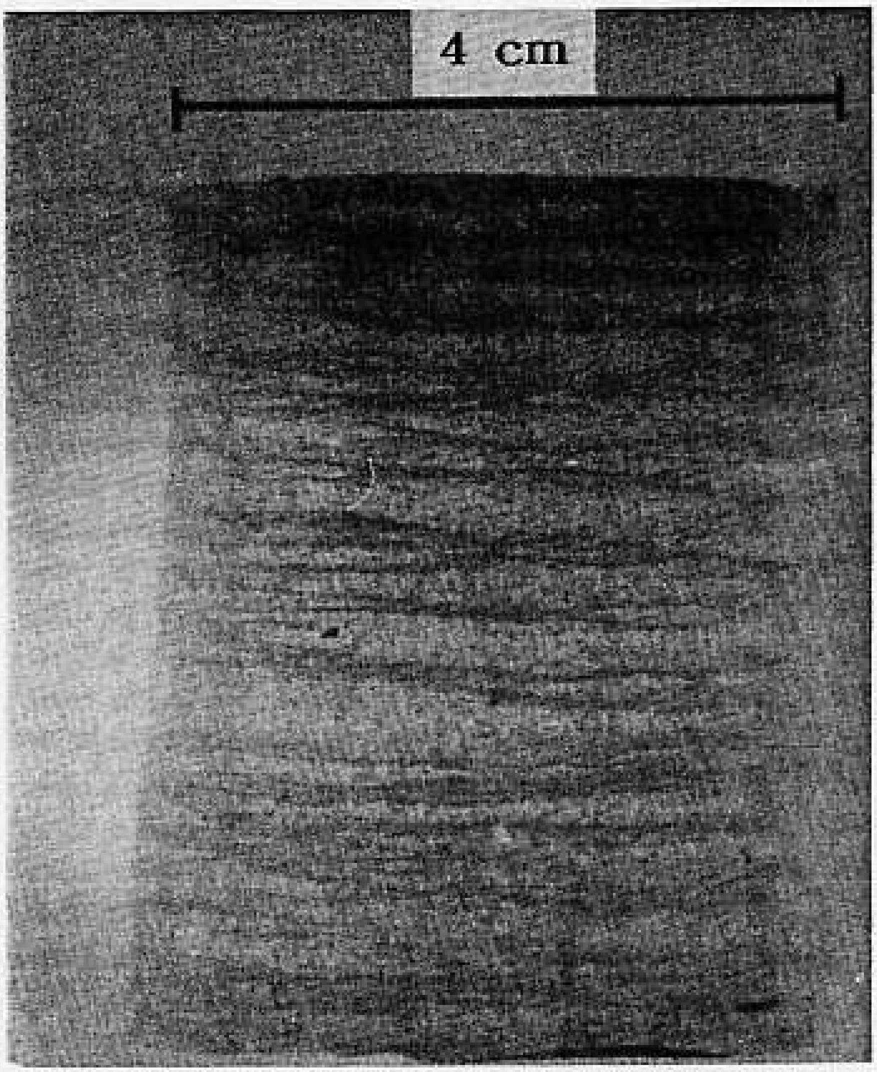

Fig. 7. Photograph in transmitted light of the inner part of an ice core from the Mizuho Plateau (East Antarctica), depth 356 m, 7 years after thermal drilling. Four centimeters of external ice was removed. Note the dense structure (stockwork) of healed macro-cracks.

schematically in Fig. 6. The same remnants of the old cracks are clearly visible in a photograph of the Vostok ice core published by Schneider (1989).

The visible and invisible cracks, both in the shallow and deep cores, are an important factor influencing the CO_2 content and isotopic composition of gases recovered from the gas inclusions.

CONTAMINATING DRILLING FLUIDS

In a classic paper on the CO_2 content of the Vostok core there is no information given on the method of drilling, and on its eventual effects on the state of the ice core (Barnola et al., 1987). The reader is not informed that the core was thermally drilled with a hydrocarbon liquid used in the borehole as a wall- retaining fluid (Kudryashov et al., 1984b). This 'drilling fluid' consisted of a mixture of a regular military airplane fuel 'TS-1', and a 'loading material' composed of trichloroethylene, tetrachloroethylene and 'Khladon-II' added for density regulation and antifreeze purposes (Kudryashov et al., 1984a). According to Gielo-Klepacz (1991), 'Khladon-II' is the ethyl ether of ethylene glycol ($CH_3–CH_2–O–CH_2–CH_2–OH$), heavily contaminated with Zn (dissolved from containers), and 'TS-1' fuel is contaminated with resins, sulfates, inorganic acids, alkalies (NaOH and KOH), traces of metals and suspended particulates. About 0.3 mg KOH per 100 ml is usually needed to neutralize the acidity of the 'TS-1' fuel.

As may be inferred from Koudelka (1964a,b), due to the highly increased solubility of CO_2 in mixtures of organic solvents, the drilling fluid is probably enriched in CO_2 from the atmosphere. This fluid, mixed with meltwater, transferred external pollutants into the Vostok core.

CONTAMINATED ICE CORES

The traces of hydrocarbon drilling fluids contained in the macro- and micro-cracks of the ice cores may be counted as CO_2 in the gas chromatograph in which a flame ionization detector converts CO_2 to methane (Stauffer et al., 1981). A proportion of the hydrocarbons entering the sample chamber will be converted to methane by cracking. This methane will mix with the methane formed from the CO_2 and give apparently higher readings.

The solubility of CO_2 in mixtures of water and organic solvents present in the drilling fluid is even higher than in the pure solvents (Koudelka, 1964a,b). Therefore, one may expect both decreases and increases of CO_2 in air recovered from the ice cores, depending on the spatial patterns and history of contamination with drilling fluid.

Some of the cracks in the Vostok core, even when annealed, were identified because they contained traces of drilling fluid (De Angelis et al., 1987). These authors tried to decontaminate the core, first by an ultrasonic bath with acetone at −15°C, and then by rinsing the samples with ultrapure water 'until all fractures were removed'. Legrand et al. (1988, 1991) reported that 50–90% (sic!) of the ice core were eliminated during a 'cleaning' procedure in which the temperature of the water was about 20°C. As indicated by field and laboratory observations, such a procedure must lead to a dramatic redistribution and removal of the bulk of impurities from the ice samples with the meltwater. Up to 80% of H^+, nitrates, sulfates and heavy metals may be contained in the first 30% fraction of water released by melting; this is also accompanied by a differentiation process, releasing some ions more quickly than others (Gjessing et al., 1976, 1991; Gjessing, 1977; Johannessen et al., 1977; Davies et al., 1982), and will lead to dramatic changes in the stable isotope ratios of the remaining ice (Segalstad and Jaworowski, in preparation).

The analytical results from such cores, subjected first to contamination by highly polluted drilling fluids and then to such cleaning procedures, were often used for paleo-climatological interpretations (e.g., Legrand et al., 1988; Petit et al., 1990). However, they cannot be regarded as representing the original chemical composition of the ice.

An indication of the magnitude of drilling effects on the chemical composition of ice cores is the finding that Pb and Zn concentrations in the Vostok core decreased by a factor of about 10 000 and 400 000, respectively, between the surface and the center of the core (Boutron et al., 1987, 1990). The concentrations of Pb and Zn in surface East Antarctic snow are similar and low (Table 3). But in the Vostok core the concentrations of Pb were found to be one to two orders of magnitude lower than the concentrations of Zn, and were 1000 and 10 000 times higher than in surface snow. In the core sections from about 2026 m depth the concentrations of Pb were found to be 31 400 pg/g, and those of Zn 300 000 pg/g. Even ~3 cm inward from the surface of the Vostok core the Pb content was more than 1000 times above the level at its center (Boutron et al., 1987). In some Vostok core sections the Pb concentrations were decreasing towards the center of the core, without showing plateaus (Boutron et al., 1988). According to Boutron et al. (1988) 'contamination has penetrated to the very center of the Vostok core either during drilling, transport and storage and/or during mechanical decontamination in the laboratory'. Other cores from shallower depths, recovered without drilling fluid, were less contaminated with Pb and Zn than the Vostok core (Table 3).

Non-heavy-metal pollutants also contaminated the Vostok core. Even in its central parts the concentrations of SO_4^{2-}, Na, and Al were one to two orders of magnitude higher than in the surface snow, as seen in Table 4.

TABLE 3

Concentrations of Pb and Zn in surface snow and contaminated ice cores from East Antarctica (pg/g)

	Pb		Zn	
Surface snow	30[a]		5.5–10[c]	
Ice cores	Part		Part	
	Outer	Central	Outer	Central
With drilling fluid				
Vostok (499 m)	20 640	38[b]	100 000	33[c]
Vostok (2026 m)	31 400	20[b]	300 000	22[c]
Without fluid				
D-55 (10 m)	198	3[d]		
Dome C (500 m)	668	3.8[e]	1800	14.3[c]

[a] Boutron (1980).
[b] Boutron et al. (1987).
[c] Boutron et al. (1990).
[d] Boutron and Patterson (1983).
[e] Boutron et al. (1988).

The highest contamination of the inner parts of the Vostok core with Pb, Zn, Al and Na were reported by Boutron et al. (1987, 1990) for a depth around 500 m, from where extensive cracking was reported (Legrand et al., 1988); and for a depth near 2000 m, where no visible fractures were found (Boutron et al., 1987), but where micro-cracks are larger and more numerous

TABLE 4

Concentrations of SO_4^{2-}, Al and Na in surface snow from Antarctica and in central parts of contaminated Vostok ice core (ng/g)

	SO_4^{2-}	Na	Al
Surface snow[a] (South Pole and Adelie Land)	19–62	4–44	0.25–0.80
Vostok core[b] (499–2026 m depth)	94–206	9–197	3–82

[a] Boutron et al. (1990).
[b] Boutron et al. (1987).

(Gow, 1971). This indicates that contaminants penetrated via the microfractures or the natural capillary network of liquid at the moment of drilling or soon after, i.e. during pulling of the core and before the fractures were 'healed'.

The high Al content at these two depths of the Vostok core were regarded by De Angelis et al. (1987), Petit et al. (1990) and Jouzel et al. (1990) as a dust index (they assumed that Al represents 7% of dust composition), and interpreted as indicating climatic changes. In the light of the foregoing discussion such an interpretation does not hold, as it is obvious that the Al content was due to contamination of the cores. Dramatic decreases in CO_2 content were reported to occur at the same two depth regions of the Vostok core.

Such a distribution of metal concentrations in the cores is obviously caused by contamination from drilling fluid and mechanical devices. However, radial redistribution of impurities in ice cores may also occur due to thermal gradients developing during drilling, transportation, storage, and handling of the cores in the laboratory. During thermal drilling at the Vostok station the original temperature of the ice in the core ranged between −35 and −57°C, but the core surface was exposed to a temperature near +100°C (Kudryashov et al., 1984a) and then cooled again to about −57°C. Post-drilling operations may increase the temperature of cores close to 0°C or more (Boutron and Patterson, 1983; Pearman et al., 1986). Thus the total thermal gradients in the Vostok core may reach up to about 150°C!

Redistribution of major ions, acids and several inorganic radioactive tracers was observed in firn and ice samples exposed to a thermal gradient of −21 to −1°C (Jaworowski et al., 1990b). Also, Satow and Watanabe (1985) observed substantial changes in the isotopic composition of oxygen in a block of Antarctic firn after it was exposed to a small thermal gradient in the laboratory.

This discussion indicates that attempts to find the 'true' concentration of gases, metals, or other substances in deep ice cores, must be regarded as a very difficult and rather unreliable exercise. The reason is that all deep ice cores have been exposed to high contamination, thermal gradients and structural disturbances.

DISCREPANCIES IN DEEP CORE DATA

The CO_2 concentrations found in air bubbles and in secondary air cavities of deep Vostok and Byrd cores range between 178 and 296 ppm, i.e. much below the current atmospheric level. These values were interpreted as representing the real composition of the ancient atmosphere and past climatic changes. This would mean that the current level of this gas, about 350 ppm, is a new and unique phenomenon, and that during the past 160 000 years the atmospheric CO_2 level never approached the current value, not even some 65 000 and 110 000 years ago when the global sea-surface temperature was 2–3°C higher than now (Shackleton and Opdyke, 1973; Ruddiman, 1985; Ruddiman and Raymo, 1988), or 6000 years ago when the air temperature between 60 and 75°N was 4.5°C higher than now (Zubakov and Borzenkova, 1990). If this low ancient CO_2 atmospheric level were true, it would mean that this gas had no influence on past climatic warmings, and that these warmings did not increase its atmospheric level by, for example, degassing from a warmer ocean.

There are numerous contradictions between the isotopic and CO_2 records from deep Antarctic and Greenland ice cores. For example, glacier isotopic data have been taken to indicate that the present warmer period occurred in Antarctica several thousand years earlier than in the Northern Hemisphere (Radok, 1985). This is obviously not a realistic estimate. The rapid variations of CO_2 concentrations of 50–70 ppm, observed by Stauffer et al. (1984) in Dye 3 and Camp Century (Greenland) ice cores from a period 30 000 to 40 000 years B.P., are not similar to the much smaller variations in the Antarctic Byrd cores (Neftel et al., 1988; Oeschger et al., 1988) or Vostok cores (Barnola et al., 1987).

$^{13}C/^{12}C$ ratio in the carbon dissolved in the deep ocean was lower during the glacial than interglacial times, suggesting higher atmospheric CO_2 content during the glacial time (Shackleton, 1977). This is contrary to the ice core data indicating that the atmospheric level of CO_2 was substantially lower in the glacial period than today. To increase the CO_2 content from 200 ppm in the glacial period to 275 ppm in the interglacial by warming the surface ocean would require a 10°C increase in sea surface temperature. However the faunal record in ocean sediments indicate that the interglacial sea surface temperature warming was only 1.7°C Broecker and Peng, 1986). We agree with Broecker and Peng's statement that 'one way out of this dilemma would be to challenge the validity of the ice-core-based glacial to interglacial atmospheric CO_2 change'.

The reduction in the atmospheric concentration of CO_2 during the last glaciation, deduced from ice core measurements, was explained by more efficient 'biological pumping' of carbon into deep oceanic waters, due to increased bioproductivity of the ocean (Martin, 1990). However, records of the accumulation rates of diatom shells, the ratio of germanium to silicon in diatomacous opal, and the carbon isotope ratio in foraminiferal carbonate indicate lower productivity during the last glaciation (Mortlock et al., 1991). According to Barnola et al. (1987) the levels of CO_2 in the global atmosphere during many tens of thousand of years spanning 30 000 to 110 000 B.P. were below 200 ppm. If this were true then the growth of C_3 plants should be limited at the global scale because their net photosynthesis is depressed as the CO_2 concentration in air decreases to less than ~250 μbar (less than ~250 ppmv) (McKay et al., 1991). This would lead to the extinction of C_3 plant species. This has, however, not been recorded by paleobotanists (Manum, 1991).

Stauffer et al. (1984) noticed a serious discrepancy in their own analytical results from Dye 3 (Greenland): a lack of lag between their CO_2 and $\delta^{18}O$ data which should be observed if the results were representing the ancient atmosphere.

According to Fairbanks (1990) the assertion based on the $\delta^{18}O$ anomaly in the Dye 3 (Greenland) ice core that the climate during the Younger Dryas (10 000 to 11 000 years B.P.) rapidly shifted (within less than a century) into and out of 'glacial conditions' has been repeated so often that many believe it has been firmly established. This author, however, found from corrected ^{14}C data that the end of the $\delta^{18}O$ anomaly in Dye 3 is neither correlative with the end of the Younger Dryas climatic event identified in pollen records as marking vegetation changes in Europe, nor with its dating based on marine faunal indices. Also, data from the Byrd core (Antarctica) do not show the rapid $\delta^{18}O$ changes indicating warm periods (Oeschger et al., 1988). Robin (1985) pointed out that the paleotemperature changes reconstructed from the Vostok ice dated 106 000 to 116 000 B.P. do not agree with other ice, marine and terrestrial data.

Perhaps even more serious is the discrepancy in CO_2 data for Antarctic cores from the Byrd and Vostok stations. The first important decrease in CO_2 concentrations occurred in the Byrd core between about 500 and 600 m depth (Neftel et al., 1982), and in the Vostok core at a similar depth of about 400 m. But the assigned age of the ice in both these cores is totally different: 1500–1600 years B.P. in the Byrd core and 18 000 years B.P. in the Vostok core. The second CO_2 decrease, of about 50 ppm, occurred in the Byrd core in a region between 950 and 1200 m depth, where the age of the ice was about 8000 to 14 000 years B.P. In the Vostok ice of this age (at about 250–300 m depth), CO_2 concentrations were rather stable, and in the ice deposited 12 000 to 16 000 years ago were higher by about 60 ppm than in the Byrd core. On the other hand, at a depth of about 1100–1150 m the CO_2 concentrations were similar in the Byrd and Vostok cores (about 235 ppm), although the assigned age of the ice differed by about 65 000 years.

An ad hoc attempt to explain some of these discrepancies by Oeschger et al. (1988) by: (1) 'a process which has not yet been identified', (2) wrong modelling, and (3) 'not overlapping time intervals, perhaps due to rheological irregularities', is ambiguous and inconclusive.

All these similarities and differences are rather fortuitous, as they are due to artifacts in the ice sheets and in the ice cores. In some cases these artifacts have a random distribution, but they may also depend on processes related to depth in the ice sheet, and therefore show some regularities.

AGE OF AIR IN ICE

The validity of the hypothesis that the age of the occluded air is younger than that of the ice matrix is of crucial importance for the estimates of CO_2 levels in the pre-industrial atmosphere. This hypothesis was proposed by Berner et al. (1980) who assumed that for Greenland the typical age difference is 200 years. The hypothesis was then accepted by Craig and Chou (1982) who assumed that the air trapped in ice at 68 m depth at Dye 3 (Greenland) is 90 years younger than the age of the ice. Schwander and Stauffer (1984) elaborated the hypothesis and estimated the age difference for eight Greenland and Antarctic sites ranging from 90 to 2800 years. It should be noted that the hypothesis is purely speculative, neither based on experimental nor empiric evidence, and has an ad hoc flavor.

The hypothesis was based on the assumption that the air in the porous firn strata is well mixed with the atmosphere at least down to the beginning of the firn–ice transition. Furthermore, it was assumed that air trapped in the ice sheets is isolated from the atmosphere only after a complete enclosure of air bubbles, at an ice density of 0.83 g/cm^3. At the Antarctic ice sheet this density is reached between about 50 and 100 m depth (Gow, 1968a; Watanabe et al., 1978; Barnola et al., 1987). To satisfy this assumption the condition is needed that the whole firn column, down to the density level of 0.83 g/cm^3, is devoid of layers impermeable to air. It was believed that this condition can be met at the cold Antarctic sites with mean annual temperatures of about −24°C, where, as was assumed, no summer melting occurs. This supposition is not true, as radiational melting was observed in Antarctica even at locations with summer temperatures near −20°C (see section Liquid in Ice), and the existence of thick melt layers and thin ice crusts was reported from many Antarctic localities (the Siple, Byrd, Mizuho and Vostok stations) with mean annual temperatures ranging from −24 to about −57°C.

At the Siple station (mean annual temperature −24°C), Neftel et al. (1985) reported the existence of one 10-mm thick melt layer at a depth of 7 m. But from the Siple Coast (mean annual temperature −26.5°C) Alley and Bentley (1988) reported nine melt layers, some of them more than 20 mm thick, distributed randomly in a 100 m deep core. At the Byrd station, hundreds of thin ice layers were reported from several cores by Gow (1968a). At this site, layers of bubble-free ice, up to 1 mm thick, were reported to occur in the firn with a frequency ranging from one to eight layers per meter. These ice crusts could be identified in cores from as deep as 240 m (Gow, 1968a). Several refrozen melt layers up to 100 mm thick were observed in the Byrd core at between 1300 and 1700 m depth (Gow, 1970).

One of the proponents of this hypothesis stated that 'the ice layers do not cover a large region continuously but are more or less frequently interrupted by holes or dislocations. According to my knowledge, there exist no extensive investigations on the geometry of ice layers' (Schwander, 1989). But meticulous Japanese studies, covering a vast Antarctic region, indicate the opposite.

At the Mizuho station, Watanabe et al. (1978) observed ice layers with a frequency of about 5 to 15 per metre down to a depth of 110 m. A stratigraphic study of several meters thick upper firn strata at 38 sites in Enderby Land (Northeastern Antarctica) was carried out by Watanabe (1977) along a traverse reaching about 1200 km inland and an altitude up to 3382 m, where the average annual air temperature is –48°C. This study demonstrated that ice layers are ubiquitous within the Antarctic ice sheet. They form a complex multilayer structure in which merging neighboring layers separate firn in horizontal pockets (Fig. 8). Watanabe (1977) found that the ice layers maintain their continuity along the whole studied cross-section of firn, and that they continue horizontally for at least several tens of kilometers (Watanabe, 1978).

In a 6 m deep snow and firn layer at the Vostok station, eight sun ice crusts and 19 wind crusts were found by Kotlyakov (1961). A well-defined stratification was also observed in the Vostok core down to several tens of meters below the surface (Korotkevich et al., 1978).

In the top 200 cm of firn at a site at Dronning Maud Land (Antarctica), where the mean annual temperature is about –19.2°C (Orheim et al., 1986), Repp (1978) found several 1–2 cm thick ice layers, some of them clustered together to a total thickness of 6 cm.

In very cold regions, thin sun ice crusts, about 1 mm thick, form near the surface of the firn due to insolation and refreezing of water vapor, evaporated or sublimated from ice crystals below. The vapor migrates upwards along the decreasing temperature gradient, and condenses in the interstices between grains of cold snow at the surface or below a less permeable glaze or sublimation crust. These processes are discussed in detail by Gow (1968a) and illustrated in Fig. 9. The changes in the state of H_2O in these processes have an important impact on the stable isotope, elemental and molecular composition of ice and of air entrapped in it.

The load pressure in the firn forces the air up through the leaks in the thin ice layers. This permanent upward stream of air prevents atmospheric air from penetrating downwards through the laminated structure of firn.

As proof of the 'age of air' hypothesis, Schwander and Stauffer (1984)

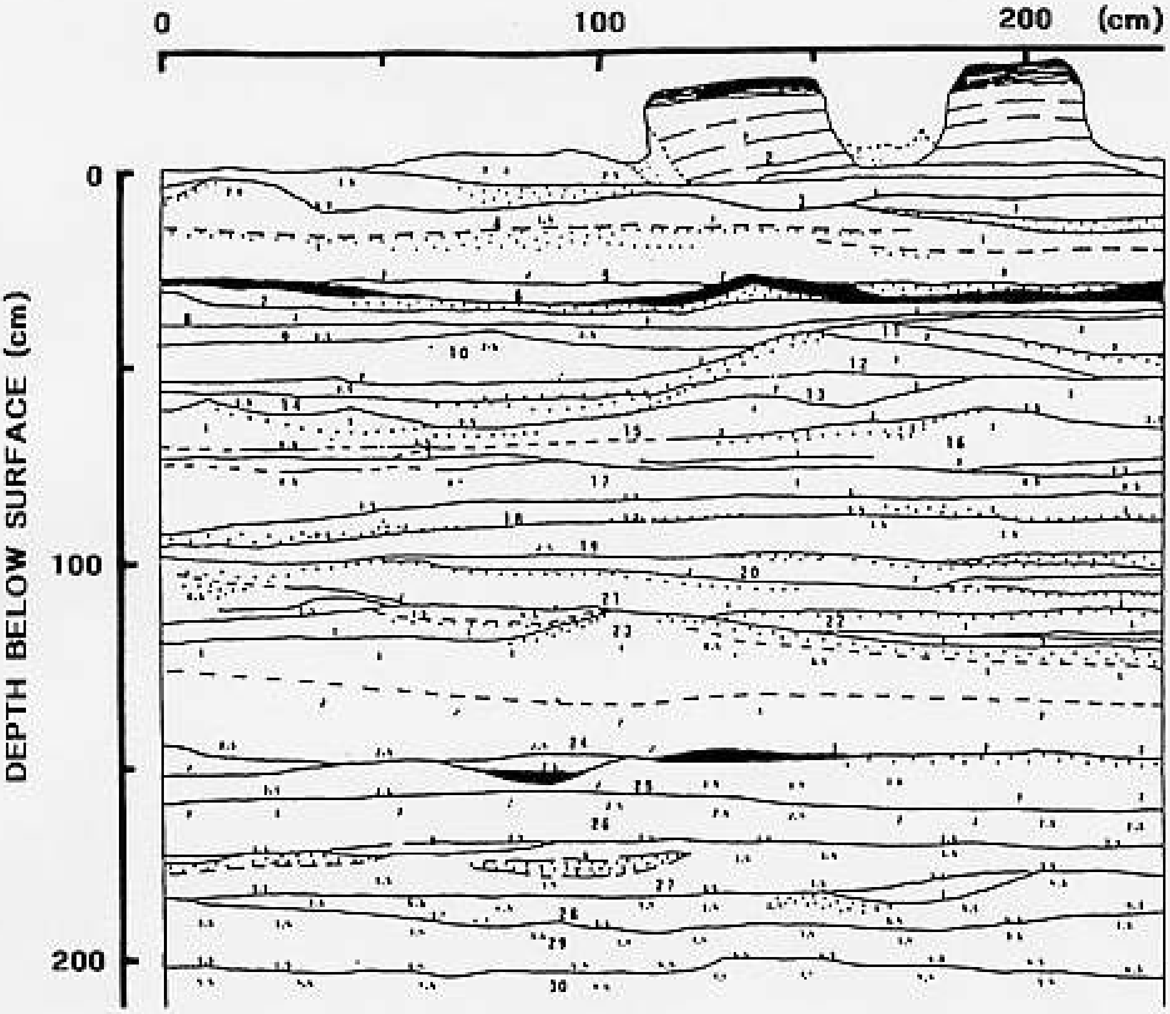

Fig. 8. Firn stratigraphy in a pit at the Mizuho Plateau, West Enderby Land (East Antarctica) at an altitude of 3386 m a.s.l.; average annual temperature –48°C. Thin solid lines indicate the numerous ice crusts in firn. Adapted from Watanabe (1977).

cited measurements of radioactive atmospheric trace gases in polar ice cores of Loosli (1983), and stated that ‘^{39}Ar measurements provide evidence that the air in the open pore volume is well mixed at least down to the beginning of the firn–ice transition’. However, the results in Loosli’s (1983) paper indicate the opposite. At 70 m depth at Dye 3 (Greenland), the age of natural radioactive ^{39}Ar gas trapped in air bubbles was about 70 years, i.e. the same as the age of the ice determined by other methods. Also, at a depth of about 100 m at the Byrd station (Antarctica) the age of the air measured by the ^{39}Ar method was the same as the age of the ice estimated from the precipitation rate (Oeschger et al., 1977). However, all these argon age determinations were highly uncertain, because Loosli (1983) found that all ice samples were contaminated by ambient air, and even in the 3000 years old ice of high den-

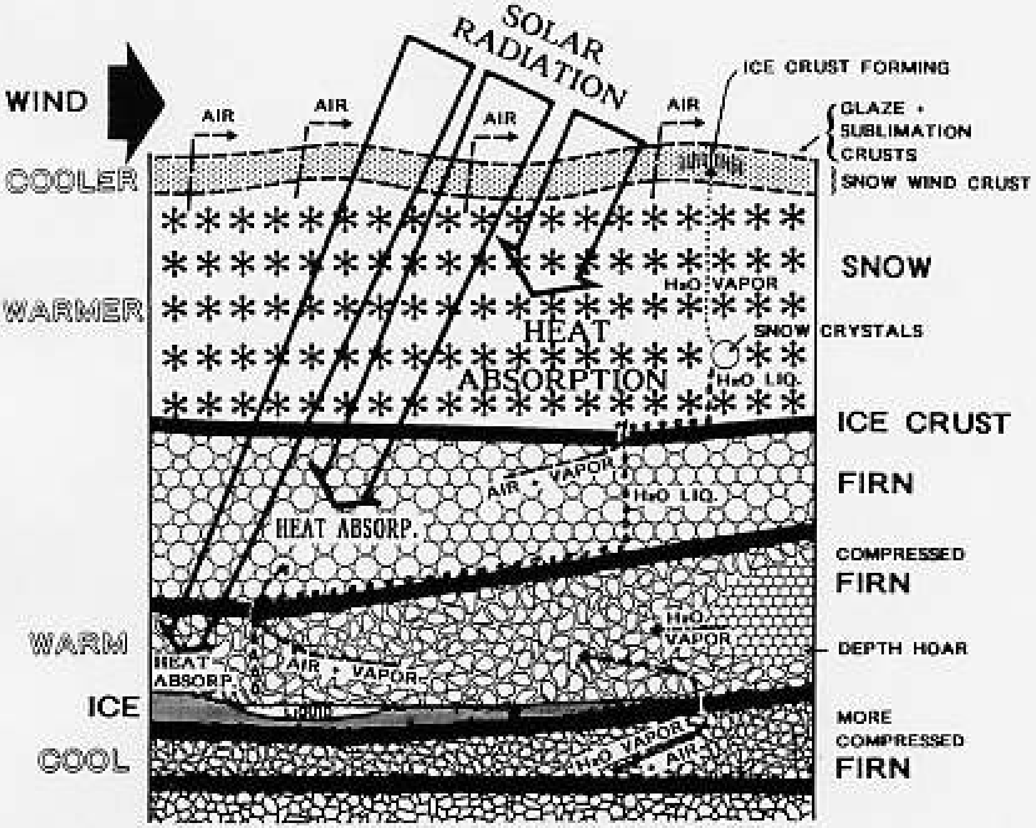

Fig. 9. Schematic illustration of processes occurring in the top 1–2 m of snow and firn strata in cold polar ice sheets (not to scale). Absorption of solar radiation at low temperature partly volatilizes and melts the snow flakes. Snow is metamorphosed to firn. The thermal gradient and gravitational compression of snow cause upward movement of gas. Some air escapes from snow and firn back to the atmosphere, and H_2O vapor condenses near the wind-cooled surface. Depth hoar forms due to loss of material by sublimation. Meltwater seeps down and collects over impermeable layers.

sity, the total measured ^{39}Ar activity has to be attributed to contamination by atmospheric air during field and laboratory processing. By measuring ^{85}Kr, a radioactive gas produced in nuclear reactors and bomb explosions, Loosli (1983) demonstrated that up to 36% ambient air was found in gas samples extracted from ice cores. These cores were stored for about 8–13 years before analysis, and exposed to the ambient atmosphere.

This finding has an important implication. It indicates that unsealed ice cores, such as those used for CO$_2$ and stable isotope measurements, are contaminated by ambient air. Some of these cores were even exposed to cigarette smoke (Jaworowski et al., 1990a), which indicates that contamination problems are not seriously considered in gas analysis of ice cores.

Discussing the age of entrapped air, Schwander (1989) did not quote Loosli (1983), and stated instead, incorrectly, that 'at present no data from [radioactive atmospheric] tracer methods are yet available'. He also, rightly, did not quote the circular argument of Neftel et al. (1985) that the same concentrations of CO_2 found in the recent South Pole atmosphere and in air bubbles trapped in nineteenth century Antarctic ice prove that air from bubbles is 82 years younger than the ice. This finding suggests rather that the atmospheric CO_2 concentration 82 years ago was the same as now.

Craig et al. (1988a) revoked their earlier assumption that trapped air at Dye 3 is 90 years younger than the ice in which it is sealed (Craig and Chou, 1982). They stated that results of their isotopic measurements of methane recovered from the Greenland ice 'preclude such a large difference in age'.

Craig et al. (1988b) observed enrichments of ^{15}N and ^{18}O isotopes and of N_2 and O_2 in air trapped in polar firn strata effects resulting from molecular diffusion and other processes. This strongly indicates that the air in porous firn is protected from convective and other motions.

The above discussion demonstrates that the hypothesis that entrapped air is much younger than the ice enclosing it disagrees with glaciological evidence. In polar ice sheets, the air in firn is isolated from the atmosphere by several hundred thin ice layers, before the firn pores close off completely at the firn–ice transition. This means that the age of the gas in a primary air bubble is approximately the same as the age of the ice that encloses it.

This hypothesis was posed at the time when the CO_2 concentration in air bubbles from ice deposited in the nineteenth century or earlier was found to be similar to the current atmospheric level. The ad hoc hypothesis was needed to make this finding consistent with the man-made global warming paradigm. This is shown in Fig. 10a, which illustrates that the CO_2 concentrations in pre-industrial ice from Antarctica were made to overlay exactly the recent atmospheric concentrations at Mauna Loa (Hawaii) (Siegenthaler and Oeschger, 1987).

Figure 10a was prepared in connection with 'model calculations that are based on the assumption that the atmospheric [CO_2] increase is due only to fossil CO_2 input' and other human activities. The curve in this figure is based on data of Neftel et al. (1985) and Friedli et al. (1986) from the Siple ice core, which was partially melted during transportation. The overlaying was done after assuming that the age of the air is 95 years younger than the ice. However, as shown in Fig. 10b, without this speculative assumption the Mauna Loa and Siple data do not overlay. Rather than representing past atmospheric changes, the ice CO_2 concentrations in the Siple core decrease with increasing load pressure up to about 15 bars, due to clathrate formation, differential dissolution of gases in the liquid water at the surface of ice crystals, and other processes in the ice sheet and in the ice core. As discussed above, studies at other locations, carried out before 1985, recorded higher CO_2 levels in air from pre-industrial ice than in that from both the Siple core and at Mauna Loa.

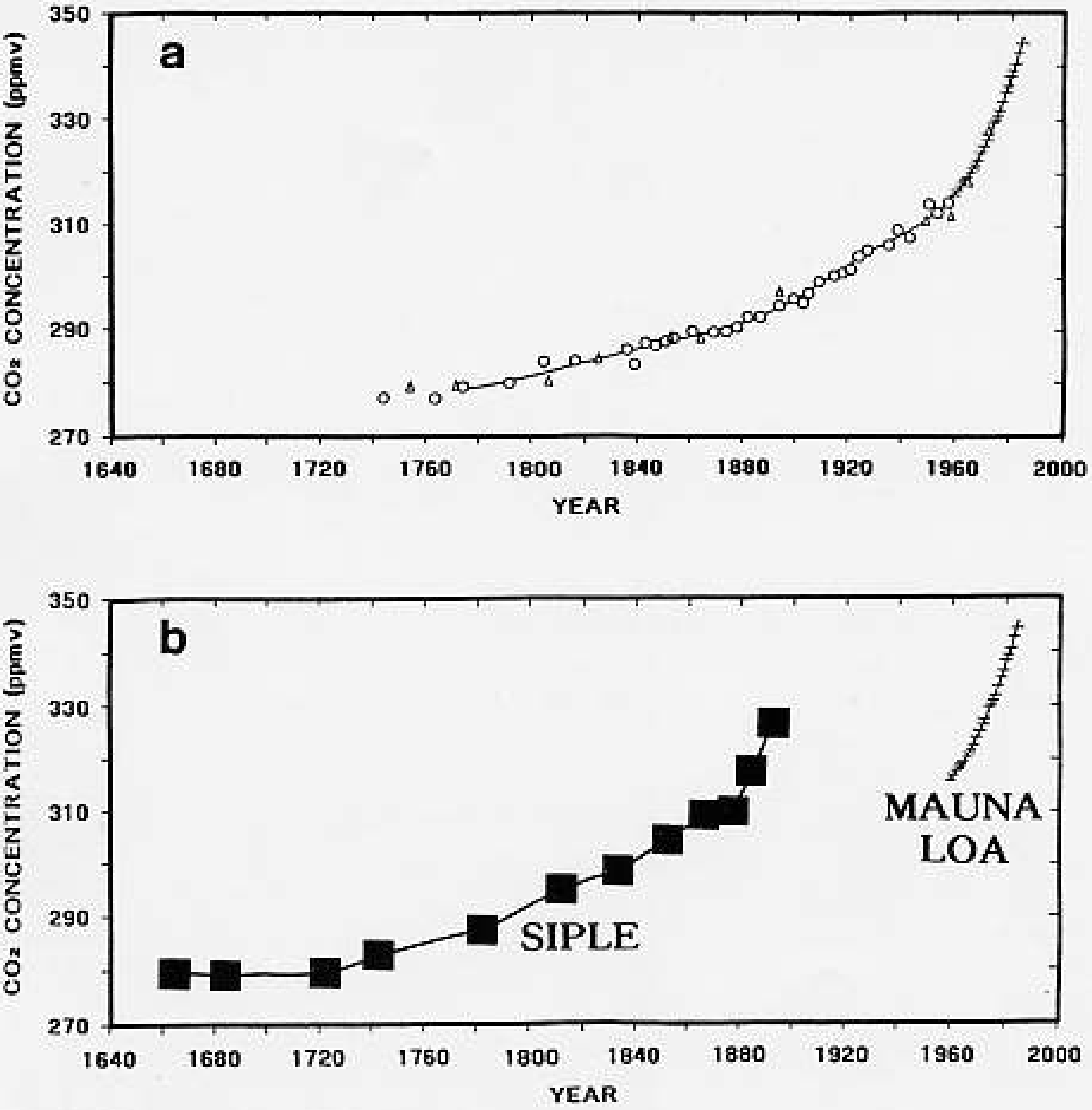

Fig. 10. Concentrations of CO_2 in the Siple (Antarctica) ice core: (a) with, and (b) without assuming a 95-year younger age of air than the age of the enclosing ice. The crossed line represents the reported atmospheric CO_2 concentrations at Mauna Loa (Hawaii). The reported analytical uncertainty, ≥ ± 3 ppm, is larger than the size of the data points. The core was partially melted during transportation (Etheridge et al., 1988). Without assuming the age difference, the Siple and Mauna Loa curves cannot be made to overlay each other. (a) Adapted from Siegenthaler and Oeschger (1987) and Bolin et al. (1989); (b) from Fig. 3.

Figure 10a was reproduced in countless publications and used as proof that the burning of fossil fuels, deforestation and changing land use by man have changed the global carbon cycle very significantly during the last two centuries. The figure was used as the basis for other speculative estimates of changes in the global carbon cycle (e.g., Bolin et al., 1989). It is in this context that one should note that Fig. 10a does not represent real CO_2 changes in the global atmosphere, but rather processes in the ice sheets, artifacts in the partially melted ice core, and unsubstantiated assumptions on the age of air inclusions. It is astonishing that such non-representative and misleading data have been so widely and uncritically accepted.

CHANGES IN THE CHEMICAL COMPOSITION OF TRAPPED AIR

The trapping of CO_2 in glaciers starts in the atmosphere when this gas associates with snowflakes by dissolution in water droplets prior to freezing and in a liquid present at the surface of the flakes, and by adsorption onto crystal surfaces. A liquid containing sulfuric acid is incorporated into snow crystals as a film on a solid nucleus or added by riming, and it is expected to remain as a liquid on the outside of the ice grain crystals (Wolff et al., 1988). About 2–3% (by weight) of supercooled liquid water may be mixed within the entire mass of snowflakes (Matsuo and Miyake, 1966). The mechanisms of in-cloud and below-cloud scavenging of gases by supercooled water were reviewed by Davidson (1989).

The presence of liquid water in polar ice sheets is supposedly the main factor involved in suppressing the seasonal acidity peaks in Pleistocene ice (Hammer et al., 1985), and in rapid smoothing in the upper strata and obliteration of δD and $\delta^{18}O$ short-term variations in ice older than 10 000 years (e.g., Langway, 1967; Dansgaard, 1977; Johnsen, 1977; Grootes et al., 1990).

Dissolution and adsorption of CO_2 continues after deposition of snow on the glacier. Due to large solubility differences of particular air gases, the composition of air trapped within snow changes at this early stage and during firnification. At high pressures deep in the ice sheets, the equilibrium pressures of gases dissolved in water increase at different rates, and are higher for CO_2 than for other air gases (Enns et al., 1965). Therefore, one may expect that the composition of the air trapped in firn and ice will be different from that in the atmosphere: the air in the whole ice will be enriched in CO_2; the air in voids of firn and in ice bubbles will be depleted in CO_2; and the O_2/N_2 and Ar/N_2 ratios will be changed in the whole ice and in the air bubbles.

Several in situ processes in the ice sheets and in the cores cause changes in the composition of entrapped gases. Both types of processes depend on pressure and temperature varying with depth in the ice sheets. Therefore, one may expect that these changes should reveal some regularities at a greater vertical or temporal scale. At a smaller vertical scale, of the order of a few meters or centimeters, and also at the same horizons, one should expect a random distribution of these changes.

These processes usually lead to a low CO_2 content of voids in the firn and bubbles in the ice. They were also reflected in large local fluctuations in CO_2 concentrations in air bubbles collected from a 30 cm long ice core from Dome C (Antarctica), where annual precipitation is 3.6 cm water equivalent. The precision of determinations was 3%. The ice samples (1–2 g) were taken from 1.5 cm thick slices of core, i.e. about two slices per year of ice accumulation. The concentration of CO_2 fluctuated by more than 13% (32 ppm) between neighboring slices, and by about 10% (25 ppm) in the same slice (Barnola et al., 1983). As mentioned before, these fluctuations are twice as high as the 'CO_2 glacier signal' used in support of claims of anthropogenic increase of this gas, and they certainly do not reflect the atmospheric fluctuations in the same year.

Oeschger et al. (1985) stated that various processes could lead to insignificant CO_2 enrichments in ice of not more than 10 ppm, and that 'the analysis of the $N_2/O_2/Ar$ ratios in ice originating from very cold areas with no summer melting shows that, within experimental uncertainty, the measured ratios agree with those in air' (Raynaud and Delmas, 1977). But Raynaud and Delmas (1977) interpreted their analytical results from the Pionerskaya and Vostok stations differently: 'par rapport a la composition atmospherique ... les effets observes sont donc faibles mais significatifs et indiquent un appauvrissement relatif des teneurs en O_2 et Ar'. In the interstitial air pumped from the upper firn layer at these two stations, Raynaud and Delmas (1977) found negative enrichment, corresponding to $\Delta O_2/N_2$ and $\Delta Ar/N_2$ values of –5.3 and –0.11‰ in comparison with the free atmosphere. As mentioned before, they also found CO_2 depletion of about 90 ppm in interstitial air from recent firn at Vostok and 170 ppm at Pionierskaya.

Large negative and positive enrichments of heavy gases' (O_2 and Ar) ratios to N_2 were reported by Craig et al. (1988b) in air recovered from Antarctic and Greenland cores. The values for $\Delta O_2/N_2$ ranged from –14 to +3.5‰ and those for $\Delta Ar/N_2$ from –7 to +4.2‰. The authors suggested that differential capillary flow during the loss of gas from core samples via micro-cracks is responsible for this effect.

In the early studies it was found that the concentration of O_2 in ice from Greenland and Antarctica decreases with depth, and that the concentration of N_2 increases (Lorius et al., 1968; Alder et al., 1969). This may be due to gravitational separation of heavier and lighter gas molecules (O_2, mol. wt = 31.9988; N_2, mol. wt = 28.0134) in the porous firn.

Also, Horibe et al. (1985) found negative enrichment for $\Delta O_2/N_2$ and $\Delta Ar/N_2$ in an ice core from Camp Century (Greenland). These authors reported depletion of oxygen by up to 1.5% in air bubbles trapped in the 20 000 years old ice in comparison with the ambient atmosphere; the depletion increased with depth in the ice sheet between 559 and 1248 m.

The results of measurements of N_2, O_2, Ar and CO_2 trapped in ice, compiled in Table 5, indicate that the composition of air in the whole ice and in the air bubbles differs greatly from that in the atmosphere, both in temperate glaciers and in polar ice sheets.

TABLE 5

Composition of air in the atmosphere and in glacier ice

Site and reference	N_2 (%)	O_2 (%)	Ar (%)	CO_2 (ppm)
Atmosphere	78.08	20.95	0.934	330
Greenland (Scholander et al., 1961)				
Single bubbles		22.8 -38.2		
Ice[a]		19.7 -21.5		
Antarctica (Matsuo et al., 1966)				
Shirase Gl. ice	78.3	20.7	0.93	280
Breidvågnippa Gl. ice	73.2	25.3	1.22	2900
Antarctica (Lorius et al., 1968)				
Terre Adelie[b] ice	78.29 -79.66	19.46 -20.73	0.905 -0.935	80 -320
Greenland (Alder et al., 1969)				
Camp 3[c] ice	79.79 -86.41	13.06 -19.34	0.53 -0.85	
Alps (Weiss et al., 1972)				
Jungfraujoch[d] ice	78.08	20.90	1.02	
Greenland (Raynaud and Delmas 1977)				
Camp Century[e] ice	78.11 -78.51	20.55 -20.81	0.936 -0.953	1700 -7400
Antarctica (Raynaud and Delmas, 1977)				
Byrd St.[f] ice	78.25 -78.60	20.45 -20.81	0.932 -0.947	900 -1800
Pionerskaya St.[g]	See text			160
Vostok St.[g]	See text			240
Greenland (Stauffer et al., 1985)				
Dye 3[h] ice	63.00 -75.62	22.74 -32.50	1.05 -1.65	4070 -28 000

TABLE 5 (*continued*)

Site and reference	N_2 (%)	O_2 (%)	Ar (%)	CO_2 (ppm)
Greenland (Horibe et al., 1985)				
Camp Century bubbles[i]		20.59 -20.66		
Greenland (Clausen and Stauffer, 1988)				
Camp 3[j] ice	80.7	18.4	0.83	
Crête	78.1	20.8	0.97	

[a] Ice = in whole ice.
[b] Upper 30–50 m.
[c] Upper 0–1 m.
[d] Tunnel in old ice.
[e] From 108.5–1345 m depth.
[f] From 71–300 m depth.
[g] Interstitial air, 0–1 m depth.
[h] 0–34.5 m depth.
[i] In air bubbles.
[j] ~2–21 m depth at Camp 3 and ~400 m at Crête (Clausen, 1990).

LIQUID IN ICE

Faraday (1850) postulated that a thin water layer exists on ice surfaces at temperatures below the melting point. Later it was found that snow and ice consist of crystals, separated by thin films of intercrystalline brine, which contains soluble impurities (Buchanan, 1908). But it was only recently recognized that this phenomenon also occurs at very low temperatures.

Large numbers of under-ice puddles of meltwater were found in Antarctica at a depth of 10–20 cm below the surface of sea ice. The puddles, up to 70 cm deep, were formed at a mean air temperature of -2°C, and the temperature of meltwater under the ice cover in the puddles reached up to +10°C. The mode of formation of the puddles suggested that the cause of their formation was sun radiation absorbed in the interior of the ice (Endo, 1970).

In Dronning Maud's Land (Antarctica) a firn layer, soaked with liquid water, was observed at a site where the average annual temperature is about -19°C (Repp, 1978). Large amounts of meltwater were also found in ponds at a depth of about 1 m under the ice surface in Dronning Maud Land, at an altitude of about 1200 m, where the summer air temperature was below -20°C (Hagen, 1991). This phenomenon may contribute to the formation of impermeable layers in the firn in very cold regions of Antarctica and to the redistribution of CO_2.

Field observations have shown the existence of unfrozen water in porous media at temperatures between -30 and -50°C (Anderson and Morgenstern, 1973). This has been attributed to various mechanisms, including dipolar forces, density variations and pressure melting of ice (Dash, 1989).

Thermodynamic models suggested that a layer of a definite thickness, with properties similar to those of the surface of liquid water, exists at the surface of ice crystals to a temperature of -15°C (Fletcher, 1973). Nye and Frank (1973) proposed that liquid water in ice is located at the triple junctions between the crystals which form an interconnecting network in the ice. The presence of a quasi-liquid layer on the surface of ice crystals at a temperature of about -35°C was postulated by Orem and Adamson (1969) on the basis of N_2 adsorption studies. Also, Ocampo and Klinger (1982) deduced from CO_2 adsorption onto ice that the ice surface is covered by a quasi-liquid layer at temperatures above -35°C.

The existence of a quasi-liquid in ice was detected by proton magnetic resonance spectroscopy. With this method Kvilidze et al. (1970), Bell et al. (1971) and Kvilidze et al. (1974) demonstrated that liquid water is present in ice down to temperatures of about -13°C. Photoemission studies with ultraviolet radiation (Nason and Fletcher, 1975) provided evidence for the presence of a water-like layer on the surface of ice down to -160°C. This layer becomes progressively thinner as the temperature decreases. The thickness of this layer was estimated to range between a few nanometers and a few tens of nanometers (Golecki and Jaccard, 1978). We postulate that such a layer covers the inner surfaces of air bubbles in ice sheets and the secondary gas cavities in ice cores, and that it contributes to the depletion of CO_2 from the gas inclusions and to isotopic equilibration of gases with the ice.

This is in agreement with the observed oxygen isotope equilibration between CO_2 gas inclusions in ice and H_2O observed by Siegenthaler et al. (1988). These authors asked the question whether this could be due to the existence of a liquid-like layer at the air bubble–ice interface.

Maccagnan (1981) and Maccagnan and Duval (1982) proposed, on the basis of direct current conductivity measurements, that the liquid in polar glacier ice is a water–sulfuric/nitric acid mixture, located at the ice grain boundaries. A model study by Wolff and Paren (1984) suggested that these mixtures are located at triple junctions between ice crystals. This vein system may provide a means of draining liquids out of ice sheets.

Liquid sulfuric acid in deeply frozen glacier ice was discovered by Mulvaney et al. (1988). By scanning electron microscopy and X-ray spectra they found that high concentrations of sulfuric acid are located at the triple junctions, but they could not rule out the presence of some liquid in films at two-grain boundaries. This study, performed on 125-year-old ice from the Antarctic Peninsula, indicates that the concentration of sulfuric acid in the veins may range between 2.5 and 4.9 M. At this higher concentration the acid–water mixture may remain liquid down to the eutectic temperature of -73°C. Sulfuric and nitric acids are common impurities in polar ice sheets. Studies by Wolff and Paren (1984) and Mulvaney et al. (1988) indicate that most of these impurities are eliminated from the ice crystal lattice and located as a highly concentrated brine in the intercrystalline veins. As may be seen from a photograph in the paper by Mulvaney et al. (1988) the air bubbles are intersected by these veins and films. This provides conditions for diffusion of gas from bubbles to or from the intergranular liquid.

When alkaline dust neutralizes acids in the liquids contained in ice, the resulting salt–H_2O mixtures may cause freezing point depressions. The extent of the freezing depression is dependent on the types and concentrations of salts in the intercrystalline brines; polyvalent ions will generally depress the freezing point further than monovalent ions (Shepherd et al., 1985). For example, the experimentally determined freezing point depression for the $NaCl–CaCl_2–H_2O$ system was found to reach –51°C at 30.59% salinity (Oakes et al., 1990).

From a low salinity water–salt solution, pure H_2O ice will precipitate with decreasing temperature, hence decreasing the volume and increasing the salt concentration of the brine. In sea ice, for a temperature range of -0.1 to -54°C, a brine volume decrease by a factor of 320 was found by Assur (1958). From nuclear magnetic resonance and chemical analyses it has been found that such a brine can maintain its liquid state down to -70°C (Nelson and Thompson, 1954; Richardson and Keller, 1966; see also review by Weeks and Ackley, 1982). One may expect that, at greater depths in the Antarctic ice sheet, where the temperature increases, for example, by 21°C at 2040 m depth at Vostok (Vostretsov et al., 1984), and by 21°C at 1700 m depth at the Byrd station (Gow and Williamson, 1976), salinity and acidity will decrease as more H_2O enters the liquid phase. This will lead to a volume increase of intercrystalline voids containing brine. As a first approximation, one may infer from the data of Assur (1958) that this volume increase factor could be near 100 at a depth of about 2000 m at Vostok, considering a brine with similar ionic composition as that of standard sea ice.

The depression of the freezing point of brine (salinity 27–35‰) under a load pressure has a slope of about -0.0076°C/bar (Fujino et al., 1974). Therefore, and because of increasing temperature with depth, one may expect that deep in the ice sheet there will be melting of the ice. On a macroscale the brine migrates downward in the ice sheets due to gravity and the density difference between ice and brine. Under a temperature gradient the brine in the veins will tend to migrate toward higher temperatures, i.e. downward, because the brine density will be higher at lower than at higher temperatures (Leeder et al., 1987). The permeable ice acts as a sieve for the brine, thereby redistributing elements, isotopes and micro-particulates.

The drainage may contribute in part to the formation of pockets or lakes of liquid water below ice sheets, observed by radio-echo sounding in Eastern Antarctica (Oswald and Robin, 1973) and near Vostok (Zotikov, 1986). Budd et al. (1971) calculated near basal temperatures of –23.5°C to –26.2°C in the Vostok region. Vostretsov et al. (1984) measured temperatures in the Vostok borehole down to a depth of about 2000 m. Linear extrapolation of these latter data to a depth of 3700 m gives a basal temperature of about –4°C.

Oswald and Robin (1973) reported a marked increase in radar echo strength of 10–20 dB (decibel) as the radar signals moved from the ice to the sub-sheet lakes. The reflection coefficient from an ice–pure water interface would be around –3 dB, while the reflection coefficient from an ice–rock interface would be –14 to –20 dB (Oswald and Robin, 1973). The increased radar echo strength means that the radar signals were reflected from a medium with a much higher conductivity than ice or pure water. This medium could be saline water, moraine, clay, graphite-rich rocks, ore minerals, or a mixture of such materials (Segalstad, 1985). Because the radar echo targets are extraordinarily smooth and have an area of up to 8000 km^2 (Drewry, 1987), they probably represent a substantial layer of liquid water in the form of sub-sheet lakes (Oswald and Robin, 1973).

This water will have to be saline to be such a strong radar reflector. Using the data of Fyfe (1964), Fujino et al. (1974) and Potter (1978) on freezing point depression versus salinity and pressure, one can calculate that for a temperature of –4°C in such lakes the corresponding salinity should be about 4% (weight) NaCl equivalents at the 3700 m basal ice depth at Vostok, under a pressure of about 330 bars. The salt solution is not likely to consist of dissolved NaCl only, but rather a mixture of different dissolved mono- and multi-valent salts.

Gow et al. (1968) detected pressurized liquid water at the ice–rock interface beneath the ice sheet at the Byrd station at a depth of 2164 m. Its chemical composition was not determined, but its specific conductance of 45 μmho/cm^2 was higher than that of melted ice (1.7–3.1 μmho/cm^2).

Changes in salt concentrations influence the solubility of gases in the brine. Yasunishi and Yoshida (1979) found that the solubility of CO_2 in aqueous solutions of electrolytes commonly present in polar ice decreases slightly with increasing concentration of salts. The decreasing salinity and increasing intercrystalline brine volume at great depths in the ice sheet may be partly responsible for the observed variation in the CO_2 content of the gas inclusions from Antarctic cores.

The discovery of a liquid phase in ice at very low temperatures is extremely important. It indicates that, in ice sheets, even in the coldest regions, there is a quasi-infinite network of liquid-filled veins in which dissolved substances and suspended micro-particles can migrate and interact.

The use of Antarctic and Greenland ice cores for studies on the chemical and isotopic composition of the atmosphere of past epochs is based on the assumption that cold polar ice sheets lack a liquid phase. Therefore, diffusion effects and mass transport in the fluid phase were ignored, and it was generally accepted that Antarctic ice can preserve unchanged the original composition of entrapped gas for long periods of time. Recent studies have provided convincing evidence that this fundamental assumption is wrong.

STRUCTURAL CHANGES AND PHYSICO-CHEMICAL PROCESSES

Changes caused by increasing load pressure in the ice sheets, and by its relaxation in the ice cores, are of great importance for understanding processes that influence the elemental and isotopic composition of air inclusions in the ice. Some of the processes are listed in Table 6, and their effects are illustrated in Fig. 11. We discuss them in relation to concentrations of CO_2 recorded in the Vostok core. Most of the arguments for the Vostok core are also valid for the CO_2 record in a 1900 m deep Byrd core (Neftel et al., 1988) and for other deep cores.

A striking feature of the data shown in Fig. 11 is that the vertical distribution of CO_2 concentrations is similar to the distribution of brittle cracks, pressure of air inclusions in relaxed cores, core volume expansion, crystal size, and disappearance of primary air bubbles and formation of secondary cavities. Such similarities strongly suggest that the concentrations of CO_2 in the gas recovered from the Vostok core are artifacts caused by in situ and post-coring processes.

A total disappearance of primary air bubbles in the ice sheet was observed at the Byrd station by Gow et al. (1968) and Gow (1971) below a depth of 1200 m. The secondary gas cavities reappeared in the bubble-free deep ice cores after the load pressure was removed by drilling (Fig. 11).

Miller (1969) postulated that the formation of air clathrates causes the disappearance of air bubbles at greater depths in polar ice sheets, and that the reappearance of the secondary gas cavities is caused by dissociation of clathrates. He predicted that N_2 and O_2 clathrates start to form at a temperature of −30°C at depths of 850 and 600 m, respectively. This was confirmed by Shoji and Langway (1982, 1983), who found that air clathrates appeared at Dye 3 (Greenland) near a depth of 994 m. They also found that secondary gas cavities, having irregular shapes, were gradually forming by dissociation of single clathrate inclusions during 86 and 180 h after core cutting in the borehole. The newly formed cavities grew exponentially with

TABLE 6

In situ and in-core processes influencing elemental and isotopic composition of air inclusions in polar ice

Sub-surface melting, sublimation, refreezing and regelation	in situ, in cores
Formation of CO_2, O_2, Ar, CH_4 and N_2 clathrates	in situ
Dissociation of clathrates	in cores
Disappearance of air bubbles	in situ
Formation of secondary air cavities	in cores
Core volume increase due to:	
elastic relaxation, dilatation of existing air bubbles and formation of secondary air cavities and cracks	in cores
Formation of sheeting fractures	in situ
Formation of fractures by core relaxation	in cores
Formation of fractures by thermal shocks	in cores
Formation of cracks by mechanical shocks	in cores
Formation of plate-like inclusions	in cores
Recrystallization, annealing	in situ, in cores
Diffusion in gases, liquids and crystals:	
(a) at constant temperature	in situ, in cores
(b) at thermal gradient	in situ, in cores
Dissolution and chemical reactions of gases in intercrystalline brine	in situ, in cores
Fractionation during phase transitions:	
ice ↔ liquid, ice ↔ vapor, liquid ↔ vapor, liquid ↔ salt hydrates	in situ, in cores
Changes of volume, salinity, and acidity of brine	in situ, in cores
Contamination by drilling fluid	in cores
Flushing of brine through ice sheets	in situ
Migration of brine	in cores

time, driven by high O_2 and N_2 clathrate dissociation pressures in the decompressed cores.

The N_2/O_2 composition ratio of the clathrates trapped in deep ice cores collected at Dye 3 (Greenland) was 1.7, i.e. markedly lower than the N_2/O_2 ratio of 4 in atmospheric air. This is because oxygen molecules form hydrate clathrates earlier and at shallower depth than nitrogen molecules (Nakahara et al., 1988). This separation mechanism changes the elemental composition of clathrates and that of the gas in the air bubbles.

The depth compression of ice is relaxed elastically before the cores reach the surface (Gow, 1971). At the Byrd station this period of relaxation results in a volume increase of about 0.2% for near-bottom samples. Subsequent relaxation of the load pressure occurs in the cores over a longer period, and is governed by the bubbliness of the ice and orientation of the ice crystals.

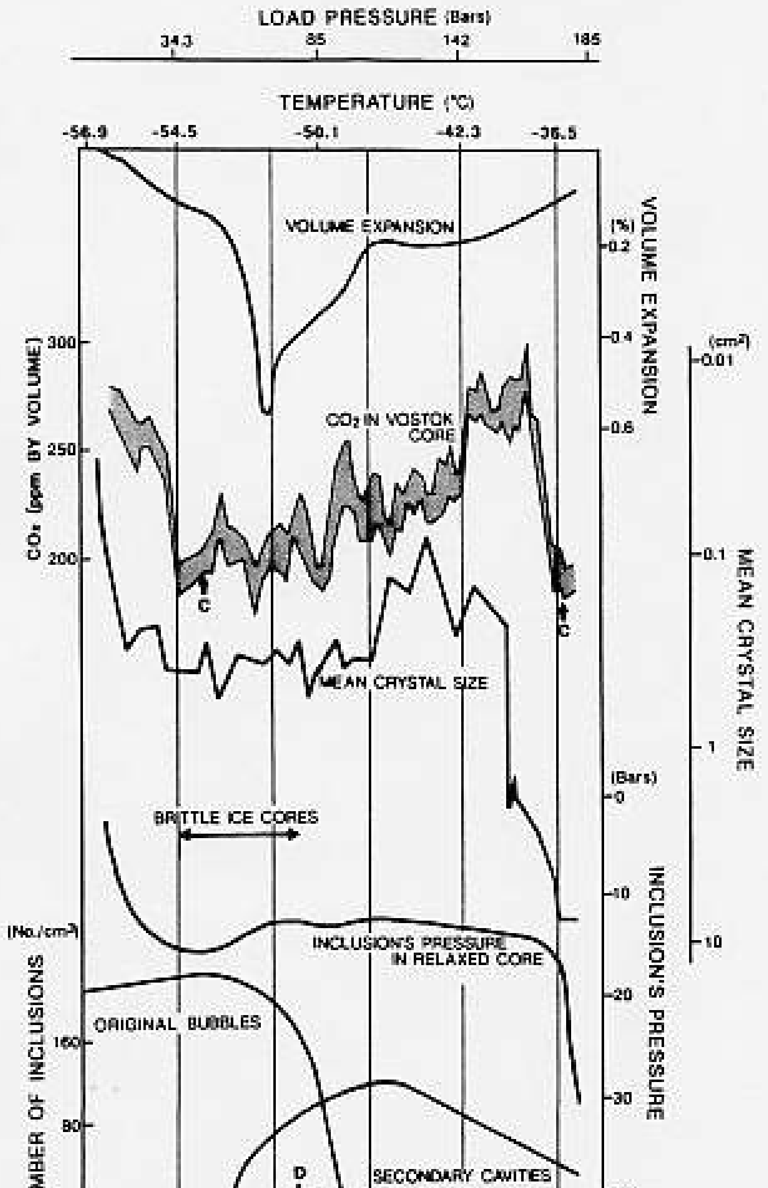

Fig. 11. Processes influencing the chemical and isotopic composition of air inclusions in ice. Depth is the dependent abscissa. Adapted after: Barnola et al. (1987) — CO_2 concentration in gas inclusions in the Vostok core and their assigned age; Gow (1971), Gow and Williamson (1975), Gow and Williamson (1976) — core volume expansion, air bubble disappearance, formation of secondary cavities, brittle ice, pressure in air inclusions 3 years after drilling, crystal size in the Byrd core; Vostretsov et al. (1984) — temperature in the Vostok borehole; the vertical arrow D indicates the total disappearance of air bubbles in the Vostok core, after Korotkevich et al. (1978); the vertical arrows C indicate the sites of highest contamination of the inner parts of the Vostok core with Pb, Zn, Al and Na from drilling fluid, after Boutron et al. (1987, 1990).

This relaxation may cause up to 0.6% expansion of the volume of the core (Fig. 11). Gow (1971) found that the volume expansion and decrease in ice density after relaxation was accompanied by more than a two-fold dilation of pressurized air bubbles in which disk-like cracks were formed intersecting the air bubbles. The cores still continued to relax 27 months after they were drilled.

Sections of the Byrd core from depths between 400 and 900 m exhibited brittle fractures. These stressed cores tended to fracture at the slightest mechanical shock. The ice contained abundant air bubbles (Fig. 11), in which the air pressure in situ was between 40 and 80 bars, decreasing to about 15 bars 1 year after drilling (Gow and Williamson, 1975). In the Vostok core, fractured ice was already present at a depth of 125 m (Legrand et al., 1988).

An improvement in the mechanical condition of the Byrd core, associated with the gradual disappearance of air bubbles, was observed below 900 m depth. Some relaxation effects, such as volume expansion and density decrease, diminished in the deeper core sections (Fig. 11), but other effects appeared. Three distinctive types of inclusions were observed after the deep core sections were brought to the surface: secondary gas cavities, plate-like inclusions, and cleavage cracks. All three types are of secondary origin, because none were observed in the initial examinations immediately after the core sections were pulled to the surface, but only after a longer period (Gow, 1971).

Secondary gas cavities started to appear in the Byrd core at around 600 m depth. They were faceted in reflected light, had a knobby external appearance, and were easily distinguished from primary air bubbles, which possess smooth outlines. The secondary cavities were filled with gas, the quantity of which increased with time (Gow, 1971). The cavities were surrounded by crystal disturbances (Shoji and Langway, 1983) possibly formed by quasi-explosive (decrepitation) dissociation of air clathrates.

Cleavage cracks made their first appearance at about 600 m depth. They were not uniformly distributed in cores, especially in the deep ones. There the cleavage cracks were clumped together in layers. The number of these cracks increased with time. Their thickness was 1–10 μm, and their volume was about 10% of that of the secondary cavities. In the very deep ice, below 2000 m, cleavage cracks were larger and more numerous. Plate-like inclusions appeared after a period of storage of the core sections from a depth below 800 m. They were 1.0 μm thick. The formation of these voids can probably be attributed to strain-induced vacancies (Gow, 1971).

Gow and Williamson (1976) found that the crystal size in the Antarctic ice sheet changes with depth in an irregular way. They observed a constantly increasing crystal size from the firn–ice transition to a depth of 400 m, an irregular plateau in the size distribution between 400 and 1200 m, a sharp decrease in size with a peak near 1600 m, then a dramatic crystal size increase at 1800 m and below (Fig. 11). Similar observations were reported from other Antarctic and Arctic locations (Herron et al., 1985; Langway et al., 1988; see also review by Paterson, 1981).

In a Dome C (Antarctica) core, between 400 and 550 m depth, Duval and Lorius (1980) found a coincidence between a sudden decrease in crystal size and a sudden change of $\delta^{18}O$ values in the ice. They interpreted this as a climatic signal. However, they were unable to offer a plausible mechanism to explain the relationship between crystal size and climatic changes. We propose that these $\delta^{18}O$ changes are due to recrystallization of ice in the ice sheet and in the ice core. Crystal growth was also observed when the ice cores were stored for a few days (Duval and Lorius, 1980), 1 month, or 1 year (Narita and Nakawo, 1985).

Later, Petit et al. (1987) reiterated the idea of a correlation between climate and ice crystal size in the Dome C (Antarctica) core, but they noted that it suffers limitations due to in situ processes. The temperature memory of crystals proposed by Petit et al. (1987) was criticized by Alley et al. (1988). Alley et al. (1988) found that this memory lasts only hours rather than thousands of years, and that the small crystal sizes in Wisconsinian ice are probably caused by impurities in the ice. Langway et al. (1988) and Shoji and Langway (1989) observed an inverse correlation between sulfate concentration and crystal size in the Dye 3 core. The reason for this variability remains unknown (Paterson, 1981; Shoji and Langway, 1989).

The strikingly similar vertical distribution of CO_2 and crystal size in the Vostok core is more likely caused by physico-chemical processes in the ice sheet and in the ice core than to past climatic changes.

The first dramatic decrease in CO_2 concentrations in the Vostok core, at a depth of about 400 m, coincides with the region where major brittle cracks appear (Fig. 11) associated with disk-like cracks intersecting the air bubbles. In this zone the relaxation stresses exceeded the tensile strength of the ice. This part of the core was characterized by an abundance of air bubbles with a high initial (in the ice sheet) pressure of 34 bars, and by a rapid increase of core volume after relaxation of pressure in the bubbles to about 15 bars. At such an initial pressure and at a temperature near −50°C, gaseous CO_2 enters the solid clathrate form (Takenouchi and Kennedy, 1965), but not other air components (Miller, 1969). During dry crushing of such samples in the laboratory at low temperature, solid CO_2 clathrate may be left in the ice and may not be included in the gaseous CO_2 recovered from the bubbles. This will lead to erroneously lower analytical results.

The low CO_2 concentrations near 750 m depth coincide with the highest core volume expansion, accompanied by dramatic dilation of air bubbles and by crack formation (Gow and Williamson, 1975). The dilation of bubbles was accompanied by a decrease in bubble pressure. This must be associated with differential escape of gas from the bubbles into the micro-cracks and liquid veins within the ice, and also out of the cores. Depletion of CO_2 is clearly dependent on changes in ice structure, which are reflected in core volume expansion, crystal size distribution, and disappearance and reappearance of air inclusions (Fig. 11). This depletion can be due to lower viscosity and smaller molecular volume of CO_2 than of other air components. Contamination by drilling fluid was probably one of the factors influencing the changes in gaseous components of the core.

Below about 900 m all original air bubbles disappear in the Vostok core (Korotkevich et al., 1978). All gas cavities from which CO_2 was determined below this depth were secondary, and formed by dissociation of N_2 and O_2 clathrates, and by degassing from crystals, intercrystalline liquid, and contaminating drilling fluid. Both these processes, and those that earlier caused the disappearance of the air bubbles, must have led to chemical and isotopic fractionation of the air components. The CO_2 and δD changes in the Vostok core, which are out of phase by about 1000 to 13 000 years, are supposedly an artifact of this fractionation, rather than due to ancient climatic fluctuations as assumed by Barnola et al. (1987).

The steady increase in CO_2 concentrations between about 900 and 1876 m depth parallels the volume expansion curve, and that between 900 and 1500 m the secondary cavities' curve and the crystal size's curve in Fig. 11. The sudden decrease in CO_2 concentrations below 1876 m in the Vostok core is probably due to slower release of CO_2 than of N_2 and O_2 from clathrates to poorly developed secondary cavities. In cores from this depth, secondary cavities retain much higher gas pressure than cavities in shallower cores.

The extent of contamination of the Vostok core by drilling fluid and its impact on the gaseous composition of the core is different at different depths, depending on the vertical distribution of post-coring processes. In different ice cores the greatest contamination occurred at similar depths (near 500 and 2000 m) at which abrupt CO_2 decreases were reported.

CONCLUSIONS

Ice is not a rigid material suitable for preserving the original chemical and isotopic composition of atmospheric gas inclusions.

Carbon dioxide in ice is trapped mechanically and by dissolution in liquid water. A host of physico-chemical processes redistribute CO_2 and other air gases between gaseous, liquid and solid phases, in the ice sheets in situ, and during drilling, transport and storage of the ice cores. This leads to changes in the isotopic and molecular composition of trapped air. The presence of liquid water in ice at low temperatures is probably the most important factor in the physico-chemical changes. The permeable ice sheet with its capillary liquid network acts as a giant sieve which redistributes elements, isotopes and micro-particles.

Carbon dioxide in glaciers is contained: (1) in interstitial air in firn; (2) in air bubbles in ice; (3) in clathrates; (4) as a solid solution in ice crystals; (5) dissolved in intercrystalline veins and films of liquid brine; and (6) in dissolved and particulate carbonates. Most of the CO_2 is contained in ice crystals and liquids, and less in air bubbles. In the ice cores it is also present in the secondary gas cavities, cracks, and in the traces of drilling fluid.

The concentration of CO_2 in air recovered from the whole ice is usually much higher than that in atmospheric air. This is due to the higher solubility of this gas in cold water, which is 73.5- and 35-times higher than that of nitrogen and oxygen, respectively. The composition of other atmospheric gases (N_2, O_2, Ar) is also different in ice and in air inclusions than in the atmosphere.

Argon-39 and ^{85}Kr data indicate that 36–100% of air recovered from deep Antarctic ice cores is contaminated by recent atmospheric air during field and laboratory processing.

Until about 1985, CO_2 concentrations in gas recovered from primary air bubbles and from secondary gas cavities in pre-industrial and ancient ice were often reported to be much higher than in the present atmosphere. After 1985, only concentrations below the current atmospheric level were published. Our conclusion is that both these high and low CO_2 values do not represent the real atmospheric content of CO_2.

Recently reported concentrations of CO_2 in primary and secondary gas inclusions from deep cores, covering about the last 160 000 years, are much below the current atmospheric level, although several times during this period the surface temperature was 2–4.5°C higher than now. If these low concentrations of CO_2 represented real atmospheric levels, this would mean (1) that CO_2 had not influenced past climatic changes, and (2) that climatic changes did not influence atmospheric CO_2 levels. There are numerous other contradictions between the CO_2 records from deep Antarctic and Greenland ice cores and stable isotopic records, and also between the CO_2 records from different sites.

In air bubbles from shallow ice cores, collected in Antarctica just below the firn/ice transition depth, the CO_2 concentrations were found to be similar to those in the current atmosphere. The ice at this depth was deposited in the 19th century. The CO_2 concentrations in these ice cores decreased proportionally to increasing depth and load pressure. Such a vertical distribution of CO_2 in shallow cores has been incorrectly interpreted as indicating an anthropogenic increase of atmospheric CO_2 in the 19th and 20th century. This interpretation was based on the speculative assumption that the air in bubbles in ice deposited during the 19th century and earlier is much younger than the ice, due to a free exchange of air contained in the deep polar firn with the atmosphere. However, stratigraphic studies and radioactive and stable isotope data demonstrate that this assumption is not valid, because the air in firn is sealed off by hundreds of ice layers.

In samples of gas from pre-industrial ice, CO_2 concentrations fluctuated by a factor of about 10, and were the same, considerably higher, or lower than in the present atmosphere. The reported analytical errors of CO_2 measurements at a 95% probability level were of the same magnitude as the hypothesized recent rise in atmospheric CO_2 levels.

In deep cores the vertical distribution of CO_2 represents the effects of in situ physico-chemical processes, artifacts in cores, and arbitrary rejection of high readings, rather than original concentrations in an ancient atmosphere. The most important among these processes are the dissolution and diffusion of gases in intercrystalline liquids, the formation and dissociation of clathrates, the disappearance of air bubbles and the formation of secondary air cavities, the formation of macro- and micro-cracks, thermal gradients during drilling, transportation and storage of cores, and contamination of cores by drilling fluid. Contamination led to fluctuations in heavy metal and Al readings in the cores, incorrectly interpreted as being due to ancient climatic changes.

During the disappearance of air bubbles in ice sheets and the formation of new secondary cavities in the ice cores, the chemical and isotopic fractionation of gases occurs in two stages.

First, when the air bubbles disappear sympathetically with increasing load pressure, the gas dissolves in liquid water and in ice crystals, and condenses to solid-state clathrates. At various depth, pressure, and time, the individual gases are transferred at different rates from bubbles to ice crystals and to intercrystalline liquid veins and films. In the liquids and crystals they may remain in solution or as solid clathrates, mixed with gases which were present there before the disappearance of the bubbles. Isotope ratios and gas composition are changed at each state transition (between ice, liquid and vapor). Thus during this first stage the molecular and isotopic composition of gases will change both in the air bubbles and in the ice itself.

During the second stage, when the load pressure decreases in the bubble-free ice cores, particular gases are successively released from the ice crystals, liquids and clathrates, forming new secondary gas cavities. During this process the state transitions are reversed, i.e. from solid and liquid to gas. The contribution of gases that were originally trapped in the ice crystals and liquids to the air in the new cavities, remains to be determined. But it is highly improbable that, following such dramatic changes, the gas in the secondary cavities should have the same composition as in the original atmosphere.

Changes in current and past atmospheric CO_2 levels cannot be established from the available data on CO_2 in polar ice with any confidence. Even the fundamental information on the relation between CO_2 concentration in the air contained in 10-year-old glacier strata and in the contemporary atmosphere is not available. In such a situation this relation cannot be realistically determined for 100 or 100 000-year-old ice, for example. More than 20 physical and chemical processes in the ice sheets and in the ice cores (listed in Table 6) make the gas samples recovered from both shallow and deep cores unrepresentative of the original elemental and isotopic composition of paleo-atmospheres.

With the methodology currently used the glaciers cannot divulge the true CO_2 and paleo-climatic story. The idea that this is the case has dawned on CO_2 students, who recently started to realize that the CO_2 variation observed in ice cores 'is an artifact, due to the enclosure process or ice–gas interaction' (Siegenthaler et al., 1988). But harm has already been done: in the past decade, unidirectional and uncritical conclusions from ice core studies, repeated in myriad publications, have led to a widely accepted false tenet that the man-made climatic warming hypothesis is based on solid ground. This dogma has already had political consequences, and may have an enormous impact on the future economy and development of society. But it was never critically evaluated in depth.

In order to study man's hypothetical impact on climate, of paramount importance is information on changes in atmospheric composition during the last 150 years, and not the prehistorical changes. We therefore propose that, in future CO_2 studies of glaciers, the emphasis should be placed on the firn and ice deposited in this period. Drilling cores, even from shallow depths, is an extremely brutal procedure leading to drastic changes in the ice samples, precluding their reliability for gas analyses. Other methods of sampling should be considered. Collecting the gas in situ may possibly be the best of them. If firn and ice samples are to be considered they should be sealed off at the moment of collection, and their temperature kept constant until analysis. The gas should be extracted from the ice at the sampling site during or immediately after collecting the samples. The samples should be collected from the ice sheet starting at the surface down to layers deposited in the first half of 19th century. Processes which change the elemental composition of air inclusions in snow and ice should be carefully studied before deciding whether the upper parts of polar ice sheets can be used for reconstruction of the pre-industrial atmosphere.

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ADDENDUM

After the present paper was submitted for publication we read the paper by Wahlen et al. (1991), in which the authors presented results of CO_2 measurements made in a 95 m long ice core, drilled below the firn-ice transition in Greenland. The ice at the starting depth was deposited in 1720, the CO_2 concentration in this air was 310 ppm. By assuming that the age of air was 220 years younger than the age of ice, the authors smoothly connected their results to the recent atmospheric observations from Mauna Loa. The criticism and reservations for similar interpretation of ice core data in sections *Shallow cores* and AGE OF AIR IN ICE are valid also for this paper.

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