Atmospheric methane between 1000 A.D. and present: Evidence of anthropogenic emissions and climatic variability

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Abstract. Atmospheric methane mixing ratios from 1000 A.D. to present are measured in three Antarctic ice cores, two Greenland ice cores, the Antarctic firn layer, and archived air from Tasmania, Australia. The record is unified by using the same measurement procedure and calibration scale for all samples and by ensuring high age resolution and accuracy of the ice core and firn air. In this way, methane mixing ratios, growth rates, and interpolar differences are accurately determined. From 1000 to 1800 A.D. the global mean methane mixing ratio averaged 695 ppb and varied about 40 ppb, contemporaneous with climatic variations. Interpolar (N-S) differences varied between 24 and 58 ppb. The industrial period is marked by high methane growth rates from 1945 to 1990, peaking at about 17 ppb yr^{-1} in 1981 and decreasing significantly since. We calculate an average total methane source of 250 Tg yr^{-1} for 1000-1800 A.D., reaching near stabilization at about 560 Tg yr^{-1} in the 1980s and 1990s. The isotopic ratio, $\delta^{13}CH_4$, measured in the archived air and firn air, increased since 1978 but the rate of increase slowed in the mid-1980s. The combined CH_4 and $\delta^{13}CH_4$ trends support the stabilization of the total CH_4 source.

1. Introduction

Methane (CH_4) is a radiatively active and relatively long lived gas that also has important chemical roles in the atmosphere. Methane now contributes about 20% to the increased direct radiative forcing by greenhouse gases compared to preindustrial times [*Shine et al.*, 1995]. Oxidation of CH_4 in the troposphere produces carbon monoxide (CO), can lead to the production of ozone (O_3), and involves the major atmospheric oxidant, the hydroxyl radical (OH). In the stratosphere, methane oxidation is an important source of water vapor.

The amount of methane in the atmosphere has been observed from modern direct measurements and from the analysis of air inclusions in polar ice to be growing since about 200 years ago [e.g., *Craig and Chou*, 1982; *Etheridge et al.*, 1992; *Matsueda et al.*, 1996; *Rasmussen and Khalil*, 1984; *Stauffer et al.*, 1985; *Steele et al.*, 1992]. This growth is mainly attributed to increased anthropogenic CH_4 sources during the industrial and agricultural period. Changes in emissions from natural sources and in the global level of OH (the main CH_4 sink) may also have contributed to CH_4 changes.

Attempts to understand the global atmospheric CH_4 budget from modern, systematic direct measurements of the atmosphere have been made difficult by their short duration (beginning in 1978) and the variability of CH_4 growth rates over this period. Reduced growth in fossil fuel CH_4 emissions was suggested as a cause of the decline in the growth rate since 1983 [*Steele et al.*, 1992]. A major growth rate decrease in 1992 was partly attributed to a reduced fossil fuel source [*Dlugokencky et al.*, 1994a]. *Hogan and Harriss* [1994] and *Lowe et al.* [1997] suggested that reduced wetland emissions

resulting from the atmospheric cooling following the 1991 eruption of Mount Pinatubo, and reduced biomass burning, respectively, were more likely causes. In contrast, a transient increase in the CH_4 growth rate immediately after the eruption was found to be consistent with reduced tropospheric UV flux, leading to decreased OH levels [*Dlugokencky et al.*, 1996]. A clear understanding of the frequency of occurrence of, and responses to, natural forcing on atmospheric CH_4 is a prerequisite to predictions and monitoring of future effects of anthropogenic forcing.

Ice core records can place the recent changes in a longer term perspective. However, to improve the understanding of the recent atmospheric CH_4 budget, measurements need to have a precision better than 1% and have sufficiently fine time resolution to record relatively small and rapid changes. Furthermore, ice core measurements need to be extended into recent decades to bridge the gap to the first reliable direct measurements of CH_4 in the atmosphere.

An earlier study [*Etheridge et al.*, 1992] used the DE08 ice core from Law Dome, Antarctica, where the extremely high rate of snow accumulation enclosed air into bubbles in the ice with a fine age resolution, and with mean ages as recent as the 1970s. It was found that CH_4 growth rates stabilized during 1920-1945 and possibly since 1970, showing that there have been large variations in the CH_4 growth rates throughout the industrial period. The ice core results, and the contemporary record, led to speculation that the observed growth rate changes were likely to have been caused by changes to the anthropogenic sources such as fossil fuel utilization.

We present new high-resolution measurements of CH_4 in air from polar ice and firn, from the past decade back to 1000 A.D. We remeasure the DE08 ice core and measure a newer core, DE08-2, also from the high accumulation rate side of Law Dome that now provides mean air ages as recent as the 1980s. The Cape Grim Air Archive (Tasmania) also provides air samples since 1978 [*Langenfelds et al.*, 1996]; we have reselected and deseasonalized the CH_4 results to link them

with the ice record. New procedures improve the CH_4 measurement precision, and the considerable overlap of the ice measurements with the CH_4 record from atmospheric measurements and air archive tanks is used to check the accuracy of the ice technique. The late preindustrial period is represented by the deep Law Dome ice core, DSS. Using CH_4 measurements of the Greenland ice cores, Eurocore (E. Michel et al., manuscript in preparation, 1998) and GISP2 [*Sowers et al.*, 1997], made in the same laboratory, we accurately determine how the interpolar difference in CH_4 has varied in the past.

To link the ice core air with the atmosphere, and to quantify the effects of the air enclosure process on the air age and composition, we analyzed the air from the firn layer (the permeable upper 85 m) at DE08-2 for CH_4 and other key atmospheric species. The firn layer holds an additional atmospheric archive [e.g., *Battle et al.*, 1996; *Schwander et al.*, 1993; *Trudinger et al.*, 1997]. At DE08-2 the firn air provides a record from 1993 back to just before the first reliable direct atmospheric measurements of CH_4. The mean age and age spread of the firn air and ice core air have been calculated with a numerical model of air diffusion and enclosure [*Trudinger et al.*, 1997] and confirmed with direct measurement of the bomb-produced pulse of $^{14}CO_2$ [*Levchenko et al.*, 1996, 1997).

We also use measurements of the isotopic composition of methane ($^{12}C/^{13}C$) in air from the Cape Grim Air Archive and DE08-2 firn, covering the last 17 years. The measurements were made using recently developed techniques [*Francey et al.*, 1996b] and some have appeared in preliminary form [*Trudinger et al.*, 1997]. Here the $\delta^{13}CH_4$ measurements are presented more fully and used in conjunction with the mixing ratios of CH_4 to provide constraints on causes of its changing atmospheric budget. Bacterial CH_4 emissions have markedly lower $\delta^{13}C$ values than those of thermogenic or biomass burning origin [*Conny and Currie*, 1996], whereas the main sink for CH_4, reaction with atmospheric OH, strongly favors the lighter molecule. The resulting atmospheric $\delta^{13}CH_4$ level and its trend reflect these source and sink contributions to the CH_4 budget.

The new CH_4 measurements show in detail the changes since the start of major industrial and agricultural activity, including significant variations in preindustrial times and in the decades leading up to the contemporary measurements. The $\delta^{13}CH_4$ record helps identify the possible causes of the strongly declining growth of CH_4 mixing ratios in recent decades.

2. Ice Cores

The Antarctic cores were drilled on Law Dome, East Antarctica (summit 66°44' S, 112°50' E, 1390 m elevation) during the last decade. Ice cores DE08 and DE08-2 were drilled in a region of extremely high accumulation rate (1100 kg m^{-2} yr^{-1}, equivalent to about 1.2 m of ice), 16 km east of the summit. The DSS core was drilled 4.6 km SSW of the summit in a region of lower accumulation (600 kg m^{-2} yr^{-1}). Drilling techniques were thermal (DE08 and DSS to 96 m) and electromechanical (DE08-2 and DSS below 96 m) and drilling fluid was used only at DSS below 96 m. The ice layering at all sites is regular and essentially undisturbed by wind scouring at the ice sheet surface or by ice flow at the depths considered here. The cores contain only a few melt layers (all thinner than

10 mm) and there are no clathrates. Further details of the Law Dome ice cores are given by *Etheridge et al.* [1996] and *Morgan et al.* [1997].

The Greenland cores are from the Summit region (72°34' N, 37°37' W, 3200 m elevation) and were drilled electromechanically and without fluid. Because the accumulation rate (about 200 kg m^{-2} yr^{-1}) is lower than for the Law Dome cores, they have lower air age resolution, and the measurements used here cover only the preindustrial period. The Eurocore ice core samples were measured for CH_4 as part of investigations into the cause of the Greenland-Antarctic ice CO_2 difference (E. Michel et al., manuscript in preparation, 1998). The GISP2 samples (selected from the ("F") core) were measured as part of a measurement intercomparison between ice core laboratories [*Sowers et al.*, 1997].

3. Measurement Techniques

The ice core air extraction, collection, and analysis procedures are similar to those described by *Etheridge et al.* [1996]. Our "cheese grater" dry extraction technique was used to quickly extract relatively large air samples without the risk of contamination from CH_4 produced by friction between stainless steel components. The released air was dried cryogenically at -100°C and collected cryogenically in stainless steel traps which were cooled to about -255°C by a closed-cycle helium cooler. The CH_4 mixing ratio of the ice core air samples (warmed to ambient temperature) was measured with a Carle series 400 gas chromatograph (GC) equipped with a flame ionization detector. From one to five analyses were made, depending on the sample size. Precision of the GC analysis was 0.15% (1σ). The response was almost perfectly linear over the range 300 ppb to at least 1850 ppb (parts per billion in dry air). The calibration scale, denoted the CSIRO94 CH_4 scale, is indistinguishable from the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory calibration scale [*Dlugokencky et al.*, 1994b; *Sowers et al.*, 1997; *Steele et al.*, 1996].

Several refinements made to our earlier procedures [*Etheridge et al.*, 1988, 1992] significantly improved the CH_4 measurements. The sample traps were shorter and wider and required no internal mixing ball. The trap surfaces where the sample condensed were electropolished and had no welds, ensuring reliable and quantitative sample transfer and storage. One bellows-sealed valve with a copper-tipped stem closed each trap without the risk of CH_4 production during actuation. A new GC inlet manifold removed traces of laboratory air at the trap connection by evacuation, which was more effective and used less sample than by flushing only. This enabled the ice core air samples to be analyzed with the same GC and with the same calibration strategy as that used to measure the much larger atmospheric flask air samples [*Francey et al.*, 1996a] and firn air samples. Estimated precision (1σ) of the ice core CH_4 measurements (air extraction and analysis) is 5 ppb.

3.1. System Tests

Tests of the integrity of the ice core air extraction and analysis system were made by simulating the procedure by crushing air-free ice in the presence of standard gas samples with CH_4 mixing ratios ranging from 677 to 1655 ppb. This would readily detect possible contamination or CH_4 production from surfaces. More than 50 tests were made over the duration

of this study, with CH_4 returned on average 6 ± 4 ppb enhanced, and with no systematic dependence on the mixing ratio of the standard. This represents a significant improvement on our earlier procedure. Suspected causes of the previous higher and more variable enhancement were sporadic CH_4 production in earlier trap valves and contamination by residual laboratory air in dead spaces of the trap needle valve and GC inlet line.

In a recent intercomparison of ice core extraction and analysis procedures, our ice core CH_4 measurements were found to be within 16 ppb of the average value of 748 ppb found by 5 ice core laboratories on adjacent ice samples [Sowers et al., 1997], after allowance for small differences identified in the calibration scales of the laboratories. A consistent difference of about 20 ppb at CH_4 levels of about 760 ppb was found between techniques using dry extraction and melt extraction, with the dry techniques being higher. We have no explanation for this difference but note that the application of the results of our system tests coupled with the excellent overlap of our ice core measurements with the recent direct atmospheric record (see below) confirm our CH_4 measurements presented here to within about 10 ppb.

Several differences exist between the ice core CH_4 measurements presented here and the earlier measurements of the DE08 ic4e core [Etheridge et al., 1992]. First, improved dating of the ice at DE08 has made the mean air ages older by up to 3 years (see Appendix). Second, the new data are more precise ($1\sigma = 5$ ppb compared with 23 ppb, based on the CH_4 variability of samples with the same air age). Third, the earlier measurements are typically about 40 ppb higher for last century, and less enhanced for the younger samples. A comparison by Steele et al. [1996] shows a high degree of consistency in the CH_4 calibration scale between the two analysis periods. The higher ice core values were therefore probably caused by the small contamination discussed above. The contamination was undetected at the time due to the lesser precision of the earlier measurements and because the earlier system tests used standard air samples with CH_4 mixing ratios comparable to ambient modern air. Also, the good overlap of the earlier DE08 measurements with the modern record was fortuitous, because the effect of the contamination was much less for higher CH_4 mixing ratios, and was compensated by the small dating error. System tests with low-CH_4 standard gases show that the new traps, valves, and GC inlet manifold used for the measurements reported here have eliminated this contamination problem.

3.2. Firn Air Measurements

The DE08-2 firn air samples were collected at intervals of typically 5 m from the surface to 85 m, using the procedure described by Etheridge et al. [1996]. Briefly, when the required drilling depth was reached, a firn air sampling device (FASD) was inserted which sealed the borehole and pumped air from pores in the firn into flasks at the surface. The total volume pumped at each level (to initially purge 1000 standard liters of air and to flush and fill up to 7 flasks) was less than 1900 standard liters. This represents distances of less than 2 m from the FASD inlet, and it had no observable effect on the composition of the samples. The sample pumps, containers (0.5-L glass flasks and 22-L stainless steel tanks) and the two FASDs were proven to be benign for the CH_4 mixing ratio of the samples. The CH_4 mixing ratio was analyzed by the same GC technique described above.

3.3. Cape Grim CH_4 Measurements

Air from Cape Grim, Tasmania, has been archived in 35-L stainless steel tanks and 48-L aluminium cylinders 2 to 10 times per year since 1978 [Langenfelds et al., 1996, and references therein]. These provide relatively large and reliably-stored air samples from before the recent end of the Law Dome ice core record to the present day. The archived air samples were measured for CH_4 using similar GC techniques and the same calibration scale as the ice core samples. They were selected to include only samples that were taken during "baseline" wind conditions (back trajectories over the southern ocean) and stored in containers with demonstrated CH_4 stability [Langenfelds et al., 1996].

Routine flask air samples have also been collected at Cape Grim quasi-weekly since 1984 [Steele et al., 1996]. These were also taken during baseline wind conditions and measured with the same GC technique as the archive samples.

3.4. The $\delta^{13}CH_4$ Measurements

Measurement of $\delta^{13}CH_4$ involved quantitative conversion of CH_4 to CO_2 then analysis of $\delta^{13}C$ by mass spectrometry, based on the techniques of Stevens and Rust [1982] and Lowe et al. [1997], further modified to reduce sample volume requirement [Francey et al., 1996b]. Even then the measurement required typically 5 standard liters of air and was thus restricted to the larger air volumes available from the Cape Grim Air Archive and the DE08-2 firn. Briefly, the air samples were stripped of CO_2, water vapor, nonmethane hydrocarbons, N_2O and CO. The CH_4 in the remaining air was converted by heated platinized alumina to CO_2 (and H_2O) and the CO_2 transferred to a sample tube. The $\delta^{13}C$ of the CO_2 was then measured by isotope ratio mass spectrometry [Francey et al., 1996a].

A number of systematic biases can influence the $\delta^{13}C$ of CH_4, particularly when the isotopic composition of working gas (pure CO_2) is significantly different from the sample values. Francey et al. [1996b] discuss the various influences and the calibration strategies which minimize their influence. The results reported here benefit from: (1) having a working gas relatively close in $\delta^{13}C$ to the sample (within 10‰), (2) referencing all sample values to the value in a natural air standard in a high-pressure cylinder, measured bracketing, or close to the time of, each sample analysis, and (3) analyzing air samples spanning almost two decades in repeat analysis sessions of weeks for both the firn and the air archive. Results are given in the V-PDB scale, and analytical precision for both air archive and firn air data is about ±0.05‰. Full details are given by R.J. Francey et al. (manuscript in preparation, 1998).

4. Air Enclosure and Chronology

The age and composition of the air enclosed in an ice sheet can be affected by several processes that occur during enclosure. A thorough understanding of these processes is required to accurately date the air in the ice and firn and to correct for the fractionation processes, which can be especially significant for isotopic ratios.

The upper layer of the ice sheet is characterized by the increase of firn density with depth and associated decreases in open porosity (i.e., interconnected air channels) and in

diffusivity. Air in the firn moves through the open porosity primarily by molecular diffusion to the sealing depth where it eventually becomes slowly enclosed in bubbles. The air is therefore younger than the surrounding ice and has a spread of ages. Diffusion also promotes gravitational fractionation, as mentioned below. Processes competing with diffusion are the downward advection of air with the accumulating firn, the resistance to mixing presented by stratigraphic barriers in the firn, and the convection of air due to turbulence near the surface and to air expulsion at depth due to the decrease of open porosity. The results from the firn air experiment at DE08-2 show that diffusion is the dominant mechanism influencing the flux of air in the firn to the sealing depth and that there is only a small contribution from the competing effects [Etheridge et al., 1996; Trudinger et al., 1997].

4.1. Gravitational and Isotopic Fractionation

Gases tend to fractionate gravitationally in the diffusive firn air column [Craig et al., 1988b; Schwander, 1989], as identified by the enrichment of the heavy isotope of nitrogen, $^{15}N^{14}N$. The CH_4 mixing ratios were corrected for gravity by increasing them by the amount $\Delta M \times \delta^{15}N_2 \times [CH_4]$ [Sowers et al., 1989], where $\Delta M = 13$ is the difference between the molecular masses of dry air and CH_4. At DE08-2, the firn air $\delta^{15}N_2$ increases with depth to a maximum of about 0.3‰ at the sealing depth of 72 m [Etheridge et al., 1996], as expected for fractionation by gravity and a small opposing effect primarily from the downward advection of the accumulating firn layers. The firn diffusion model [Trudinger et al., 1997] produces nearly identical corrections for gravity.

The corrections for the firn air CH_4 mixing ratios were based on the firn air $\delta^{15}N_2$ measurements, which increased them by a maximum of 0.39% (about 6 ppb) at the sealing depth, reducing to zero at the surface. The maximum correction was also applied to the Law Dome ice core CH_4 measurements. The Eurocore and GISP2 ice-core CH_4 mixing ratios were corrected up by 0.43%, based on $\delta^{15}N_2 = 0.33‰$ measured at the base of the firn air column at Summit [Schwander et al., 1993]. Subsequent measurements of $\delta^{15}N_2$ in GISP2 ice are in the range 0.31‰ to 0.39‰ [Sowers et al., 1997] and confirm this result.

In addition to fractionation by gravity, the isotopic ratios of the firn air are potentially modified by the effects of gas diffusion in the firn. This may have significant effects on CH_4 isotopic ratios when rapid atmospheric growth creates gradients in the CH_4 mixing ratio in the firn, such as during the industrial period. Fractionation by both gravity and diffusion have been modeled by Trudinger et al. [1997] and the corrections for each effect on the isotopic ratios and mixing ratios at DE08-2 have been determined.

4.2. Air Dating

A mean age or effective age is used to relate the ice and firn air sample measurements to past atmospheric composition. The effective age of the air at any one depth in the firn or ice is the time (reported as either years ago or date A.D.) when the mixing ratio of the species of interest was seen at the surface.

The effective ages of the firn air samples were found by using gas species measured in the firn as tracers and by using the firn air model. Both methods are described in the Appendix. The two dating methods determine very similar effective ages (within about 1 year) for CH_4 in the firn air at

DE08-2. The effective age of the firn air CH_4 is zero ($\equiv$1993.2 A.D.) at the surface, 8 years at the sealing depth of 72 m, and reaches a maximum of about 15 years for the deepest sample (85 m). Note that for cases other than a steadily increasing (or decreasing) atmospheric mixing ratio, such as a short-lived pulse, the effective age would become more complex [Trudinger et al., 1997].

The effective age of the ice core air is different from the age of the ice, by an amount equal to the age of the ice at the sealing depth, less the time for the air to mix by diffusion to the sealing depth (i.e., 8 years for CH_4). The age of the ice was found from the distinct annual layering of trace chemicals and isotopes. The age differences between the host ice and the CH_4 in the air are 32 ± 1 years for DE08 and DE08-2 and 60 ± 2 years for DSS.

The age spread of the firn air at DE08-2 increases with depth and reaches about 10-15 years at the sealing depth [Etheridge et al., 1996; Trudinger et al., 1997]. Enclosure of the air into bubbles usually involves further broadening of the air-age spread, because the bubble close-off process occurs over a relatively long period, which depends on the snow accumulation rate. At DE08 and DE08-2, however, the extremely high snow accumulation rate causes rapid bubble close-off, and the air age spread originates mostly from the firn air diffusion, that is, about 10-15 years. The air age spread of the DE08 and DE08-2 ice is thus the narrowest of any known ice cores. A further advantage of the fast bubble close-off is that air from recent decades is enclosed. The air in DSS is expected to have a broader age spread (about 20 years) because of its lower accumulation rate and longer duration of bubble close-off.

An independent determination of the effective age and age spread of the ice core air at DE08 and DE08-2 has been obtained by detection in the ice and firn air of the $^{14}CO_2$ pulse from weapons tests of this century [Levchenko et al., 1996]. The mean air age found by this method is younger than the host ice by 31 ± 0.5 years for CO_2 and the age spread (full width of a moving average, approximately 2σ) is about 12.5 years. This compares well (to within 1 year) with the CH_4 dating described above, when the relative diffusivities of CO_2 and CH_4 are taken into account. Note that the bomb pulse technique determines the combined effects of air diffusion and bubble close-off on the ice core air age.

The Greenland ice core samples were dated with an accuracy of ±2 years [Blunier et al., 1993]. The enclosed air has an estimated age difference and spread of about 200 years and more than 15 years, respectively [Schwander et al., 1993, 1997].

5. Results and Discussion

The DE08-2 firn air CH_4 mixing ratios are shown versus depth in Figure 1. The DE08 and DE08-2 ice core measurements (corrected for the system blank) are also shown. The firn CH_4 results show a decrease with depth, as expected for slow diffusive mixing of a species increasing with time in the atmosphere. The rate of decrease increases markedly at about 70 m. Measurements of firn physical structure identified that the firn is sufficiently closed at 72 m that diffusive mixing stops, which is consistent with changes in the gradients of other trace gases in the firn. Below 72 m the air is effectively sealed in the firn (albeit in open porosity), and its age increases
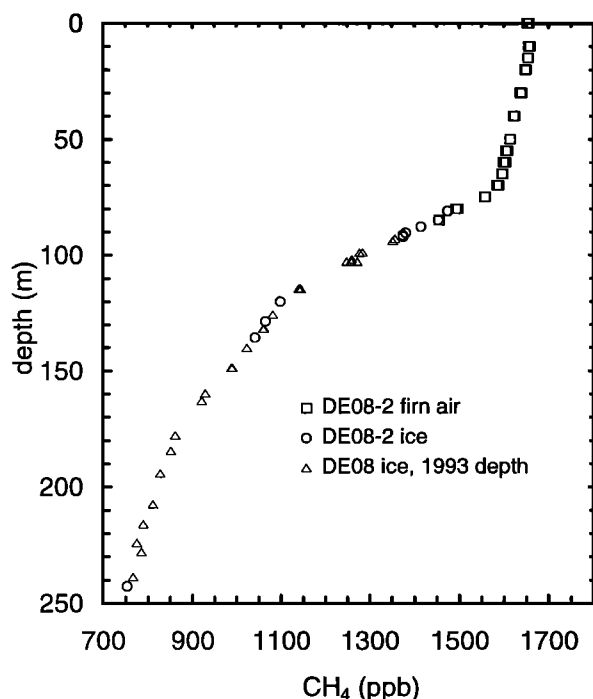
Figure 1. Methane mixing ratios in air from the firn at DE08-2 and ice at DE08 and DE08-2, versus sample depth. The DE08 depths have been increased by up to 8.3 m to allow for the 6 years of accumulation between the times that the two cores were drilled. Both firn and ice core air analyses were made using the same GC and referenced to the same calibration scale. The extraction system blank of 6 ppb has been subtracted from the ice core measurements. No corrections for gravitational fractionation have been made to the ice or firn data.

with depth at the same rate as the ice layers. In this region, the firn air CH_4 mixing ratios overlap those of the ice core air samples. The similarity of the air measured from the open porosity and closed porosity confirms that there is no detectable modification of the CH_4 composition as a result of the air enclosure process or the extraction and handling of the ice core air. Below about 90 m, all of the air is enclosed in bubbles. The CH_4 mixing ratio in the ice core air continues to decrease with depth to the bottom of the DE08 and DE08-2 cores, where the CH_4 approaches preindustrial levels.

The CH_4 mixing ratio of the surface samples is slightly lower than the firn air immediately below, by an amount consistent with the amplitude of the seasonal cycle of CH_4 at high southern latitudes. The surface samples were taken at the time of the seasonal minimum in CH_4 (February), whereas, because of diffusive mixing, the samples from within the firn represent averages over several years.

The CH_4 mixing ratios found from the three Antarctic ice cores are shown versus mean air age in Figure 2 and listed in Table 1. The CH_4 mixing ratios have been corrected for the system blank and for gravitational fractionation. A total of 32 DE08 samples, 11 DE08-2 samples, and 47 DSS samples are presented. Fifteen ice core measurements were rejected, due to unsatisfactory chromatography, system leaks, or ice samples being damaged.

The three Law Dome ice cores give almost identical CH_4 results, despite their different drilling techniques, different times since drilling, and different locations (and thus

accumulation and temperature regimes and trace chemistry). The ice core record overlaps the DE08-2 firn air measurements (also corrected for gravity) and the direct CH_4 record from Cape Grim. The annual mean CH_4 mixing ratios between the latitudes of Cape Grim and Law Dome have been nearly identical over the last decade or more [*Dlugokencky et al.*, 1994b]. The overlap of the ice core measurements with the Cape Grim record is within about 10 ppb, and further demonstrates that the ice core air faithfully represents the past atmosphere. The record shows that the mean CH_4 mixing ratio between 1000 and 1800 A.D. was about 40% of present-day levels and that small but significant variations occurred. The preindustrial period and the industrial period are discussed in detail below.

5.1. Late Preindustrial Holocene (LPIH)

The Law Dome CH_4 record for the LPIH back to 1000 A.D. is shown in Figure 3, curve a. On this expanded CH_4 scale, variations of about 40 ppb are evident over timescales of about a century. Notably lower CH_4 levels during 1550-1750 A.D. coincided with the Little Ice Age (LIA), a period of significantly cooler climate especially in the northern hemisphere [*Grove*, 1988]. Land temperatures for northern hemisphere summers reconstructed through the LIA period by *Bradley and Jones* [1993] are shown in Figure 3, curve b. *Crowley and Kim* [1996] found this record to be representative of the mean annual temperature of the northern hemisphere in general. Higher CH_4 levels predominated during 1050-1250 A.D., when temperatures in large parts of the globe were higher, contributing to the notion of a Medieval Warm Period
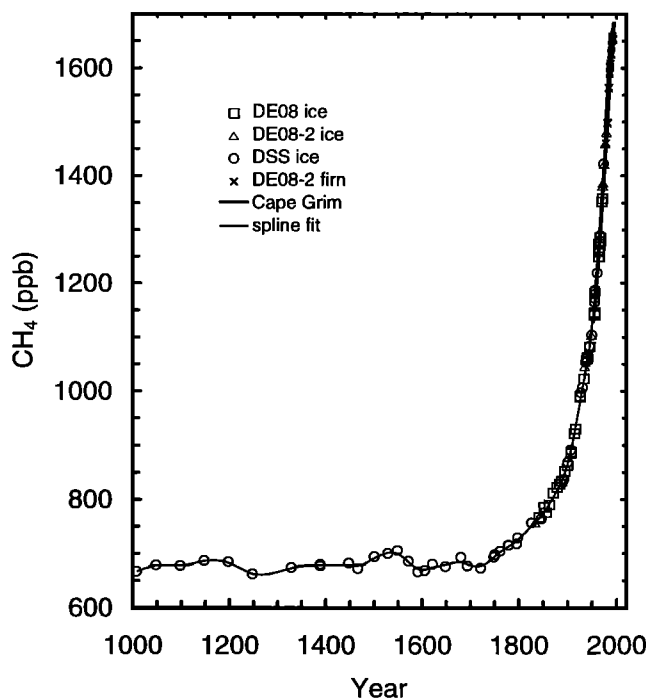
Figure 2. Methane over the last 1000 years found from the three Antarctic (Law Dome) ice cores corrected for system blank and gravitational fractionation. Precision is ± 5 ppb. The spline fit attenuates variations of 75 years periodicity by 50%. Also shown are the CH_4 records since 1978 from the DE08-2 firn air and from Cape Grim, Tasmania (see text).

Table 1. Methane Mixing Ratios From Antarctic and Greenland Ice Cores Over the Last 1000 Years

Air Age (A.D.)	CH$_4$, ppb	Depth, m	Ice Age (A.D.)	Sample
Antarctic Ice Core Results				
1008	666.0	534.2	948	DSS 038
1048	677.8	523.4	988	DSS 040
1098	676.4	505.9	1038	DSS 042
1148	685.9	488.3	1088	DSS 043
1198	683.7	467.7	1138	DSS 036
1248	660.9	447.2	1188	DSS 039
1329	672.9	414.0	1269	DSS 034
1389	676.3	387.1	1329	DSS 024
1389	678.9	387.2	1329	DSS 026
1448	681.5	360.6	1388	DSS 022
1467	671.4	351.2	1407	DSS 044
1501	693.0	336.7	1441	DSS 023
1529	698.9	323.7	1469	DSS 035
1549	704.3	313.9	1489	DSS 018
1572	684.8	302.0	1512	DSS 032
1591	665.4	293.2	1531	DSS 021
1606	667.7	285.2	1546	DSS 012
1622	679.4	276.3	1562	DSS 045
1649	674.6	263.4	1589	DSS 013
1681	692.0	245.6	1621	DSS 020
1694	676.1	238.0	1634	DSS 011
1722	671.9	223.0	1662	DSS 019
1749	692.9	207.6	1689	DSS 025
1751	696.9	206.5	1691	DSS 014
1762	703.1	200.5	1702	DSS 031
1779	714.4	190.9	1719	DSS 017
1796	716.9	181.3	1736	DSS 016
1798	728.5	180.0	1738	DSS 015
1827	755.8	163.5	1767	DSS 010
1834	756.3	242.8	1802	DE08-2 006
1842	766.9	228.7	1810	DE08 222
1847	763.7	151.6	1787	DSS 009
1852	785.5	218.0	1820	DE08 200
1856	775.9	214.1	1824	DE08 234
1863	789.9	206.1	1831	DE08 232
1871	811.9	197.5	1839	DE08 228
1879	822.3	190.2	1847	DE08 255
1884	828.5	184.3	1852	DE08 229
1888	833.6	179.5	1856	DE08 252
1893	836.8	122.8	1833	DSS 030
1894	852.3	174.4	1862	DE08 241
1900	862.4	167.9	1868	DE08 230
1901	868.4	116.9	1841	DSS 007
1907	891.0	114.3	1847	DSS 033
1907	885.3	160.6	1875	DE08 253
1907	887.8	160.8	1875	DE08 254
1914	921.6	153.0	1882	DE08 239
1917	929.9	149.9	1885	DE08 233
1926	989.0	138.8	1894	DE08 231
1926	991.1	138.8	1894	DE08 237
1928	997.0	100.3	1868	DSS 008
1931	1006.4	99.7	1871	DSS 041
1934	1023.2	130.3	1902	DE08 238
1936	1045.2	135.7	1904	DE08-2 011
1938	1053.0	94.1	1878	DSS 027
1940	1059.9	121.9	1908	DE08 240
1941	1055.7	92.7	1881	DSS 037
1941	1062.2	121.8	1909	DE08 243
1942	1069.1	128.8	1910	DE08-2 007
1944	1082.5	90.5	1884	DSS 052
1946	1081.8	115.7	1914	DE08 227
1950	1103.7	86.2	1890	DSS 029
1950	1102.9	120.2	1918	DE08-2 009
1955	1143.5	104.3	1923	DE08 236
1955	1140.0	104.4	1923	DE08 201
1955	1145.3	104.6	1923	DE08 208
1956	1164.3	81.8	1896	DSS 001

Table 1. (continued)

Air Age (A.D.)	CH$_4$, ppb	Depth, m	Ice Age (A.D.)	Sample
1956	1171.8	81.8	1896	DSS 003
1956	1183.8	81.8	1896	DSS 002
1957	1179.5	81.4	1897	DSS 047
1957	1186.4	81.4	1897	DSS 048
1961	1218.5	78.0	1901	DSS 004
1964	1258.7	92.7	1932	DE08 214
1964	1248.6	92.8	1932	DE08 215
1964	1273.3	93.0	1932	DE08 212
1964	1260.6	93.2	1932	DE08 213
1965	1261.3	92.0	1933	DE08 203
1967	1285.2	89.0	1935	DE08 226
1967	1278.4	89.2	1935	DE08 225
1967	1288.5	74.0	1907	DSS 049
1970	1351.7	84.0	1938	DE08 235
1971	1357.2	83.1	1939	DE08 205
1972	1380.3	92.2	1940	DE08-2 016
1972	1379.9	91.6	1940	DE08-2 015
1973	1385.8	90.6	1941	DE08-2 005
1974	1421.5	70.4	1914	DSS 050
1975	1420.4	88.0	1943	DE08-2 002
1977	1458.1	85.1	1945	DE08-2 003
1980	1479.7	81.1	1948	DE08-2 008
1980	1479.3	81.2	1948	DE08-2 012
Greenland Ice Core Results				
1075	701.2	272.1	871	Eurocore 495
1121	720.7	261.2	917	Eurocore 475
1165	743.1	252.3	971	Eurocore 459
1209	734.4	242.9	1015	Eurocore 442
1281	706.4	227.9	1080	Eurocore 415
1376	710.1	208.9	1177	Eurocore 353
1464	706.3	188.4	1262	Eurocore 343
1512	732.0	178.4	1308	Eurocore 325
1556	750.2	168.7	1351	Eurocore 307
1648	712.6	148.9	1442	Eurocore 271
1733	724.2	129.1	1527	Eurocore 235
1775	759.6	119.2	1572	Eurocore 217
1797	761.8	118.7	1602	GISP2
1800	766.8	118.0	1605	GISP2
1807	774.0	116.6	1612	GISP2
1842	808.8	104.1	1639	Eurocore 190
1885	875.3	94.2	1681	Eurocore 172

The mixing ratios have been corrected for system measurement blank and for gravitational fractionation. CH$_4$ measurement precision is 5 ppb (1σ).

(MWP [see, e.g., *Hughes and Diaz*, 1994]). Atmospheric CO$_2$ levels also changed during the LIA and the MWP [*Etheridge et al.*, 1996] (Figure 3, curve c), almost in phase with the CH$_4$ record. Methane levels rose immediately after 1750 A.D., probably due to the combined effects of the recovery of natural CH$_4$ sources to their pre-LIA state, and the onset of major anthropogenic emissions.

The Greenland ice core results comprise 14 from Eurocore and 3 from GISP2 and are shown in Figure 3, curve d and Table 1. They were measured with the same procedure and calibration scale as the Antarctic cores. Methane is stored reliably in both ice sheets, unlike CO$_2$ which may be affected by the high impurity content of Greenland ice [*Anklin et al.*, 1995; E. Michel et al., manuscript in preparation, 1998]. The Greenland CH$_4$ results show that similar variations occurred during the LPIH in the high northern latitudes as the Antarctic region, but to a greater degree. This is seen in the interpolar
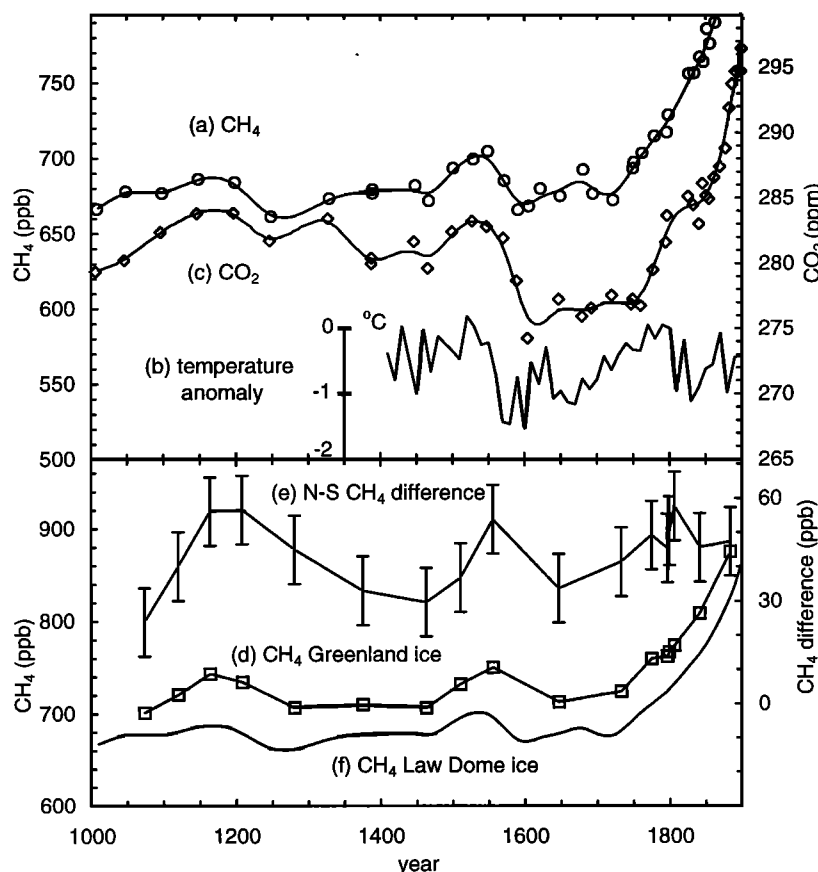
Figure 3. Methane variations during the late preindustrial Holocene. Curve a, data and line as for Figure 2. Curve b, temperature anomaly for northern hemisphere summers, decadal means, referenced to 1860-1959 A.D. [*Bradley and Jones*, 1993]. Curve c ice core CO_2 record [*Etheridge et al.*, 1996] with 75-year smoothing spline fit. Curve d, Greenland ice core CH_4 results from Eurocore (E. Michel et al., manuscript in preparation, 1998) and GISP2 [*Sowers et al.*, 1997]. The sampling interval may have missed some variations, so the interpolation of the record should be viewed as indicative only. Curve e, the interpolar difference in CH_4, calculated from the Greenland ice core results and the corresponding year of the Law Dome record (curve f), which is the line from curve a. Estimated 1σ uncertainty for the interpolar difference is 10 ppb.

difference (north polar-south polar) in CH_4 (Figure 3, curve e), which varied from 24 to 58 ± 10 ppb during the LPIH, and was larger during periods of warmer climates and smaller during the LIA. This interpolar CH_4 difference has since increased to about 143 ppb in recent times [*Dlugokencky et al.*, 1994b], due presumably to large increases in emissions from northern hemispheric (and mainly anthropogenic) sources.

Preindustrial CH_4 levels have been investigated by several other ice core studies, with varying degrees of uncertainty in air age resolution and CH_4 precision. *Khalil and Rasmussen* [1989] measured global CH_4 levels between about 675 and 850 ppb before 1800 A.D., and suggested that lower values during 1450-1660 A.D. were the result of climatic forcing of CH_4 sources. *Nakazawa et al.* [1993] found CH_4 mixing ratios in both Antarctic and Greenland ice cores for the LPIH that are slightly higher than ours (mean differences 21 and 24 ppb respectively) although the average interpolar difference (55 ± 14 ppb) was comparable to ours for a similar period (1600-1850 A.D.). The discrepancies can be largely explained by the small difference between the CH_4 calibration scale of Nakazawa et al. and that used in this study [*Dlugokencky et al.*, 1994b; *Nakazawa et al.*, 1993]. The variability during the LIA was not detected by Nakazawa et al., probably because of

the lower air age resolutions of their ice cores (120 and 42 years) and wider sampling intervals. They also found that the interpolar difference may have reversed 30-50 years ago, but this could be caused by errors in the dating of the ice core air (T. Nakazawa, personal communication, 1996). Our Greenland measurements do not cover the 20th century, so we cannot comment on this finding. Our Greenland CH_4 record has some similar features and a comparable mean LPIH mixing ratio to the CH_4 measurements of Eurocore ice by *Blunier et al.* [1993], after reducing the latter by 15 ppb according to *Chappellaz et al.* [1997]. The preindustrial CH_4 decrease in our Greenland and Law Dome records appears more prominent and more in phase with the LIA than those of *Blunier et al.* [1993], who attribute their signal to a combination of changes in OH concentration, temperature and anthropogenic sources. *Chappellaz et al.* [1997] report a mean interpolar difference for the LPIH that is comparable with our findings, and they also suggest anthropogenic emissions may have become significant in the last millennium.

Several modeling studies have found that long-term variations in the CH_4 budget were probably controlled by variations in CH_4 sources, rather than its main sink, reaction with OH radicals [*Crutzen and Brühl*, 1993; *Martinerie et al.*,

1995; *Pinto and Khalil*, 1991; *Thompson*, 1992]. Climatic influences on OH would result from a complex interplay between temperature, water vapor, solar flux, atmospheric dynamics, and levels of some key trace gases (CO, NO_x, nonmethane hydrocarbons, and CH_4 itself). Despite this, the models suggest that OH levels were remarkably stable in the past, ranging from about a 20% decrease to a 6% increase from the LPIH to present. Atmospheric measurements of methyl chloroform, which, together with emission estimates, can be used to determine globally averaged OH levels, also show that global OH has changed little ($0.0 \pm 0.2\%$ yr^{-1}) from 1978 to 1994 [*Prinn et al.*, 1995]. This is despite several factors that could have been expected to change global OH levels: increased UV radiation flux in the troposphere from recent accelerated ozone depletion in the stratosphere, and changed atmospheric temperature, humidity, and UV flux associated with the eruption of Mount Pinatubo in June 1991. In light of the apparent stability of OH levels during these major changes to the global atmosphere, we expect that OH levels, and thus the CH_4 lifetime, would not have been greatly influenced by the LIA.

Global mean CH_4 mixing ratios are used to evaluate past atmospheric CH_4 budgets. For the period 1000 to 1900 A.D., the global means are calculated from the spline fit (75 year smoothing) to the Antarctic ice core results (Figure 3, curve a) and the interpolar difference found from the Greenland minus Antarctic results (Figure 3, curve e). For this century, global CH_4 levels from the unified Antarctic/Cape Grim record are used with 12.5-year smoothing. The interpolar difference for this period is linearly interpolated from the mean difference of 50 ppb for the late 1800s to 143 ppb for the 1980s [*Dlugokencky et al.*, 1994b]. The calculation of global mean for both periods is based on the annual mean tropospheric mixing ratio of CH_4 (global mean, weighted by surface area), being greater than that of the Antarctic region by 37% of the interpolar CH_4 difference. This is found from the extensive globally-distributed CH_4 atmospheric measurements made since 1983 [*McIntosh et al.*, 1996]. Application of this result to times before 1983 assumes that the broad latitudinal pattern of CH_4 mixing ratio has not changed greatly over the past two centuries. Since most CH_4 sources are land based, and the interhemispheric exchange time is unlikely to have changed over the period of this record, we expect this assumption would lead to an error of at most about 10 ppb in the past CH_4 global means calculated in this way. Global mean CH_4 mixing ratios are listed in Table 2. When comparing variations between the two parts of the record, it should be noted that their smoothing treatments are over different periods, based on the data density and the age resolution of the ice cores.

The atmospheric CH_4 budget can be described by

$$dB/dt = S - B/T \qquad (1)$$

where S is the total annual source, B is the atmospheric CH_4 burden ($= 2.767 \times [CH_4]$ Tg, where the conversion factor 2.767 is from *Fung et al.* [1991], [CH_4] is the global mean CH_4 mixing ratio in ppb, and Tg=10^{12} g), T is the CH_4 lifetime (in years), and t is time in years. This formulation is based upon a key assumption that the atmospheric CH_4 mixing ratios are reported in a calibration scale which is correct in an absolute sense. We are confident that the CH_4 calibration scale used in this work is within about 1% of such absolute accuracy. The value of T for the present has recently been reassessed at about 9 years [*Prather*, 1996; *Prinn et al.*, 1995].

The budget lifetime, or residence time, is the appropriate quantity here, rather than the lifetime for a perturbation of CH_4, which is slightly longer [*Prather*, 1996]. The global mean CH_4 mixing ratio, averaged over the LPIH (1000-1800 A.D.) is 695 ppb, which is equivalent to an atmospheric CH_4 burden of 1923 Tg. This implies a LPIH source at steady state ($dB/dt = 0$) of about 250 Tg CH_4 yr^{-1} for a CH_4 lifetime 10% shorter than present (based on the middle of the range of LPIH OH levels discussed above), that is, 8 years, and a soil sink of 10 Tg yr^{-1}. This soil sink was the optimum value found by *Fung et al.* [1991], although estimates range up to 45 Tg yr^{-1}. A larger source would be required if the OH levels or the soil sink were at the higher end of the estimated LPIH range (shorter CH_4 lifetimes). The total CH_4 source required to maintain CH_4 at LPIH and present-day levels and for various lifetimes is shown in Figure 4. The variability in CH_4 levels observed in the ice core record during the LPIH is also represented in Figure 4. Budget terms that may have changed and contributed to the LPIH CH_4 variability are natural emissions, (predominantly wetlands), anthropogenic emissions and the reaction with OH. Methane exchange with the ocean is believed to be very small. Estimates of the ocean source are generally about 10 Tg yr^{-1} [*Ivanov et al.*, 1993] but may in fact be an order of magnitude less [*Bates et al.*, 1996]. Therefore variations of atmospheric CH_4, unlike CO_2, can be explained without considering the possible influence of changed ocean conditions.

The lower CH_4 level during the LIA would have been due to a reduction in the source strength by about 15 Tg yr^{-1}, or 6% of the estimated total LPIH CH_4 source, if the CH_4 lifetime was steady during the LPIH (at 8 years). Alternatively, a decrease in the CH_4 lifetime (higher OH) of about the same amount could have caused the LIA CH_4 decrease, but this is less likely due to reasons given above. Furthermore, if atmospheric CO and NO_x levels were largely unchanged, cooling during the LIA would be expected to have reduced the loss of CH_4 through reaction with OH (by about 2% per °C; [*DeMore et al.*, 1997]. Thus even greater reductions in CH_4 sources would be required to explain the observed lower CH_4 levels.

Lower temperatures would lower the extent and CH_4 emission flux of wetlands [*Harriss et al.*, 1993]. About 75% of the CH_4 emitted during preindustrial times was from wetlands [*Chappellaz et al.*, 1993], with about 60% of these in the northern hemisphere (NH) and about 20% at high northern latitudes [*Harriss et al.*, 1993]. The changes in CH_4 and the interpolar CH_4 difference through the LIA (Figure 3, curves a and e) closely parallel the observed temperature anomalies in the NH [*Bradley and Jones*, 1993] (Figure 3 curve b, where most wetland CH_4 emissions occur. The CH_4 decreases correspond to smaller interpolar differences, implying decreased CH_4 sources in the NH, although this could also be a result of a stronger southern hemisphere (SH) sink. Finally, the records of CO_2 [*Etheridge et al.*, 1996] and $\delta^{13}CO_2$ [*Francey et al.*, 1997] of the last 1000 years have been modeled (C.M.Trudinger et al., Long-term variability in the global carbon cycle inferred from a high-precision CO_2 and $\delta^{13}CO_2$ ice core record, submitted to *Tellus*, 1998) and suggest that the observed decrease of CO_2 during the LIA was also caused by the effect of lower temperatures on the terrestrial biosphere, reducing the CO_2 emissions. For these reasons we conclude that the lower CH_4 levels from 1550 to 1750 A.D. were predominantly due to terrestrial CH_4 emissions being

Table 2. Global Mean CH_4 Mixing Ratios Calculated From the Antarctic/Cape Grim Unified Record Plus 37% of the Interpolar Difference

Year	CH_4, ppb
1010	676
1020	679
1030	682
1040	684
1050	685
1060	686
1070	686
1080	687
1090	688
1100	690
1110	692
1120	695
1130	698
1140	701
1150	704
1160	706
1170	707
1180	706
1190	704
1200	701
1210	698
1220	694
1230	690
1240	686
1250	682
1260	680
1270	679
1280	678
1290	679
1300	680
1310	682
1320	684
1330	685
1340	686
1350	687
1360	688
1370	689
1380	689
1390	689
1400	689
1410	689
1420	689
1430	689
1440	689
1450	688
1460	687
1470	689
1480	693
1490	698
1500	703
1510	708
1520	712
1530	715
1540	716
1550	716
1560	713
1570	707
1580	700
1590	695
1600	692
1610	691
1620	692
1630	691
1640	691
1650	691
1660	693
1670	695
1680	696
1690	694
1700	693

Table 2. (continued)

Year	CH_4, ppb
1710	692
1720	693
1730	696
1740	702
1750	710
1760	717
1770	725
1780	730
1790	734
1800	741
1810	750
1820	760
1830	769
1840	779
1850	791
1860	805
1870	821
1880	837
1890	856
1900	879
1902	887
1904	896
1906	905
1908	914
1910	924
1912	933
1914	944
1916	955
1918	966
1920	978
1922	989
1924	1001
1926	1013
1928	1025
1930	1036
1932	1047
1934	1058
1936	1068
1938	1078
1940	1088
1942	1099
1944	1109
1946	1120
1948	1133
1950	1147
1952	1163
1954	1182
1956	1202
1958	1224
1960	1247
1962	1272
1964	1298
1966	1326
1968	1355
1970	1386
1972	1417
1974	1449
1976	1481
1978	1514
1980	1547
1982	1580
1984	1614
1986	1644
1988	1671
1990	1694
1992	1714

See section 5.1. For the period 1000 to 1900 A.D., the Antarctic values were first smoothed and interpolated every 10 years using a spline (50% attenuation at 75 years). For this century, the smoothing period is 12.5 years and the interpolation is every 2 years.
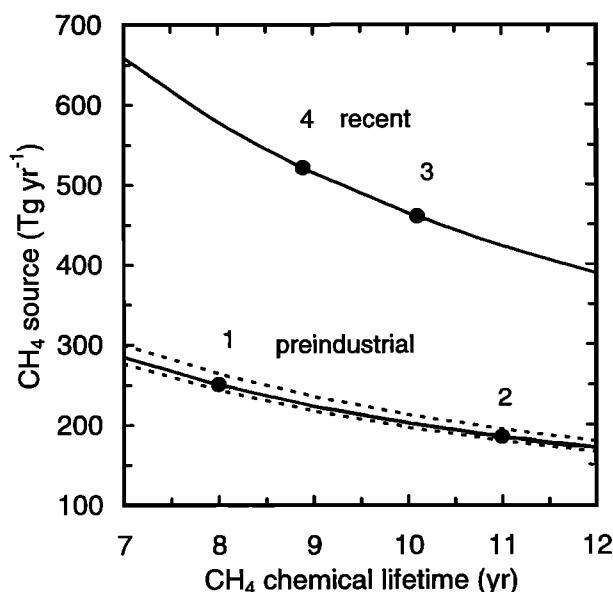
Figure 4. Total source of atmospheric CH_4 for the late preindustrial Holocene (LPIH) (1000-1800 A.D.) and for recent times (1984-1987 A.D.), for a range of possible chemical lifetimes, soil sink of 10 Tg yr^{-1}, and assuming steady state. Shown are the sources based on the following points: 1, the mean LPIH global mean CH_4 mixing ratio of this study and a lifetime 10% less than the present-day value of 8.9 years [*Prinn et al.*, 1995]. The dashed lines indicate the range of CH_4 levels observed during the LPIH; 2, the natural CH_4 source inventory and CH_4 lifetime of *Chappellaz et al.* [1993] for the LPIH; 3, the model synthesis of *Fung et al.* [1991] for 1984-1987 A.D.; 4, the same as point 3 but adjusted to the revised CH_4 lifetime of Prinn et al.

decreased by lower temperatures. Similarly, higher CH_4 levels in both hemispheres in the 12th century and a doubling of the interpolar difference may be explained by the effect of increased emissions from the northern hemisphere, such as from higher temperatures increasing the wetland CH_4 emissions.

The inventory study of *Chappellaz et al.* [1993] estimated that the total natural source of CH_4 was 190 Tg CH_4 yr^{-1} during the LPIH (allowing for a soil sink of 10 Tg yr^{-1}). Several other inventory studies estimate that anthropogenic CH_4 sources grew to significant levels, ranging from 7 to more than 55 Tg CH_4 yr^{-1}, in the centuries leading up to the industrial period [*Kammen and Marino*, 1993; *Subak*, 1994]. The larger emissions of this range would account for most of the difference between the natural source estimate of Chappellaz et al. and the total LPIH source of 250 Tg yr^{-1} calculated here (see Figure 4). Growing anthropogenic CH_4 emissions may also account for other observed CH_4 increases before the LIA, such as from about 1250 to 1550 A.D.

High-resolution, precise records of long-lived atmospheric species can provide globally integrated evidence of the climatic response of trace gas sources and sinks. Proxy evidence for [e.g., *Keigwin*, 1996; *Thompson et al.*, 1995] and against [*Hughes and Diaz*, 1994] the existence of Little Ice Age and the Medieval Warm Period continues to mount, yet the generalizing of patterns of climate into such periods has recently come into question. The evidence of these climate changes is not always spatially or temporally consistent, and the ways that temperature and precipitation changes were manifested in different climate proxies add further

complications. However, we find that both CH_4 and CO_2 changed significantly and synchronously, despite the different characteristics of their budgets, for at least a century centered at about 1150 and 1700 A.D., and in directions consistent with the suggested temperature changes. The atmospheric composition records thus offer new evidence of natural climate variability over large portions of the global land surface during periods classically identified as the LIA and the MWP.

5.2. Industrial Period

Most of the increase of CH_4 during the industrial period has occurred in the last 100 years. The CH_4 record for high southern latitudes this century is shown in more detail in Figure 5, curve a. It comprises the Law Dome ice core and firn air results and the Cape Grim record since 1978. The Cape Grim CH_4 mixing ratios were deseasonalized using techniques described by *Dlugokencky et al.* [1994b]. These measures, and the very small CH_4 difference between the latitudes of Cape Grim and Law Dome, ensure that the CH_4 mixing ratios from the Law Dome ice cores and the direct atmospheric measurements can be unified.

Global growth rates of methane this century are shown in Figure 5, curve b. They are found from the global mean mixing ratios calculated in section 5.1, based on the spline in Figure 5 curve a. Thus features of only a few years duration, such as the 1991 and 1992 growth rate anomalies, are expected to be heavily smoothed. The major growth of CH_4 from 1945 to 1990 is the largest single feature in the last 100 years, and indeed for the entire 1000 years of this record. This followed gradually increasing growth rates since the 1800s, and a period from 1920 to 1940 when the growth rate stabilized or decreased slightly (i.e., $d^2[CH_4]/dt^2 \leq 0$). This stabilization was suggested in the earlier DE08 ice core record [*Etheridge et al.*, 1992] and is now confirmed with the new ice cores and greater measurement precision. The CH_4 growth rate peaked at about 17 ppb yr^{-1} in 1981, then dropped sharply to about 4 ppb yr^{-1} by the mid 1990s, which is similar to the rate observed at the start of this century. The recent part of this decrease has been observed in direct atmospheric measurements [*Dlugokencky et al.*, 1994b; *Lowe et al.*, 1997; *Matsueda et al.*, 1996; *Steele et al.*, 1992] with global growth rates dropping from 14-17 ppb yr^{-1} in the early 1980s to 5 ppb yr^{-1} or less since 1992. *Etheridge et al.* [1992] found evidence in ice core CH_4 measurements of the growth rate beginning to stabilize by 1978. *Dlugokencky et al.* [1994b] used these ice core results and CH_4 measurements at the south pole since 1983 and found that the growth rate decrease began in the 1970s. The unified ice core/firn air/Cape Grim record, which has continuity and improved precision of measurement and ice core air dating throughout this period, shows that the rate of increase in the CH_4 growth rate ($d^2[CH_4]/dt^2$) decreased in the early 1970s and that the growth rate decrease began in 1981.

The total global CH_4 source during the last century is shown in Figure 5, curve c. It is derived from (1), the global mean CH_4 mixing ratio and the global CH_4 growth rate, a soil sink of 10 Tg yr^{-1}, and a CH_4 chemical lifetime of 8.9 years for 1978 to present, decreasing linearly before 1978 to 10% less (about 8 years) by preindustrial times (1800 A.D.). The total CH_4 source calculated in this way grew strongly during this century until the early 1980s when it rapidly began to approach stabilization. The average source during 1984-1987 was about 560 Tg yr^{-1}, similar to that for the same period determined by *Fung et al.* [1991] when adjusted to the revised lifetime of
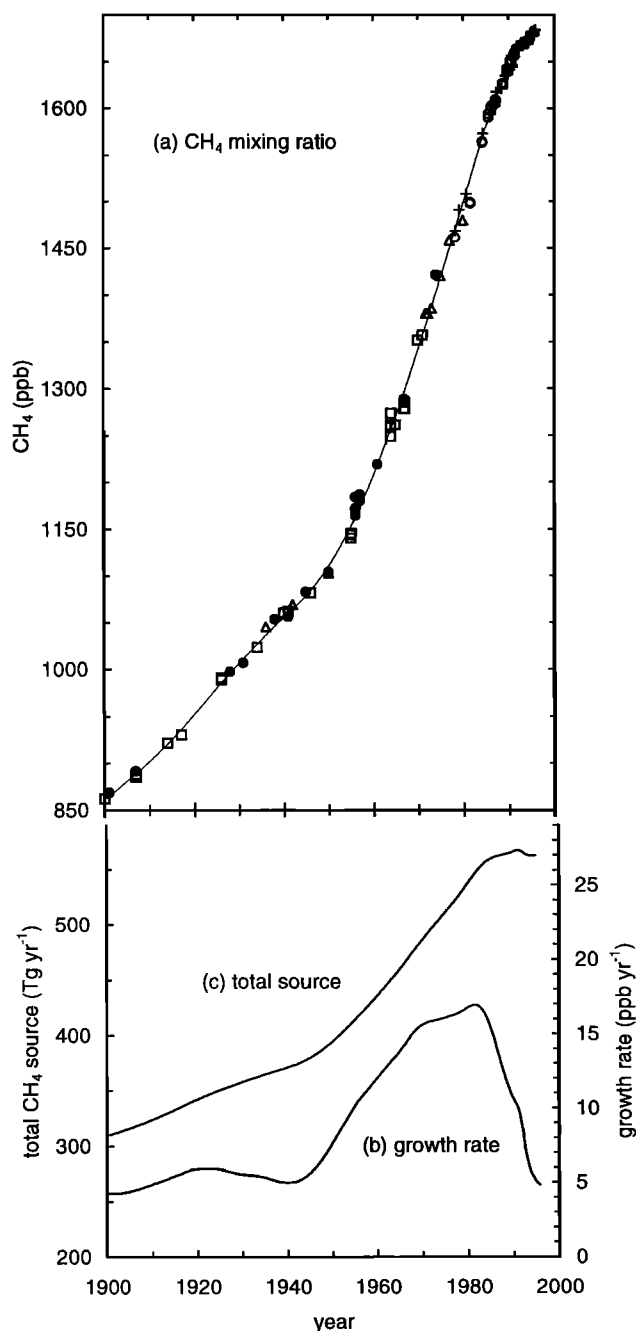
Figure 5. Curve a shows methane mixing ratios in the mid-high latitude southern hemisphere this century, found from the Antarctic (Law Dome) ice cores (DE08, squares; DE08-2, triangles; DSS, solid circles), DE08-2 firn air (open circles), and Cape Grim air (crosses). The Cape Grim record is combined from GC measurements from glass flasks since 1984 [*Steele et al.*, 1996] and recent GC measurements from air archived in tanks since 1978 [*Langenfelds et al.*, 1996], and deseasonalised (see text). A smoothing spline fitted to the combined data sets attenuates variability of 12.5 years period by 50%, which is judged as most suitable for the air age spread and data density of the ice cores. Curve b shows the global CH_4 growth rate, found from the derivative of the spline in Curve a after first adjusting it to global mean mixing ratios (see section 5.1). Estimated uncertainty is ± 1 ppb yr^{-1}. Curve c shows the total CH_4 source, found from the global mean CH_4 mixing ratio, the global CH_4 growth rate, a soil sink of 10 Tg yr^{-1}, and a chemical lifetime increasing linearly from 8.5 to 8.9 years. Uncertainty of the total source magnitude is 9% (1σ), derived mostly from the uncertainty of the lifetime.

Prinn et al. [1995] (Figure 4). The small difference is mainly due to the inclusion of CH_4 growth in the source calculation. Total CH_4 sources ranging from 562 to 592 Tg yr^{-1} were found by inverse modeling of atmospheric observations for 1983-1989 [*Hein et al.*, 1997]. The maximum derived CH_4 source in this work was 570 Tg yr^{-1} in 1991.

Changed fossil fuel CH_4 emissions were tentatively attributed to the growth rate changes of the last two decades and of 1920-1940 [*Dlugokencky et al.*, 1994a; *Etheridge et al.*, 1992; *Steele et al.*, 1992]. This speculation was based on trends in the amounts and practices of fossil fuel exploitation and usage, the observation that the recent growth rate decrease was most rapid in the most industrialized region of the globe (30°-90°N), and the estimates that 15-25% of the present total CH_4 source is associated with fossil fuel. However, CH_4 growth at the rates observed in 1920 and 1980 was caused by sustained imbalances in the CH_4 budget corresponding to only about 4% and 9% respectively of the total CH_4 source at the time, so only relatively small changes to the fossil source, or any of a large number of possible other sources, could have caused the observed growth rate trends.

Climate change may also have contributed to the observed CH_4 changes of this century. The overall temperature increase this century of about 0.6°C [*Nicholls et al.*, 1996] would have led to an increase of about 10 Tg yr^{-1} in the natural emissions (about 4% of the increase in total annual emissions this century), if natural CH_4 sources responded in the same way as suggested for the LPIH. This would have partially offset the reduction in natural CH_4 emissions expected to have occurred since the LPIH due to the loss of wetlands and wild animals (about 30 Tg yr^{-1} [*Chappellaz et al.*, 1993]. Changing temperature alone is unlikely to explain the growth rate changes during 1920-1940 A.D. and 1975-1996 A.D., as temperatures (global and northern hemispheric) increased on average during these periods, and would probably have increased natural CH_4 emissions.

Extrapolation of the global atmospheric CH_4 observations between 1983 and 1990 suggested that the decrease in the growth rate would lead to CH_4 stabilization around the year 2006 if the trend continues [*Steele et al.*, 1992]. The unified record presented here confirms that the growth rate change is a longer term feature. Extrapolation of this trend, which depends on the mechanisms causing the present situation continuing, shows that zero growth could be expected before 2006.

5.3. The $\delta^{13}CH_4$ Results

Measurements of $\delta^{13}C$ of CH_4 can help identify the causes of the observed atmospheric CH_4 changes. The length of our isotope record (1978-1993) is limited by the relatively large sample requirements and is thus currently restricted to analyses of air from the Cape Grim Air Archive and the DE08-2 firn. The trend we determine from the archive samples is independently supported by results from the firn air samples. Both data sets are shown in Figure 6. The data employed here are described in detail by R.J. Francey et al. (manuscript in preparation, 1998).

In Figure 6 the archive air results have been modified by removing a fixed seasonal component, simply estimated by a harmonic fit to several years of $\delta^{13}CH_4$ data from Baring Head and Scott Base [*Lowe et al.*, 1997]. The error bars reflect instrumental uncertainties, but do not reflect uncertainty in the seasonal correction; the additional error could be substantial for some points (±0.05‰), but is unlikely to affect the overall
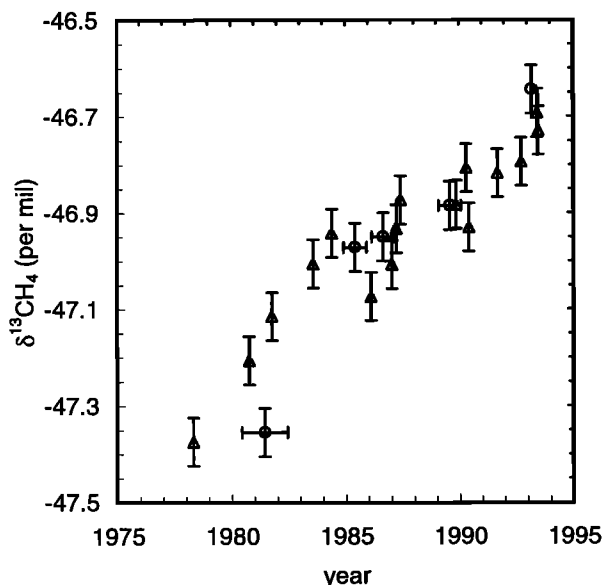
Figure 6. The $\delta^{13}CH_4$ results obtained from the Cape Grim Air Archive tanks over the period 1978-1992 (triangles) and the firn air samples from DE08-2, corrected for gravitational fractionation and then for diffusion using a firn diffusion model [*Trudinger at al.*, 1997] (circles). The measurements are deseasonalized and in the V-PDB scale. Error bars show estimated uncertainties (1σ) of the $\delta^{13}CH_4$ measurements and of the firn air age.

trend. Apart from the surface sample at DE08-2, seasonal correction is not required for the firn samples. However, the firn samples represent air spread over several years and are also subject to a large correction for diffusive fractionation. Because the firn correction is well constrained by the measurements of several other species [*Trudinger et al.*, 1997], we interpret the reasonable agreement between the archive and firn results as good evidence for a common atmospheric signal. Our results show $\delta^{13}CH_4$ generally increasing (i.e., becoming isotopically heavier) and at a decreasing rate since the mid 1980s.

The direction of the $\delta^{13}CH_4$ trend agrees with that of *Stevens* [1995], but we note that the magnitude of the total change in our results is significantly smaller than (about half) that reported by him for the southern hemisphere during the period 1978-1989. In assessing the difference in the trend between the two studies, it is useful to appreciate the very different analysis strategies involved. Because we had the benefit of measuring all archived air samples in a limited period (weeks), we could avoid the demanding requirement of maintaining strict analytical and calibration procedures over a decade or more.

We also note that decreases in $\delta^{13}CH_4$ were observed in the early 1990s [*Gupta et al.*, 1996; *Lowe et al.*, 1997] when our measurements show only a short stabilization. However, in both these other studies the decrease persisted for relatively short periods, and the different sampling locations to ours may have sampled air masses of somewhat different origin. The more recent measurements of Lowe et al. show a recovery of the increasing $\delta^{13}CH_4$ trend in 1993.

In an ice core study by *Craig et al.* [1988a], a 2‰ increase of $\delta^{13}CH_4$ was found over the industrial period by measurements of several large (~25 kg) ice samples. When

corrected for gravitational fractionation, the increase was adjusted to 1.7‰ [*Craig et al.*, 1988b]. Comparison of this result with our findings is difficult because of the very different time scales covered. *Gupta et al.* [1996] suggest that the $\delta^{13}CH_4$ increase found by Craig et al. may have been a result of kinetic isotope fractionation resulting from increased stratospheric chlorine radical concentrations (i.e., an increased sink) and that most of the 1.7‰ increase would have occurred during the 1970s and 1980s. It is difficult to reconcile this scenario with our finding of an increase in $\delta^{13}CH_4$ of only 0.5‰ from 1978 to 1990.

It is a coincidence that the period covered by our $\delta^{13}CH_4$ measurements corresponds almost exactly with the period over which our analysis of the long-term CH_4 record indicates near stabilization of the global source. A consequence of a stable source and a constant sink (destruction by OH) over this period will be a continuing rise in the CH_4 burden but at a steadily slowing rate as the system approaches equilibrium. Such a behavior of the global methane system would also be reflected in $\delta^{13}CH_4$, simply because the CH_4 sink causes an isotopic fractionation (about -5.4‰ [*Cantrell et al.*, 1990], and, if the fractionation due to the loss of methane in soils is included, the weighted average fractionation is slightly more negative [*Quay et al.*, 1991]). This isotopic fractionation preferentially removes the lighter isotope, thus leaving the atmosphere enriched in the heavier isotope. The observed decrease in the growth rates of both CH_4 and $\delta^{13}CH_4$ in recent decades cannot therefore be caused by an increase in the CH_4 sink, which would cause a greater rate of increase in $\delta^{13}CH_4$ and is anyway inconsistent with the deduced OH stability since 1978 [*Prinn et al.*, 1995]. The CH_4 and $\delta^{13}CH_4$ trends are consistent with a scenario of a constant total source (with a fixed isotopic signature) and a constant sink since the early 1980s at the latest. The magnitude of our $\delta^{13}CH_4$ change can also be consistent with this scenario. However, we cannot exclude the possibility that the average source isotopic signature associated with a stable annual release of methane may have changed over this period. These possibilities will be explored more fully elsewhere with the use of appropriate models (R.J. Francey et al., manuscript in preparation, 1998).

6. Conclusions

We have produced a record of atmospheric methane over the last 1000 years unified from several Antarctic ice cores, Antarctic firn air, the Cape Grim Air Archive and Cape Grim air flasks. The record features high measurement precision and high air age resolution. Interpolar CH_4 differences are precisely determined from measurements of Greenland ice cores using consistent procedures.

The global mean CH_4 mixing ratio was 695 ppb during the late preindustrial Holocene (1000-1800 A.D.). LPIH CH_4 levels varied by up to about 40 ppb, in unison with indicators of climate variation. Simultaneous variations in the interpolar CH_4 difference, and CO_2 and $\delta^{13}CO_2$ trends in the Law Dome ice cores, suggest that the CH_4 variations were most likely a result of changes in the CH_4 terrestrial emissions. Positive climate feedbacks (where warming increases the CH_4 mixing ratio which increases radiative forcing) may thus be expected in the future at these small levels of climate variability.

The CH_4 global mean for the LPIH, combined with new estimates of the OH sink strength and a small soil sink,

correspond to a global CH_4 source of 250 Tg yr^{-1}. The difference between this and prior estimates of the total natural source found from inventory studies (190 Tg yr^{-1}) is consistent with estimates of substantial anthropogenic CH_4 emissions before the start of industrialization (i.e., the 1800s). Such emissions may also explain earlier increases in CH_4 levels, such as in the 13th to 16th centuries.

The atmospheric methane budget this century is characterized by a major peak in the growth rate that began about 1945, reached a maximum in the 1981 and has since declined to pre-1945 levels. The likely cause of the trend in recent decades is that the total global CH_4 source reached near stabilization. The calculated average source in the 1980s and 1990s was 560 Tg yr^{-1}. Measurements of $\delta^{13}CH_4$ are used to provide additional information about source and sink changes in the last few decades. The trends in both CH_4 and $\delta^{13}CH_4$ are both consistent with a stabilized total source and a constant sink since the early 1980s.

Overall, the industrial period shows that small sustained changes in emissions can lead to large changes in CH_4 growth. The unified record presented here shows that extrapolation of the growth rate decrease since about 1981 would lead to zero growth before 2006. The causes of the declining growth rate are still not known unambiguously, however, and the magnitudes of some of the individual components of the current global CH_4 source remain uncertain. Elucidation of these uncertainties remains an important task. The relatively short atmospheric lifetime for CH_4 combined with the modest (less than 10%) reductions in anthropogenic CH_4 emissions required to achieve stabilization of the atmospheric CH_4 near current levels suggest that appropriate mitigation measures can be designed to achieve this goal.

Appendix: Firn Air and Ice Core Air Dating

A1. Firn Air

The first method found the effective age of the firn air samples by comparing their measured CO_2 and SF_6 mixing ratios with past atmospheric measurements. In a firn column where gases move only by diffusion, the relative effective ages of CH_4 and the gas tracers would be inversely related to their relative diffusion coefficients, i.e., $\tau_{CH_4}/\tau_{tracer} = D_{tracer}/D_{CH_4}$. In reality, the effects competing with diffusion shift the relative effective ages closer to unity (i.e., less dependence on diffusion coefficients) by an amount which is greater for the slower diffusing gases. The effective age (i.e., the time before the sampling date, February 1993) of CH_4 at depth z, between the surface and the sealing depth z_S, is thus

$$\tau_{CH_4}(z) = \tau_{tracer}(z) \times (D_{tracer} / D_{CH_4}) \times f \qquad 0<z<z_S \qquad (A1)$$

where f accounts for the effects competing with diffusion. Variable f is expected to be large at DE08-2 compared to other sites because the high accumulation rate causes significant advection of air in the firn. At DE08-2, f ranges from about 1.1 for fast diffusing gases to about 1.4 for gases with low diffusion coefficients such as SF_6, found from the measured firn air profiles of CO_2, SF_6, and CFC-12, and from the model-produced profiles [Trudinger et al., 1997, Figure 13].

Below the sealing depth, where diffusion ceases, the change in the effective ages of gas species is independent of their diffusion coefficients, so that

$$\tau_{CH_4}(z) = \tau_{CH_4}(z_S) + \tau_{tracer}(z) - \tau_{tracer}(z_S) \qquad z>z_S \qquad (A2)$$

This dating procedure does not allow for past changes in the atmospheric growth rates of the tracers, but the changes during the relevant period (up to 1992) are small enough for such effects to be minimal.

The second dating method used the finite difference model of firn air diffusion and close-off [Trudinger et al., 1997]. This was also central to determining the effects of fractionation. Briefly, the model's equations are based on Fick's laws of diffusion, the barometric equation and conservation of mass. Vertical advection is caused by snow accumulation, which has a constant rate in the model. Inputs include the vertical profiles of density and porosity measured in the DE08 and DE08-2 cores and the dependence of diffusivity on porosity.

Dating differences between the two methods are within about 1 year. Differences are largest in the region below the sealing depth where variations in the accumulation rate may cause variations in the age-depth relationship but are not included in the model. A dating error of 1 year for the model firn air age at 80 m would account for the difference between the two CH_4 mixing ratios and the $\delta^{13}CH_4$ value of the 80 m firn air, and the measurements of the Cape Grim Air Archive (Figures 5, curve a and 6). The measurement of the bomb pulse of $^{14}CO_2$ [Levchenko et al., 1997] also suggests that this firn air sample is older than the model prediction by up to 1 year. The age spread of the firn air at DE08-2 increases with depth and reaches about 10-15 years at the sealing depth [Etheridge et al., 1996; Trudinger et al., 1997].

A2. Ice Core Air

The effective age of the air a_a in each ice sample was found as follows, where ages are given as calendar years A.D.:

$$a_a = a_i + \tau_s - \tau(z_s) \qquad (A3)$$

where a_i is the age of the host ice layer from which the air is extracted, τ_s is the time between when the layer was deposited as snow and when it reached the sealing depth, and $\tau(z_s)$ is the mean time for air in the firn to reach the sealing depth.

The age of the ice a_i was found from the annual layering in the ice oxygen isotope ratio ($\delta^{18}O$ of H_2O), hydrogen peroxide (H_2O_2) concentration, and electroconductivity measurements. Ice dating accuracy was ±2 years at 1805 A.D. for the three cores and ±10 years at 1350 A.D. for DSS. The ice dating was verified by detection of the volcanic acid layers of the eruptions of Agung (1963 A.D.), Tambora (1815 A.D.), and large eruptions accurately dated at 1259 A.D. and about 1450 A.D. but of uncertain origin. The DE08 ice chronology has been revised by up to 3 years compared to the earlier CH_4 record in that core [Etheridge et al., 1992], by using new ice $\delta^{18}O$ and H_2O_2 data and by crosschecking with the DE08-2 profiles.

The sealing depth was determined from measurements of density and porosity [Etheridge et al., 1996]. It is also marked by the sudden increase in gradient of the firn trace gas profiles at DE08-2. At DE08 and DE08-2, sealing occurs at about 72 m depth, where the ice is 40 ± 1 years old. At DSS the sealing depth and ice age are 66 m and 68 years, respectively.

The time for air to reach the sealing depth, $\tau(z_s)$, was found to be 8 years, based on the firn air age for CH_4 at DE08-2. This value also applies to DE08, which has nearly identical firn characteristics, but is only an estimate for DSS and may introduce a small dating error. The age differences between air

and ice are thus 32 ± 1 years for DE08 and DE08-2 and 60 ± 2 years for DSS.

The air age spread of the DE08 and DE08-2 cores, that is, about 10-15 years, originates mostly from the firn air diffusion. If a significant proportion of the bubbles formed above the sealing depth, or if air leaked past the sealing depth (possibly through breaks in the horizontal layering), then the bubble close-off process would have a greater control of the air age spread. This is unlikely to broaden the air age spread at DE08 or DE08-2, where 80% of the bubbles close over only 8 years and at depths below the sealing depth of 72 m. However, the air age spread may be broadened at sites with lower accumulation rates than DE08 and DE08-2 because bubble close-off can take several decades (e.g,. DSS and Siple, Antarctica, or Summit, Greenland) or even centuries (e.g., Vostok and Byrd, Antarctica). A slightly broadened age distribution of air in DSS ice may have smoothed high-frequency features in the CO_2 record [Etheridge et al., 1996].

Several additional effects could slightly alter the air ages. Large changes in accumulation rate would change the times τ_s and $\tau(z_s)$ but are small enough over the last 1000 years not to have significant effects on the air dating used here [Etheridge et al., 1996]. Melt layers would also affect τ_s if they are sufficiently thick and horizontally extensive to impede the vertical mixing of air in the firn. A 10 mm layer at 8.7 m in the DE08-2 firn was found to have influenced the upper 10-15 m of the firn air profiles. However, melt layers are otherwise rare and very much thinner in the DE08, DE08-2, and DSS ice cores. Measurements of air extracted from samples selected across the thickest melt layers in the DE08 and DE08-2 ice showed nearly identical composition (CH_4, CO_2, N_2O), whereas a step change would be expected if the layers were impermeable.

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