Z. JAWOROWSKI, T. V. SEGALSTAD and
V. HISDAL:

ATMOSPHERIC CO$_2$ AND GLOBAL WARMING:

A CRITICAL REVIEW

Z. JAWOROWSKI, T. V. SEGALSTAD and
V. HISDAL:

ÁTMOSPHERIC CO_2 AND GLÓBAL WARMING:

A CRITICAL REVIEW

Zbigniew Jaworowski and Vidar Hisdal
Norsk Polarinstitutt
Postboks 158
N-1330 Oslo Lufthavn, Norway

Tom V. Segalstad
Mineralogisk-Geologisk Museum
Universtitetet i Oslo
Sars' gate 1
N-0562 Oslo 5, Norway

CONTENTS

SUMMARY

The projections of man–made (anthropogenic) climate change through burning of fossil carbon fuels (coal, gas, oil) to CO_2 gas are mainly based on interpretations of measured CO_2 concentrations in the atmosphere and in glacier ice.

Dominant factors in the Earth's CO_2 cycle are the ocean, and mineral equilibria. Due to their vast buffer capacity, they stabilize the geochemical equilibrium of CO_2 gas between the hydro–, atmo–, litho– and biosphere. A new radiocarbon (^{14}C) study indicates that the turnover time of the dissolved organic carbon in the upper ocean is of a few decades' duration. This suggests that CO_2 produced by burning the Earth's whole fossil carbon fuel reservoir would be dissolved in the ocean, before reaching the double concentration of its current atmospheric level.

The 19th century measurements of CO_2 in the atmosphere were carried out with an error of up to 100%. A value of 290 ppm (parts per million by volume) was chosen as an average for the 19th century atmosphere, by rejection of "not representative" measured values, which were 10% or more different from the "general average for the time". This introduced a subjective factor in the estimates of the pre–industrial level of CO_2 in the atmosphere.

The Mauna Loa (Hawaii) observatory has been regarded as an ideal site for global CO_2 monitoring. However, it is located at an active volcano, which has on the average one eruption every 3.5 years. There are permanent CO_2 emissions from a rift zone situated only 4 km from the observatory, and the largest active volcanic crater only 27 km from the observatory. These patterns of the site have made "editing" of the results an established procedure, which may introduce a subjective bias in the estimates of the "true" values given. A similar procedure is used at other CO_2–observatories.

The CO_2 concentrations in air bubbles trapped in glacier ice are often interpreted as previous atmospheric concentrations, assuming that the composition of the air in the bubbles remained unchanged. This was again based on the assumption that there is no liquid phase in the ice below a mean annual temperature of about $-25°C$, and that therefore no changes due to diffusion may be expected. However, it was recently found that in the Antarctic ice the veins of liquid can be present at temperatures as low as $-73°C$. Numerous studies indicate that, due to various chemical and physical processes, the CO_2 content in the ice can be largely enriched or depleted in comparison with the original atmospheric

level. In several studies the CO_2 levels in the pre–industrial ice were found to be twice or more the current atmospheric level.

Methods using dry extraction of CO_2 from crushed ice release only about half of this gas present in the ice. CO_2 in the air inclusions can penetrate the ice by diffusion or dissolution into the liquid present at the ice grain boundaries, at a rate different from those of other gases in the air. A problem for the determination of CO_2 levels in gas inclusions is the formation of solid CO_2 clathrates (hydrates). Other gases in air also form clathrates, but at different temperatures and pressures. This leads to important changes in the composition of the inclusion air at different core depths, and indicate that glacier ice cannot be regarded as a steady state matrix suitable for observation of long–term atmospheric trends. Thus the results of CO_2 determinations in air inclusions in ice cannot be accepted as representing the original atmospheric composition.

Another difficulty is the determination of the age of air inclusions in ice, introducing uncertainties, even in the analytical results obtained from the upper ~100 m deposits in Greenland and Antarctica. $N_2/O_2/Ar$ ratios in air are not preserved. Instead the ratios agree with those from aqueous solubility data. Hence the inclusions must have been formed by exsolution from freezing water, and not from sealed channels in ice originally open to air.

Paleo–temperature calculations based on light stable isotope ratios (D/H and $^{18}O/^{16}O$) in ice have large uncertainties. After discovery of liquids between ice crystals in the deeply frozen antarctic ice, considerable isotopic exchange and fractionation should be expected in the ice, making calculated paleo–temperatures meaningless if phase changes occurred in the presence of a mobile fluid phase.

Attempts have been made to calculate the paleoatmospheric CO_2 content from $^{13}C/^{12}C$ carbon stable–isotope ratios in tree rings. It is concluded here that the CO_2 content in the atmosphere calculated from such carbon isotope analyses cannot be considered a valid tool in paleoclimatology, and cannot be used as evidence of changing atmospheric CO_2.

The so–called increasing "greenhouse effect" signal, i.e. anthropogenic increase of the global air temperature, which was claimed to have been observed during the last decades, is not confirmed by recent studies of long temperature series.

In the Arctic, according to model calculations, this warming signal should be most explicit. However, cooling rather than warming has been recorded in this region during the last two decades. The glacier balance studies in the Norwegian and Canadian Arctic, and of the Greenland and Antarctic ice caps, do not provide evidence for a recent increase in the temperature of the atmosphere.

1.   INTRODUCTION

Solar radiation entering the Earth's atmosphere gets a mixed reception. On a mean annual global scale only about half the incoming solar energy is absorbed by the Earth's surface. The rest is scattered back and to some extent absorbed by the atmosphere (clouds included), or reflected by the ground.

The Earth itself radiates at wavelengths much longer than those of solar radiation. This Earth radiation, unlike the solar radiation, is strongly absorbed in the atmosphere. The absorbtion is mainly caused by water vapor and clouds, but also by some trace gases. Only a very small part of the radiation emitted by the ground escapes directly to space. In this way the atmosphere is heated, and returns radiative energy to the Earth's surface, where it is again absorbed and re–radiated, and so on. Thus a remarkable exchange of thermal energy takes place between the ground and the lower atmosphere. These processes, somewhat misleadingly called the **"greenhouse"** effect, are responsible for the relatively high mean surface temperature on the Earth, about 14°C. If the Earth had no atmosphere the corresponding temperature would be about –18°C.

The term "greenhouse effect" is now often used to name a predicted increase in the temperature of the lower atmosphere, as a consequence of man's release of CO_2 and other heat–absorbing trace gases to the atmosphere. This predicted additional effect will in the following be referred to as an **increasing "greenhouse effect"** or **"greenhouse" warming**.

In the Earth's atmosphere dry air consists of nearly 78% (by volume) nitrogen (N_2), about 21% oxygen (O_2) and about 1% argon (Ar). In humid air the water vapor content varies from about 3% in the tropics to a small fraction of this quantity in the Arctic. Carbon dioxide (CO_2) is just a trace component, with a concentration of about 0.035% (= 350 ppm). This gas plays an important part in life processes (both the plant photosynthesis and oxidation, and animal/human metabolism), and the concentration varies with time and place. Thus, it has been found that the concentration may double during one single day over a wheat field (Fergusson, 1985).

During the 1970s and the first half of the 1980s several climatic model computations predicted that for a hypothetical doubling of the average atmospheric CO_2 concentration during the next 60 years, the average global temperature will increase by 1 to 5°C (see e.g. review by Braathen et al., 1989), that the polar regions will warm more than the lower latitudes, up to 8 to 10°C (Schneider, 1975; Manabe and Wetherald, 1980), and that the seasonal variations will be greatest in the north polar regions (Ramanathan et al., 1979).

These models also predicted considerable changes in the geographical distribution of precipitation. At the end of the 1980s more sophisticated models revised the earlier predictions substantially, decreasing the net impact on the climate and changing its geographical distribution. A recent estimate is 1.2°C increase in the surface and tropospheric temperature due to doubling the atmospheric CO_2 (Lorius et al., 1990), assuming no feedback processes.

To the present natural global atmospheric flow of CO_2, man's burning of fossil carbon fuels may add an amount somewhere in the range of 0.1 to 3.6%. CO_2 is one of about 40 trace "greenhouse gases" present in the atmosphere (Ramanathan et al., 1985). CO_2 contributes about 22% (~33 W/m^2) to the total "greenhouse" effect of the lower atmosphere. The effect of other trace gases to this warming of the lower atmosphere is about 3% (4 to 5 W/m^2). Water vapor contributes the most, about 75% (~113 W/m^2), to the total "greenhouse" effect of the lower atmosphere (Braathen et al., 1989).

The present level (approximately 350 ppm by volume) of CO_2 in the atmosphere contributes, as seen above, to about 1/5 of the total "greenhouse" effect. All past human activity has contributed about 1% (~2 W/m^2) to the current total average "greenhouse" effect of the atmosphere (of about 150 W/m^2), and a doubling of CO_2 would contribute about 2.2% (~4 W/m^2) (Raval and Ramanathan, 1989). Landsberg (1974) estimated that only 3% decrease in atmospheric water vapor, and 1% increase in cloudiness can compensate the warming due to an anticipated CO_2 doubling (other conditions held constant). As a whole, the influence of clouds on the atmospheric temperature is still an unsolved problem (e.g. Schlesinger and Mitchell, 1987).

The level of CO_2 in the atmosphere depends on an equilibrium between its sources and sinks. Oceanic flows of this gas in and out of the global atmosphere are important for the CO_2 budget. Even very small natural fluctuations of these oceanic flows can mask the man–made CO_2 inputs into the global atmosphere.

A doubling of atmospheric CO_2 would lead to a decrease of the long–wave flux through the tropopause by about 4 W/m^2 (Ramanathan et al., 1989 a). Several studies have suggested that such radiative heating of 4 W/m^2 would lead to a global warming of 3.5 to 5°C (Hansen et al., 1984; Wilson and Mitchell, 1987; Washington and Meehl, 1984; Wetherald and Manabe, 1988). At present the total positive global mean forcing of all trace "greenhouse" gases (CO_2; CFCs; methane, etc.) is claimed to be about 2.2 W/m^2, i.e. below the uncertainty of about ± 5 W/m^2 for estimates of the global net radiation (Ravel and Ramanathan, 1989). The positive (warming) forcing of water in the clouds is about 30 W/m^2;

this is the "greenhouse" effect of clouds, approximately seven times larger than that resulting from a hypothetical doubling of CO_2. The CO_2 concentration in the atmosphere has to be increased by more than one hundred times to produce a "greenhouse" effect comparable to that of clouds (Ramanathan et al., 1989 b). The negative cloud forcing (due to a high albedo at the upper cloud surface) is of the order of –50 W/m^2. From such figures (30 minus 50) one gets a net cloud forcing of about –20 W/m^2, i.e. several times higher than the claimed man–made positive forcing of CO_2 doubling.

Ramanathan et al. (1989 b) demonstrated that the clouds have a large net cooling effect on the Earth. As mentioned above, the negative cloud–radiative forcing is much larger than that of a doubled CO_2 positive forcing, and according to Ramanathan et al. (1989 b) it offsets the possible increasing "greenhouse effect" warming. This is because an increase in the global temperature will increase the amount of water vapor and clouds in the troposphere, introducing a strong negative radiative feedback. As indicated before, the total past anthropogenic "greenhouse" forcing (due to CO_2 and other trace gases) between 1850 and 1985, was 2.2 W/m^2 (Ramanathan et al. 1989 b). According to model predictions, this should commit the planet to a global surface warming of 0.8 to 2.4°C. However, no such warming has been observed, which indicates that the negative cloud forcing of about –20 W/m^2 (or perhaps also some other negative forcings) is sufficiently large to stabilize the increasing "greenhouse effect" warming. This was confirmed by Slingo (1989) who found that the top-of–atmosphere radiative forcing by doubled CO_2 concentrations can be balanced by modest increases in the amount of low clouds.

Wigley et al. (1989) have pointed out that SO_2–derived negative forcing may offset considerably the "greenhouse–gas" positive forcing. SO_2 originates from dimethylsulfide from the oceans (Charlson et al., 1987), volcanic emissions, and by man–made sources. The cooling effect is partly due to the absorption of incoming solar radiation by sulfuric acid in the stratosphere, and partly due to an increase of cloud condensation nuclei in the atmosphere. The latter effect, due to H_2SO_4 and sea–salt aerosols (Latham and Smith, 1990) serves to "brighten" clouds (increase their albedo), and in this way reflecting a part of the incoming solar radiation back into space. Satellite data now confirm that the ocean-stratocumulus cloud (one of the most common cloud types on Earth, and the variety most likely to be affected by an increasing number of condensation nuclei) is indeed considerably brighter in the lee of the regions of major anthropogenerated SO_2 emissions (Cess, 1989).

A main feature of the predictions of almost all climate models is a relatively large warming at high latitudes. Therefore polar regions may be assumed to be the most

promising areas for detection of any current increasing "greenhouse effect" warming, where temperature and glacier records can be used for checking the model predictions. A discussion of computer modelling with the help of General Circulation Models (GCM) is, however, beyond the scope of this report. For a comparison of different models of this kind, reference is made to Cess et al. (1989).

As will be seen from the discussion below, the hypothesis of an imminent climatic change is based on evidences which are subject to serious uncertainties and inconsistencies. These uncertainties should be factored into the policy decisions in view of the staggering costs of implementation of anti-"greenhouse" economic decisions on a global scale. Only in the United States these costs may reach 3.6 trillion dollars (Passel, 1989). This might have serious negative social consequences both for the developed and third world countries, reaching beyond the 21st century.

In most cases the scientists are aware of the weak points of their basic assumptions and simplifications needed to interpret the results of measurements or to create models. These uncertainties are mostly ignored or banished to a subordinate clause, when the results are presented by politicians or mass media. In the process of forming the environmental policy, the preliminary hypotheses are transformed into "reliable facts" when presented to the public. The magnitude of "normal" natural reservoirs, fluxes, and variations are not presented and compared to claimed "abnormal" anthropogenic contributions. A more balanced view is certainly needed.

The hypothesis of man-made climatic warming due to burning of fossil carbon fuels is to a large extent based on measurements of CO_2 in air and in glacier ice, hydrogen and oxygen isotopes in glacier ice, carbon isotopes in tree rings, and atmospheric temperature records, interpreted as an indication of a long-term increasing level of this gas in the atmosphere. In this paper we critically review these measurements and their interpretations, to test the nowadays widely accepted postulate that "the change in atmospheric CO_2 is not just a fluctuation of nature, but is predominantly the consequence of the activities of mankind – chiefly the burning of fossil fuels such as coal, gas and oil" (Rowland and Isaksen, 1988). We also compare the quantities of anthropogenic contributions with known fluxes of natural reservoirs, and discuss air temperature and glacier balance records, which should reveal signals of an increasing "greenhouse effect".

2.   THE CO_2 BUDGET

2.1 CO_2 FLOWS AND RESERVOIRS

Most of the recent attempts at predicting an increasing "greenhouse effect" have assumed a doubling of the present atmospheric CO_2 level, of about 350 ppm, due to fossil fuel burning during the next 30 – 60 years. To estimate the reliability of this basic assumption, the order of magnitude of the various sources and sinks of atmospheric CO_2 should be taken into account.

Iansiti and Niehaus (1989) estimated that fossil carbon fuel burning contributes 4.9 GT C (carbon equivalents in gigatonnes = 10^{15}g) per year, i.e. about 3.6% to the global natural flux of CO_2 of 169 GT C per year, whereas Fergusson (1985) estimated the man–made contribution to be only about 0.1%. Fluctuations in the natural flux of CO_2 (Table 1) are generally higher than this man–made contribution.

The yearly CO_2 exchange between atmosphere and ocean, and between atmosphere and biosphere, amounts to about 23% of the estimated pre–industrial atmospheric CO_2 content. In contrast, the present annual man–made input due to fossil fuels amounts to 0.8% of atmospheric CO_2 (Oeschger and Siegenthaler, 1988). This means that a small fluctuation in the natural exchange rate would mask the fossil fuel contribution.

If all fossil fuel resources (approximately 7000 GT C) were burned immediately, the current atmospheric content of CO_2 (700 GT C; Rose et al., 1983) would suddenly increase by a factor of 11, before it would dissolve in the ocean and be precipitated as carbonates in the bottom deposits (Walker and Drever, 1988). Such an assumption is of course rather unrealistic, as the existing resources are supposed to be exhausted in approximately 300 years, and as the CO_2 residence time in the atmosphere is only 4 to 12 years (Bolin and Keeling, 1963; Stumm and Morgan, 1970; Broecker and Peng, 1974; Sundquist, 1985).

CO_2 consumed annually by the photosynthesis of land plants give fluxes in the range 10 – 70 times more than produced by man; photosynthesis by marine plants give fluxes in the range 50 to 250 times more (Revelle and Suess, 1957). Such powerful natural sources and sinks would most likely mask the effect of fossil carbon fuel burning, which accounts for just a tiny fraction of the global atmospheric flux of this gas. Just small fluctuations in the dissolved marine carbon reservoir (38,000 GT C; Bolin, 1989), sedimentary carbonate carbon reservoir (60,000,000 GT C; Walker and Drever, 1988), the vast carbon reservoir of the Earth's interior (constantly being tapped by volcanic activity), or short–term fluctuations

Table 1. Current reservoirs of carbon at the Earth's surface and annual fluxes of CO_2 (expressed as carbon equivalents in gigatonnes = 10^{15}g) into the atmosphere.

	GT of carbon	References
RESERVOIRS		
Sediments[1]	60,000,000	Walker and Drever, 1988
Marine dissolved organics	1,000	Bolin, 1989
Marine dissolved inorganics	38,000	Bolin, 1989
Fossil fuels	7,200	Walker and Drever, 1988
Atmosphere	727	Rose et al., 1983
Soil	1,300	Prentice et al., 1990
Terrestrial biomass	834	Prentice et al., 1990
Marine biomass[2]	230	
ANNUAL FLUXES		Iansiti et al., 1989
NATURAL		
Ocean	106	
Land	63	
TOTAL	169	
MAN–MADE		
Fossil fuels and land use	6	

---

[1] Near surface.

[2] Calculated from a total mass of marine biota of 1×10^{18} g (Nriagu, 1978) and from carbon concentration in these biota assumed to be the same as in terrestrial mammals, i.e. 0.23 gram carbon per gram body weight (ICRP, 1975).

such as due to the El Niño – Southern Oscillation (ENSO) phenomenon occurring every few years (about 2 GT C per event; Gaudry et al., 1987), may probably obscure the fossil fuel contribution of about 5 GT C per year.

As recently found in a modelling computation, for simulations run with twice the present–day CO_2 levels, strong negative feedbacks appear, due to carbon storage in terrestrial biota and soils (Prentice and Fung, 1990). These negative feedbacks remove 235 GT of carbon from the atmosphere. The marine reservoir contains as dissolved carbonic acid at least 35% of the fossil fuel CO_2 produced in the past (Broecker et al., 1979). If the same fraction may be expected for the future releases, it would correspond to about 87 GT C. The terrestrial biota, soils and marine sinks would then be large enough to remove 322 GT of carbon from the atmosphere. This is more than enough to remove the anthropogenic amount introduced into the atmosphere during the next 50 years, at the current consumption rate of fossil fuels.

2.2 CO_2 EQUILIBRIA

As may be seen in Table 1 the ocean is the dominant factor in the CO_2 cycle of the Earth's surface. Therefore, we discuss shortly the biogeochemical equilibria and dynamic processes that govern the relationship between atmospheric and oceanic CO_2. The inorganic part of the CO_2 cycle in the atmosphere/hydrosphere/lithosphere system is buffered with respect to H^+ by the carbonate equilibria (see below). The salinity of the ocean is held constant by erosional and depositional processes and by mineral equilibria. All parts of the system, including CO_2 in the atmosphere, are therefore thermodynamically buffered, and reach a chemical equilibrium at a given temperature. For a change in temperature, new chemical equilibria apply, and a new value for the partial pressure of CO_2 will be established (Rubey, 1951; MacIntyre, 1970). It appears from the work by Smith and Jones (1985) that the wind is capable of pumping CO_2 into the water, and thereby establishing a partial pressure of CO_2 in the surface water, which is higher than that in the air. This is due to pressurization of bubbles generated by breaking waves.

The oceans down to about 4 km depth are supersaturated with respect to calcium carbonate (Broecker et al., 1979), which facilitate calcium carbonate to precipitate for any additional input of CO_2 through the atmosphere/ocean interface, and thereby consume any excess CO_2 in the atmosphere.

CO_2 in the atmosphere is in chemical equilibrium with carbonic acid dissolved in the hydrosphere (sea, lakes, rivers, etc.) (e.g. Gonfiantini, 1981; Mozeto et al., 1984; Etcheto and

Merlivat, 1988; Horita, 1989; Ohmoto and Rye, 1979), which again is in chemical equilibrium with calcium carbonate making up limestone and lime shells of aquatic organisms (see e.g. Rubey, 1951; Garrels and Thompson, 1962; Garrels and Christ, 1965; Pytkowicz, 1967; Stumm and Morgan, 1970; Plummer et al., 1978; Plummer and Busenberg, 1982; Talsman et al., 1990). Several chemical reactions are stabilizing this atmosphere/hydrosphere equilibrium, working for at least during the last some 600 million years (Holland, 1984).

The vast calcium carbonate buffer is not the only buffer acting in the atmo–sphere/hydrosphere/lithosphere system. The Earth has a set of equilibrium systems working simultaneously. The geochemical equilibrium system anorthite $CaAl_2Si_2O_8$ – kaolinite $Al_2Si_2O_5(OH)_4$ at the pH of sea water has a buffer capacity one thousand times higher than that of a 0.001 M carbonate solution (Stumm and Morgan, 1970). In addition, there are clay mineral buffers, and the calciumsilicate + CO_2 <—> calciumcarbonate + silica buffer (e.g. MacIntyre, 1970; Krauskopf, 1979). These are all working as "security nets" under the main buffer controller: the CO_2 (gas) – HCO_3^- (aqueous) – $CaCO_3$ (solid) buffer system. This suite of mineral buffers attain, in principle, an **infinite buffer capacity** (Stumm and Morgan, 1970). As Kramer (1965) expresses it: "A few simple calculations will show that only very large additions or subtractions of carbon dioxide (from the lithosphere) could overwhelm these equilibria".

The solubility of CO_2 in water can be expressed by the Henry's Law Constant, K_H (Drummond, 1981; Henley et al., 1984; Barta and Bradley, 1985). This constant is numerically expressing the decreasing solubility of CO_2 in water for increasing temperature (up to about 200 °C). As the temperature rises, less CO_2 may remain in the water, as a new equilibrium between gas and liquid is obtained, and the water will degas CO_2 from the ocean to the atmosphere. The effect of this "thermally driven solubility pump" is accounting for approximately 70% of the total ocean degassing, while the remaining 30% is accounted for by the organic nutrient "biologic pump" (Volk and Liu, 1988). The thermal solubility pump and the biological pump increase the atmospheric level of CO_2 when the sea and air temperature rises due to natural climatic fluctuation. The powerful negative feedback mechanisms, such as e.g. due to increase in cloudiness, lower the temperature again and keep the naturally fluctuating global air temperature in balance (see Chapter 1).

It has been estimated that approximately 4000 GT of CO_2 was fluxed from the ocean via the atmosphere to the continental biosphere, during transition from a glacial to an interglacial stage (Faure, 1990). Other natural carbon flows (weathering, volcanism, carbonate sedimentation and dissolution, degassing by metamorphism, etc.) are not

and enormous surface of droplets exposed to atmospheric CO_2 must contribute largely to a flow of inorganic carbon from the atmosphere to the hydrosphere. This contribution is related to the volume of the atmosphere occupied by the cloud droplets, and to their residence time. If this residence time were sufficiently long, the total amount of CO_2, which at a temperature of e.g. 10°C might be dissolved in the global annual precipitation, would reach ~1,000,000 GT CO_2, i.e. ~270,000 GT C. This is several hundred times more than the amount of CO_2 present in the atmosphere. Although several other factors enter into the picture, this illustrates the CO_2 scavenging potential of the global precipitation.

Another sink for CO_2 is weathering of silicate minerals. It has been demonstrated by Walker et al. (1981) that the partial pressure of CO_2 in the atmosphere is buffered, over geologic time scales, by a negative feedback mechanism in which the rate of weathering of silicate minerals (followed by deposition of carbonate minerals) depends on surface temperature. The higher the temperature the greater removal of CO_2 from the atmosphere by deposition of carbonates. This negative feedback is an important factor in the long–term stabilization of the global surface temperature. Schwartzman and Volk (1989) have sug- gested that biota amplifies this negative feedback.

Holland (1984) has tested whether the atmospheric CO_2 content has been extremely low or extremely high during the Earth's history. At low partial pressure of CO_2 gypsum $CaSO_4 \cdot 2H_2O$ would be formed at the expense of calcium carbonate. This has not been found in marine sediments. At high partial pressure of CO_2 dolomite $CaMg(CO_3)_2$ would be expected to precipitate directly from the ocean instead of calcium carbonate (aragonite or calcite). This has not been found either. The conclusion is that the atmosphere/hydro- sphere equilibria operating at the Earth's surface today, have been working through hund- reds of millions of years, even during periods of e.g. intense volcanic release of CO_2. A correlation between increased volcanic production and contemporaneous increasing marine carbonate sedimentation has been presented by Budyko et al. (1987).

3. AIR CONCENTRATIONS OF CO_2

3.1 CONTEMPORARY MEASUREMENTS

An important component of the "greenhouse" warming hypothesis is the analysis of CO_2 concentrations in the atmosphere. These measurements have been carried out systematically at the Mauna Loa observatory in Hawaii since 1958 (Bacastow at al., 1985) and later on at several other stations. The annual mean concentrations reported from the Mauna Loa observatory increased from 312.8 ppm in 1958 (Pales and Keeling, 1965) to 345.8 in 1985 (Thoning et al., 1989). The Mauna Loa data have been regarded as representative for the global concentration of CO_2 in the atmosphere. This seems to be rather doubtful as the site is exposed to vast local natural emissions of CO_2 and also man-made sources.

The published results of the Mauna Loa measurements indicate a systematic increase during the last 30 years of about 10% in the atmospheric CO_2. Taken together with the concentrations found in the air bubbles trapped in glacier ice, these results have been taken to indicate a rise of about 25% in the atmospheric CO_2 since about 1850 (Schneider, 1989). The predictions of doubling the CO_2 atmospheric level around the year 2030 are based on extrapolating the compiled results of glacier and air measurements, and on an assumption that the 25% increase is solely due to man-made sources.

We shall discuss here some aspects of the Mauna Loa measurements, to illustrate the difficulties involved in estimating the current levels of CO_2 in the global atmosphere. The general increasing CO_2 trend over the last some 30 years is not questioned. Here the accuracy, precision, sensitivity and methodology are discussed.

The observatory is located at the slope of the Mauna Loa volcano which averaged one eruption every 3.5 years since 1832 (Encyclopaedia Britannica, 1974; Simkin et al., 1981). Following an eruption in 1975, the Mauna Loa volcano remained at rest until March 1984, when about 220 million tons of lava covered an area of about 48 km^2, but pre-eruption activity had been going on since about 1980 (Koyanagi and Wright, 1987; Koyanagi et al., 1987). The CO_2 content of volcanic gases emitted, associated with various types of lava, was reported by Rubey (1951). The concentration of CO_2 in the gases emitted from the Mauna Loa and Kilauea volcanos of Hawaii reaches about 47%. This is more than 50 times higher than in volcanic gases emitted in other regions of the world. The reason for this is the alkaline nature of this volcanism, strongly associated with mantle CO_2 degassing.

The observatory is also exposed to permanent CO_2 vents from the volcanic caldera and a rift zone situated only 4 km upslope from the observatory (Pales and Keeling, 1965), and from some distant sources downslope (Keeling et al., 1976). Pales and Keeling (1965), in their description of methodology and the sampling site, did not mention that the world's largest active volcanic mass, Kilauea, is situated with the largest active volcanic crater (5 km long and 2 km wide) only 27 km southeast of the Mauna Loa observatory. Frequent eruptions of this volcano were observed during the 1960s and 1970s. CO_2 emission from Kilauea is observed also in non–eruption periods (Decker and Koyanagi, 1983; Decker et al., 1987). Emissions of up to 5000 tons of CO_2 per day were recorded from the summit crater of this volcano in non–eruption periods (Gerlach and Taylor, 1990).

More recently increased activity of Kilauea started in January 1983 and continued throughout 1984. There were 16 major gas charged eruptions in 1984, with several hundred meters high fountains of lava, and with an average production of lava of about 10 million tons per episode.

To account for the influence of volcanic emissions from the neighboring 10 km long rift zone and caldera at Mauna Loa, Pales and Keeling (1965) calculated an increase in CO_2 concentration of 2 ppm for a certain "weather type", which is about three times higher than the observed 0.68 ppm average increase per year. The eruption events of the Mauna Loa and Kilauea volcanoes, or for quiescent emission of CO_2 from the gigantic Kilauea crater, were not discussed by these authors. Eleven years later Keeling et al. (1976) mentioned the prolonged period of Kilauea activity which commenced in November 1967 and ended March 1971. In March 1971 a locked chain gate was erected across the road to the Mauna Loa observatory 0.5 km from the CO_2 intakes. Both the (temporary) cessation of the Kilauea volcanic activity and the erection of the gate coincided with the dramatic decrease in frequency of the large peaks of CO_2 concentrations.

An example of the variations of hourly average atmospheric concentration of CO_2 during three consecutive days at Mauna Loa is given in Figure 1. It demonstrates that it seems extremely difficult at this locality to determine values representing global concentrations. This may be illustrated by Figure 2, in which the effect of data selection at the Cape Matatula Station in Samoa is presented. The description of the methods used at both stations, for elimination of irregularities to get a representative value, confirms this conclusion.

The effects of different kinds of local vegetation on the concentrations of CO_2 in air have not been satisfactorily treated, and a number of features of the published curves for

atmospheric variation of CO_2 through approximately the last 30 years have not been explained (Keeling et al., 1989). Pales and Keeling (1965) discuss the depletion of atmospheric CO_2 by a tropical forest downhill, which was supposed to cause "dips" in their readings. Grassland production of CO_2 may have a large influence on CO_2 levels in the air, as will respiration and decay of organic matter. Daily fluctuations of CO_2 concentration over a grassland were found to reach 40 ppm, and the seasonal variations (between June and September) reached about 25 ppm (Spittlehouse and Ripley, 1977). Daily variations over a wheat field can almost double the amount of CO_2 in the air (Fergusson, 1985). Pales and Keeling (1965) noticed the existence of the CO_2 sources at the Mauna Loa observatory itself, such as exhausts of a diesel engine–driven generator and automobile pollution which have become a problem (Keeling et al., 1976). In view of these points of criticism the claim of Pales and Keeling (1965) that "the observatory is thus an excellent, if not ideal, site for measuring CO_2 in the upper air" seems to be exaggerated.

Throughout the whole period of measurements the results were "edited" (Bacastow et al., 1985) to account for local disturbances causing both higher and lower CO_2 concentrations. As Pales and Keeling (1965) stated, the measurements are clearly locally influenced. The authors applied "omissions of variable periods from the daily averages" to eliminate both high and low readings.

The values that were omitted were defined as "measurements that occur when the air trace shows significantly more variation than the reference gas" (Bacastow et al., 1985). When estimating daily averages the "too high" or "too low" values were eliminated by "visual inspection". This clearly introduced a subjective factor in the estimates of temporal trends.

Other long series of CO_2 air concentration were recorded at stations not exposed to vast local volcanic emissions of CO_2. They show an increasing long–term trend similar to that of the Mauna Loa data, but with different amplitudes for the seasonal changes. In view of the above discussion the observations from these stations should be preferred to those from Mauna Loa. A similar "editing" procedure as for the Mauna Loa records was applied also for data from these other stations, to account for (assumed) local disturbances.
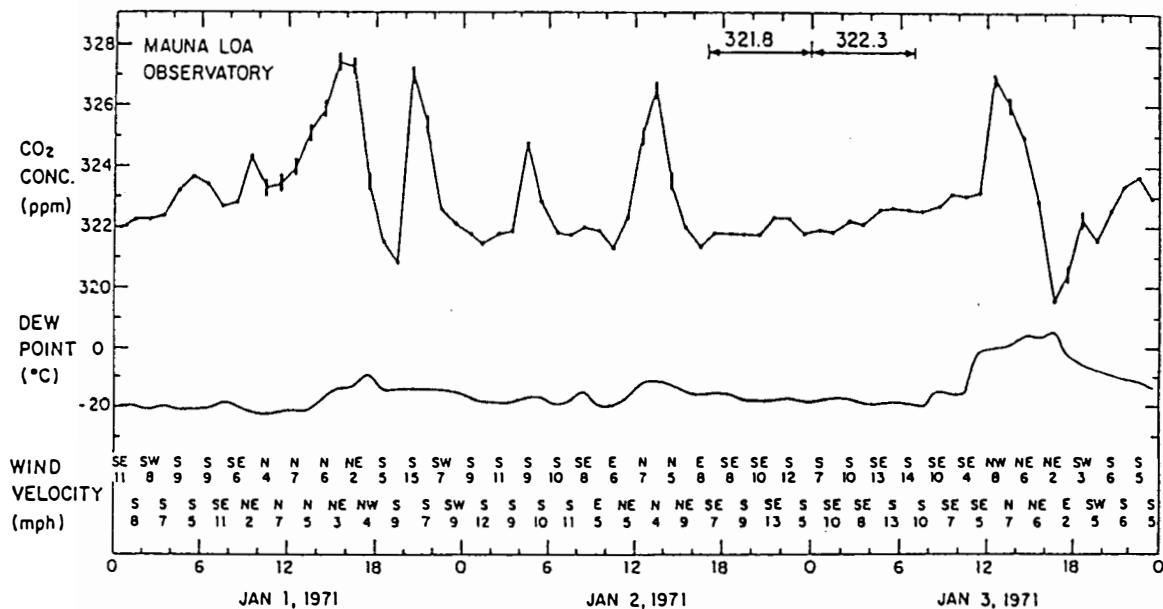
Figure 1. Hourly average atmospheric CO_2 concentration at Mauna Loa (Hawaii). Vertical bars indicate periods rejected from the records, as local CO_2 releases were suspected. Horizontal arrows indicate "steady periods" supposed to give a more representative concentration. (After Keeling et al., 1976.)
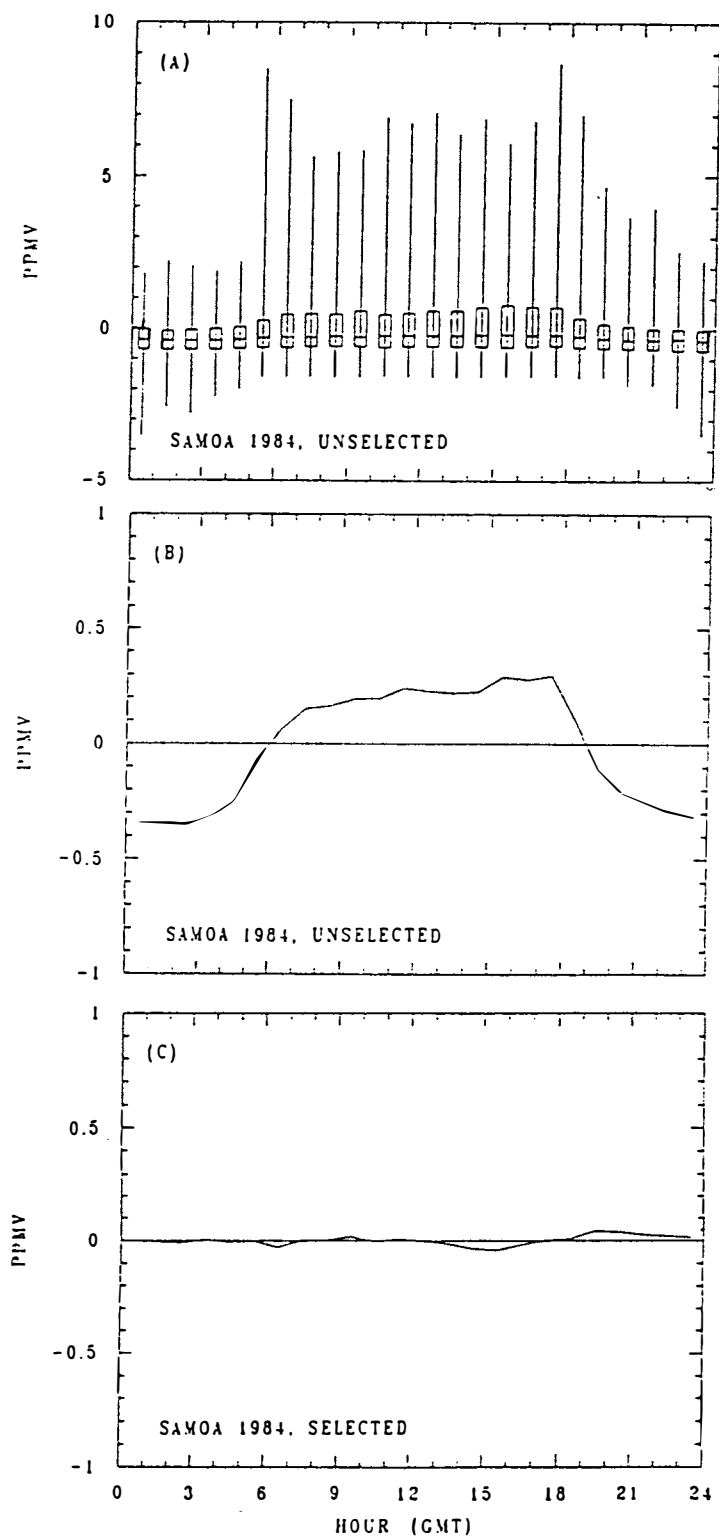
Figure 2. Results of the CO_2 concentration selection procedure at Cape Matatula, Samoa. (After Waterman et al., 1989.)

It seems difficult to understand that the effect of a powerful natural injection of 6 GT of CO_2 (equivalent to 2 GT C) by the El Niño – Southern Oscillation (ENSO) 1982–1983 event (Gaudry et al., 1987), and of nine other ENSO events, are not visible in the Mauna Loa and the South Pole records (Siegenthaler, 1990). On the other hand it has been claimed that the records detect the annual anthropogenic CO_2 releases, which are just 2–3 times higher than the ENSO events. This may mean that the "editing" procedure produces records not reflecting important large–scale CO_2 variations in the atmosphere.

3.2 NINETEENTH CENTURY CONCENTRATIONS

On the basis of the nineteenth century measurements of CO_2 in the atmosphere, compiled by Callendar (1940, 1958), its pre–industrial level was estimated to be about 290 ppm. Callendar based his estimate mainly on the measurements carried out since 1873 at the Montsouris observatory near Paris. According to Callendar (1958) the 19th century measurements might often be up to 100% in error. He noticed that the 19th century data do not "show a significant trend between 1870 and 1900", i.e. at a period when the annual emissions of CO_2 from fossil fuels increased by a factor of 3, from 0.15 to 0.5 GT of carbon (Elliott, 1983).

The Montsouris data show large shifts of monthly means (>10 ppm from one month to the next) and they show no seasonal variations. This is incompatible with the modern records showing much less daily scatter and a clear seasonality (Waterman, 1983). The most obvious jump occurred at Montsouris between June and July 1890, when a change of 27 ppm was reported. This change is about the same as the increase observed at the Mauna Loa observatory during 22 years from 1958 to 1980. Some of the Montsouris measurements indicate extremely high or low values (355 ppm and 243 ppm, respectively). This has been interpreted as an evidence of analytical and sampling shortcomings (Stanhill, 1983).

In 1880 and 1881 Müntz and Aubin determined CO_2 in the center of Paris. The measured concentrations averaged 62 ppm more than those at the same period at Montsouris. Of their ten non–urban sites, seven reported CO_2 concentrations greater than at Montsouris, the mean difference being 12 ppm. In Paris the concentrations recorded in 1880 and 1881 averaged 325 ppm (Wigley, 1983).

It is difficult to believe that a monthly mean of 355 ppm for December 1878 and a mean of 243 for April 1880, reported for the Montsouris Observatory, are truly representative

of global background values (Waterman, 1983). The Montsouris investigators were probably not running any blanks or duplicate measurements that could shed light on the precision of their measurements.

The chemical method used at Montsouris was similar to the procedure used by Müntz and Aubin. This method could lead to erroneously low results due to incomplete stripping of the CO_2 from the airstream by a reaction with KOH. Another source of error was probably a reaction of the reagents on the laboratory apparatus (Waterman, 1983). The enormous temporal scatter of the Montsouris results (of 27 ppm) and the geographical scatter of the Müntz and Aubin data (of 40 ppm) do not represent the "natural noise", but was due to sampling and analytical shortcomings, and indicates that these data cannot be regarded as reliable as contemporary measurements.

It is interesting to note that there is a tendency to choose a low average value for the CO_2 concentration in 19th century atmosphere, because "the most compelling support for a 270 ppm pre–industrial CO_2 level comes from direct measurements of CO_2 in the ice cores" (Wigley, 1983). But those who measured CO_2 in the ice cores also preferred to select as true the lower values, because they were "within the range of the estimated (by Callendar, 1958) pre–industrial atmospheric content of 290 ppm" (Berner et al., 1978).

This demonstrates that a subjective factor biased the CO_2 values chosen by the contemporary researchers, which resulted in a too low estimate of the pre–industrial level of this gas.

4. TREE RINGS AS INDICATORS OF CO_2 IN THE ATMOSPHERE

It has been proposed to use $\delta^{13}C$, an expression for the $^{13}C/^{12}C$ stable (non-radioactive, non–radiogenic) carbon isotope ratio, of tree rings as a way to calculate the CO_2 contents of the atmosphere in the past.

The results of Stuiver et al. (1984) are often used to draw a curve showing the contents of CO_2 in the atmosphere during historic time (e.g., Miljøverndepartementet, 1988–1989). The original article by Stuiver et al. (1984) and other works (e.g. Deines, 1980) demonstrate that contemporaneous trees show large variations in their carbon isotope ratios. Some trees increase their ratios, while others decrease their ratios, at the same time.

Stuiver et al. (1984) emphasize that after normalizing and averaging the data from different trees, there was still a remaining variability in the data resulting in a standard error of ± 16 ppm (assumed 68 % confidence level) in the calculated CO_2 contents (analytical and sampling errors not included). For the computational uncertainty alone, a 95 % confidence level would give ± 31 ppm. A large part of the variation calculated by Stuiver et al. (1984) is less than this statistical uncertainty.

Recent systematic studies on stable isotope geochemistry in plants cast serious doubts on the usefulness of this method in paleoclimatology, because of isotopic inhomogeneity in the plants themselves (e.g. Yakir et al., 1989) and post–photosynthetic modifications in the wood cellulose (e.g. DeNiro and Cooper, 1989). A systematic study by Tans and Mook (1980) of carbon isotopic ratios of the complete circle of a single tree ring, revealed that the carbon isotope variations were up to **3.5** units ($\delta^{13}C$ units expressed in per mil). (See Tans and Mook, 1980).

The maximum variation in the same isotopic ratios given by Stuiver et al. (1984) for the last 1800 years was **3** units, most of the variation was within 2 units (± 1 unit from the mean value). The calculated curve for the atmospheric CO_2 variation for the last 1800 years from carbon isotope ratios in tree rings is hence based on isotope variations which are less than the variations expected in a single tree ring. This fact supports the objections to the use of tree ring isotope analysis in paleoclimatology.

The $\delta^{13}C$ methodology calculates the CO_2 contents of the atmosphere through time by isotopic mass balance calculations in a simplified physical box model (e.g., Oeschger et al., 1975) between the atmosphere, biosphere and the sea at **constant temperature**. The ratios of light stable isotopes, like the carbon isotopes, are strongly changed by temperature. This is the reason why such isotopes find their major use in science as paleothermometers. The

surface temperature of the Earth has varied considerably throughout the last 1800 years (see Figure 7). A temperature change of a few degrees C alone would be able to account for the observed carbon isotope variations by Stuiver et al. (1984). Variations in rainfall would have influence on the photosynthesis and hence the resulting carbon isotope ratios of the tree cellulose (governed to a large part by biologic kinetic isotope effects). The model also neglects CO_2 releases (or accumulations) from the largest reservoirs of carbon involved, namely the lithosphere and the Earth's interior. Furthermore the model assumes that the global source of CO_2 always has a constant carbon isotopic composition. With so many sources and sinks of carbon, each with its distinct carbon isotopic signature (Ohmoto and Rye, 1979), this assumption may represent a too strong simplification.

Finally, the carbon isotopic composition of corals and contemporaneous trees do not correlate (Nozaki et al., 1978). However, they should correlate if all the assumptions were valid and the methods suitable.

It must be concluded that the CO_2 contents in the atmosphere calculated from carbon isotope analysis of tree rings cannot be considered a valid tool in paleoclimatology, and cannot be used as evidence of changing atmospheric CO_2 levels.

5. CO_2 IN GLACIER ICE

Studies of CO_2 concentrations in glacier snow and ice are a corner stone of the increasing "greenhouse effect" hypothesis. Therefore, they deserve a wider discussion.

The early determinations of CO_2 in air bubbles trapped in glacier ice, carried out in the 1950s to the 1970s, recorded much higher concentrations in the pre-industrial samples than the mean value of about 290 ppm estimated by Callendar (1958) for the nineteenth century air. It was in the 1980s that the CO_2 levels in the pre-industrial ice started to be interpreted as being in agreement with the Callendar estimate.

The very first CO_2 studies in glacier ice were initiated at the University of Oslo, and the first measurements were carried out at the Storbreen glacier in Jotunheimen, Norway (Coachman et al., 1956; Coachman et al., 1958 a; Nutt, 1959). These studies indicated that the CO_2 content in air bubbles in the pre-industrial ice was ranging between 200 and 1000 ppm, and that in the older parts of the glacier it was reduced by a factor of three, due to leaching by liquid water. In samples of old ice from the Greenland ice cap, Coachman et al. (1958 b) found that the oxygen values were close to those of the present-day atmosphere, but the values for CO_2 were twice as high as today. They concluded that the atmosphere might have been richer in carbon dioxide at the time this ice was formed. It was recognized in these early studies that the original composition of the air trapped in the ice is changed due to various physical and chemical processes (Scholander et al., 1961).

Coachman et al. (1958 a) stated that the loss of CO_2 from the ice might occur during melting, both at the site of ice formation and near the snout of the glacier. They also noticed that the ice could be contaminated by organic dust, which subsequently became oxidized, enriching the CO_2 of the air in the bubbles. Hemmingsen (1959) observed a great mobility of CO_2 in the glacier ice, which he supposed to be an effect of diffusion in the intercrystalline liquid brine films. Such films and veins of liquid exist in ice even at extremely low Antarctic temperatures (see below).

Alder et al. (1969) found that CO_2 can be adsorbed at the ice surface and remain adsorbed even in **vacuo**, and that this adsorption is not reversible. This effect might decrease the level of this gas in the air bubbles, and also increase its content in the ice by adsorption from the laboratory air. They, and also Scholander et al. (1961), found an evidence that, in the Greenland ice, oxygen is removed by oxidation of organic matter. This may lead to an increase of CO_2 in the ice.

These early studies posed the question whether glacier ice is a reliable matrix for study of the composition of the ancient atmosphere. As will be seen later, after three decades the question is still entirely open.

5.1 CHANGES IN ORIGINAL GAS COMPOSITION

Stauffer et al. (1984) supposed that, among the factors influencing the CO_2 levels in the air bubbles, are the presence of clathrates (gas hydrates), melt layers, and microbubbles. To this list Stauffer and Oeschger (1985) added adsorption of air components on the firn grain surfaces and enclosing the air during snowflake formation, zone refining processes parallelling crystal growth, interaction of CO_2 with the ice itself, fracturing of the ice, chemical reactions between CO_2 and impurities trapped in the ice, and oxygen exchange between CO_2 and water. They found that the increase of the CO_2 concentration parallels the dust content in all the measured ice cores. They also recognized a dependence of CO_2 levels on the acidity of the ice: the samples showing the highest pH values had the lowest CO_2 contents.

But perhaps the most important factor changing the original composition of atmo–spheric air trapped in the glaciers is liquid water present in the ice even at extremely low temperatures.

5.1.1 LIQUID IN ICE AT LOW TEMPERATURES

The Antarctic and Greenland ice cores, used for historical studies of CO_2 changes in the atmosphere, are usually regarded as a steady state matrix in which the original concentrations of this gas are preserved indefinitely. The main argument used in support of this assumption is that the existence of a liquid phase in the polar ice can be neglected at a mean annual temperature of –24°C (Berner et al. 1978; Reynaud and Barnola, 1985). This liquid phase would enable diffusion processes to change the original composition of air contained in the ice. However, the presence of liquids in Antarctic ice was found even at much lower temperatures (see below), so this argument seems now to be invalid. A part of the studies on CO_2 behavior in the temperate glaciers, where a liquid phase is a common feature, may therefore be relevant for ice from the polar caps as well.

Berner et al. (1978) stated that the high content and wide variations of CO_2 observed in ice could be understood if, during the sintering processes of snow to ice, a liquid phase

was present. They believed that with mean annual temperatures at a polar ice cap of −24°C, the influence of the liquid phase can be neglected. This is why the later CO_2 studies in the ice were carried out only on the polar ice caps. This opinion is, however, not correct, in view of the evidence that at low Antarctic temperatures both melt layers and intercrystal-line liquids occur in the ice (see discussion below).

Scholander et al. (1961) listed several processes that could change the original composition of gas inclusions in ice. One of their most important findings was an observation of enrichment of CO_2, oxygen and argon (relative to nitrogen) in air bubbles, by freezing them out from the liquids present in the firn or ice containing dissolved atmospheric gases. They also noticed that supercooled fog, carrying dissolved gases, leads to CO_2 enrichment when freezing on the surface of ice sheets. This is what should be expected in view of the changes in gas ratios when air dissolves in water. On a molar basis the solubility of CO_2 in water at a temperature of 0°C is 73.5 times higher than that of nitrogen, the solubility of oxygen is 2.0 times that of nitrogen, and the solubility of argon 2.4 times higher than that of nitrogen. Therefore, at 0°C temperature the concentration of oxygen in the air dissolved in water is 35%, and not 21% as in the atmosphere (Hodgman et al, 1962; Weast et al., 1989). Such gas ratios, different from atmospheric air, should be characteristic of primary gas inclusions (see below) in ice.

The dissolution of air gases in the liquid contained in ice is likely to start with the formation of snow crystals in the atmosphere. The 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 grain crystals (Wolff et al., 1988). Therefore it seems that at least a part of enrichment of CO_2, O_2 and Ar observed in glacier ice was already reached during the atmospheric history of the snow crystals.

In later studies of ice cores from both central Greenland and Antarctica (see e.g. Neftel et al., 1982; Raynaud and Barnola, 1985), melt layers were commonly observed. Also Boutron (1986) notes the possibility of disturbing the old ice deposits in Greenland and Antarctica by percolating water during the summer months. During the antarctic summer, meltwater was found at a depth of about 1 m in the ice sheet at the station Troll, Dronning Maud Land (Antarctica), 250 km inland, where the summer air temperature was below −20°C (Hagen, 1990). Veins of liquid are also present in the capillary network between the ice crystals, even at extremely low temperatures in the Antarctic ice-sheet (Maccagnan, 1981; Mulvaney et al., 1988).

Acid–water mixtures in layers at ice grain boundaries have been found to remain liquid down to the eutectic point of –73°C (Wolff et al., 1988). In antarctic ice high aqueous concentrations of 4.9 M sulfuric acid H_2SO_4 were found in veins at triple–junctions, where the ice grains meet (Mulvaney et al., 1988). When alkaline dust neutralizes acids in the ice, the resulting salt–H_2O mixtures may cause freezing point depressions. The extent of freezing depression is dependent on type and concentration of salts in the intercrystalline brines. In this way the brine can keep its liquid state down to –50°C or even lower (Roedder, 1984; Shepherd et al., 1985; Oakes et al., 1990). When freezing salt aqueous solutions, pure ice crystallizes, leaving an increasing saline solution. It may be mentioned that for inclusions of sea water in sea ice, there was still liquid brine down to temperatures as low as –70°C (Weeks and Ackley, 1982). As an example this effect may for instance influence the behavior of gases in the deep ice strata of the Vostok core. The high content of Na at Vostok at depths of about 500, 850, and 2000 m coincided with the low CO_2 content recovered from the air inclusions. The low content of Na at the depths of about 1420, 1770, and 1850 m coincided with the increasing CO_2 concentrations (see Barnola et al., 1987).

The importance of the discovery of a liquid phase in ice at extremely low temperatures is difficult to overestimate. This suggests that in glacier ice there is a quasi infinite network of liquid–filled veins, through which dissolved substances can migrate during long periods of time. The validity of antarctic and Greenland ice cores as reliable objects for study of chemical and isotopic composition of the atmosphere of the past epochs is highly questionable.

Considerable knowledge of gas and fluid inclusions in solids has been gained from the geological sciences (e.g. Hollister and Crawford, 1981; Roedder, 1984; Shepherd et al., 1985; Bodnar et al., 1985). The fundamental principle underlying all gas/fluid inclusion studies is that the gases and fluids inside the inclusions are representative portions of the gases and fluids present in the phase from which the host mineral grew (provided the gas/fluid is homogenous at the time of trapping). Such inclusions are called primary inclusions.

Changes may occur inside the inclusions after they were trapped, even if the inclusion volume remains constant. The temperature may change and give rise to phase changes or chemical reactions within the inclusion phases or with the inclusion walls. Solids may precipitate from dissolved species in the inclusion liquids, gases or vapors. Then, the measured characteristics may not be the same as the original ones.

The inclusion volume may change after inclusion trapping, and a chemical re-equilibration internally between phases or with the inclusion wall may take place after the change in temperature, pressure or volume. Solid, liquid and gas inclusions can readily migrate through crystals, and even metals, under the influence of strong thermal gradients (Shepherd et al., 1985). There is also evidence that the inclusions may leak, even from such sturdy materials as quartz, giving wrong information about the CO_2 content of the inclusions (Bakker and Jansen, 1990).

Inclusions formed after the host crystal has been formed are regarded as secondary inclusions. These are commonly formed in post-crystallization fractures initiated during mechanical or thermal stress. These cracks are later sealed to form characteristic trails of secondary inclusions. Such inclusions are unrelated to and not representative of the original volatile environment during the growth of the host mineral. In a similar way, pseudosecondary inclusions may develop, but the fracturing and healing take place before the crystal growth has terminated. Pseudosecondary inclusions should reflect the volatile environment during the last growth stages of the host mineral, but not necessarily the initial stages of growth.

Stauffer et al. (1981) and Oeschger et al. (1985) have described the trapping of air in glacier ice and snow. The uppermost part of a glacier contains snow flakes, and deeper down the firn grains and ice. The pore space between the snow flakes and firn grains is filled by air. In the investigated glaciers, at a depth of about 70–80 m, corresponding to an ice age of about 100–120 years, air bubbles were formed, sealing off the channels to the atmosphere. Hence the air inclusions in ice can be considered as pseudosecondary inclusions, although they did not trap the bulk of the atmosphere gases in inclusions at the time the bulk of the ice formed.

The ice is, however, not a rigid material. It is constantly subject to interaction with water, refreezing, solid phase changes (annealing), fracturing, and plastic deformation. Compression of the air bubbles will occur. Pressure, temperature, volume and density of the ice change. Under these circumstances the ice will not behave as a rigid host material to the inclusions. No textural evidence has been presented that the original pseudosecondary inclusions have been preserved, and that no new secondary inclusions have been formed. We will expect that the secondary inclusions will dominate in a deep ice core sample (the drilling may even destroy the integrity of the remaining original pseudosecondary inclusions present), and that their validity for the paleoatmospheric research may be questioned until such documentation exists. It is also known that the deep

blue ice has lost practically all its inclusions. From a depth of 1200 m no bubbles are visible, neither to the naked eye nor by the microscope (Gow and Williamson, 1975). This suggests that the gases diffused into the ice structure (or were lost through fractures). This leads to problems connected with later release of these gases, and makes it difficult to distinguish between air originally trapped in the ice structure and air recovered from the bubbles in ice (or recently adsorbed in the ice core sample).

The release of gases from inclusions in minerals is commonly done by decrepitation (e.g. Walder and Segalstad, 1987) or crushing (e.g. O'Reilly et al., 1990). The same methods have been used for inclusions in ice. Stauffer et al. (1981) discuss the different experimental methods for analyzing atmospheric CO_2 concentrations in air enclosed in inclusions in ice. The major differences between rock silicates and ice as a host mineral for the inclusions are the much lower melting point for ice (close to ambient temperatures) and higher vapor pressures, influencing the much higher solubilities of gases in the H_2O phases than in, for instance, quartz. Furthermore the ice is physically not a very good container for the inclusions.

Free CO_2 is a very common major constituent of inclusions in a wide range of geological environments. On crushing in the presence of liquid water or water vapor a large fraction of the CO_2 forms aqueous carbonic acid (Roedder, 1984). In glacier ice the measured CO_2 in the gas phase will not represent the total CO_2 in the gas inclusions, because much CO_2 will have been dissolved in the (not analyzed) cold water, both present in the ice and produced at crushing. It seems that this has not been considered by Stauffer et al. (1981), when they described the "missing CO_2" during their ice melting runs. Barnola et al. (1987) report that the presence of water vapor in inclusions gave low values for CO_2 when crushing the ice. They therefore added a flat "best estimate" of 5 ppm to the lower CO_2 concentrations found. Unfortunately the papers usually give no information on the $CO_2/N_2/Ar$ ratios. Hence it is not possible to inspect the data as to the validity of their claimed atmospheric paleocompositions.

5.1.2 NITROGEN/OXYGEN/ARGON RATIOS

For estimation of the age of the air trapped in the upper 80 m of antarctic and Greenland firn and ice Oeschger et al. (1985) assumed that "the entrapment of air in ice is essentially a mechanic process ... which occurs with no differentiation of the gas components". They stated also that the $N_2/O_2/Ar$ ratios in ice are the same as in the ambient atmosphere. However, this assumption, which is crucial for age estimates, is not in agreement with the analytical results.

In the cold Antarctic environment at the Byrd Station (Antarctica), and at Camp Century (Greenland), Raynaud and Delmas (1977) found that the oxygen content in gas in the ice was reduced by 0.83 – 1.2% in comparison with atmospheric air, (i.e. an effect opposite to that expected from the solubility data; Hodgman et al., 1962; Weast et al., 1989), and enriched by 0.75 to 1.2% in argon. This is also opposite to the earlier findings of Scholander et al. (1961). In the firn samples from the Pionerskaya and Vostok stations in Antarctica these authors found the concentrations of both these gases reduced in relation to nitrogen. The error of measurement of these gases was reported to be 0.5%. The authors stated that "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". It is therefore difficult to understand why Oeschger et al. (1985) interpreted the Raynaud and Delmas (1977) finding as an evidence that "$N_2/O_2/Ar$ ratios in ice originating from very cold areas with no summer melting show that, within experimental uncertainty, the measured ratios agree with those in air". This statement Oeschger et al. (1985) used in support of an assumption that the gas trapped in the ice is about 100 years younger than the frozen water which encompasses it. However, the early data of the Oeschger group demonstrated that the Ar/O_2 ratio in various parts of a glacier may reach a value of 0.95%, i.e. much lower than the 1,19% in the ambient air (Berner et al., 1977). According to Berner et al. (1977) the Ar content in the ice (0.948%) is slightly higher than in the atmosphere (0.934%) and the O_2 content slightly lower (20.34% and 20.95%, respectively).

Stauffer et al. (1981) have measured the Ar/O_2 ratio in the old Greenland ice, but refrained from presenting the results. The value of this ratio was given by Stauffer et al. (1985) for ice samples from Dye–3 (Greenland) collected between 0 and 35 m depth. In these samples they found extremely high CO_2 concentrations, up to 28,000 ppm. In the surface layer the ratio of N_2/O_2 was 51.6 % (while being 26.8 % in the atmosphere), N_2/Ar was 2.6 % (1.19 % in atmosphere), and N_2/CO_2 was 4.4 % (0.042 % in atmosphere). This

means that the claim of the gas inclusion age estimates of 90 to 2800 years younger than the age of ice (Oeschger et al., 1985) is based on a false assumption. The $N_2/O_2/Ar$ ratio in the glacier ice is of great importance for estimating the validity of this matrix for the studies of temporal changes of gases in the global atmosphere. The observed changes of this ratio in the ice mean that this matrix is not suitable for studying the original composition of the ancient atmosphere.

5.1.3 DEPLETION OF CO_2 IN SURFACE SNOW

An important finding of Raynaud and Delmas (1977) was the observation that in surface firn (up to 1 m depth) at the Pionerskaya and Vostok stations, the concentration of CO_2 in the interstitial air was 160 to 240 ppm, respectively, whereas in the atmospheric air this concentration was 310 ppm. They stated that in the air trapped in the snow the concentration of CO_2 is reduced as compared with the atmospheric level. This demonstrates that, even in the snow that was not subject to longer firnification and firn–ice transition processes, the CO_2 content may be up to 150 ppm lower, i.e. about 48% lower, than in the ambient air of the same age.

5.1.4 EFFECT OF CARBONATES

In 13 samples (of Holocene and Wisconsin age) from an ice core from Camp Century (Greenland) Raynaud and Delmas (1977) found an average CO_2 concentration of 3500 ppm, and in a core from Vostok (Antarctica) 1300 ppm. These values were determined in whole samples of ice, and not only in the air bubbles. The authors added some drops of sulfuric acid to the ice before melting it. This probably added CO_2 to the original gas composition, by reactions of acid with carbonates present in the samples. Sulfuric acid and sulfates are commonly present in the polar ice. They may possibly react with carbonates in situ, as well as after sampling of the cores of old ice. This may lead to a wide range of CO_2 values, as found in many studies of these cores. Also Delmas et al. (1980) suggested that the presence of carbonates in the ice may influence the CO_2 measurements.

High concentration of dissolved organic carbon (up to 0.32 mg per kg) was found in the Greenland snow (Twickler et al., 1986). They noticed that, in contrast to oxygen, the diffusion of CO_2 in the ice was measurable. This could change the original concentration of this gas in the air inclusions.

5.1.5 CHANGES OF AIR INCLUSIONS IN ICE

Stauffer et al. (1984) supposed that 20% of the observed temporal changes in CO_2 content in air inclusions ("bubbles") is due to enrichment in microbubbles. In the inter-pretation of their results from the Dye–3 (Greenland) core they assumed a 40 ppm surplus CO_2 from the microbubbles, and subtracted it from the measured values. Without this sub-traction, the CO_2 level which they found in the approximately 100 year old ice was about 340 ppm, i.e. similar to the present atmosphere.

In polar glaciers, notably in Antarctica, the air bubbles migrate and form inclusion clusters leaving several hundred meter long outcrops of bubble–free ice. It seems that gas inclusions migrate from less to more bubbly areas (Stehle, 1967). Migration of bubbles was also observed by Maeno (1967). At the Byrd Station (Antarctica) shrinkage of bubbles with increasing depth was observed to be faster below 800 m than expected from hydrostatic pressure; at a depth of 1200 m and on, no bubbles were visible. After several months storage of ice cores, bubbles started to form due to decompression (Gow and Williamson, 1975). Maeno (1967) also observed disappearance of air bubbles in the ice, which he interpreted as due to dissolution of air molecules into ice, or a mass transportation through diffusion of some kind of defects in the ice crystal. Both dissolution and diffusion are quite probable in the open lattice configuration of an ice crystal (Maeno and Kuroiva, 1967).

The internal pressure in the air bubbles trapped in the ice ranges from 2 to 20 atmospheres (Scholander and Nutt, 1960). Langway (1958) found that, in the ice from a deep core in Greenland, the internal pressures of more than 13 atmospheres relaxed after a year's storage, a period shorter than usually encountered in glacier core studies. Such high internal pressures may influence the diffusion of CO_2 in the ice In situ and in the cores, and facilitate the forming of clathrates (hydrates) of gases in the intercrystalline liquid. Cracking of ice occurs due to relaxation of the geostress when the ice cores are removed from the deep layers. Pressurized gases may then escape from the bubbles through the microcracks.

The air bubbles collected from ice by the dry extraction technique contain half or less of CO_2 present in the ice. This low concentration, and not the content in the whole ice sample, is taken into account in the estimates of the CO_2 level in the pre–industrial atmosphere (see Chapter 5.2).

In view of the preceding discussion, a tacit assumption of constant mass, volume, pressure and chemical composition, preserved indefinitely, applied in determination of CO_2 concentration of the gas trapped in the ice, cannot be accepted.

A striking illustration of the effects of glacial processes on the CO_2 content in ice, recovered from great depths, is presented in Figure 3. The air and CO_2 content fluctuations in the ice are more or less parallel between ~900 and 1130 m depth. But below this level a dramatic decrease in the CO_2 concentration was found, not accompanied by a similar decrease in air content (Berner et al., 1980). At corresponding depths the air bubbles disappear in the ice. This phenomenon was observed by Gow and Williamson (1975) below 1200 m in the Byrd Station (Antarctica) core. The authors found that air was present in the ice, and after decompression of the ice core during storage, the bubbles formed again. A decrease in CO_2 content also occurred at a depth of about 1200 m at Camp Century (Greenland) and the Byrd Station was observed by Neftel et al. (1982).

At a certain depth, when the gas pressure exceeds the dissociation pressure, the gas is converted to the clathrate hydrate (solid) form, provided that there is enough liquid H_2O. At the Byrd Station (Antarctica) this pressure is reached at a depth of 800 m (Miller, 1969). At Vostok the predicted depth is 400 m, however sporadic bubbles were observed below 800 m (Korotkevich et al., 1978). The dissociation pressure of the CO_2 clathrate is about 13 to 20 times, depending on temperature, lower than that of N_2 and O_2 in air (Miller, 1969 and 1973; Takenouchi and Kennedy, 1965). This means that at the same temperature the CO_2 clathrates will be formed at much shallower depth than those of the major components of air. This phenomenon is a plausible cause for the decrease of the CO_2 concentration in ice below 1130 meters, observed in Greenland and Antarctic cores by Berner et al. (1980) and Neftel et al. (1982).

Spacial fractionation of gases may occur due to selective formation of clathrates and different solubilities of the different air gases. This is coupled with the migration of liquids in the extensive capillary network of the glaciers. After decompression of the cores the different components of air reenter the gaseous phase, at different rates, forming new secondary air bubbles. At low temperature at this stage a greater part of CO_2 than of other air gases may remain in solution, due the higher retrograde solubility of CO_2 (≥ 74, ≥ 35, and ≥ 31 times higher solubility than that of N_2, O_2, and Ar, respectively, on a molar basis) whereas most of the other air constituents enter the secondary air bubble. The dissociation pressure depends on the temperature. At greater depths in the polar ice caps, where temperature rises, one may expect release of gases from the clathrates. However, the
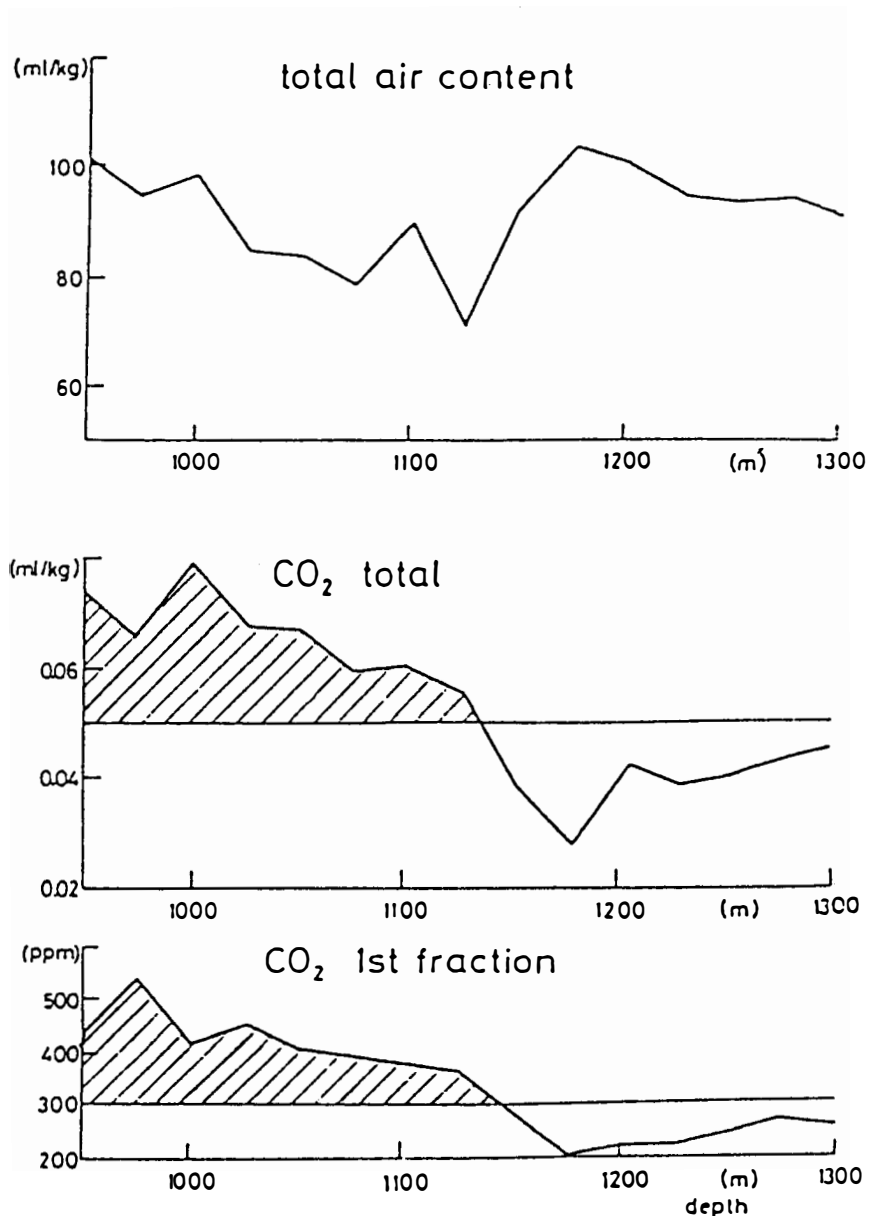
Figure 3. Changes of air and CO_2 content in glacier Ice from Camp Century (Greenland) versus depth (after Berner et al., 1980). Note the decrease in CO_2 content below ~1130 m, where air bubbles were reported to disappear.

clathrates remain stable because the pressure increases. The gases remaining in solids will be subject to diffusion and chemical processes. They may migrate in the intercrystalline liquid during very long periods of time. Their original composition is changed. After release of the geostress the clathrates will dissociate in the recovered cores, at various rates, depending on the differences between the temperature and pressure at the sampling site and that of the storage.

A sudden decrease in the CO_2 concentration from 250 to 180 ppm occurred in the Vostok core at a depth of 400 m (Barnola et al., 1987). This is at a depth that can be predicted for this location for conversion of CO_2 to the clathrate form (Miller, 1969).

5.1.6 MELT LAYERS

The melt layers can not only change the chemical composition of the gases in the ice, but they are also important impermeable barriers for the penetration of gases from the atmosphere into the deeper layers of firn. Even in Antarctica such impermeable layers can be observed down to a depth of ~68 m (Neftel et al., 1985; Raynaud and Barnola, 1985). Raynaud and Barnola (1985) stated that the air in the Antarctic firn cannot be well mixed with the atmosphere due to the existence of these impermeable layers, which isolate the air in the firn from the free atmosphere, even at shallower depth. It is therefore astonishing that some researchers assumed that the air bubbles in ice from a depth of more than 68 m could represent the composition of the 1983 atmosphere (Neftel et al., 1985). In this assumption, based on an observation that the air bubbles became trapped at a depth of 70 m, and on porosity measurements (Berner et al., 1978; Schwander and Stauffer, 1984), the sealing effect of the impermeable layers was not taken into account, even though such layers were observed (Neftel et al., 1985) (see discussion in Chapter 5.1). The physical and chemical processes, which may change the original composition of atmospheric air along its long migration route in porous material to such a depth, were also neglected.

5.1.7 EFFECTS OF DRILLING

Cracking of the ice, in some cases due to rapid decompression, and contamination with drilling fluid (a mixture of diesel oil and trichlorethylene or kerosene), was reported from deep cores, including those from Camp Century (Greenland), Vostok, and Byrd Station (Antarctica), regarded as classic for CO_2 studies (Ng and Patterson, 1981; Neftel et al., 1982;

Kudryashov et al., 1984 a and b; Petit et al., 1990). These factors can lead to significant changes in the composition of air in the ice core inclusions.

5.1.8 CONCLUSIONS

The physical phenomena discussed above, and chemical reactions between CO_2 and chemical species dissolved in the intercrystalline liquid, must change the proportion of gases in the secondary air inclusions (trapped in fractures and between ice crystals), as well as in the primary (gases originally dissolved in water, trapped when the water froze to ice) and pseudosecondary gas inclusions (trapped in channels in the ice crystals, before the channels closed), compared to the original atmospheric composition. Therefore the concentrations of gas species (like CO_2) determined in the air bubbles from deep Greenland and antarctic cores, e.g. from the Vostok core (Barnola et al., 1987), cannot be regarded as representing original atmospheric concentrations of gas species (like CO_2) in the ancient atmosphere.

5.2 MEASURED CO_2 LEVELS IN GLACIER ICE

The early measurements were made by melting the ice samples, weighing up to several kilograms, from which CO_2 was extracted after ice melting and boiling of the meltwater. Later smaller samples (usually ~300 g) were used, and extraction was carried out first during a short time, 7 – 15 minutes, before ice had completely melted. The second extraction was carried out during several hours. The first fraction was interpreted as representing CO_2 contained in the air bubbles trapped in the ice. The second fraction was believed to represent the total content of this gas in the ice. The microanalysis of gas in single gas inclusions in ice was developed already in 1947 (Scholander et al, 1961). Since 1980 a new method, consisting of crushing the ice samples in low temperature, was introduced. With this method the gas was extracted only from the air bubbles, and the weight of samples used by various authors ranged from 1 to 1400 g.

The early determinations of CO_2 in melted ice samples produced a very wide range of results, with peak values reaching several thousands ppm, found after several hours of extraction, i.e. in the total volume of gas contained in the ice structure. The short–term extraction (up to 15 minutes) from melted samples, and crushing the small cubes of ice, produced much lower results, i.e. less than half of total volume results. In the air trapped

in the near surface snow in Antarctica the CO_2 level was up to about 50 % lower than in the atmosphere (Table 2).

The first determinations carried out at a temperate Norwegian glacier showed rather high concentrations, similar to those found later at the polar ice caps. In the Greenland ice cap Scholander et al. (1961) found, in 20 samples of approximately 2700 year old ice (Murozumi et al. 1969), CO_2 concentrations in the air bubbles ranging from about 100 to 900 ppm. Old ice samples from other localities in this region had CO_2 concentrations from a few to more than 1500 ppm. They found large differences between the chemical composition of single air bubbles from the same ice samples. This suggests that, when using small samples with a mass near one gram containing few air bubbles, the analytic uncertainty is increased.

In an antarctic ice core Matsuo and Miyake (1966) found a CO_2 concentration range of 280 to 2900 ppm.

Raynaud and Delmas (1967) measured CO_2 concentrations ranging between 1700 and 7400 ppm in a 108.5 to 1345 m deep ice core from Camp Century, Greenland, and between 900 ppm and 1800 ppm in a 71 to 300 m deep core from Byrd Station, Antarctica.

Berner et al. (1978) found CO_2 levels ranging between 400 ppm and 1200 ppm in 180 year old ice from the Camp Century core at a depth between 90.2 and 90.9 m. These values are quoted here after Stauffer et al. (1981), who noticed that during the process of extraction CO_2 is desorbed from the walls of the extraction container. These authors stated that "this contribution (of ~20%) was estimated and subtracted from the earlier given values". This illustrates the analytical difficulties in the determination of CO_2 in the glacier ice.

Delmas et al. (1980) found high concentrations of CO_2 in ice from two Antarctic cores. At a depth between 113 and 670 m the concentrations ranged from 210 to 740 (average 440) ppm in gas from the melted samples. These values were determined not in the original ice samples, in which the authors found concentrations by an order of magnitude higher (1050 to 6100 ppm), but in the samples that were rinsed "copiously" with water or ethylalcohol. This procedure, which might change the original chemical composition of the samples, was used because the authors supposed that the carbonates present in the sample might have influenced the CO_2 readings.

From the same ice cores Delmas et al. (1980) released about 75% of the gas by pulverization of the frozen "dry" samples. In 22 samples from one core, at various depths between 37 and 893 m, they found concentrations randomly ranging between 160 and 360 ppm. In a second core, in 13 samples from various depths between 37 and 301 m, they

TABLE 2. CONCENTRATIONS OF CO_2 IN GLACIER ICE (ppm by volume).

Age of ice	Locality	Concentration	Reference
PI[3]	Storbreen (Norway)	~200–1000	Coachman et al., 1956 Coachman et al., 1958 a
	Greenland		Coachman et al., 1958 b
PI	11 localities	~100–2500	Scholander et al., 1961
2700 BP[4]	Tuto Tunnel	~100–800	Scholander et al., 1961
PI	Antarctica	280–2900	Matsuo and Miyake, 1966
Holocene and Wisconsin	Greenland	1700–7400	Raynaud and Delmas, 1977
	Antarctica		Raynaud and Delmas, 1977
>100 BP	Byrd Station	900–1800	
Few years BP	Pionerskaya[6]	160	
Few years BP	Vostok[6]	240	
180 BP	Greenland	400–1200	Berner et al., 1978
PI	Antarctica		
	whole ice[5]	210–740	Delmas et al., 1980
	air bubbles[6]	160–335	
PI up to	Greenland[6]	200–800	Berner et al., 1980
40,000 BP	Antarctica[6]	230–400	
5000–30,000 BP	Greenland	200–700	Stauffer et al., 1981
180 BP	Greenland	250–1000	Stauffer et al., 1981
180 BP	Greenland[6]	300–550	Stauffer et al., 1981

---

[3] PI pre-industrial, exact age not given.

[4] Years before present.

[5] Samples washed in water or alcohol.

[6] In gas inclusions after dry extraction, otherwise in melted ice.

TABLE 2 – continued.

Age of Ice	Location	Concentration	Reference
1000?–30,000 BP	Antarctica	200–520	Stauffer et al., 1981
	Greenland		
>100 BP	Dye–3[6]	300–2350	Neftel et al., 1982
600–40,000 BP	Camp Century[6]	1–470	Neftel et al., 1982
~680 BP	North Central Antarctica[6,7]	271	Neftel et al., 1982
600–40,000 BP	Byrd Station[6]	100–500	Neftel et al., 1982
PI	Greenland Dye–3	135–275	Stauffer et al., 1984
~1850	Antarctica[6]	276–295	Raynaud and Barnola, 1985
~1620[6]		258–284	Raynaud and Barnola, 1985
	Antarctica		
1663–1891 BP	Siple[6]	279–328	Neftel et al., 1985
110–820 BP	South Pole[6]	278–281	Neftel et al., 1985
1530–1900 BP	Antarctica[6]	268–326	Pearman et al., 1986
4050–163,670 BP[6]	Antarctica	191–296	Barnola et al., 1987

---

[7] In one 11 cm thick layer at 103 m depth.
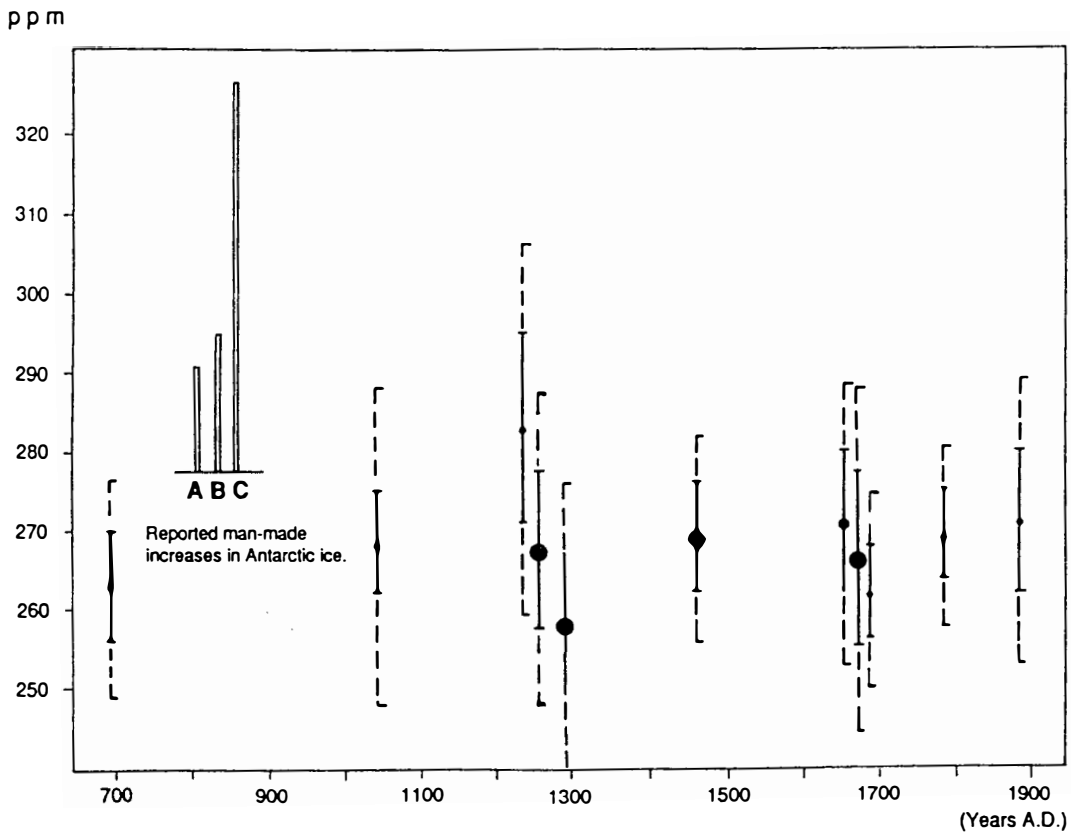
Figure 4. Errors of measurement of CO_2 in air bubbles in ice cores from Greenland and Antarctica (modified after Oeschger et al., 1985) and reported increase of CO_2 level in recent ice samples due to fossil fuel burning (A: Pearman et al., 1986; B: Raynaud and Barnola, 1985; C: Neftel et al., 1985). Solid line indicates ±1 standard deviation (assumed to include ~68% of the observations), broken line indicates ±2 standard deviations (assumed to include ~95% of the observations).

found concentrations ranging between 160 and 350 ppm. The lowest values were measured in the cracked parts of the core, which "lost important volumes of gases". The question arises: how the cracks could deplete CO_2 in the bubbles, instead to allow for CO_2 increase due to contamination by the contemporary air? In both cores exactly the same average concentration of 250 ppm CO_2 was calculated.

Very high concentrations of CO_2 were found by Neftel et al. (1982) in the air bubbles in the several hundred year old ice from a Dye–3 core in southern Greenland, ranging between about 300 and 2350 ppm. At Camp Century in another region of Greenland, they found CO_2 concentrations ranging from about 1 to 470 ppm in several hundred to 40,000 years old ice. At the Byrd Station (Antarctica) in ice of similar age they found CO_2 concentrations ranging between about 100 and 500 ppm. They stated that only the lowest values (which they fail to specify) "best represent the CO_2 concentrations of the originally trapped air", and assumed that the higher readings were due to contamination of the samples with a mixture of diesel oil and trichlorethylene, used as a drilling fluid, which penetrated the cracks in the core. From this description, the cores sampled with such a technique should not be qualified for CO_2 determinations.

In a very cold region at the North Central Station (Greenland) Neftel et al. (1982) found in 22 samples from a 13 cm long part of core from a depth of 103 m a low average CO_2 value of 271 ppm (the detailed results and range not presented). This value is much lower than their readings in ice samples from other regions in Greenland (Camp Century), ranging up to about 440 ppm; the average concentration during a period between 500 and 5000 years ago was about 380 ppm. However, this low value of 271 ppm, from a 13 cm long core, and not an average from all determinations in Greenland (which is similar to, or higher, than the present atmospheric level) is often used in climatological estimates as representative for the pre–industrial period (e.g. Schneider, 1989).

Raynaud and Barnola (1985) measured the CO_2 concentrations in air bubbles from a core collected at the D57 Site in Antarctica. The ice was sampled from the core at various depths below 89 m. The measured annual snow accumulation rate at this region, upslope of the sampling site, ranged between 4.4 and 45 cm. The authors assumed for the bubble air age calculations two average values for the accumulation rate of 45 cm and 18 cm of ice equivalents per year. They do not report the age of the ice, which, however, can be calculated from the assumed accumulation rate values. The accumulation rate of 45 cm per year corresponds to an ice age of about 1849 A.D. at the depth of about 89 m, and 1622 A.D. at the depth of about 197 m. The authors were aware of the occurrence of

impermeable layers, and therefore it is not clear from the presented evidence why they assigned an age of 1940 A.D. for the air bubbles in ice from a depth of 89 m, and 1560 A.D. from 197 m depth. They stated, however, that the age of bubbles "may be, in fact, older by several tens of years ... because the air can be isolated (with impermeable melt layers)". In addition to this error, the uncertainty of the age estimates of the gas bubbles for the recent samples reached ±50 years (from 1940 to 1890), and for the older samples ±225 years (from 1745 to 1520).

In the air bubbles preserved in the ice deposited about 1849 A.D. they found an average CO_2 concentration of 288 ppm (range 275.5 to 294 ppm), and in the ice deposited about 1622 A.D. a concentration of 271 ppm (range 258 to 284 ppm). These results were obtained by "dry crushing" the ice at low temperature, representing the concentrations found in the gas bubbles and not in the ice itself. They do not account for CO_2 which was lost from the bubbles due to diffusion in intercrystalline liquids, and due to numerous other factors discussed in Chapter 5.1.5.

The obvious flaw of this paper is a lack of data from the first few meter depth of firn, which would serve as a contemporary reference. As discussed in Chapter 5.1.3, in the 1 m thick layer of surface firn in Antarctica, the recorded concentrations of CO_2 were up to ~50% lower than in the atmospheric air at the same time. No statistical evaluation of the temporal trend of data was presented. The authors compared their results with the current Mauna Loa atmospheric measurements, and stated that their results "indicate clearly the increase in atmospheric CO_2 due to burning of fossil fuels, and probably also due to the anthropogenic influence on the biosphere over the nineteenth and twentieth centuries". This conclusion is not consistent with the presented results, which probably represent a random fluctuation of CO_2 concentrations in ice, due to natural physical and chemical processes at the snow/air interface in the atmosphere and in glaciers. From the difference of 17 ppm between the mean CO_2 concentration of 288 ppm (st. dev. 6.3) and 271 ppm (st. dev. 8.5); recorded in 1849 and 1622 A.D. ice, respectively, it is not possible to judge if this difference is significant. With the reported errors of the age estimate the authors were even unable to state with a reasonable level of confidence whether they collected the air samples from the twentieth century.

Similar flaws in connection with estimation of the age of air in the bubbles, neglecting the possible enrichment and depletion processes in the snow and ice, lack of analysis of near surface layers, and not accounting for CO_2 in the ice itself, can be found in the Neftel et al. (1985) paper. They measured the CO_2 content in the air bubbles from an ice core

collected in 1983 at the Siple Station, Antarctica. The accumulation rate at that site was about 50 cm (water equivalent) per year. At a depth of 7 m they found an impermeable ice layer formed from melt water, 2 – 10 cm thick. They also noted that at a depth between ~68 and 69 m two impermeable layers occurred. At this depth, corresponding to an ice age of 1891 A.D. they found an average CO_2 concentration of 328 ppm (range not indicated), and interpreted this as an evidence of an effect of fossil fuel burning, because the value of 328 ppm was the same as recorded in the atmosphere at the South Pole ten years earlier.

Neftel et al. (1985) assumed that the air bubbles in the ice deposited about 1891 A.D. had an age corresponding to 1962 – 1983 A.D. They did not measure this age. Among arguments in support of this assumption, they used rather fortuitous coincidence of the CO_2 concentration in the ice from 1891 A.D. and in the South Pole atmosphere in 1973/74. When estimating the difference between the age of the air in bubbles and the age of the ice they have not taken into account the sealing effect of the impermeable layers.

They assumed an age of 95 years for the air in the open pore volume at the firn–ice transition zone, on the basis of an argument that the air in the open pore volume is well mixed at least down to the beginning of the firn–ice transition (Schwander and Stauffer, 1984). They supported this argument by citing the results from the ^{39}Ar dating of the Greenland ice (Loosli, 1983). However, the results in Loosli's (1983) paper indicate the opposite: at 70 m depth at Dye–3, Greenland, an ice core shows the age of the ^{39}Ar gas trapped in the bubbles to be ~70 years, i.e. the same as the age of ice, determined by the ^{35}Si method.

The assumption on the difference of age of ice and age of the trapped air, ranging between ~60 and 4,300 years, was also applied in interpretation of CO_2 measurements by Pearman et al. (1986) and Barnola et al. (1987).

The ice cores can be easily contaminated by ambient air during the field work (Loosli, 1983). This contribution can reach up to 36% as indicated by the measurements of ^{85}Kr, a radioactive gas isotope produced in nuclear reactors and bomb explosions. This suggests that other ambient gases, including CO_2, may contaminate the ice cores during the field work and storage. Oeschger (1989) presented a photograph showing handling of an ice core used for CO_2 studies in the presence of persons smoking cigarettes. Under such circumstances the ice was exposed to higher than ambient CO_2 air concentration, which could change the original composition of the ice core samples. This possibility was noted by Alder et al. (1969) and Stauffer et al. (1981) who noticed "that ice, and especially firn, samples in contact with an atmosphere enriched in CO_2 get contaminated".

Neftel et al. (1985) did not take into account the processes which may enrich CO_2 in deep layers of firn and ice, discussed above, neither the evidence that the snow collected at a depth of 0 to 1 m at two Antarctic sites showed CO_2 concentrations reduced by up to 48% (160 ppm) as compared with the atmosphere (Chapter 5.1.3). Nor have they measured the CO_2 concentrations in the near–surface layers of firn, which would enable comparison with the recent deposits. They concluded that around 1750 A.D. the atmospheric concentration was 280 ppm, and has increased since, because of human factors, by 22.5% to 345 ppm in 1984. This conclusion is difficult to accept in view of the discussion above, and seems to be partially based on circular logic.

It is interesting to note that Raynaud and Barnola (1985) and Neftel et al. (1985), at corresponding depths, observed totally different concentrations of CO_2 in the trapped air, 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 of atmospheric CO_2. This suggests that there exists a tendency of a unidirectional interpretation of the analytical results.

An example of an unusual selection of results is a paper by Pearman et al. (1986). The authors collected 74 ice samples from an Antarctic ice core, from which they rejected 32, because the CO_2 concentrations differed by more than 7 ppm from "at least one other sample of comparable age". They stated that between 1850 and 1900 an increase in CO_2 concentration of 13 ppm occurred, and that this corresponds to a net global CO_2 input of 48 GT, "which cannot be explained by the small amount of fossil fuel consumed during this period". As the authors have not presented all analytical results both conclusions are of little value.

Finally, one should compare the range of analytical uncertainty with the temporal differences in CO_2 concentration in ice, used recently to demonstrate the atmospheric increase of this gas. This difference in the case of Raynaud and Barnola (1985) was 17 ppm, in the case of Neftel et al. (1985) 49 ppm, and in the case of Pearman et al. (1986) 13 ppm. According to Oeschger et al. (1985) the "errors" (at assumed 68% probability) of the single measurements of CO_2 in the air trapped in the 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. It is clear from this comparison that the claims of a recent increase in atmospheric CO_2 content, found in the glacier gas inclusions, is based on rather spurious evidence; the "errors" of measurements at a 95% probability level are larger than or close to the claimed rise in atmospheric CO_2 (see Figure 4).

Classical examples of CO_2 measurements in the Greenland and Antarctic ice are given in Figures 5 and 6. These measurements show typical long–term (6000 to 30,000 years B.P.) random variations of 200 and 700 ppm (Figure 5), and short–term random variations in a 90 cm long core of 180 years old ice, of ~280 and 1000 ppm (Figure 6). It would be difficult to believe that these variations represent the real changes in CO_2 levels in the atmospheric air. Rather they resulted from the physical and chemical processes in the glacier ice, or are due to artifacts during sampling and analyses of the ice. As may be seen in Figures 5 and 6, after a 15 minutes extraction the concentration of CO_2 recovered from the melted ice was much lower than after a 7 hour extraction. N_2, O_2 and Ar did not reveal such behavior. Only ~50% of the CO_2 is extracted after the melting process is terminated. Many hours are needed in order to make the extraction complete. The dry extraction by crushing the frozen samples releases the air contained in bubbles but does not allow measurements of the total CO_2 content (Stauffer et al., 1981).

Stauffer et al. (1981) assumed that, in spite of these difficulties, the CO_2 concentrations measured in the air released from the ice (after 15 minutes extraction) represent the atmospheric content with an accuracy of 22 ppm. This assumption does not seem to be supported by experimental evidence.

Stauffer et al. (1981) stated that "with high probability during the last 30,000 years the atmospheric CO_2 content was in a band of 200 ppm to 400 ppm", and compared their 15 minutes extraction results with the Callendar (1958) value of 290 ppm for the 19th century atmosphere. In the discussion of the long–term changes they ignored the results from 7 hours extraction fractions, which ranged between ~280 ppm and 1300 ppm.

As may be seen in Figure 5, the dry extraction method recovers probably only a half or less of the total CO_2 present in the ice. This method was used in recent studies in which a pre–industrial level of CO_2 in the atmosphere was postulated to be similar to the Callendar (1958) value. The results of the dry extraction methods were interpreted as representing the original atmospheric load of CO_2, although Stauffer et al. (1981) found that these methods "directly released the air contained in the bubbles but do not allow to measure the total CO_2 content".

Therefore, it does not seem possible to accept from the 15–minutes–extraction–from–melted–ice data and from the dry–extraction data discussed above, that the average pre–industrial level of CO_2 in the atmosphere should be about 290 ppm. This value is not justified by the analytical techniques used up to today.
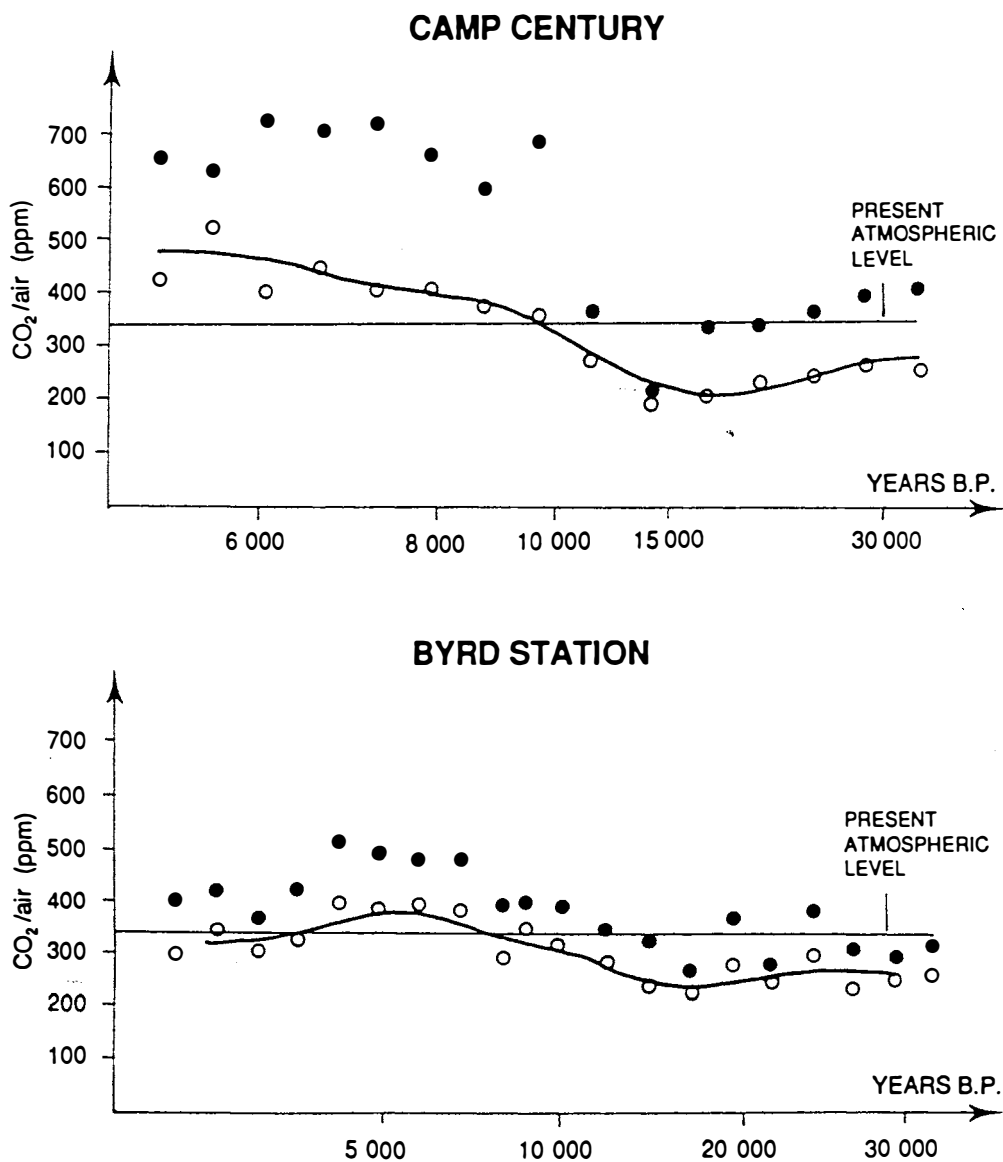
Figure 5. Concentrations of CO_2 in air from the Camp Century (Greenland) and the Byrd Station (Antarctica) ice cores. White dots represent CO_2 concentrations after 15 minutes extraction; black dots after 7 hour extraction. After Stauffer et al., 1981.
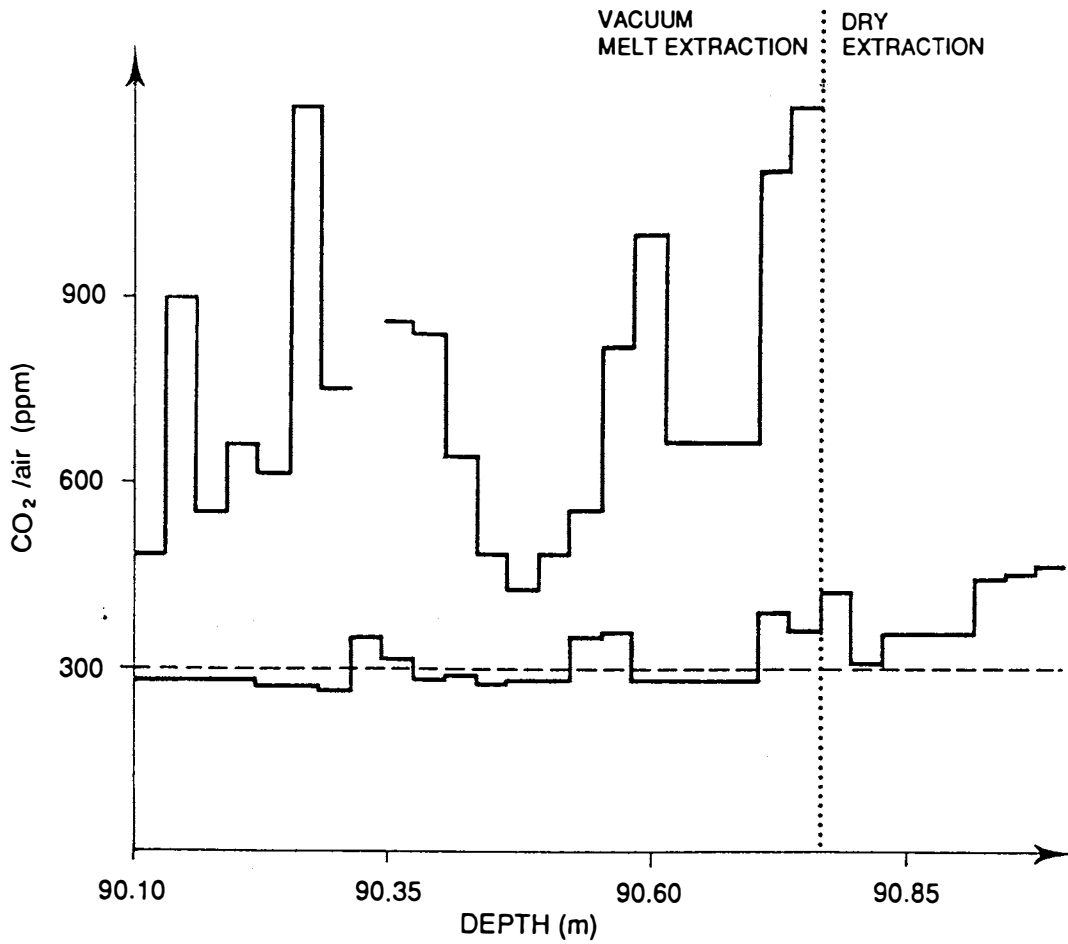
Figure 6. Concentration of CO_2 in a 90 cm long piece of the Camp Century (Greenland) ice core. The lower curve represents the values after 15 minutes extraction from melted ice and the results after dry extraction. The upper curve shows the CO_2 content after 7 hours extraction. After Stauffer et al., 1981.

5.3. CONCLUSIONS

(1) The air trapped in recent (near surface) glacier deposits has lower CO_2 contents than the ambient atmosphere. Therefore the recent deposits are not representing the original CO_2 level in the atmosphere.

(2) Chemical and physical processes during early (atmospheric) history of the snow crystals, and in the old glacier firn and ice, can both decrease or increase the CO_2 content in air trapped in the ice, compared to the original atmospheric concentration. Probably the most important cause of these changes is the presence of liquid in snow and ice, even at extremely low temperatures. CO_2 easily dissolves in cold water because of its retrograde solubility. CO_2 may form solid clathrate. CO_2 may also migrate in the solid ice, as well as in its gaseous inclusions. Other air components have different solubilities in water, and this leads to changes in the concentration ratios between the gases in the ice.

(3) Air bubbles migrate, disappear and reappear in the ice under varying physical conditions. The physical and chemical processes in the bubbles and in the ice are changing the original composition of air trapped in them. Therefore ice cores cannot be regarded as a steady state matrix for the studies of past atmospheric concentrations of CO_2.

(4) Also the sampling and analytical methods used for CO_2 determination in the glacier ice may change the original content of this gas in the samples, by incomplete release of the gas, by loss of CO_2, or by contamination.

(5) The results of CO_2 measurements in pre–industrial ice indicate that the concentrations of this gas trapped in ice fluctuate by a factor of about ten. In ice from the 19th century and before, these concentrations were found to be either the same, or considerably higher or lower than the present atmospheric levels. The "errors" of measurements at a 95% probability level are larger than or close to the claimed rise in atmospheric CO_2. Hence a rise, fall, or steady level of CO_2 in the atmosphere cannot be established from the available CO_2 gas inclusion data. The value of about 290 ppm, often accepted as representing the average global concentration of CO_2 in the pre–industrial atmosphere, is highly uncertain and speculative.

(6)   The establishment of the true pre–industrial level of CO_2 in the atmosphere with the help of polar ice analysis is of great importance and needs further studies. Investigations of the validity of ice as a representative matrix, should be a primary object of these studies.

6.   HYDROGEN AND OXYGEN ISOTOPES IN GLACIERS

Hydrogen and oxygen stable isotope determinations have provided stimulating and fruitful results in the field of glaciology (e.g. see Hoefs, 1980, and Arnason, 1981, for references). The seasonal variation of δD and $\delta^{18}O$ values of snow and firn can be used to date snow and firn layers as a function of depth. The isotope ratios are set by temperature plus the accumulation rate (mass of water precipitated). For example, Epstein et al. (1965) used hydrogen and oxygen isotopes to find an average annual accumulation rate of 7 cm of water at the South Pole between 1958 and 1963, in good agreement with stratigraphic and radioactive dating results.

Snow drift can affect the isotopic composition of the snow after it has been deposited (Arnason, 1981). The isotopic ratios for the light isotopes are changed considerably every time there is a phase change (between vapor/liquid/solid), more at low temperatures than at higher temperatures, and as a function of mass ratios involved in the phase change reaction (e.g. Hoefs, 1980). Kinetic isotope effects, common at low temperatures, may further obscure the picture as calculated by equilibrium isotope effects.

As a result, the seasonal fluctuations of δD and $\delta^{18}O$ in snow and ice are gradually eliminated due to homogenization processes, such as melting and refreezing of water percolating through snow, firn and ice. Thus, detailed comparisons between these isotope records of the ice sheets in Greenland and Antarctica are unreliable (Hoefs, 1980). Arnason (1981) gives examples of isotope variations in ice cores from the Byrd Station in Antarctica where it was impossible to interpret successive summer and winter layers. The isotopic variation was too irregular to be acceptable for paleoclimatic use. Still the hydrogen and oxygen isotope values have been used as record of climatic conditions in terms of calculated mean air temperatures, like for the Vostok ice core (Jouzel et al., 1987; Barnola et al., 1987).

For the Vostok ice core Jouzel et al. (1987) correlate the recent annual averages of the surface temperature with the recent snow hydrogen isotope ratio, using a correction model for the kinetic isotope effect. This relation is then used to calculate temperature deviations from the present surface temperature ($-55.5°C$) for the whole 2083 m ice core covering 160,000 years. The authors must assume that the water precipitation rate was constant throughout this long time span covering several glacial and interglacial stages. This assumption is highly questionable. Nor is it likely that the ice has been unattacked by phase changes and melt/ice–interactions (see Chapter 5) that will alter the original light isotope ratios.

Regarding the kinetic isotope effects Jouzel et al. (1987) point out that "obviously, a change with time in the relative strength of this kinetic effect, possibly associated with changes in saturation conditions, could partly obscure the relation between the isotopic content of polar precipitation and its [calculated] temperature of formation". They therefore conclude from their considerations that "deviations of up to 20% in the estimate of the temperature change cannot be excluded". Taking into account the considerations discussed in Chapter 5.1, it seems that the unfortunately highly uncertain temperature calculations have been widely adopted uncritically by non–scientists as well as scientists (e.g. Houghton and Woodwell, 1989), without taking the uncertainty or the systematics of the method into consideration.

7. LAG BETWEEN CO_2 LEVELS AND TEMPERATURE CHANGES

The noticeable warming tendency of the Northern Hemisphere surface air, which started around 1910 and reached a maximum in the late thirties, took place prior to the major "greenhouse gas" emissions (Michaels, 1990). In the Mauna Loa record of CO_2 atmospheric concentration (Keeling et al., 1989) the peak values lag behind the global continental temperature increases by about five months (Kuo et al., 1990). Kuo et al. (1990) noted that changing temperatures lead to changes in the amount of CO_2 outgassing or dissolution in the ocean, and to variation in biological activity, and thus to CO_2 level changes in the atmosphere. The five month lag time of CO_2 level behind temperature level changes, indicates that the causality is: temperature–to–CO_2. If CO_2 trapping heat was the cause, an opposite sequence of maxima should be observed. Barnett (1990) stated that the

interrelation between the two variables, i.e. CO_2 and temperature, may be due to temperature changes arising from natural climate variability, and has nothing to do with an increasing "greenhouse effect".

The ocean is a large sink for CO_2 dissolved in water. Because of CO_2's retrograde solubility in water, increased temperature causes degassing of CO_2 from the ocean to the atmosphere (Segalstad, 1990). This "thermal solubility pump" accounts for 70% of the CO_2 flux from the ocean to the atmosphere, while "the biologic pump" accounts for the remaining 30% (Volk and Liu, 1988). It has been estimated that 4000 GT of CO_2 (equivalent to 1000 GT of carbon) is fluxed from the ocean via the atmosphere to the continental biosphere when going from a glacial to an interglacial stage (Faure, 1990), owing to these two "CO_2 pumps" only. Other natural carbon fluxes (weathering, volcanism, hot springs, carbonate sedimentation, degassing by metamorphosis of rocks, El Niño – Southern Oscillation, etc.) are not included in this figure.

8. TEMPERATURE RECORDS

As indicated before, it was assumed that since the middle of the 19th century the concentration of CO_2 increased in the atmosphere by ~25%. According to the General Circulation Models (GCMs) this should have increased the global mean air temperature by up to about 2.5°C today. The measurements do not confirm this prediction.

Attempts to find a warming trend signal in the long temperature records are to a large extent based on inspection of smoothed curves ("running means") and not on more reliable time series analyses. The way in which smoothing procedures may totally change the statistical properties of the original time series, and lead to unrealistic conclusions, has been treated by several authors (see e.g. Hisdal, 1956). Variations with long periods are emphasized in a fascinating manner, and short period "noise" is suppressed, the final result depending on the type of smoothing filter applied. Even completely random series may, on the basis of visual inspection, show convincing "climatic changes" after having been beautified by such linear operations (cf. Haavelmo, 1951).

Hansen and Lebedeff (1987, 1988) found that the average global land temperature increased about 0.7°C during the past one hundred years. Other studies suggested that the global land and sea–surface temperatures rose by about 0.5°C (see review in Monastersky, 1989). Hansen (1988) stated in front of the U.S. House of Representatives that he had "99%

confidence" in the reality of the global warming trend, and in the cause/effect relationship between a 0.7°C global warming and anthropogenerated "greenhouse" alterations. This statement was criticized on theoretical grounds (see e.g. review in Kerr, 1989) and it was also found that the uncertainty of the estimated past global temperatures is about the size of the warming signal (Barnett, 1989 – after Monastersky, 1989).

A recent study of the NASA climate records in the United States showed a warming of 0.4°C in the twentieth century. However, this temperature increase could be strongly influenced by an urbanization effect on measurements taken at meteorological stations situated in or near the cities (Karl and Jones, 1989). Also a part of the increase turned out to be due to an error of the computer program when NASA supplied data to NOAA for analysis (Karl – after Michaels, 1990). A study of rural–station temperatures in the Soviet Union, China, and Australia suggests that the urbanization effect could be lower than expected (Jones et al., 1990).

Hanson et al. (1989) found that the records from the 48 contiguous United States do not indicate any statistically significant evidence of an overall increase in annual temperatures or change in annual precipitation between 1895 and 1987.

A new study of the worldwide ocean temperatures since 1850, carried out by a group from MIT (Newell et al., 1989), shows little or no global warming over the past century. The authors found that the average ocean surface temperature is now virtually the same as it was in the 1940s. If two thirds of the buildup of CO_2 have taken place since 1940, the MIT data do not support the model predictions.

Reynolds et al. (1989), analyzing surface and satellite measurements, concluded that there is no evidence of any warming trend in the ocean surface water between January 1982 and June 1988. This finding refuted an earlier claim by Strong (1989) that the sea surface temperatures increased in this period by as much as 0.1°C per year.

The variability of natural climatic fluctuations, and human influence on temperatures (urban and "heat island" effects), have been described e.g. by Landsberg (1974) and Groveman & Landsberg (1979). These factors make it difficult to obtain homogeneous time series of annual global temperatures. During the winter, temperature variations over continents are, on the average, 4–6 times larger than over oceans, and 2–3 times larger on a yearly basis. The area ratio continents/oceans between 15 and 70° North is 0.88, but only 0.14 between 0 and 70° South. For an area weighed arithmetic mean calculated for the Northern and Southern Hemisphere, the temperatures measured over continents will dominate for the Northern Hemisphere. A major problem lies in making the weighed global

annual mean temperatures representative when more temperature data are available over continents than over oceans. This problem has still not been satisfactorily solved.

Long, relatively reliable series exist for the Northern Hemisphere from Europe, North America, Soviet, and Japan. These data were used by Borzenkova et al., (1976) and by Groveman and Landsberg (1979) for calculating weighted annual average temperatures for the Northern Hemisphere (Figure 7). In order to extend the time series back in time (between 300 – 400 years B.P.) Groveman and Landsberg used records of tree ring thickness from Finland and Alaska, which had correlated well with later instrumental temperature records. The older part of their time series is the least reliable one.

A spectral analysis of the almost 400 years long time series reveals that almost half of the variance can be explained by a periodic variation with a wavelength of 99 years (Groveman and Landsberg, 1979). A possible explanation of this is cataclysmic volcanic eruptions occurring at about this time interval, e.g., Laki (Iceland) 1783–1785 and Krakatau (Indonesia) 1883. These released sulfurdioxide explosively to the stratosphere, where the SO_2 combined with water to sulfuric acid, effectively blocking a part of the incoming solar radiation (Segalstad, 1983; Palais and Sigurdsson, 1989). It has been calculated from geologic evidence that Laki's 1983 eruption caused the formation of some 90 million tons of sulfuric acid in the stratosphere, while the 1983 Krakatau eruption contributed some 30 million tons. Other volcanic eruptions also contribute steadily to the atmospheric input of sulfur. For example the small 1981 eruption of the Krafla volcano (Iceland) contributed to the formation of some 100,000 tons of sulfuric acid (Palais and Sigurdsson, 1989).

Because of the irregular influence of volcanoes on the Earth's climate, it is important to look at time series which are several times longer than the periodicity of about 100 years. For a discussion on time spans and resolution of various climatic records see e.g. Webb (1985).

It is interesting to compare the almost 400 years long series with a shorter portion from the years 1850–1975. Both data sets show the same arithmetic means and standard deviations, and are both normally distributed. Adapting a linear trend to the data, the long time series shows almost no change at all (+0.076°C per 100 years), while the short series (1850 – 1975) gives a small increase (+0.33°C per 100 years). It is important to note, however, that the calculated trends "explain" only about 15% of the respective variances. If one assumes that the current (and future) increase in CO_2 releases from human burning of fossil fuels follows an exponential or logarithmic trend instead, and that this trend would be seen in the

temperature record, one should note that exponential or logarithmic trends will not fit the data any better.

Using statistical methods it is hardly possible to predict future temperature changes. It is necessary to find the geophysical mechanisms behind climatic changes before reliable predictions can be made.

The rescaled range methods of Mandelbrot and Wallis (1968, 1969 a, 1969 b) are appropriate for examination of certain long geophysical records. They were used, e.g., for studying the many thousand year long record of water level, flooding and drought of the river Nile. Such records have in most cases been found to be "fractal noise", and statistics based on random series cannot be used. This method tests the persistence tendency of the data, i.e. if high or low levels tend to occur over a long time. It can also put constraints on the likelihood of getting extreme values in the future.

Using this procedure Frøyland (1990) found for the almost 400 years long temperature series, in Figure 7, a strong tendency for the temperature to remain within the same range for times much longer than what would be expected if there was statistical independence in the series. This means that there is a strong persistence tendency in the series, i.e. a warm year is likely to be followed by another warm year, a warm decade is likely to be followed by another warm decade, etc.

Based on examination of rather short (100–150 year) time series many researchers have concluded that a recent rise in temperatures is caused by only one, anthropogenic, cause. This signal is by the same researchers projected into the future to give 1.5 to 4.5°C higher annual global temperatures 60 years from now.

By inspection of the long time series (Fig. 7) we see three other similar temperature rises (starting at about 1835, 1675, 1605). If it is true that the anthropogenic influence by burning of fossil fuels started about 1750, we should be able to see this as a signal in the temperature data over the last 200 years, and different from the foregoing 200 years. We see no obvious difference between these two halves of the series. Even a claimed recent rise in the 1980s (not shown in Figure 7) is less dramatic than the rise in temperatures from about 1812–1830.

In the past, excursions much larger than those in the 400 year record have taken place (Holocene warming, etc.). It is also well known from dynamic systems theory that phenomena like intermittent bursts can commonly occur in nonlinear systems.
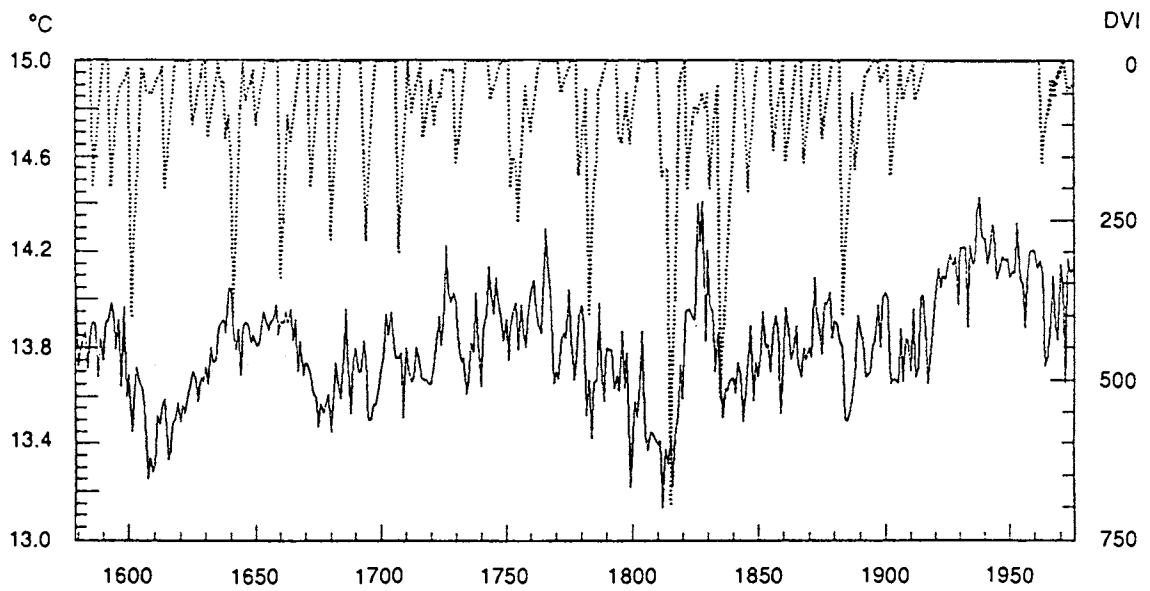
Figure 7. Lower curve: Northern Hemisphere annual temperatures (data from Borzenkova et al., 1976 and Groveman and Landsberg, 1979). Upper curve: Volcanic Dust Veil Index, D.V.I. (data from Lamb 1970, 1978), with increasing values downwards.

We therefore conclude that the nature of the temperature data is such that no signal of human–induced global warming is significantly traced in the best available temperature data for the Northern Hemisphere. High recent temperatures are not significantly different from earlier similar excursions (Fig. 7), and are not of a magnitude or duration (part of a 200 year long increasing trend) that is unique or alarming in the long–term (400 years) natural temperature fluctuations. Recent high temperatures are not different from what can be expected from statistical properties (dynamic systems theory).

The 3.3% annual rise in the release of CO_2 from burning of fossil fuels (Elliott et al., 1985) since about 1750 should give a statistically significant signal in the temperature. It is very difficult to test the significance of a trend, because the temperature record represents a series with a strong persistence tendency. The temperature record may be characterized as resembling "fractal noise". From numerical analysis, the last 400 years temperature record is not showing characteristics that would make the prediction of 1.5 to 4.5°C global heating by the year 2050 very likely from a process that was acting in this period, regardless its cause.

9. AIR TEMPERATURES AND GLACIERS AT HIGH LATITUDES

Temperature data from the Scandinavian peninsula and Denmark for the last 120–130 years give no evidence of any increasing trend during this period (Hanssen–Bauer, 1990). There seems to be a slight increasing tendency up to the 1940s, followed by a slight decrease towards the end of the series. The warmest period in the 1930s coincided with the lowest volcanic dust loading of the global atmosphere during the last several hundred years (Lamb, 1970) (see Figure 7).

Long–term temperature records in Svalbard started in 1912 at Green Harbour. During the first years the smoothed mean temperature rose considerably until the 1920s, particularly during the winter season (Birkeland, 1930; Hesselberg and Birkeland, 1940). Since then there have been several "nice" waves in the Svalbard temperature records, as in all smoothed series, but no definite sign of an increasing "greenhouse" warming, that would justify a statistical analysis (Figure 8).

Five studies of other arctic temperature records (presented by Michaels, 1990) show similar variations as those found in the Norwegian Arctic.
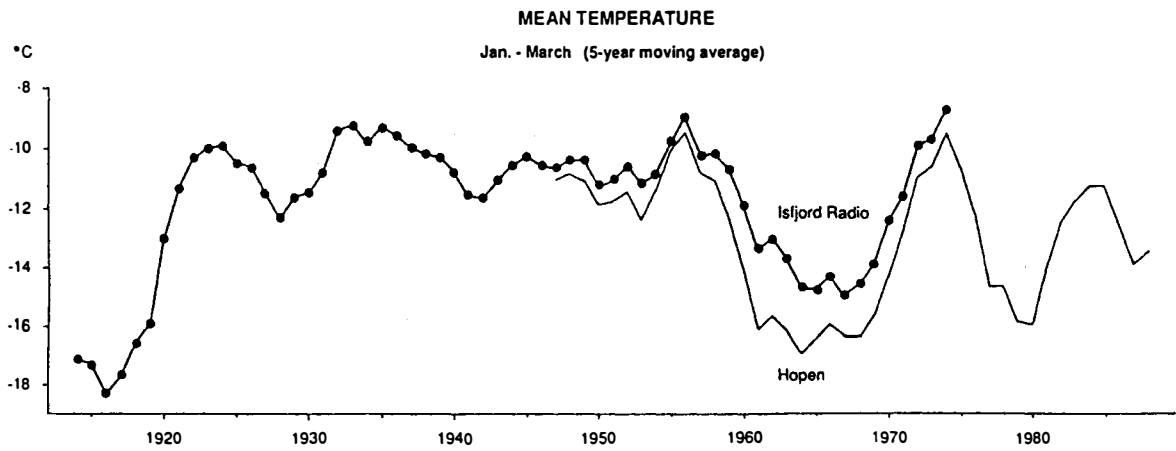
Figure 8. Five–year moving average temperature for January–March for the stations Isfjord Radio (78°04'N, 13°38'E) and Hopen (76°30'N, 25°04'E).

Using the melt layers at the Devon Ice Cap in the Canadian Arctic, Koerner and Fisher (1990) reconstructed the summer Arctic temperatures during the last 10,000 years. Their data suggest that the warmest summers occurred 8,000 – 10,000 years ago, and the coldest ones only 150 years ago (end of "The Little Ice Age"). The cooling from about 9,500 years ago to the present was estimated to be about 2.5°C.

Stratospheric temperatures, which according to climatic models should decrease in a "greenhouse–gas" enriched atmosphere, did not show a statistically significant decline since 1960 (Angell, 1986).

Because of the combined effect of the "greenhouse gases", we should, according to Michaels (1990), have effectively gone beyond half way to a doubling of CO_2. But the high latitude temperatures have simply not responded in the predicted fashion. In fact the data indicate a rise in temperature **prior to** the major "greenhouse gas" emissions, followed by a decline, or on a longer time scale, no trend at all.

Lefauconnier and Hagen (1990) and Hagen and Liestøl (1990) found at the Brøgger-breen and Lovenbreen glaciers in Svalbard an indication of a recent deceleration of loss of ice mass. This is in agreement with the study of Koerner et al. (1989) who have determined the ice mass balance for the past 10 to 30 years at four ice caps in the Canadian Arctic, and found no indication of increasing ablation. These ice caps and the Svalbard glaciers are likely to be good detectors of increasing "greenhouse effect", especially if it is true that the warming should be most pronounced at high latitudes. In the Canadian ice cap Koerner et al. (1989) found that the conditions during the last years constitute a marked contrast to the heavy melting years that characterized the warm period from the 1960s to the early 1980s. During the second half of the 1980s, there was an increase in the ice mass at the Melville South and Meighen ice caps. Since about 1968, the advance of small glaciers in West Greenland coincided with a period of decreasing summer temperatures, and could be seen as a direct response to this climatic deterioration. Six out of the nine glaciers studied continued to advance at least until 1978 (Gordon, 1980).

One should also note that new satellite surveys indicate that both the ice caps of Greenland and Antarctica are now increasing, corresponding to a lowering of the sea water level of 0.45 and 0.75 mm per year, respectively (Meier, 1990). Hence the thermal expansion of the sea water during a warming period can thus be counterbalanced. Of course during cooling periods the water of the oceans will tend to show thermal contraction.

The above evidence supports the opinion (Wigley et al., 1989) that the anthropogenic increasing "greenhouse" warming signal has **not** yet been detected in a rigorous way.

10. CONCLUDING REMARKS

★   The atmosphere is a contemporary, rather short–term, storage for the trace gas CO_2, in which this gas has a residence time of about 5 years.

★   The atmospheric CO_2 is constantly changing and adjusting its concentration according to the natural changes in the Earth's temperature. This is governed by inorganic thermodynamic gaseous, aqueous and mineral equilibria, and by biologic processes. The anthropogenic CO_2 is negligibly small compared to these strong CO_2 "pumps" and other natural fluxes of CO_2.

★ CO_2 has a high solubility in water. Lower aqueous solubility of CO_2 at higher temperature will make the oceans degas CO_2 to the atmosphere, when the sea and air temperature rises as a natural result of climate change. This leads to an increase of CO_2 concentration in the atmosphere, which in this case is an effect and not a cause of climatic change. The CO_2 increases in the 20th century were found to lag behind increases of the surface air temperature. A warming effect of the increased atmospheric CO_2 may be counterbalanced by powerful negative feedback mechanisms, such as increased cloudiness.

★   Radiocarbon (^{14}C) studies show that the upper ocean turn over the dissolved atmo–spheric CO_2 in a short time (a few decades).

★   The total fossil fuel carbon reservoir is only 11 times larger than the atmospheric carbon reservoir. About fifty parts of CO_2 are dissolved in the oceans for each part released to the atmosphere. Therefore, a permanent doubling of the atmospheric CO_2 cannot be realized from burning of fossil fuels only, all other things being held constant.

★   The estimate of "pre–industrial" atmospheric CO_2 concentration cannot be based on studying gas inclusions in ice cores, or carbon isotopes in tree rings, the way it has been done up to now. The sampling and analytical methods used give results that have an uncertainty larger than the claimed variations.

★ The presence of liquid water in glacier ice at low temperatures, and the physical and chemical processes involved, is likely to make ice core results not representative of the original chemical and isotopic composition of the ancient atmosphere.

★ Temperature estimates from hydrogen and/or oxygen isotopes in glacier ice are highly uncertain, and in most cases meaningless if ice/water–interactions took place in the glacier ice.

★ Clear indications of atmospheric heating caused by anthropogenic releases of CO_2 or other "greenhouse" gases have not been proved in the temperature records.

★ For several arctic glaciers a reduction of the negative mass balance was found. Both in Greenland and Antarctica an increase of ice mass was recently observed, which indicates, for instance, that an imminent rise in sea level is not likely. Thermal expansion of sea water during the last warming period can thus be counterbalanced.

11. REFERENCES

Abelson, P.H., 1990. Uncertaintles about global warming [edltorial]. **Science, 247: 1529.**

Alder, A., J. Gelss and A. Renaud, 1969. Gas composltlon In lce samples collected by E.G.I.G. in Greenland. **Medd. Grønland, 177 (2): 100-115.**

Angell, J.K., 1986. Annual and seasonal global temperature changes in the troposphere and low stratosphere. **Mon. Weather Rev., 107: 1922-1930.**

Arnason, B. 1981. Ice and snow hydrology. *In:* Gat, J.R. and R. Gonfiantini (Eds.): Stable Isotope hydrology. Deuterium and oxygen–18 In the water cycle. Internat. **Atomic Energy Agency, Tech. Report Serles, 210: 143-175.**

Bacastow, R.B., C.D. Keellng and T.P. Whorp, 1985. Seasonal amplitude increase in atmospheric CO_2 concentration at Mauna Loa, Hawaii, 1959–1982. **J. Geophys. Res. 90 (D6): 10529-10540.**

Bakker, R.J. and J.B.H. Jansen, 1990. Preferential water leakage from fluid inclusions by means of mobile dislocations. **Nature, 345: 58-60.**

Barnett, 1990. Beware greenhouse confusion. **Nature 343, 696-697.**

Barnola, J.M., D. Raynaud, Y.S. Korotkevich and C. Lorius, 1987. Vostok ice core provides 160,000–year record of atmospheric CO_2. **Nature, 329: 408-414.**

Barta, L. and D.J. Bradley, 1985. Extension of the specific Interaction model to include gas solubllltles In high temperature brine. **Geochlm. Cosmochlm. Acta, 49: 195-203.**

Battam, L.J., 1979. **Weather** (Polish transl.). Panstwowe Wydawnlctwo Naukowe, Warsaw: 182 pp.

Berner, W., P. Bucher, H. Oeschger and B. Stauffer, 1977. Analysis and interpretation of gas content and compositlon in natural ice. *In:* Isotopes and Impurities in Snow and Ice. **Internat. Assoc. of Hydrol. Scl. (Washington, D.C.), Publ. 118: 272-284.**

Berner, W., B. Stauffer and H. Oeschger, 1978. Past atmospheric composition and climate, gas parameters measured on Ice cores. **Nature, 276: 53-55.**

Berner, W., H. Oeschger and B. Stauffer, 1980. Information on the CO_2 cycle from ice core studies. **Radlocarbon, 22: 227-235.**

Birkeland, B.I., 1930. Temperaturvariationen auf Spitsbergen. **Met. Zeltschr. 47 (6): 234-236.**

Bodnar, R.J., T.J. Reynolds and C.A. Kuehn, 1985. Fluid–inclusion systematics in epithermal systems. *In:* Berger, B.R. and P.M. Bethke (Eds.): Geology and geochemistry of epithermal systems. **Soc. Econ. Geol., Rev. In Econ. Geol., 2: 73-97.**

Bolin, B. and C.D. Keellng, 1963. Large–scale atmospheric mlxing as deduced from the seasonal and meridlonal variations of carbon dloxide. **J. Geophys. Res., 68: 3899-3920.**

Bolln, B. 1989. How much CO_2 will remain in the atmosphere. *In:* B. Bolin, B.R. Döös, J. Jäger and R.A. Warrick (Eds.): **The Greenhouse Effect, Cllmatic Change and Ecosystems. (SCOPE 29).** John Wiley & Sons, Chichester: 93–155.

Borzenkova, I.I., K.Y. Vinnikov, L.P. Spirina and D.I. Stekhnovskii, 1976. Variation of Northern Hemisphere air temperature from 1881 to 1975. **Meteorol. I Gidrol., 7: 27-35.**

Boutron, C.F., 1986. Atmospheric trace metals and metalloids in the snow and ice layers deposlted In Greenland and Antarctica from prehistoric times to present. **Advances In Envlron. Scl. Technol., 17: 467-506.**

Braathen, G.O., H. Dovland and B. Aune, 1989. Foreløpig rapport fra NILU og DNMI om drivhuseffekten og klimautviklingen. **Norsk Instltutt for Luftforskning, Report NILU OR: 79/89: 76 pp.**

Broecker, W.S. and T.–H. Peng, 1974. Gas exchange rates between air and sea. **Tellus, 26: 21-35.**

Broecker, W.S., T. Takabashi, H.J. Simpson and T.-H. Peng, 1979. The fate of fossil fuel carbon dioxide and the global carbon budget. **Science, 206: 409-418.**

Budyko, M.I., A.B. Ronov and A.L. Yanshin, 1987. **History of the Earth's atmosphere.** Springer-Verlag, 139 pp.

Callendar, G.S., 1940. Variations in the amount of carbon dioxide in different air currents. **Quart. J. Roy. Meteorol. Soc. 66: 395-400.**

Callendar, G.S., 1958. On the amount of carbon dioxide in the atmosphere. **Tellus, 10: 243-248.**

Cess, R.D., 1989. **Presentation to U.S. Department of Energy meeting on research planning for Global Change, Germantown, MD, April, 1989** – After Michaels, 1990.

Cess, R.D., G.L. Potter, J.P. Blanchet, G.J. Boer, S.J. Ghan, J.T. Kiehl, H. Le Treut, Z.-X. Liang, J.F.B. Mitchell, J.-J. Morcrette, D.A. Randall, M.R. Riches, E. Roeckner, U. Schlese, A. Slingo, K.E. Taylor, W.M. Washington, R.T. Wetherald and I. Yagai, 1989. Interpretation of cloud–climate feedback as produced by 14 atmospheric general circulation models. **Science, 245: 513-516.**

Charlson, R.J., J. E. Lovelock, M.O. Andreae and S.G. Warren, 1987. Oceanic phytoplancton, atmospheric sulphur, cloud albedo and climate. **Nature, 326: 655-661.**

Coachman, L.K., E. Hemmingsen and P.F. Scholander, 1956. Gas enclosures in a temperate glacier. **Tellus, 8: 415-423.**

Coachman, L.K., T. Ennis and P.F. Scholander, 1958 a. Gas loss from a temperate glacier. **Tellus, 10: 493-495.**

Coachman, L.K., E. Hemmingsen, P.F. Scholander, T. Ennis and H. DeVries, 1958 b. Gases in glaciers. **Science, 127: 1288-1299.**

Decker, R. and R. Koyanagi, 1983. *In:* Annual Report of the World Volcanic Eruptions. **Bull. Volc. Eruptions 21: 65-66.**

Decker, R.W., T.L. Wright and P.H. Stauffer (Eds.), 1987. Volcanism in Hawaii. **US Geol Surv. Prof. Pap., 1350: 845-1667.**

Deines, P., 1980. The isotopic composition of reduced organic carbon. *In:* Fritz, P. and J.C. Fontes (Eds.): **Handbook of environmental isotope geochemistry, Vol. 1.** Elsevier: 329–406.

Delmas, R.J., J.-M. Ascencio and M. Legreand, 1980. Polar ice evidence that atmospheric CO_2 20,000 yr BP was 50% of present. **Nature, 284: 155-157.**

DeNiro, M.J. and L.W. Cooper, 1989. Post–photosynthetic modification of oxygen isotope ratios of carbohydrates in the potato: Implications for paleoclimatic reconstruction based upon isotopic analysis of wood cellulose. **Geochim. Cosmochim. Acta, 53: 2573-2580.**

Druffel, E.R.M. and P.M. Williams, 1990. Identification of a deep marine source of particulate organic carbon using bomb ^{14}C. **Nature, 347: 172-174.**

Drummond, S.E., Jr., 1981. **Boiling and mixing of hydrothermal fluids: chemical effects on mineral precipitation.** Ph.D. thesis, The Pennsylvania State University: 381 pp.

Elliott, W.P., 1983. A note on the historical industrial production of carbon dioxide. **Climatic Change, 5: 141-144.**

Elliott, W.P., L. Machta and C.D. Keeling, 1985. An estimate of the biotic contribution to the atmospheric CO_2 increase based on direct measurements at Mauna Loa Observatory. **J. Geophys. Res., 90 (D2): 3741-3746.**

Encyclopaedia Britannica, 1974. Helen Hemingway Benton Publisher, Chicago.

Epstein, S., R.P. Sharp and A.J. Dow, 1965. Six–year record of oxygen and hydrogen isotope variations in South Pole firn. **J. Geophys. Res., 70: 1809-1814.**

Eriksson, E., 1963. Possible fluctuations in atmospheric carbon dioxide due to changes in the properties of the sea. **J. Geophys. Res., 68: 3871-3876.**

Etcheto, J. and L. Merlivat, 1988. Satellite determination of the carbon dioxide exchange coefficient at the ocean – atmosphere interface: A first step. **J. Geophys. Res. 93, 15669-15678.**

Faure, H., 1990. Changes in the global continental reservoir of carbon. **Paleont., Paleo-geography, Paleoecol. (Global and Planet. Change Sect.), 82: 47-52.**

Fergusson, J.E., 1985. **Inorganic Chemistry and the Earth, Chemical Resources, their Extraction, use and Environmental Impact.** Pergamon Series on Environmental Sciences, Pergamon Press: 400 pp.

Flohn, H., 1980. Possible climatic consequences of a man–made global warming. **Internat. Inst. Applied Systems Anal. (Laxenburg, Austria), Rep. RR-80-30.** – After Jäger, 1981.

Frøyland, J., 1990. Private communication.

Garrels, R.M. and C.L. Christ, 1965. **Solutions, minerals, and equilibria.** Harper & Row: 450 pp.

Garrels, R.M. and M.E. Thompson, 1962. A chemical model for sea water at 25°C and one atmosphere total pressure. **Am. J. Sci., 260: 57-66.**

Gaudry A., P. Monfray, G. Polian and G. Lambert, 1987. The 1982–1983 El Niño: a 6 billion ton CO_2 release. **Tellus, 39 B: 209-313.**

Gerlach, T.M. and B.E. Taylor, 1990. Carbon isotope constraints on degassing of carbon dioxide from Kilauea Volcano. **Geochim. Cosmochim. Acta, 54: 2051-2058.**

Gonfiantini, R., 1981. The δ–notation and the mass–spectrometric measurement techniques. **Internat. Atomic Energy Agency Tech. Rep. Ser., 210: 35-84.**

Gordon, J.E., 1980. Recent climatic trends and local glacier margin fluctuations in West Greenland. **Nature, 284: 157-159.**

Gow, A.J. and T. Williamson, 1975. Gas inclusions in the Antarctic ice sheet and their glaciological significance. **J. Geophys. Res. 80 (36): 5101-5108.**

Groveman, B.S. and H.E. Landsberg, 1979. Reconstruction of Northern Hemisphere temperature: 1579–1880. **Meteorol. Prog., Univ. Maryland, Publ. 79-181: 46 pp.**

Haavelmo, T., 1951. **Inføring I teoretisk statistikk. Del II.** Memorandum fra Sosial–økonomisk Institutt, University of Oslo: 123 pp.

Hagen, J.O., 1990. Personal communication.

Hagen, J.O. and O. Liestøl, 1990. Long–term mass balance investigations in Svalbard 1950–1988. **Annals of Glaciol. - In press.**

Hansen, J., A. Lacis, D. Rind, G. Russell, P. Stone, I. Fung, R. Ruedy and J. Lerner, 1984. Climate sensitivity: Analysis of feedback mechanisms. **Climate Processes and Climate Sensitivity, Maurice Ewing Series, Am. Geophys. Union, Washington, D.C., 5: 368 pp.**

Hansen, J., 1988. **Testimony to U.S. House of Representatives, 6/88.** – After Michaels, 1990.

Hansen, J. and S. Lebedeff, 1987. Global trends of measured surface air temperature. **J. Geophys. Res., 92: 13345-13372.**

Hansen, J. and S. Lebedeff, 1988. Global surface temperatures: update through 1987. **Geophys. Res. Lett., 15: 323-326.**

Hanson, K., G.A. Maul and T.R. Karl, 1989. Are atmospheric "greenhouse" effects apparent in the climatic record of the contiguous U.S. (1895–1987)? **Geophys. Res. Lett., 16: 49-52.**

Hanssen–Bauer, I., 1990. Personal communication.

Hemmingsen, E., 1959. Permeation of gases through ice. **Tellus, 11: 355-359.**

Henley, R.W., A.H. Truesdell and P.B. Barton, Jr. (Eds.), 1984. Fluid–mineral equilibria in hydrothermal systems. **Soc. Econ. Geol., Rev. In Econ. Geol., 1: 267 pp.**

Hesselberg, T. and B.J. Birkeland, 1940. Säkulare Scwankungen des Klimas von Norwegen. Die Lufttemperatur. **Geofys. Publ. (Oslo), 14: 106 pp.**

Hisdal, V., 1956. Statistical description of pressure. *In:* **Norwegian-British-Swedish Antarctic Expedition, 1949-52. Scientific Results.** Norsk Polarinst., Oslo: 7–34.

Hoefs, J. 1980. **Stable Isotope geochemistry, 2nd. ed.** Minerals and Rocks, Vol. 9. Springer–Verlag: 208 pp.

Hodgman, C.D., R.C. Weast, R.S. Shankland and S.M. Selby, 1962. **Handbook of Chemistry and Physics, 44th ed.** Chem. Rubber Publ. Co., Cleveland, Ohio: 3604 pp.

Holland, H.D., 1984. **The chemical evolution of the atmosphere and oceans.** Princeton University Press: 582 pp.

Hollister, L.S. and M.L. Crawford, 1981. Short course in fluid Inclusions: applications to petrology. **Mineral. Assoc. of Canada, Short Course Handbook, 6: 304 pp.**

Horita, J., 1989. Analytical aspects of stable isotopes in brines. **Chem. Geol. (Isotope Geoscl. Sect.), 79: 107-112.**

Houghton, R.A. and G.M. Woodwell, 1989. Global climatic change. **Scl. Am., 260 (4): 18-26.**

Iansiti, E. and L. Niehaus, 1989. Impact of energy production on atmospheric concentration of greenhouse gases. **IAEA Bull., 31 (2): 12-20.**

ICRP, 1975. Report of the Task Group on Reference Man. **International Commission for Radiological Protection.** ICRP Publ. 23., Pergamon Press, Oxford: 480 pp.

Jäger, J., 1981. A critical review of recent studies of the impact on climate of an increased atmospheric carbon dioxide concentration. *In:* Fazzolare, R.A. and C.B. Smith (Eds.): **Beyond the Energy Crisis - opportunity and challenge. Vol. 2.** Pergamon Press, 529–537.

Jones, P.D., P.Y. Groisman, M. Coughian, N. Plummer, W.C. Wang and T.R. Karl, 1990. Assessment of urbanization effects in time series of surface air temperature over land. **Nature, 347: 169-174.**

Jouzel, J., C. Lorius, J.R. Petit, C. Genthon, N.I. Barkov, V.M. Kotlyakov and V.M. Petrov, 1987. Vostok ice core: a continuous isotope temperature record over the last climate cycle (160,000 years). **Nature, 329: 403-408.**

Karl, T.R. and P.D. Jones, 1989. Urban bias in area–averaged surface air temperature trends. **Am. Met. Soc. Bull., 70: 265-270.**

Keeling, C.D., R.B. Bacastow, A.E. Bainbridge, C.A. Ekdahl, Jr., P.R. Guenther and L.S. Waterman, 1976. Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. **Tellus, 28: 538-551.**

Keeling, C.D., R.B. Bacastow, A.F. Carter, S.C. Piper, T.P. Whorf, M. Heimann, W.G. Mook and H. Roeloffzen, 1989. A three–dimensional model of atmospheric CO_2 transport based on observed winds: 1. Analysis of observational data. *In:* Peterson, D.H. (Ed.): Aspects of climate variability in the Pacific and the Western Americas. **Am. Geophys. Union, Geophys. Mono., 55: 165-236.**

Kuo, C., C. Lindberg and D.J. Thomson, 1990. Coherence established between atmospheric carbon dioxide and global temperature. **Nature, 343: 709-714.**

Kerr, R.A., 1989. Greenhouse skeptics out in the cold. **Science, 244: 1041-1043.**

Koerner, R., R. Dubey and M. Parnandi, 1989. Scientist monitor climate and pollution from the ice caps and glaciers. **Geos, 18: 33-38.**

Koerner, R.M. and D.A. Fisher, 1990. A record of Holocene summer climate from a Canadian high–Arctic ice core. **Nature, 343: 630-631.**

Korotkevich, Y.S., V.N. Petrov, N.I. Barkov, L.I. Sukhonosova, D.N. Dmitriyev and V.G. Portnov, 1978. Results of studies of the vertical structure of the Antarctic Ice Sheet near Vostok Station. **Informatslonnyy Byulleten' Sovetskoy Antarktlcheskoy Espeditsil, 97: 135-148** (in Russian).

Koyanagi R. and T. Wright, 1987. **Bull. Volcanol., 49: 42-43.**

Koyanagi, R., G. Ulrich and T. Wright, 1987. **Bull. Volcanol., 49: 44-45.**

Kramer, J.R., 1965. History of sea water. Constant temperature–pressure equilibrium models compared to liquid inclusion analyses. **Geochim. Cosmochim. Acta, 29: 921-945.**

Krauskopf, K.B., 1979. **Introduction to geochemistry, 2nd ed.** McGraw–Hill, Inc.: 617 pp.

Kudryashov, B.B., V.K. Chistgakov, E.A. Zagrivny and V.Y. Lipenkov, 1984 a. Preliminary results of deep drilling at Vostok Station, Antarctica, 1981–82. Proceedings of the Second International Symposium on Ice Drilling Technology, Calgary, Canada, 30–31 August, 1982. **US Army Cold Region Res. and Eng. Spec. Rep. (Hanover, N.H.) 86-340: 123-124.**

Kudryashov, B.B., V.K. Chistgakov, V.H. Pashkevich and V.N. Petrov, 1984 b. Selection of a low temperature filler for deep holes in the Antarctic ice sheet. Proceedings of the Second International Symposium on Ice Drilling Technology, Calgary, Canada, 30–31 August, 1982. **US Army Cold Region Res. and Eng. Spec. Rep. (Hanover, N.H.) 86-340: 137-138.**

Lamb, H.H., 1970. Volcanic dust in the atmosphere, with a chronology and assessment of its meteorological significance. **Phil. Trans. Roy. Soc. London, Ser. A, Vol. 266: 425-533.**

Lamb, H.H., 1978. Introduction to the volcanic Dust Veil Index. **Climate Monitor, 6: 57-67.**

Landsberg, H.E., 1974. Man–made climatic changes. *In:* **Physical and dynamic climatology. Proceedings of the symposium on physical and dynamic climatology. World Meteorol. Org., 347: 262-303.**

Langway, C.C., Jr., 1958. Bubble pressures in Greenland glacier ice. Physics on the movement of ice, Symposium of Chamonix 16–24 Sept. **Internat. Assoc. Sci. Hydrol., Publ. 47: 359-369.**

Latham, J. and M.H. Smith, 1990. Effect on global warming of wind–dependent aerosol generation at the ocean surface. **Nature, 347: 372-373.**

Lefauconnier, B. and J.O. Hagen, 1990. Glaciers and climate in Svalbard, statistical analysis and reconstruction of the Brøgger Glacier mass balance for the last 77 years. **Annals Glaciol., In press.**

Loosli, H.H., 1983. A dating method with ^{39}Ar. **Earth Planet. Sci. Lett., 63: 51-62.**

Lorius, C., J. Jouzel, D. Raynaud, J. Hansen and H. Le Treut, 1990. The ice–core record: Climate sensitivity and future warming. **Nature, 347: 139-145.**

Maccagnan, M., 1981. Contribution a l'etude des proprietes dielectriques de la glace antarctique; application geochimique. **Laboratoire de Glaciologie et Gephysique de l'Environment du CRNS, Publ. 373.**

MacIntyre, R., 1970. Why the sea is salt. **Sci. Am., 223 (5): 104-115.**

Maeno, N., 1967. Air bubble formation in ice crystals. *In:* H. Oura (Ed.): **Physics of Snow and Ice.** The Institute of Low Temperature Science, Hokkaido University: 207–218.

Maeno, N. and D. Kuroiwa, 1967. Metamorphism of air bubbles in a snow crystal. **J. Glaciol., 6: 561-564.**

Manabe, S. and R.T. Wetherald, 1980. On the distribution of climatic change resulting from an increase in CO_2 content of the atmosphere. **J. Atmosph. Sci., 37: 99-118.**

Mandelbrot, B.B. and J.R. Wallis, 1968. Noah, Joseph, and operational hydrology. **Water Resources Res., 4: 909-918.**

Mandelbrot, B.B. and J.R. Wallis, 1969 a. Some long–run properties of geophysical records. **Water Resources Res., 5: 321-340.**

Mandelbrot, B.B. and J.R. Wallis, 1969 b. Robustness of the Rescaled Range R/S in the measurement of noncyclic long run statistical dependence. **Water Resources Res., 5: 967-988.**

Matsuo, S. and Y. Miyake, 1966. Gas composition in ice samples from Antarctica. **J. Geophys. Res., 71 (22): 5235-5241.**

Meier, M.F., 1990. Reduced rise in sea level. **Nature, 343: 115-116.**

Michaels, P.J., 1990. The greenhouse effect: beyond the popular vision of catastrophe. **Liberty, 3: 27-33.**

Miljøverndepartementet, 1988–89. **Miljø og utvikling. Norges oppfølging av Verdenskommisjonens rapport. Stortingsmelding, 46 (1988-89).** Miljøverndepartementet, 180 pp.

Miller, S.L., 1969. Clathrate hydrates of air in Antarctic ice. **Science, 165: 489-490.**

Miller, S.L., 1973. The clathrates – their nature and occurrence. *In:* Whalley, E., S.J. Jones and L.W. Gold (Eds.): **Physics and chemistry of ice.** Roy. Soc. Can. (Ottawa): 42–50.

Monastersky, R., 1989. Looking for Mr. Greenhouse. **Sci. News, 135: 216-221.**

Mozeto, A. A., P. Fritz and E.J. Reardon, 1984. Experimental observations on carbon isotope exchange in carbonate – water systems. **Geochim. Cosmochim. Acta 48, 495-504.**

Mulvaney, R., E.W. Wolf and K. Oates, 1988. Sulphuric acid at grain boundaries in Antarctic ice. **Nature, 331: 247-249.**

Murozumi, M., T.J. Chow and C.C. Patterson, 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dust and sea salts in Greenland and Antarctic snow strata. **Geochim. Cosmochim. Acta, 33: 1247-1294.**

Neftel, A., H. Oeschger, J. Schwander, B. Stauffer and R. Zumbrunn, 1982. Ice core sample measurements give atmospheric CO_2 content during the past 40,000 years. **Nature, 295: 220-223.**

Neftel, A., E. Moore, H. Oeschger and B. Stauffer, 1985. Evidence from polar ice cores for the increase in atmospheric CO_2 in the past two centuries. **Nature, 315: 45-47.**

Newell, N.E., R.E. Newell, J. Hsiung and W. Zhogxiang, 1989. Global marine temperature variation and the solar magnetic cycle. **Geophys. Res. Lett. 16: 311-314.**

Ng, A. and C.C. Patterson, 1981. Natural concentrations of lead in ancient Arctic and Antarctic ice. **Geochim. Cosmochim. Acta, 45: 2109-2121.**

Nozaki, Y., D.M. Rye, K.K. Turekian and R.E. Dodge, 1978. A 200 year record of carbon–13 and carbon–14 variations in a Bermuda coral. **Geophys. Res. Lett., 5: 825-828.**

Nriagu, J.O., 1978. Properties and the geochemical cycle of lead. *In:* Nriagu, J.O. (Ed.): **The Biogeochemistry of lead in the Environment.** Part A. Elsevier, North Holland Biomedical Press,Amsterdam: 1–14.

Nutt, D., 1959. Recent studies of gases in glacier ice – a summary. **Polar Notes, Occasional Publication of The Stephansson Collection, Dartmouth College Library (Hannover, NH) 1: 57-66.**

Oakes, C.S., R.J. Bodnar and J.M. Simonson, 1990. The system $NaCl-CaCl_2-H_2O$: I. The ice liquidus at 1 atm total pressure. **Geochim. Cosmochim. Acta, 54: 603-610.**

Oeschger, H. U. Siegenthaler, U. Schotterer and A. Gugelmann, 1975. A box diffusion model to study the carbon dioxide exchange in nature. **Tellus, 27: 168-192.**

Oeschger, H., B. Stauffer, R. Finkel and C.C. Langway Jr., 1985. Variations of the CO_2 concentration of occluded air and of anions and dust in polar ice cores. *In:* E.T. Sundquist and W.S. Broecker (Eds.): The carbon cycle and atmospheric CO_2: natural variations Archean to present. **Am. Geophys. Union Geophys. Mono., 32: 132-142.**

Oeschger, H. and U. Siegenthaler, 1988. How has the atmospheric concentration of CO_2 changed? *In:* Rowland, F.S. and I.S.A. Isaksen (Eds.): **The Changing Atmosphere.** John Wiley & Sons, Ltd., Chichester: 5–23.

Oeschger, H., 1989. Variations in composition of the atmosphere (summary). Symposium on "Hva skjer med klimaet i Polarområdene?" Oslo, 25–26 April, 1989. **Norsk Polarinstitutt, Rapportserie Nr. 53.**

Ohmoto, H. and R.O. Rye, 1979. Isotopes of sulfur and carbon. *In:* Barnes, H.L. (Ed.): **Geochemistry of hydrothermal ore deposits, 2nd. ed.** John Wiley & Sons: 509–567.

O'Reilly, S., W.L. Griffin and T.V. Segalstad, 1990: The nature and role of fluids in the upper mantle: Evidence in xenoliths from Victoria, Australia. *In:* Herbert, H. K. and S.E. Ho (Eds.): Stable isotopes and fluids in mineralization. **Geol. Dept. & Univ. Extension, Univ. of West. Australia Publ., 23: 315-323**.

Palais, J. M. and H. Sigurdsson, 1989. Petrologic evidence of volatile emissions from major historic and pre–historic volcanic eruptions. *In:* Berger, A., R.E. Dickinson and J. W. Kidson (Eds.): Understanding Climate Change. **Am. Geophys. Union, Geophys. Mono., 52; and Internat. Union of Geodesy and Geophysics, 7 (Washington, D.C.): 31-53**.

Pales, J.C. and C.D. Keeling, 1965. The concentration of atmospheric carbon dioxide in Hawaii. **J. Geophys. Res., 70: 6053-6076**.

Passel, P., 1989. Curing the greenhouse effect could run into the trillions. **The New York Times, November 19: 1**.

Pearman, G.I., D. Etherige, F. de Silva and P.J. Fraser, 1986. Evidence of changing concentrations of atmospheric CO_2, N_2O and CH_4 from air bubbles in Antarctic ice. **Nature, 320: 248-250**.

Petit, J.R., L. Mounier, J., Y.S. Korotkevich, V.I. Kotlyakov and C. Lorius, 1990. Palaeoclimatological and chronological implications of the Vostok core dust record. **Nature, 343: 56-58**.

Plummer, L.N., T.M.L. Wigley and D.L. Pankhurst, 1978. The kinetics of calcite dissolution in CO_2–water systems at 5° to 60°C and 0.0 to 1.0 atm CO_2. **Am. J. Sci., 278: 179-216**.

Plummer, L.N. and E. Busenberg, 1982. The solubilities of calcite, aragonite and vaterite in CO_2–H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$–CO_2–H_2O. **Geochim. Cosmochim. Acta, 46: 1011-1040**.

Prentice, K.C. and I.Y. Fung, 1990. The sensitivity of terrestrial carbon storage to the climate change. **Nature, 346: 48-51**.

Pytkowicz, R.M., 1967. Carbonate cycle and the buffer mechanism of recent oceans. **Geochim. Cosmochim. Acta, 31: 63-73**.

Ramanathan, V., M.S. Lian, and R.D. Cess, 1979. Increased atmospheric CO_2: zonal and seasonal estimates of the effect on the radiation balance and surface temperature. **J. Geophys. Res., 84: 4949-4958**.

Ramanathan, V., R.J. Cicerone, H.B. Singh, and J.T. Kiehl, 1985. Trace gas trends and their potential role. **J. Geophys. Res. 90: 5547-5565**.

Ramanathan, V., R.D. Cess, E.F. Harrison, P. Minnis, B.R. Barkstrom, A. Ahmad, and D. Hartmann, 1989 a. Cloud–radiative forcing and climate: results from the Earth radiation budget experiment. **Science, 243: 57-63**.

Ramanathan, V., B.R. Barkstrom and E. F. Harrison, 1989 b. Climate and the Earth's radiation budget. **Physics Today, 42 (5): 22-32**.

Raval, A. and V. Ramanathan, 1989. Observational determination of the greenhouse effect. **Nature, 342: 758-761**.

Raynaud D., and R. Delmas, 1977. Composition des gaz contenus dans la glace polaire. *In:* Isotopes and Impurities in Snow and Ice. **International Association of Hydrological Sciences (Washington, D.C.), Publ. 118, 371-381**.

Raynaud, D. and J.M. Barnola, 1985. An Antarctic ice core reveals atmospheric CO_2 variations over the past few centuries. **Nature, 315: 309-311**.

Revelle, R. and H.E. Suess, 1957. Carbon dioxide exchange between atmosphere and ocean and the question of an increase of atmospheric CO_2 during the past decades. **Tellus, 9: 18-27**.

Reynolds, R.W., C.K. Folland and D.E. Parker, 1989. Biases in satellite–derived sea-surface–temperature data. **Nature, 341: 728-731**.

Roedder, E., 1984. Fluid inclusions. An introduction to studies of all types of fluid inclusions, gas, liquid, or melt, trapped in materials from earth and space, and their application to the understanding of geologic processes. **Mineral. Soc. Am., Rev. In Mineral., 12: 644 pp.**

Rose, D.J., M.M. Miller and C. Agnew, 1983. **Global energy futures and CO_2-induced climate change.** Report MITEL 83–015, Cambridge MA, MIT Energy Laboratory.

Rowland, F.S. and I.S.A. Isaksen, 1988. Introduction. *In:* Rowland, F.S. and I.S.A. Isaksen (Eds.): **The Changing Atmosphere.** John Wiley & Sons, Ltd.: 1–4.

Rubey, W.W., 1951. Geologic history of sea water. **Geol. Soc. Am. Bull., 62: 1111-1148.**

Sakshaug, E., 1990. Mot en ny istid? **UnitNytt 20 (4): 3-4 & 18-19.**

Schlesinger, M.E. and J.F.B. Mitchell, 1987. Climate model simulations of the equilibrium climatic response to increased carbon dioxide. **Rev. Geophys., 25: 760-798.**

Schneider, S.H., 1975. On the carbon dioxide–climate confusion. **J. Atmosph. Sci. 32: 2060-2066.**

Schneider, S.H., 1989. The greenhouse effect: Science and policy. **Science, 243: 771-779.**

Scholander, P.F. and D.C. Nutt, 1960. Bubble pressure in Greenland icebergs. **J. Glaciol., 3: 671-678.**

Scholander, P.F., E.A. Hemmingsen, L.K. Coachman and D.C. Nutt, 1961. Composition of gas bubbles in Greenland icebergs. **J. Glaciol., 3: 813-822.**

Schwander, J. and B. Stauffer, 1984. Age difference between polar ice and the air trapped in its bubbles. **Nature, 311: 45-47.**

Schwartzman, D.W. and T. Volk, 1989. Biotic enhancement of weathering and the habitability of Earth. **Nature, 340: 457-460.**

Segalstad, T.V., 1983. Eksplosive vulkanutbrudd – 100 år siden Krakatau–utbruddet. **Naturen, 107: 163-169.**

Segalstad, T.V., 1990. Temperatur og CO_2. **Teknisk Ukeblad, 137 (17): (4)-(5).**

Shackleton, N. and N.G. Pisias, 1984. **The Chapman Conference on "Natural variations in carbon dioxide and the carbon cycle".** Tarpon Springs, Florida, 9–13 January, 1984. – After Campbell, 1984. Nature, 307: 688–689.

Shepherd, T.J., A.H. Rankin and D.H.M. Alderton, 1985. **A practical guide to fluid inclusion studies.** Blackie & Sons, Ltd.: 239 pp.

Siegenthaler, U., 1990. El Niño and atmospheric CO_2. **Nature, 345: 295-296.**

Simkin, T., L. Siebert, L. McClelland, D. Bridge, C. Newhall and J. H. Latter, 1981. **Volcanoes of the World.** Smithsonian Institution, Hutchinson Ross Publishing Co., PA: 232 pp.

Slingo T., 1989. Wetter clouds dampen global greenhouse warming. **Nature, 341: 104.**

Smith, S.D. and E.P. Jones, 1985. Evidence of wind–pumping of air–sea gas exchange based on direct measurements of CO_2 fluxes. **J. Geophys. Res., 90 (C1): 869–875.**

Spittlehouse, D.L. and A.E. Ripley, 1977. Carbon dioxide concentrations over a native grassland in Saskatchewan. **Tellus, 29: 54-65.**

Stanhill, G., 1983. Comments on "The Montsouris series of carbon dioxide concentration measurements. 1877–1910". **Climatic Change, 4: 221-237.**

Stauffer, B., W. Berner, H. Oeschger, J. Schwander, 1981. Atmospheric CO_2 history from ice core studies. **Zeitschr. für Gletcherkunde und Glaziol., 17: 1-15.**

Stauffer, B., H. Hofer, H. Oeschger, J. Schwander and Siegenthaler, 1984. Atmospheric CO_2 concentration during the last glaciation. **Annals of Glaciol., 5: 160-164.**

Stauffer, B. and H. Oeschger, 1985. Gaseous components in the atmosphere and the historic record revealed by ice cores. **Annals of Glaciol., 1985: 54-59.**

Stauffer, B., A. Neftel, H. Oeschger and J. Schwander, 1985. CO_2 concentration in air extracted from Greenland ice samples. *In:* Langway, C.C., Jr., H. Oeschger and W.

Dansgaard (Eds.): Greenland ice core: geophysics, geochemistry, and the environment. **Am. Geophys. Union, Geophys. Mono., 33: 85-89.**

Stehle, N.S., 1967. Migration of bubbles in ice under a temperature gradient. *In:* Oura, H. (Ed.): **Physics of Snow and Ice.** The Institute of Low Temperature Science, Hokkaido University: 119–232.

Strong, A. E., 1989. Greater global warming revealed by satellite–derived sea–surface–temperature trends. **Nature, 338: 642-645.**

Stuiver, M., R.L. Burk and P.D. Quay, 1984. $^{13}C/^{12}C$ ratios in tree rings and the transfer of biospheric carbon to the atmosphere. **J. Geophys. Res., 89: 11731-11748.**

Stumm, W. and J.J. Morgan, 1970. **Aquatic chemistry. An Introduction Emphasizing Chemical Equilibria in natural waters.** John Wiley & Sons, 583 pp.

Sundquist, E.T., 1985. Geological perspectives on carbon dioxide and the carbon cycle. *In:* Sundquist, E.T. and W.S. Broecker (Eds.): The carbon cycle and atmospheric CO_2: natural variations Archean to present. **Am. Geophys. Union, Geophys. Mono., 32: 5-59.**

Takenouchi, S. and G.C. Kennedy, 1965. Dissociation pressures of the phase $CO_2 \bullet 5^3/_4H_2O$. **J. Geol., 73: 383-390.**

Talsman, S.J., B. Wiwchar, W.D. Gunther and C.M. Scarfe, 1990. Dissolution kinetics of calcite in the H_2O-CO_2 system along the steam saturation curve to 210°C. *In:* Spencer, R.J. and I.–M. Chou (Eds.): Fluid–mineral interactions: A tribute to H.P. Eugster. **The Geochem. Soc., Spec. Publ., 2: 41-55.**

Tans, P.P. and W.G. Mook, 1980. Past atmospheric levels and the $^{13}C/^{12}C$ ratios in tree rings. **Tellus, 32: 268-283.**

Thoning, K.W., P.P. Tans and W.D. Komhyr, 1989. Atmospheric carbon dioxide at Mauna Loa Observatory. 2. Analysis of the NOAA GMCC Data, 1974–1985. **J. Geophys. Res., 94 (D6): 8549-8565.**

Toggweiler, J.R., 1990. Bombs and ocean carbon cycles. **Nature, 347: 122-123.**

Twickler, M.S., M.J. Spencer, W.B. Lyons and P.A. Mayewski, 1986. Measurement of organic carbon in polar snow samples. **Nature, 320: 156-158.**

Volk, T. and Z. Liu, 1988. Controls of CO_2 sources and sinks in the Earth scale surface ocean: temperature and nutrients. **Glob. Biogeochem. Cycles, 2: 73-89.**

Walder, I.F. and T.V. Segalstad, 1987. Hydrothermal vein molybdenite deposits associated with the Drammen granite in the Permian Oslo Rift, Norway. **American Current Research on Fluid Inclusions. New Mexico Inst. of Mining and Technol., 60.**

Walker, J.C.G. and J.I. Drever, 1988. Geochemical cycles of atmospheric gases. *In:* Gregor, C.B., R.M. Garrels, F.T. Mackenzie and J.B. Maynard (Eds.): **Chemical Cycles in the Evolution of the Earth.** John Wiley & Sons, Ltd.: 55–76.

Walker, J.C.G., P.B. Hays and J.F. Kasting, 1981. A negative feedback mechanism for the long–term stabilization of Earth's surface temperature. **J. Geophys. Res., 86 (C10): 9776-9782.**

Washington, W.M. and G.A. Meehl, 1984. Seasonal cycle experiment on the climate sensitivity due to doubling CO_2 with an atmospheric general circulation model coupled to a simple mixed–layer ocean model. **J. Geophys. Res., 89: 9475-9503.**

Waterman, L.S., 1983. Comment on "The Montsouris series of carbon dioxide concentration measurements, 1877–1910 by Stanhill". **Climatic Change, 5: 413-415.**

Waterman, L.S., D.W. Nelson, W.D. Komhyr, and T.B. Harris, 1989. Atmospheric carbon dioxide measurements at Cape Matatula, American Samoa, 1976–1987. **J. Geophys. Res., 94: 14817-14829.**

Weast, R.C., D.R. Lide, M.J. Astle and W.H. Beyer (Eds.), 1989. **CRC Handbook of Chemistry and Physics, 70th ed.** CRC Press, Boca Raton, Florida.

Webb, T., III, 1985. Holocene palynology and climate. *In:* Hecht, A.D. (Ed.): **Paleocllmate analysls and modellng.** Wiley & Sons, Ltd.: 163–195.

Weeks, W.F. and S.F. Ackley, 1982. The growth, structure, and properties of sea ice. **Cold Reglons Research and Eng. Lab. Mono., 82-1.** – After Roedder, 1984.

Wetherald, R.T. and S. Manabe, 1988. Cloud feedback processes in a general circulation model. **J. Atmos. Scl., 45: 1397-1415.**

Wigley, T.M.L., 1983. The pre–industrial carbon dioxide level. **Cllmatlc Change, 5: 315-320.**

Wigley, T.M.L., P.D. Jones and P.M. Kelly, 1989. Empirical climatic studies. *In:* Bolin, B. and J. Döös (Eds.): **The Greenhouse Effect Cllmatlc Change and Ecosystems.** J. Wiley & Sons: 271–322.

Wilson, C.A. and J.F.B. Mitchell, 1987. A double CO_2 climate sensitivity experiment with global climate model. **J. Geophys. Res., 92: 13315-13343.**

Wolff, E.W., R. Mulvaney and K. Oates, 1988. The location of impurities in antarctic ice. **Ann. Glaclol., 11: 194-197.**

Yakir, D., M.J. DeNiro and P.W. Rundel, 1989. Isotopic inhomogeneity of leaf water: Evidence and implications for the use of isotopic signals transduced by plants. **Geochlm. Cosmochlm. Acta, 53: 2769-2773.**

12. SAMMENDRAG (SUMMARY IN NORWEGIAN)

Forutsigelsene om en menneske–skapt (antropogen) klimaendring gjennom brenning av fossile karbon-brennstoffer (kull, gass, olje) til CO_2–gass, er hovedsakelig basert på fortolkninger av målte konsentrasjoner av CO_2 i atmosfæren og i bre–is.

Viktig for Jordens CO_2–syklus er havet og mineralenes kjemiske likevekter. På grunn av deres enorme buffer–kapasitet, stabiliserer de den geokjemiske likevekt for CO_2–gass mellom hydro–, atmo–, litho– og biosfæren. Nyere studier av radiokarbon (^{14}C) viser at sirkulasjonstiden for oppløst organisk karbon i de øverste vannlag i havet bare er noen få tiår. Dette betyr at CO_2 dannet ved brenning av hele Jordens forråd av fossile karbon–brennstoffer vil bli oppløst i havet før atmosfærens konsentrasjon av CO_2 kan dobles i forhold til det nåværende nivå.

Målinger av CO_2 i atmosfæren i det nittende århundre ble foretatt med en unøyaktighet på opptil 100%. En verdi på 290 ppm (volumdeler av en million) ble valgt som en gjennomsnittsverdi for det nittende århundre, ved å forkaste "ikke–representative" verdier, som var 10% eller mer forskjellige fra "det generelle gjennomsnitt for denne tiden". En avgjørende subjektiv faktor inngår derfor i anslaget for det før–industrielle nivå for CO_2 i atmosfæren.

Mauna Loa–observatoriet på Hawaii har vært regnet som et ideelt sted for måling av det globale CO_2–nivå. Imidlertid er observatoriet lagt til toppen av en aktiv vulkan, som har gjennomsnittlig ett utbrudd hvert 3,5 år. Det er uavbrutt utstrømming av CO_2 fra en sprekkesone bare 4 km fra observatoriet, og det største aktive vulkankrateret ligger bare 27 km fra observatoriet. Disse spesielle forhold gjorde det nødvendig å innføre "redigering" av målingene som fast prosedyre. CO_2–verdiene har derfor vært gjenstand for en viss skjønnsmessig vurdering før publisering. Lignende prosedyrer blir også brukt ved andre CO_2–observatorier.

CO_2–konsentrasjonene i luftbobler innesluttet i bre–is blir ofte tatt som representative for tidligere atmosfæriske konsentrasjoner. Det ble antatt at sammensetningen av luften i boblene forble uendret. Dette var igjen basert på den antagelse at det ikke kunne være væske i isen ved en gjennomsnittlig årstemperatur på rundt –25°C, og at det derfor ikke kunne ventes noen forandringer som skyldtes diffusjon. Imidlertid ble det nylig funnet årer fylt med væske i isen i Antarktika ved temperaturer helt ned til –73°C. Talrike studier viser at flere kjemiske og fysiske prosesser kan gjøre at CO_2–innholdet i isen enten øker eller avtar kraftig i forhold til innholdet i den samtidige atmosfære. Ved flere undersøkelser ble det funnet at CO_2–nivået i før–industriell is var det doble av nivået i dagens atmosfære.

Metoder som benytter tørr ekstraksjon av CO_2 fra knust is, frigjør bare omtrent halvparten av denne gassen fra isen. CO_2 i luftboblene kan trenge gjennom isen ved

diffusjon eller oppløsning i væske til stede langs korngrensene, med en hastighet forskjellig fra luftens andre gasser. Dannelse av faste CO_2 klatrater (hydrater) er et problem for bestemmelsen av CO_2-mengden i gassinneslutninger i is. Andre gasser danner også klatrater, men ved andre temperaturer og trykk. Dette kan lede til betydelige forandringer i gass-sammensetningen i inneslutninger ved forskjellige dyp. Derfor er CO_2-målinger av luftbobler innesluttet i is ikke representative for den opprinnelige atmosfære. Dette innebærer at bre-is ikke kan betraktes som et bestandig materiale. Iskjerner vil derfor ikke være et tilfredsstillende materiale for observasjon av atmosfærens utvikling gjennom lange tidsrom.

Det kan også være vanskelig å fastsette alderen til luftbobler innfanget i is. Dette medfører nok en usikkerhet i måleresultatene, til og med fra de øvre ~100 m is avsatt på Grønland og i Antarktika. Det opprinnelige $N_2/O_2/Ar$-forhold i luften er ikke bevart. Forholdene er mer lik de man finner for oppløselighet av gasser i vann. Gassblærene må i hovedsak ha blitt dannet ved utskillelse da vannet frøs, og ikke fra gjenlukkede kanaler, som opprinnelig var åpne til luften.

Beregninger av tidligere tiders temperaturer basert på lette stabile isotoper (D/H og $^{18}O/^{16}O$) i is er også beheftet med stor usikkerhet. Etter oppdagelsen av væske mellom iskrystaller i dypfrosset is i Antarktika, vil faseforandringer måtte ventes. Det kan regnes med stor isotop-utbytting og stor forandring i isotop-forholdene, noe som medfører at beregnete paleo-temperaturer fra isotop-forholdene vil være meningsløse når faseforandringer oppstår i nærvær av en mobil væskefase.

Det har vært gjort forsøk på å beregne den tidligere konsentrasjon av CO_2 i atmosfæren fra stabil-isotopforholdet for karbon ($^{13}C/^{12}C$) i træs årringer. Det konkluderes her med at CO_2-innholdet i atmosfæren beregnet fra slike analyser ikke kan bli brukt som en gangbar metode i paleoklimatologi, og ikke som bevis for forandring i atmosfærens CO_2-innhold.

Det mest omtalte "drivhuseffekt-signalet", dvs. en antropogen økning av den globale luft-temperatur, påstått å ha funnet sted gjennom de siste tiår, er ikke blitt bekreftet gjennom studier av lange temperatur-serier.

Det har vært hevdet, i henhold til modellberegninger, at denne oppvarmingen skulle være mest merkbar i Arktis. Imidlertid er det ikke påvist noen temperaturøkning i dette området i løpet av de siste to tiår. Målinger av breenes massebalanse i norsk og kanadisk Arktis, og av isdekkene på Grønland og i Antarktika, gir ingen holdepunkter for at det har funnet sted en økning av luft-temperaturen gjennom de senere år.

13. INDEX