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Natural and anthropogenic changes in atmospheric CO_2 over the last 1000 years from air in Antarctic ice and firn

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Abstract. A record of atmospheric CO_2 mixing ratios from 1006 A.D. to 1978 A.D. has been produced by analysing the air enclosed in three ice cores from Law Dome, Antarctica. The enclosed air has unparalleled age resolution and extends into recent decades, because of the high rate of snow accumulation at the ice core sites. The CO_2 data overlap with the record from direct atmospheric measurements for up to 20 years. The effects of diffusion in the firn on the CO_2 mixing ratio and age of the ice core air were determined by analyzing air sampled from the surface down to the bubble close-off depth. The uncertainty of the ice core CO_2 mixing ratios is 1.2 ppm (1 σ). Preindustrial CO_2 mixing ratios were in the range 275-284 ppm, with the lower levels during 1550-1800 A.D., probably as a result of colder global climate. Natural CO_2 variations of this magnitude make it inappropriate to refer to a single preindustrial CO_2 level. Major CO_2 growth occurred over the industrial period except during 1935-1945 A.D. when CO_2 mixing ratios stabilized or decreased slightly, probably as a result of natural variations of the carbon cycle on a decadal timescale.

Introduction

The changes in atmospheric CO_2 before precise, direct atmospheric measurements began in 1958 [*Keeling*, 1991a] have been investigated by analyzing air enclosed in polar ice sheets [*Neftel et. al.*, 1985; *Raynaud and Barnola*, 1985; *Etheridge et al.*, 1988; *Wahlen et al.*, 1991; *Barnola et al.*, 1995]. Ice core measurements indicate that the CO_2 mixing ratio has increased by about 25% during the past few hundred years, consistent with industrialization and large-scale land use modification. Long-term ice core records show that CO_2 has varied with the Earth's climate with about 80 ppm lower levels during glacial periods [e.g., *Barnola et al.*, 1987; *Neftel et al.*, 1988]. Smaller natural CO_2 variations over the millennium before industrialization appear in some ice core records, possibly caused by the influence of changed climate on the carbon cycle [*Raynaud and Barnola*, 1985; *Etheridge et al.*, 1988; *Siegenthaler et al.*, 1988; *Wahlen et al.*, 1991; *Barnola et al.*, 1995]. However, these CO_2 variations are rather small compared to the measurement precision and their timing is not always well defined. Further information on past CO_2 levels is required to improve the understanding of the natural and human-perturbed carbon cycle and the climatic impact of CO_2 as a greenhouse gas.

Measuring air extracted from polar ice is the most direct way of reconstructing past atmospheric CO_2 mixing ratios. Less direct techniques are based on measurement of the isotopic ratios of carbon preserved in organic matter. They suffer from larger measurement error, uncertainties caused by physiological influences on photosynthetic fractionation, and by the assumptions required to derive atmospheric mixing ratios from isotopic values in a carbon exchange model.

Ice cores, in particular those from cold Antarctic sites, offer the following advantages: (1) whole air is enclosed in bubbles in the ice; (2) the ice is a relatively inert storage medium for CO_2 and many other atmospheric trace gases; (3) the enclosed air generally represents the "background" atmosphere, remote from biological or anthropogenic CO_2 sources or sinks; (4) timescales ranging from tens of years to hundreds of thousands of years can be investigated by selecting appropriate sites; and (5) other relevant physical and chemical information resides in the same stratigraphy, such as trace acids for dating [*Hammer*, 1980], or water isotopic ratios as climatic indicators (in the case of Law Dome, *Morgan* [1985]).

There are several possible difficulties in the ice technique: (1) reactions involving CO_2 may occur if the ice approaches melting [*Neftel et al.*, 1982], or if it contains high concentrations of impurities, conditions that may have affected the CO_2 in some sections of Greenland ice cores [*Delmas*, 1993; *Staffelbach et al.*, 1991]; (2) cracks in cores may release air or allow contamination to enter; (3) ice core samples must be carefully refrigerated to avoid post coring melting (PCM) which may change the composition of the air bubbles [*Pearman et al.*, 1986]; (4) the pressure in the ice at about 500 m and deeper may be sufficient (depending on temperature) for the bubbles to disappear and form clathrates

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[*Miller*, 1969] which may complicate air extraction; (5) dating the ice by annual stratigraphy becomes difficult at sites with low-accumulation rate or where ice flow disturbs the layered sequence at depth; (6) the age resolution of the enclosed air can be limited by the progressive closure of the air bubbles and, to a lesser degree, diffusion of air from the ice sheet surface through the firn layer to the closure depth; and (7) associated with the diffusion are possible fractionation effects [*Craig et al.*, 1988; *Schwander*, 1989] which are small for CO_2 mixing ratios but significant at the precision level of carbon isotope ratio measurements.

Most of these difficulties can be avoided by appropriate selection of the drilling site and careful handling of the ice sample. Desirable characteristics of ice core sites for CO_2 studies are negligible melting of the ice sheet surface, low concentrations of impurities, regular stratigraphic layering which is undisturbed at the surface by wind or at depth by ice flow, and high snow accumulation rate.

Sites with high-accumulation rate enclose air with a narrow age distribution, because the time required for an ice layer to complete the bubble close-off process is short. This has two advantages: more temporal detail of atmospheric variations survives, and air from most recent times is closed off in the upper ice layers so the ice core results can be compared with modern atmospheric records. Such a comparison reveals any modification of the original atmospheric CO_2 mixing ratio during air enclosure and storage in the ice, or during laboratory extraction and measurement.

We measured CO_2 in air extracted from three Antarctic ice cores that meet the above requirements. Two of the cores (DE08 and DE08-2) originate from an area with an extremely high rate of snow accumulation. The DE08 ice core has previously provided a high-resolution record of atmospheric methane over the industrial period [*Etheridge et al.*, 1992). Air samples from a range of depths in the firn layer at the DE08-2 ice core site were also analyzed to find the effects of diffusion on the composition and age of the enclosed air and to better establish the link between it and the atmosphere. The third core, the new Australian deep ice core, DSS, extends the CO_2 record back into the late Holocene. The resulting record of atmospheric CO_2 has an unparalleled time resolution and high analytical precision which reveals previously unseen changes in CO_2 levels over the past 1000 years.

Ice Cores

The three ice cores are from Law Dome, East Antarctica (summit 66°44' S, 112°50' E, 1390 mean annual sea level (M.A.S.L); Figure 1). Law Dome is presently isolated from the ice flow of the main inland ice sheet by the drainage effect of the adjacent glaciers. The summit region is consequently an ice divide, with accumulating snow layers moving to greater depths without significant deformation by shear for at least the top 50% of ice thickness [*Budd and Jacka*, 1989]. The ice surface topography also reduces the incidence of strong katabatic winds on the dome [*Goodwin*, 1990]. Prevailing

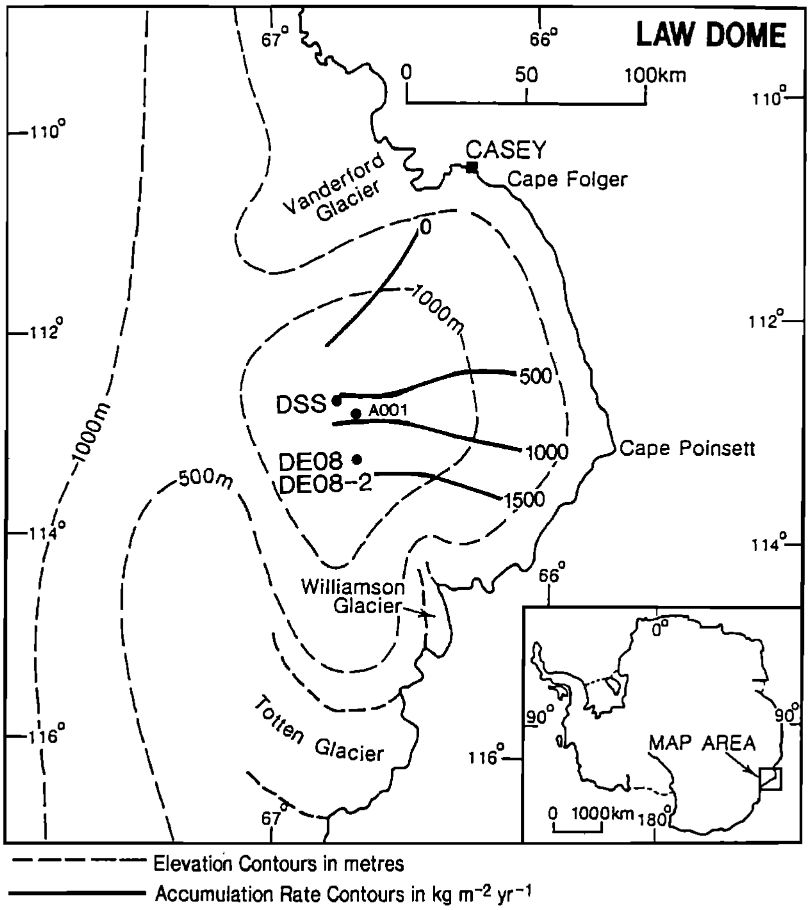

Figure 1. Map of Law Dome showing the locations of the ice cores studied and the approximate elevation and accumulation contours (adapted from *Hamley et al.* [1986]). A001 marks the approximate summit.

winds are easterly and usually snow-laden, promoting even, regular layering.

DE08 was drilled in 1987 [*Etheridge and Wookey*, 1989], 16 km east (windward) of the summit where the snow accumulation rate is extremely high (approximately 1100 kg m^{-2} yr^{-1}, or about 1.2 m ice equivalent). DE08-2 was drilled in 1993 about 300 m southeast of the DE08 site and has nearly identical site characteristics. DSS was drilled between 1988 and 1993, 4.6 km south-southwest of the summit where the accumulation is lower (600 kg m^{-2} yr^{-1}). This core reached bedrock at about 1200 m but CO$_2$ measurements so far cover only the upper 45%. The details of the cores are given in Table 1. The sites are shown in Figure 1.

All three ice cores and their sites have the following characteristics: (1) the snow accumulation is high and regular. There is minimal redistribution by scouring or dune formation caused by strong winds; (2) the stratigraphic layering is not disturbed by ice flow over the range of depths considered here; (3) snow surface melting is rare, thus avoiding aqueous chemistry or impedance by ice layers of air mixing to the enclosure zone. At most five melt layers, less than 1 cm thick, were identified in each of the DE08 cores and even fewer in DSS; (4) impurity levels are low, minimizing any possible interactions with the CO$_2$ in the air bubbles; (5) no clathrates were observed in any of the cores, which is consistent with the dissociation relation with temperature and pressure [*Miller*, 1969]; and (6) the core quality is generally very high, and PCM has been avoided.

The drilling methods used were thermal, electromechanical and fluid-immersed electromechanical for DE08, DE08-2 and DSS, respectively. This allowed a useful confirmation that the ice core CO$_2$ was not influenced by effects such as ice heating during thermal drilling or the presence of drill fluid or stress cracks (occasionally caused by thermal and electromechanical coring and subsequent pressure release after removal from the ice sheet).

Firn Air Samples

To characterize the air mixing in the firn and how it affects the age and composition of the air enclosed in the ice, air was sampled from the open pore space of the firn layer at DE08-2. Samples were taken from the surface to a depth of 85 m, using the following procedure. When the ice drill reached the desired sampling depth it was withdrawn and a firn air sampling device (FASD) lowered to the bottom of the borehole. The FASD consisted of an inflatable bladder with several air lines passing through. The bladder sealed the borehole and air samples were drawn from the firn layer below. The bladder was inflated with air from the firn to reduce the possible effects of any leaks (although none were detected) on the sample. About 1 m^3 of air was purged from the firn at the bottom of the hole before the sample flasks were flushed and filled. Leak tightness of the FASD was tested in the borehole in impermeable ice at 90 and 101 m. At these depths, air could not be pumped out of the firn and the pressure in the borehole was reduced to about 0.1 bar, which was maintained with the pump isolated. This confirmed that a good seal was made between the bladder and the borehole and that the bladder and air lines were leak tight. The samples at 0 m depth were taken with the normal procedure and with the FASD inlet on the snow surface, about 30 m upwind of the camp. All firn air samples were dried through anhydrous magnesium perchlorate.

To check any possible interaction of the various component materials with the air sample, we used two FASDs. One had a natural rubber bladder and "Nylaflow" (Polymer Corporation) nylon tubes, the other had a butyl rubber bladder and "Dekabon" tubes (Furon, Dekoron Division), made of aluminium foil internally lined by ethylene copolymer. We also used two sample pumps (Metal Bellows, or KNF Neuberger with Teflon-coated Viton elastomer diaphragm) and five types of flasks (made of steel, stainless steel, or glass). The FASDs and pumps had no discernible influence on the trace species measured. However, because of anomalous CO$_2$ results for some flask types, attributed to different flask construction and surface pretreatments, only the results from the glass and stainless steel flasks are presented here. The 0.5-liter glass flasks, fitted with two Teflon O-ring stopcocks (Glass Expansion, Melbourne), and the KNF Neuberger diaphragm pump unit have achieved high performance in sampling and storing air samples from the Commonwealth Scientific and Industrial Research Organisation (CSIRO) atmospheric sampling network since 1990.

Table 1. Details of the Law Dome Ice Cores Used in This Study

Ice Core	Year Drilled	Location	Drilling Method and Ice Core Diameter	Core Depth, m	Accumulation Rate [a], kg m^{-2} yr^{-1}	Mean Temperature [b], °C
DE08	1987	66°43'S 113°12'E, 1250 m	Dry thermal, 200 mm	234	1100	-19 [c]
DE08-2	1993	66°43'S 113°12'E, 1250 m	Dry electro-mechanical, 100 mm	243	1100	-19
DSS	1988-1993	66°46'S 112°48'E, 1370 m	Dry thermal, fluid electro-mechanical, 100-120 mm	1200	600	-22

[a] Mean over section of core studied.

[b] 20-m firn temperature.

[c] *Etheridge and Wookey* [1989].

Experimental

The ice core air was dry-extracted from the ice samples using the "cheese grater" technique [*Etheridge et. al.*, 1988; 1992]. The technique quickly extracts air from the bubbles without melting the ice or exposing the released air to moving metal components, both of which could influence the trace gas composition. Briefly, samples weighing 500-1500 g were prepared by selecting crack-free ice and trimming away the outer 5-20 mm. Each sample was sealed in a polyethylene bag flushed with high purity nitrogen and cooled to -80°C. It was then placed in the extraction flask where it was evacuated and then ground to fine chips. The released air was dried cryogenically at -100°C and collected cryogenically in electropolished stainless steel "traps", cooled to about -255°C by a closed-cycle helium cooler. The traps were shorter and wider than in earlier work to expedite air sample remixing, had all-metal valves and no welds, which are potentially porous, in the region of sample condensation.

The ice core air samples, ranging from about 50 to 150 mL standard temperature and pressure (STP), were measured for CO_2 mixing ratio with a Carle 400 Series analytical gas chromatograph (GC). After separation on the GC columns, the CO_2 was catalytically converted to methane prior to flame ionization detection. From 1 to 3 separate analyzes were made on each ice core air sample, each analysis requiring about 15 mL to flush and fill the 3-mL sample loop. Each sample injection to the GC was bracketed by calibration gas injections. CO_2 mixing ratios were then found for each aliquot by multiplying the ratio of the sample peak area to calibration gas peak area (interpolated to the time of sample analysis) by the CO_2 mixing ratio assigned to the calibration gas. The detector response was shown to be almost perfectly linear. For the CO_2 mixing ratio range of 25-350 ppm, departures from linearity did not exceed 0.4 ppm. The precision of analysis of ice core air samples was improved since our earlier reported CO_2 results [*Etheridge et. al.*, 1988] to better than 0.2 ppm (1 σ) with the new sample trap design and by using a vacuum manifold to connect the trap to the GC inlet. The firn air samples were analyzed on the same GC and with the same calibration gases as for the ice core air samples yet with higher precision ($\sigma = 0.06$ ppm) made possible by the improved sample handling and transfer characteristics of their larger volumes. The CO_2 data are reported in the World Meteorological Organisation (WMO) X93 mole fraction scale. Our calibration standards are traceable to the WMO Central CO_2 Laboratory operated by C.D. Keeling at the Scripps Institution of Oceanography.

The uncertainty of the ice core air extraction and analysis procedure was determined by processing control air samples through the extraction line and collecting and analyzing as for normal ice core air samples. In many cases, air-free ice was crushed in the presence of the control air. Forty seven tests were made, with control CO_2 mixing ratios ranging from 270.5 to 352.9 ppm. There was an average enhancement of 0.8 ppm ($\sigma = 0.7$ ppm) for the air-free ice tests ($n = 17$). The cause of this small average enhancement is unknown. A valuable quality assurance test of the ice core CO_2 measurements, including possible effects from the enclosure and storage of air in the ice and subsequent extraction and analysis, can be found by comparing the results from adjacent ice core samples. CO_2 values for ice samples from within an annual layer were found to vary by less than 1.2 ppm (1 σ).

Chronology

The ice was dated by counting the annual layers in oxygen isotope ratio ($\delta^{18}O$ in H_2O), ice electroconductivity measurements (ECM), and hydrogen peroxide (H_2O_2) concentration. These three parameters display clear seasonal cycles and are well preserved throughout the cores studied. Because $\delta^{18}O$, ECM and H_2O_2 in the ice are controled by quite different processes (temperature dependent fractionation of precipitation, acid production and transport, and atmospheric photochemistry, respectively), annual layers can be identified with confidence. Dating accuracy was ±2 years at 1805 A.D. for the three cores and ±10 years at 1350 A.D. for DSS. The ice chronology was crosschecked against acidic layers detected by ECM and attributed to the following volcanic eruptions: Agung, Indonesia, 1963 A.D.; Tambora, Indonesia, 1815 A.D.; an eruption in the 1450s A.D., seen in other ice cores [*Delmas et al.*, 1992] and suspected to be near Vanuatu [*Pang*, 1993]; and the unknown eruption dated in other ice cores at 1259 A.D. [e.g., *Langway et al.*, 1994]. We redated the DE08 ice using new $\delta^{18}O$ and H_2O_2 data and by crosschecking with the DE08-2 $\delta^{18}O$ and ECM profiles. The difference between old and new chronologies was less than 3 years.

Air becomes sealed in the ice sheet and is subsequently enclosed in bubbles as the open porosity of the firn layer decreases with depth. The enclosed air at any depth in the ice has a mean age, a_a, that is younger than the age of the host ice layer, a_i, from which the air is extracted. This difference, Δa, equals the time τ_s for the layer to reach a depth d_s, where air becomes sealed in the pore space, minus the mean time τ_d for the air to mix down to that depth. The mean air age is thus

$$a_a = a_i + \Delta a = a_i + \tau_s - \tau_d, \qquad (1)$$

where ages are dates A.D.

Mixing of air from the ice sheet surface to the sealing depth is primarily by molecular diffusion. The rate of air mixing by diffusion in the firn decreases as the density increases and the open porosity decreases with depth. Diffusion is significantly impeded in layers of density 805 kg m^{-3} and greater [*Schwander et al.*, 1988], which can occur in firn at mean densities of about 795-800 kg m^{-3}, because density varies with season. The depth at which this mean density is reached is defined as the sealing depth, d_s, of the ice sheet. At DE08 the sealing density is at about 72 m depth where the age of the ice, and thus τ_s, is 40 ±1 years (43 ±3 years was used by *Etheridge et al.* [1992] before the DE08 ice redating). A similar approach gives the sealing depths (and τ_s values) for DE08-2 and DSS as 72 m (40 years) and 66 m (68 years), respectively. The sealing process is also observed in the firn porosity measurements at DE08-2 which confirm the existence of almost fully closed layers below 72 m (J.-M. Barnola, unpublished results, 1995).

The depth d_s and age τ_s of the ice where sealing occurs depend on the rates of densification and accumulation and thus on the climatic conditions during firn formation. We investigated the influence of past changes in temperature and accumulation rate on d_s and τ_s, using a firn densification model [*Barnola et al.*, 1991]. Here d_s and τ_s varied by +2 m and +2 years, respectively, for a 1°C lower temperature and by -6 m and +11 years, respectively, for a 25% lower accumulation rate. In reality, the d_s and τ_s variations were probably much smaller because the observed temperature and accumulation rate changes on Law Dome during the past 180 years [*Morgan et al.*, 1991] were smaller and lasted for a maximum of 2 decades, about half the formation time of the firn layer at DE08 and DE08-2.

The age of the air at the sealing depth, τ_d, depends mostly on the mean time required to mix from the surface by diffusion and to a much smaller degree on the slow downward advection of air with the accumulating firn. We estimate from firn air diffusion models [*Schwander*, 1989; C. Trudinger and I. Enting personal communication, 1995] that τ_d = 10 years for CO_2 at DE08 and DE08-2. This is comparable to the value of 8 years used for methane at DE08 [*Etheridge et al.*, 1992] (equivalent to about 10 years for CO_2 when the relative diffusivities of the gases are considered), and 12 years for CO_2 at 70 m depth at Summit, Greenland [*Schwander et al.*, 1993] (which has lower temperature and accumulation rate than DE08). We used τ_d = 10 years for CO_2 in the air for all three ice cores. The results from the firn air samples (see below) confirm this value for DE08-2 and also for DE08, which has nearly identical firn density and temperature profiles, but it is only an estimate for DSS. Since the DSS core is used only for the longer term CO_2 record, the small possible error in dating is not significant.

The air enclosed in the ice has an age spread caused by diffusive mixing and gradual bubble closure. The majority of bubble closure occurs at greater densities and depths than those for sealing. *Schwander and Stauffer* [1984] found about 80% of bubble closure occurs mainly between firn densities of 795 and 830 kg m^{-3}. Porosity measurements at DE08-2 give the range as 790 to 825 kg m^{-3} (J.-M. Barnola, unpublished results, 1995), which corresponds to a duration of 8 years for DE08 and DE08-2 and about 21 years for DSS. If there is no air mixing past the sealing depth, the air age spread will originate mainly from diffusion, estimated from the firn diffusion models to be 10-15 years. If there is a small amount of mixing past the sealing depth, then the bubble closure duration would play a greater role in broadening the age spread. It is seen below that a wider air age spread than expected for diffusion alone is required to explain the observed CO_2 differences between the ice cores. Table 2 summarizes the contributions of each process to the air dating for each ice core.

Results and Discussion

DE08-2 Firn Air Results

Measurements of 17 glass flasks and 6 stainless steel flasks of firn air were made at CSIRO in May and June, 1993. One (from 80 m) was found to have been contaminated by surface air and is not presented here. The CO_2 levels in the stainless steel flasks were on average 0.6 ppm (± 0.3 ppm) lower than in the glass flasks for the same depths. It is possible that this difference is caused by the different flask type or sampling duration. However, the difference is not significant compared with the overall change in CO_2 in the firn air.

The CO_2 mixing ratios of the firn and ice core air were corrected for the effect of gravitational fractionation. Diffusion in the firn causes an increase with depth of the mixing ratios of the heavier air species which, in the absence of convective mixing and in an equilibration situation, can be predicted by the barometric equation [*Craig et al.*, 1988; *Schwander*, 1989]. The stable isotopic ratio of nitrogen, $\delta^{15}N_2$, was used as an estimate of the gravitational fractionation to correct the CO_2 mixing ratios [*Sowers et al.*, 1989], where

$$\delta^{15}N = \left[\frac{\left({}^{15}N^{14}N/{}^{14}N^{14}N\right)_{sample}}{\left({}^{15}N^{14}N/{}^{14}N^{14}N\right)_{reference}} - 1 \right] \times 1000 \quad (2)$$

expressed as per mil and with the surface air sample as the reference. There should be no detectable trend in atmospheric $\delta^{15}N_2$ in recent centuries. In the firn air column at DE08-2, $\delta^{15}N_2$ increases with depth to a maximum of about 0.3 ‰ by about 70 m and then stabilizes as the diffusive mixing diminishes near the sealing depth. This compares well with the $\delta^{15}N_2$ results for the DE08 ice core [*Etheridge et al.*, 1992] of 0.25 ±0.05 ‰. The barometrically predicted $\delta^{15}N_2$ value for DE08 and DE08-2 is 0.34 ‰, using the mean temperatures and sealing depths in Tables 1 and 2, respectively. This is probably an overestimate because equilibrium is slightly disturbed by convection near the firn surface and by downward advection of air with the accumulating firn. Also, $\delta^{15}N_2$ may not be an exact measure of the gravitational fractionation of CO_2 in the firn if the atmospheric CO_2 growth rate changes rapidly (on shorter timescales than the diffusion time). However, this effect probably has a negligible influence on the gravitational correction. The CO_2 mixing ratios of the firn air and the ice core air were thus corrected for gravitational fractionation by subtracting the amount

$$\left(M_{CO_2} - M_{air}\right) \times \delta^{15}N_2 \quad (3)$$

where M is the molecular mass and measured values of $\delta^{15}N_2$ were used. In the absence of $\delta^{15}N_2$ data for DSS, the gravitational correction was based on the $\delta^{15}N_2$ of 0.30 ‰.

Table 2. Ice Core Air Dating Parameters

Ice Core	Depth Where Sealing Occurs, d_s, m	Age of Ice at Sealing Depth, τ_s, year	Mean Age of CO_2 in Air at Sealing Depth, τ_d, year	Difference Between Ice Age and Mean Air Age, Δa, year	Duration of Bubble Close-off Process, year
DE08	72	40	10	30 ± 1	8
DE08-2	72	40	10	30 ± 1	8
DSS	66	68	10	58 ± 2	21

The gravitational correction reduces the measured CO_2 mixing ratios by an amount which increases from zero at the top of the firn to a maximum of 0.45 % (about 1.5 ppm) at the base of the firn and in the ice. No allowance has been made for the possible effect of past changes of the firn sealing depth, d_s, on the gravitational fractionation. A 6 m change (the above model result for an accumulation rate change of 25 %) would change the CO_2 at the bottom of the firn by only 0.04 % (about 0.13 ppm).

The CO_2 mixing ratios of the DE08-2 firn air are given in Table 3 and plotted in Figure 2. The diffusion delay is evident in the decrease of CO_2 with depth. It appears from the firn air results that diffusion is established even in the top 10 - 20 m and that wind pumping and convection have not caused significant mixing. At the sealing depth of 72 m, the CO_2 mixing ratio is equivalent to air 10 years old (1983 A.D., based on the atmospheric record at south pole; *Keeling* [1991a]). This is the same as the τ_d value arrived at from model calculations, discussed above.

Below about 72 m the CO_2 gradient steepens markedly. This observation is consistent with the termination of air mixing, caused by the first occurrence of impermeable, almost closed-off layers and further indicated by the stabilizing of $\delta^{15}N_2$. Although the air below 72 m is immobilized in the tightly constricted firn, it can be sampled from open pores with the FASD because bubble formation is still at an early stage.

Table 3. CO_2 Mixing Ratios in Firn Air From DE08-2

Sample Identification No.	Depth, Meters	CO_2 Mixing Ratio, ppm: Measured	CO_2 Mixing Ratio, ppm: Gravitationally Corrected
	Glass Flasks, 0.5 L		
930345	0	354.8	354.8
930338	10	353.3	353.0
930351	10	353.0	352.7
930339	15	352.7	352.4
930340	20	352.1	351.6
930342	30	350.7	350.0
930343	40	349.0	348.0
930346	55	346.8	345.7
930347	55	346.7	345.5
930348	60	346.1	344.8
930335	65	345.6	344.2
930336	70	344.5	343.1
930337	75	341.6	340.1
930350	75	341.1	339.7
930341	80	337.2	335.7
930349	85	334.4	332.8
	Stainless Steel Flasks, 22 L		
930365	0	354.7	354.7
930367	30	349.7	348.9
930369	40	348.2	347.3
930366	60	345.5	344.2
930368	70	343.8	342.4
930370	80	336.6	335.2

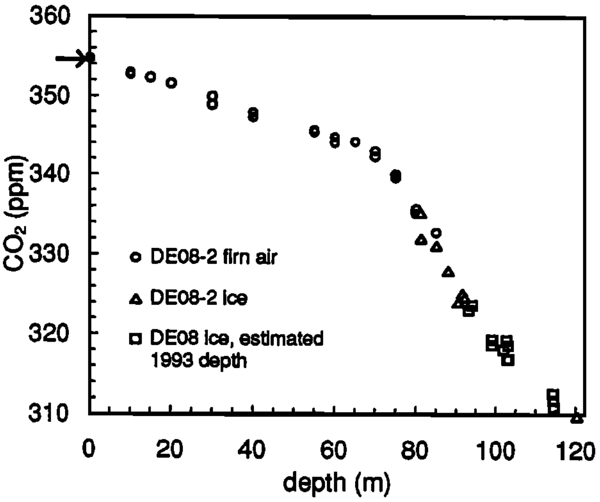

Figure 2. CO_2 mixing ratio versus depth in air from the firn at DE08-2 and from the ice at DE08-2 and DE08. The DE08 depths have been adjusted to allow for the accumulation between 1987 and 1993, when DE08 and DE08-2 were drilled, respectively. All CO_2 values have been corrected for gravitational fractionation (see text). The arrow marks the average CO_2 mixing ratio at south pole in February 1993, found from CSIRO analyses of air samples in glass flasks.

Ice Core Air Results

A total of 95 ice samples were measured. Of these, the results from 11 were discarded because the following problems were identified: leaks in the vacuum line or extraction flask (6 samples), post coring melting (2 samples), GC problems (power failure and too small sample size, 2 samples), inadequate sample cryotrapping (1 sample). Ice samples were selected away from the lower density summer layers that could complicate the air dating [*Etheridge et. al.*, 1992]. This selection also avoids a possible influence on the enclosed CO_2 by occasional high temperatures at the snow surface. Cracked ice was not measured. The measured CO_2 mixing ratios have been corrected down by 0.8 ppm to allow for the average measured system enhancement, and then by 0.45% (about 1.5 ppm) for gravitational fractionation. The results are given in Table 4.

Evidence That Ice Core Air Represents the Atmosphere

Air resides in both open porosity and closed porosity over a common depth interval at the firn-ice transition, an effect which is enhanced by the seasonal variability in density and closed porosity. A useful comparison can be made between air sampled and measured from both the open porosity (firn air) and the closed porosity (ice core air) from the same depth interval. The CO_2 results for the upper DE08 and DE08-2 ice core samples are plotted against depth together with the firn air results in Figure 2. All of the samples were analyzed with the same GC and against the same calibration gases. The results from the two types of measurement differ nonsystematically by about 1.3 ppm (1 σ), which is close to

Table 4. CO_2 Mixing Ratios in the Air From the Law Dome Ice Cores DE08, DE08-2, and DSS.

Ice Sample Code	Analysis Date	Mean Ice Depth, m	Ice Age, year A.D.	Mean Air Age, year A.D.	CO_2 Mixing Ratio, ppm
DE08					
DE08 205	Aug. 20, 1992	83.10	1939	1969	323.2
DE08 235	Aug. 12, 1993	83.98	1938	1968	323.7
DE08 225	Aug. 2, 1993	89.15	1935	1965	319.5
DE08 226	Aug. 2, 1993	89.00	1935	1965	318.8
DE08 203	Aug. 5, 1992	91.95	1933	1963	318.2
DE08 212	July 14, 1993	93.00	1932	1962	318.7
DE08 213	July 14, 1993	93.15	1932	1962	317.0
DE08 214	July 15, 1993	92.68	1932	1962	319.4
DE08 215	July 15, 1993	92.84	1932	1962	317.0
DE08 201	July 27, 1992	104.44	1923	1953	311.9
DE08 208	Nov. 13, 1992	104.61	1923	1953	311.0
DE08 236	Aug. 12, 1993	104.29	1923	1953	312.7
DE08 227	Aug. 2, 1993	115.66	1914	1944	309.7
DE08 243	Oct. 8, 1993	121.80	1909	1939	311.0
DE08 240	Aug. 19, 1993	121.90	1908	1938	310.5
DE08 238	Aug. 13, 1993	130.27	1902	1932	307.8
DE08 231	Aug. 10, 1993	138.79	1894	1924	304.8
DE08 237	Aug. 13, 1993	138.79	1894	1924	304.1
DE08 233	Aug. 11, 1993	149.86	1885	1915	301.3
DE08 239	Aug. 17, 1993	153.00	1882	1912	300.7
DE08 253	July 19, 1995	160.70	1875	1905	296.9
DE08 254	Aug. 3, 1995	160.90	1875	1905	298.5
DE08 230	Aug. 10, 1993	167.86	1868	1898	294.7
DE08 241	Aug. 19, 1993	174.39	1862	1892	294.6
DE08 252	July 19, 1995	179.50	1856	1886	293.7
DE08 229	Aug. 10, 1993	184.31	1852	1882	291.9
DE08 255	Aug. 3, 1995	190.30	1847	1877	288.8
DE08 228	Aug. 6, 1993	197.54	1839	1869	287.4
DE08 232	Aug. 11, 1993	206.09	1831	1861	286.6
DE08 234	Aug. 12, 1993	214.10	1824	1854	284.9
DE08 200	June 26, 1992	218.02	1820	1850	285.2
DE08 222	July 29, 1993	228.74	1810	1840	283.0
DE08-2					
DE08-2 008	Dec. 9, 1993	81.11	1948	1978	335.2
DE08-2 012	Dec. 15, 1993	81.30	1948	1978	332.0
DE08-2 003	Aug. 17, 1993	85.05	1945	1975	331.2
DE08-2 002	Aug. 6, 1993	87.96	1943	1973	328.1
DE08-2 005	Aug. 24, 1993	90.55	1941	1971	324.1
DE08-2 015	Aug. 3, 1995	91.69	1940	1970	325.2
DE08-2 016	Aug. 3, 1995	92.30	1940	1970	324.7
DE08-2 009	Dec. 15, 1993	120.27	1918	1948	309.9
DE08-2 007	Dec. 9, 1993	128.79	1910	1940	310.5
DE08-2 011	Dec. 15, 1993	135.82	1904	1934	309.2
DE08-2 006	Dec. 9, 1993	242.81	1802	1832	284.5
DSS					
DSS 004	Nov. 13, 1992	78.02	1901	1959	315.7
DSS 001	Aug. 20, 1992	81.82	1896	1954	313.6
DSS 002	Aug. 21, 1992	81.82	1896	1954	314.7
DSS 003	Aug. 21, 1992	81.82	1896	1954	314.1
DSS 029	Nov. 24, 1993	86.19	1890	1948	311.4
DSS 037	June 7, 1995	92.86	1881	1939	309.2
DSS 027	Nov. 18, 1993	94.13	1878	1936	307.9
DSS 041	June 15, 1995	99.82	1871	1929	305.2
DSS 008	Aug. 13, 1993	100.32	1868	1926	305.0
DSS 033	June 2, 1995	114.45	1847	1905	299.0
DSS 007	Aug. 11, 1993	116.89	1841	1899	296.5

Table 4. (continued)

Ice Sample Code	Analysis Date	Mean Ice Depth, m	Ice Age, year A.D.	Mean Air Age, year A.D.	CO_2 Mixing Ratio, ppm
DSS 030	Nov. 24, 1993	122.82	1833	1891	294.7
DSS 009	Aug. 20, 1993	151.56	1787	1845	286.1
DSS 010	Aug. 20, 1993	163.51	1767	1825	285.1
DSS 015	Oct. 8, 1993	179.97	1738	1796	283.7
DSS 016	Oct. 14, 1993	181.34	1736	1794	281.6
DSS 017	Oct. 14, 1993	190.88	1719	1777	279.5
DSS 031	June 2, 1995	200.64	1702	1760	276.7
DSS 014	Aug. 23, 1993	206.50	1691	1749	277.2
DSS 025	Nov. 10, 1993	207.58	1689	1747	276.9
DSS 019	Oct. 21, 1993	223.01	1662	1720	277.5
DSS 011	Aug. 20, 1993	238.00	1634	1692	276.5
DSS 020	Oct. 21, 1993	245.63	1621	1679	275.9
DSS 013	Aug. 23, 1993	263.35	1589	1647	277.2
DSS 012	Aug. 23, 1993	285.20	1546	1604	274.3
DSS 021	Oct. 28, 1993	293.20	1531	1589	278.7
DSS 032	June 2, 1995	302.14	1512	1570	281.9
DSS 018	Oct. 21, 1993	313.93	1489	1547	282.8
DSS 035	June 7, 1995	323.84	1469	1527	283.2
DSS 023	Nov. 10, 1993	336.73	1441	1499	282.4
DSS 044	June 30, 1995	351.30	1407	1465	279.6
DSS 022	Oct. 28, 1993	360.64	1388	1446	281.7
DSS 024	Nov. 10, 1993	387.13	1329	1387	280.0
DSS 026	Nov. 18, 1993	387.20	1329	1387	280.4
DSS 034	June 5, 1995	414.22	1269	1327	283.4
DSS 039	June 14, 1995	447.34	1188	1246	281.7
DSS 036	June 9, 1995	467.85	1138	1196	283.9
DSS 043	June 30, 1995	488.46	1088	1146	283.8
DSS 042	June 15, 1995	506.03	1038	1096	282.4
DSS 040	June 14, 1995	523.56	988	1046	280.3
DSS 038	June 12, 1995	534.27	948	1006	279.4

Values have been reduced by 0.8 ppm for extraction system enhancement and by 0.45% for gravitational fractionation, as described in the text. It should be noted that the wider age spread of the DSS ice core air may not record the detailed CO_2 changes observed in the higher air age resolution DE08 and DE08-2 cores (see text).

the uncertainty of the ice core measurements, confirming that the CO_2 results from the ice core air are representative of the air in the firn. This is further evidence that the CO_2 in the ice core air is not detectably influenced by the processes of air enclosure in the ice sheet, ice core drilling and handling, or extraction of air from the ice samples.

The comparison between the CO_2 results for the DE08, DE08-2, and DSS cores and the atmospheric CO_2 record from south pole [*Keeling*, 1991a] is shown in Figure 3. As there is virtually no atmospheric CO_2 gradient between the latitudes of Law Dome and south pole [*Conway et al.*, 1994] and because the ice core and south pole mixing ratios are reported in the same scale, any differences would most probably be due to errors in the ice core CO_2 measurement or air dating. The ice core results show a tight overlap with the south pole record, being on average 0.8 ppm higher (standard error = 1.3 ppm) which is within the measurement uncertainty. This confirms that there is no significant systematic error in the ice core CO_2 measurements. It should be noted that the overlap occurs for the three cores, which have independent air dating, and for a duration of up to 20 years. The results from the three ice cores also intercompare well, suggesting no dependence on the ice core location, accumulation rate (and thus ice depth and overburden pressure for equivalent age), ice core drilling method or storage duration. Because of these factors and other reasons discussed above, the CO_2 results presented here are a reliable measure of the atmospheric mixing ratio to within the uncertainty of 1.2 ppm.

Preindustrial Period

The complete CO_2 record from the Law Dome ice cores is shown in Figure 4. The preindustrial period, defined here as before about 1800 A.D., when emissions from fossil fuels and land use change were negligible, deserves particular note. Between 1000 A.D. and 1550 A.D., the CO_2 mixing ratio was 280-284 ppm, then dropped to a level about 6 ppm lower between 1550 A.D. and 1800 A.D., before returning to the pre-1550 A.D. level by the early 1800s. Major CO_2 growth then followed almost immediately, with the onset of the industrial period.

Small CO_2 decreases in the centuries before the industrial period appear in several other ice core records [*Raynaud and Barnola*, 1985; *Etheridge et al.*, 1988; *Wahlen et al.*, 1991] but these earlier records have larger analytical or dating

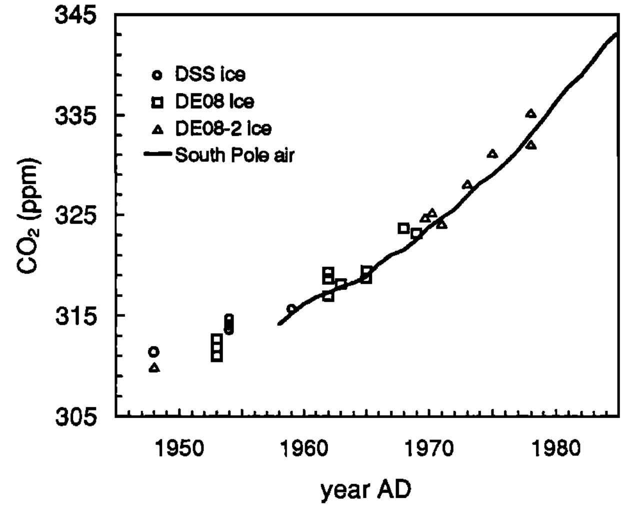

Figure 3. Comparison of CO_2 mixing ratios from the Law Dome DE08, DE08-2 and DSS ice cores and from the atmosphere at south pole. The ice core results have been corrected for average system enhancement and gravitational fractionation as described in the text. The south pole record is from the monthly means of *Keeling* [1991a], spline-smoothed to remove seasonality.

uncertainties. More recently, *Barnola et al.* [1995] observed a similar CO_2 decrease (about 6 ppm) although over a longer period (between 1350 A.D. and 1750 A.D.) than observed for DSS. Probable explanations of this difference are the smoothing procedure (100-year running mean) and the wider air age spread of the two ice cores (25-40 years and 35-40 years) of *Barnola et al.* [1995] combined with the analytical uncertainties (±1.2 ppm for this work and ±3 ppm for *Barnola et al.* [1995]). Our record does not have sufficient data density to comment on the CO_2 fluctuation of about 10 ppm seen by *Siegenthaler et al.* [1988] and *Barnola et al.* [1995] at the end of the 13th century.

The lowest CO_2 levels in our record coincide with a period of lower global temperatures often called the little ice age (LIA). There is some uncertainty about the precise timing, duration, and cause of the LIA and whether it was geographically synchronous [*Jones and Bradley*, 1992]. Evidence from glacial advances, ice core oxygen and hydrogen isotopes, tree rings, and documented records suggests that the period between about 1550 A.D. and 1850 A.D. was one of the most significant climatic events since the last ice age [*Grove*, 1988], but most proxy climatic indicators can have the limitation of being significantly influenced by local or regional effects. The Antarctic ice core CO_2 record, however, has the following characteristics:

1. The record is naturally averaged over at least a decade, which is many times the interhemispheric mixing time. Only atmospheric CO_2 changes that are sustained for several years or more are recorded.
2. The ice sheet is remote from significant local CO_2 sources or sinks. Even intense air-sea pCO_2 differences reduce the annual-average CO_2 levels near the Antarctic coast by much less then 1 ppm (southern hemisphere station network and Southern Ocean cruise data, personal communication L.P.S., R.J.F., R.L.L. and H.M. Beggs). Thus CO_2 changes observed at Law Dome are representative of the southern hemisphere, if not the globe.
3. The location is extremely remote from sources of particulate impurities such as exposed land surfaces, forest fires, or volcanos. High concentrations of such impurities in the ice may modify the trapped CO_2.

We therefore interpret the 6 ppm lower CO_2 levels observed in the Law Dome ice cores between 1550 A.D. and 1800 A.D. as a global atmospheric signal, and explore the extreme possibilities that a CO_2 decrease radiatively forced the cooler temperatures of the LIA, or alternatively, that the lower CO_2 levels were a global response to lower temperatures.

It is unlikely that the LIA cooling was solely a result of the decreased radiative forcing of an independent CO_2 change. The change in temperature for a 6 ppm CO_2 decrease found from modeling studies [*Syktus et al.*, 1994] is 0.13°-0.21°C. A similar result can be found from a rather simplistic application of the empirical temperature-CO_2 relationship derived from the Vostok ice core results [*Goreau*, 1990]. This coefficient, 0.094°C ppm^{-1}, assumes that CO_2 alone caused the observed temperature changes. Given that about 50% of the Vostok variations are attributed to radiative forcing of which about 70% is from the observed CO_2 changes [*Raynaud et al.*, 1993], a 6 ppm CO_2 decrease implies a 0.2°C lower temperature during the LIA. However, the magnitude of LIA cooling is estimated at 1°-2°C [*Grove*, 1988]. Therefore although the observed CO_2 change may have caused a global temperature feedback, it is unlikely to have been a primary cause of the LIA.

A more likely cause of the 6 ppm CO_2 change is the readjustment of the exchanges of atmospheric CO_2 with the oceans and biosphere during changing climate. Identifying which CO_2 exchanges were influenced by the LIA climate must take into account the timescales of the observed CO_2 change. The 6 ppm decrease occurred between about 1550 and 1600 A.D. The return to pre-LIA levels also occurred in about 50 years. Over these timescales or longer, the mixed layer of most of the ocean is in approximate chemical

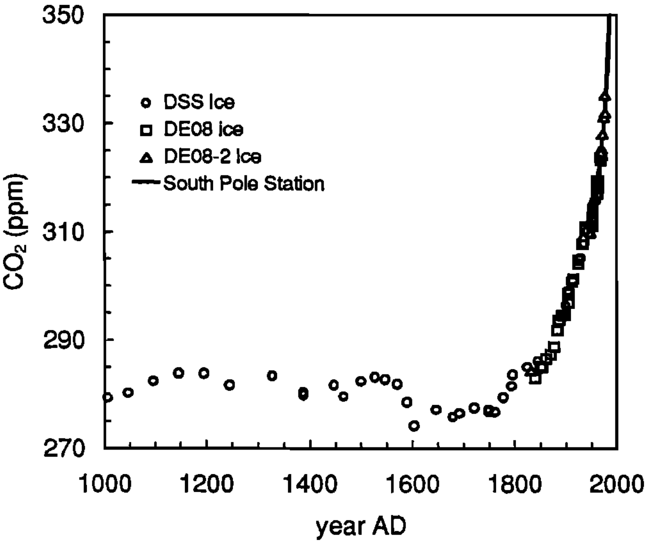

Figure 4. CO_2 mixing ratios from the DE08, DE08-2, and DSS ice cores and the modern atmospheric record from south pole as for Figure 3.

equilibrium with the atmosphere [*Broecker and Peng*, 1974] and a global change in air-sea CO_2 exchange would not by itself influence the removal rate of CO_2 into the oceans. Furthermore, the removal of atmospheric CO_2 due to increased solubility in the ocean mixed layer is limited to about 1 ppm/°C because of the buffering effect of the ocean carbonate system [*Broecker and Peng*, 1974; *Bacastow*, 1979]. Even if the maximum LIA cooling of 1°-2°C extended to the surface mixed layer, the increased solubility would amount to only about a 2 ppm CO_2 decrease. Thus the primary control that the ocean exerts on the atmospheric CO_2 level over the timescale of the LIA variations is the transport of carbon from the mixed layer into the deeper ocean. Explanations of the 80 ppm atmospheric CO_2 decrease during glacial times involve vertical redistribution of ocean carbon, either by marine biota (the "biological pump"), by changed ocean circulation and ocean chemistry (reviewed by *Broecker and Peng* [1993]), or by increased windspeeds over cooling and sinking seawater in polar regions (the "solubility pump") [*Keir*, 1993]. The shorter duration of the LIA variations compared to full glaciations excludes mechanisms such as changed whole ocean properties or increased nutrient supply associated with sea level change. However, it is conceivable that some of the processes expected to have increased CO_2 uptake in the glacial ocean occurred to a smaller degree during the LIA and contributed to the 6 ppm CO_2 decrease. Indeed, a stronger "solubility pump" and enhanced thermohaline mixing at polar regions are consistent with records of stronger winds, colder polar ocean temperatures, and greater sea ice extent during the LIA [*Lamb*, 1979].

Changed terrestrial carbon reservoirs may also have contributed to reduced LIA CO_2 levels. Colder temperatures would have reduced respiration rates, offset by lower rates of carbon uptake by photosynthesis. Model estimates [e.g., *Harvey*, 1989] suggest that the net response of terrestrial ecosystems to temperature change only would be sufficient to explain the observed CO_2 change during the LIA if the cooling were 1°-2°C. However, respiration and photosynthesis are also controlled by precipitation and nutrient levels which could offset the net temperature response by 100% or more either directly [*Dai and Fung*, 1993], or by nitrogen cycle feedback [*Schimel et al.*, 1994]. Evaluation of the net terrestrial response during the LIA, when information on precipitation and nutrients is scarce, is beyond the scope of this work.

Regardless of whether the CO_2 change during the LIA originated in the oceans or terrestrial reservoirs, it requires that large-scale shifts occurred in the cycling of carbon in these pools. The CO_2-LIA link is thus supporting evidence for the concept that the LIA was a sustained and globally significant climatic event.

Industrial Period

The Law Dome results show that the atmospheric CO_2 level has increased by around 25% since 1750 A.D. (Figure 4). Similar increases can be deduced from ice core data combined with modern atmospheric records [*Neftel et al.*, 1985; *Raynaud and Barnola*, 1985; *Etheridge et al.*, 1988; *Wahlen et al.*, 1991; *Barnola et al.*, 1995]. The CO_2 growth is attributed to fossil fuel CO_2 release that began about 1850 A.D. and biospheric CO_2 releases from land use changes that began about a century earlier [eg. *Pearman et al.*, 1986; *Siegenthaler and Oeschger*, 1987]. However, it is probable that part of the CO_2 increase in the last 200 years, namely the increase seen in Figure 4 from 1750 A.D. to 1800 A.D. and possibly later, was a recovery of the carbon cycle from the LIA perturbation. This supports the findings of carbon cycle modeling studies [*Enting*, 1992; *Siegenthaler and Joos*, 1992] that the estimated biospheric and fossil CO_2 sources since pre-industrial times are inconsistent with the Siple ice core CO_2 record: that is, the assumption that the natural carbon cycle was in steady state during the eighteenth and nineteenth centuries is invalid.

Figure 5 shows the ice core CO_2 record since 1830 A.D., corresponding to the earliest DE08 and DE08-2 results and the beginning of significant anthropogenic CO_2 emissions. CO_2 mixing ratios for this period are best described by a smoothing spline fitted to the DE08 and DE08-2 data only. Following almost a century of substantial growth, the CO_2 mixing ratio stabilized or even decreased slightly between about 1935 to 1945 A.D. CO_2 growth restarted only about 10 years before modern atmospheric measurements began. The air age resolution of the high-accumulation ice cores DE08 and DE08-2 has revealed this smaller, shorter term variation.

The spline fit to the DE08 and DE08-2 results is compared with the DSS results for the same period in Figure 6. Although only a few DSS results exist for this period, the 1935-1945 A.D. stabilization of CO_2 is not evident in the DSS record. This implies that the air age distribution is wider for DSS than for DE08 and DE08-2. Since the firn-air diffusion process is expected to be very similar for the three sites, the duration of bubble closure, which is longer at DSS, appears to have widened the air age distribution. This result is consistent with the argument made above that a certain amount of air mixes down to the bubble close-off zone. The partial control of the air age distribution by the bubble close-

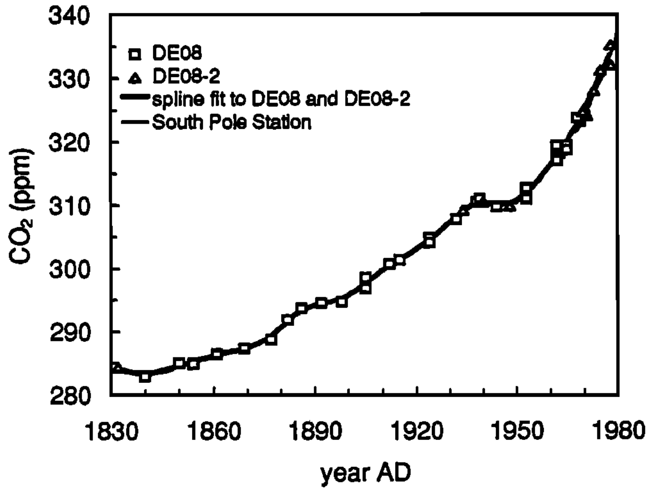

Figure 5. CO_2 mixing ratios since early last century from the ice cores DE08 and DE08-2 and the south pole record as for Figure 4. The thick line is a smoothing spline fit [*de Boor*, 1978; *Enting*, 1987] to the DE08 and DE08-2 data. The degree of smoothing has been set such that attenuation of 50% occurs for CO_2 variations of 20-years duration. Such smoothing was found to best attenuate the shorter frequency variations that, because of the averaging effect of the air enclosure process, are unlikely to be real atmospheric features and are therefore attributed to measurement errors.

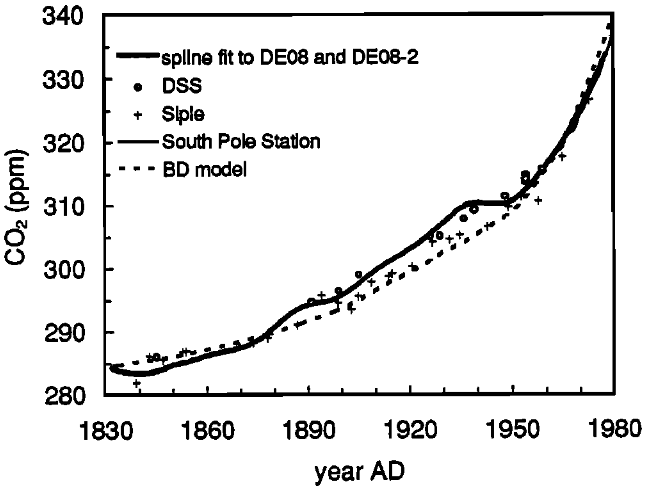

Figure 6. Comparison of CO_2 mixing ratios since 1830 A.D. from the DE08 and DE08-2 ice cores (spline fit from Figure 5) with those from the DSS ice core (circles) and from the Siple ice core [*Neftel et al.*, 1985; *Friedli et al.*, 1986] (crosses). The Siple CO_2 mixing ratios have been reduced by 0.45% to allow for gravitational fractionation, based on the $\delta^{15}N$ measurements of *Sowers et al.* [1992]. Differences may exist between the CO_2 calibration scale of the Siple results and ours. The CO_2 levels of the high-accumulation rate DE08 and DE08-2 ice cores follow the atmosphere more closely than those of the DSS or Siple ice cores for periods of rapid change. The dashed line is the atmospheric increase produced by the box diffusion carbon cycle model of *Enting and Lassey* [1993], calibrated for the Intergovernmental Panel on Climate Change (IPCC) runs. The model gives globally averaged CO_2 levels which would be expected to be only slightly higher than Antarctic levels (by about 2 ppm in 1980 decreasing to less than 1 ppm before 1960, from the latitudinal CO_2 gradient of *Keeling et al.* [1989]).

off process is the likely reason why the Siple ice core (results shown in Figure 6), which has nearly the same accumulation rate and bubble close-off duration as DSS, also damps out the CO_2 stabilization. It is likely that even the DE08 and DE08-2 ice cores have smoothed this atmospheric CO_2 feature slightly and that there was actually a small decrease in the atmospheric CO_2 level. Deconvolution of the ice core record with a model that incorporates the processes of firn diffusion and bubble closure is required to reconstruct the true atmospheric history.

The observed CO_2 mixing ratios are compared in Figure 6 with those calculated by a "box diffusion" carbon cycle model [*Enting and Lassey*, 1993]. The model incorporates CO_2 release estimates from the main anthropogenic sources, fossil fuels [*Keeling*, 1991b; *Marland and Boden*, 1991], and land use [*Houghton*, 1993]. CO_2 is exchanged between the atmosphere and the ocean. Additional uptake of carbon by enhanced growth of terrestrial biota (CO_2 "fertilization") is the only feedback process represented. The model follows the observed overall CO_2 increase except for a significant departure of the ice core results beginning about 1900 A.D. The departure reaches a maximum in 1935 A.D. and then decreases in the decade when CO_2 stabilized. The difference between the modeled and observed CO_2 levels suggests errors in the model source estimates or inadequate model parameterization of feedback processes or climate forcings.

The growth rate of the atmospheric CO_2 mixing ratio since 1830 A.D. is plotted in Figure 7. It is derived from the spline fit to the CO_2 results for DE08 and DE08-2 and given in gigatons carbon (10^9 tonnes of carbon as CO_2) per year. The growth rate increased steadily except during 1935-1945 A.D. when it dropped from about 1 Gt C yr^{-1} to zero or less. Also shown in Figure 7 are the estimates of fossil fuel and land use emissions and the growth rate derived from the carbon cycle model that incorporates these estimates. Both the fossil fuel and the land use emissions exhibit small decreases on decadal timescales, which are reflected in the model, but are too small to account for the 1935-1945 A.D. decrease in the CO_2 growth rate. Despite relatively large uncertainties in the land use term [*Houghton*, 1993], the size of the source at this time was probably too small (relative to fossil fuel emissions) for even a relatively large decrease to be the sole cause of the CO_2 growth rate decrease.

Thus a reduced respiration source or increased sink of about 1 Gt C yr^{-1} during 1935-1945 are the main likely contributors to the growth rate decrease. There is a greater abundance of information on factors affecting the biosphere for the recent century than for the LIA. Increased growth of the biosphere (i.e., an increased carbon sink) has been suggested by models incorporating the effects of observed temperature and precipitation changes [*Dai and Fung*, 1993] and temperature changes and nitrogen and CO_2 fertilization [*Hudson et al.*, 1994] on the photosynthesis and respiration of vegetation and soils. The models show that the climate and nutrient forcing could have produced a perturbation to the biospheric uptake of 1 Gt C yr^{-1} or more (with the effects of temperature and precipitation changes predominating in the first half of this century), reducing the net biospheric emissions (land use minus terrestrial biosphere) to zero or less. However, significant biospheric uptake begins at different times for each model, being either about 15 years too

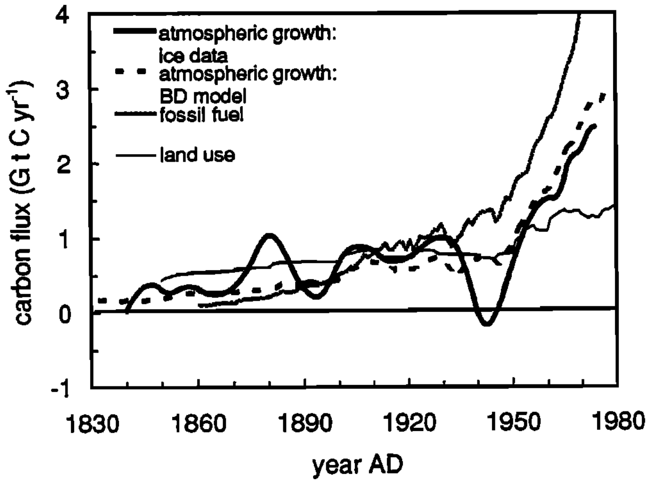

Figure 7. CO_2 growth rates (in gigatons carbon per year) in the atmosphere since last century, derived from the 20-year smoothing-spline fit to the ice core results in Figure 5 and from the carbon cycle model results, and estimates of carbon emissions from fossil fuels [*Keeling*, 1991b; *Marland and Boden*, 1991] and from land use [*Houghton*, 1993]. Positive values are defined as a net flux of carbon to the atmosphere.

early [*Hudson et al.*, 1994] or about 15 years too late [*Dai and Fung*, 1993] to fully account for the observed growth rate decrease of atmospheric CO_2.

This underlines the complexity of the natural variability of the carbon cycle and raises the possibility that ocean processes may also have varied during 1935-1945 A.D. A recent stable carbon isotope study shows that atmospheric CO_2 growth rates over the last decade have been dominated by ocean exchange [*Francey et al.*, 1995]. Low CO_2 growth rate years are also the years of El Niño events. It is therefore suggestive that an unusually persistent El Niño sequence occurred between 1939 and 1942 [R.J. Allan and R.D. D'Arrigo, Persistent ENSO sequences: How unusual was the recent El Niño?, submitted to *The Holocene*, 1995; hereinafter referred to as R.J. Allan and R.D. D'Arrigo, 1995]. The other persistent El Niño sequences identified by R.J. Allan and R.D. D'Arrigo [1995] at 1895-1898 A.D. and 1911-1916 A.D. also coincide with small decreases in the CO_2 growth rate record (Figure 7). We speculate that changes to ocean and terrestrial processes over a large portion of the globe caused by persistent El Niño sequences may have impacted on atmospheric CO_2 levels. However, the mechanistic link remains obscure, with observed reductions in equatorial ocean upwelling and advection during El Niño events accounting for only part of the observed recent CO_2 growth rate decreases [*Feely et al.*, 1995]. Thus a combination of possible causes, increases in the net carbon uptake by the ocean and terrestrial biosphere and small reductions in the fossil and land use emissions, is required to explain the CO_2 growth rate decrease during 1935-1945 and possibly at other periods in the last 100 years.

The CO_2 variations during 1935-1945 and during the LIA involved imbalances in the atmospheric CO_2 exchanges of -1 to +0.3 Gt C yr^{-1}, or about 1% or less of the gross carbon exchanges of the terrestrial biosphere and ocean with the atmosphere each year. We have discussed above how small perturbations to the exchange mechanisms could affect the net carbon exchanges and cause the observed atmospheric CO_2 variations. Clarification of the contribution of the net exchanges of carbon from different reservoirs is expected to come from the analysis of other trace species in the ice cores, in particular, the stable carbon isotopes of CO_2.

Conclusions

A detailed evolution of atmospheric CO_2 levels since 1000 A.D. has been determined using three ice cores from Law Dome, Antarctica. Measurement of air from the firn confirms the link of the ice core air with the atmosphere, permitting accurate allowances for the effects of diffusion on the composition and age of the ice core air. A substantial overlap of the results from the three, independently dated, ice cores with the modern atmospheric record is observed. This, and other tests, confirm that the CO_2 mixing ratio of the ice core air is representative of the atmosphere to within 1.2 ppm.

CO_2 mixing ratios during the 800 years before industrialization were in the range 275-284 ppm. The lowest levels coincide with the LIA period of 1550-1800 A.D. and suggest a climate-CO_2 link. We favor a climate influence on CO_2 exchange as a primary reason for the link; in this case, the globally integrated characteristics of the atmospheric CO_2 signal provide an unusual opportunity to define the timing of the LIA. The occurrence of natural CO_2 variations of this magnitude makes it inappropriate to refer to a single preindustrial level as has been customary in the past.

Major CO_2 growth is observed in the ice core record with the onset of the industrial period. Increases in CO_2 at the beginning of this period were probably caused in part by carbon releases associated with the recovery of the carbon cycle from the effects of the LIA. CO_2 mixing ratios were stable or decreased slightly between about 1935 and 1945 A.D., a feature made evident by the high air age resolution of the DE08 and DE08-2 cores. Variations in published estimates of fossil fuel and land use emissions are insufficient to explain this feature, so an increased CO_2 sink of about 1 Gt C yr^{-1} is required, caused by natural variations of carbon exchange with the biosphere or oceans. If such variations occur in the future, they could complicate predictions of anthropogenic climate forcing.

It is possible that other CO_2 changes of similar magnitude occurred in the past but with such short duration that even the Law Dome ice did not record them. However, it is unlikely that such changes would be recorded in ice cores with still higher accumulation rate than DE08 and DE08-2 (even if sites could be found without significant surface melting), because the diffusion of air through the firn will significantly smooth any variations shorter than about 10 years. The DE08 cores may be at the upper limit of air age resolution for ice cores.

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