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Changes in tropospheric methane between 1841 and 1978 from a high accumulation-rate Antarctic ice core

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ABSTRACT

To determine in detail how the concentration of tropospheric methane has changed from pre-industrial until recent times, an ice core with remarkably fine air-age resolution was investigated. The core, called DE08, contains air from as recent as 1978 with an age resolution (80% air-age distribution width) of about 14 years. It was drilled from a region of Law Dome, Antarctica with extremely high snow-accumulation rate (1160 kg m^{-2} yr^{-1}). The ice chronology was determined from the observed chemical and isotopic seasonal variations, verified against a volcanic horizon. The calculated air-age includes the effects of bubble close-off, sealing of the firn and diffusive mixing of air in the firn. The mean air-age was 35 years younger than the host ice except for air in summer ice layers which was 37 years younger than the host ice. The extracted ice-core air was analysed for methane using gas chromatography with flame-ionisation detection. Adjustments of −6 ppbv and +0.3% were made to the measured concentrations to allow for the effects of the extraction process and gravitational fractionation respectively. Methane concentrations in the DE08 record increased from 823 parts per billion by volume (ppbv, in dry air) in 1841 to 1481 ppbv in 1978. The measurement precision was ±22 ppbv (1σ). The similarity of the methane records from the DE08 ice core and from Cape Grim, Tasmania implies that there was insignificant modification during the enclosure of air in the ice or during its recovery and analysis. Methane concentrations in the period from 1951 to 1978, which were previously estimated from sporadic and inferred data, are particularly well defined in this core. The DE08 record shows that methane growth rates have generally increased since the onset of the industrial revolution to a level of 14 ppbv $year^{-1}$ (about 1% per year) by the 1970s. The exception was between about 1920–1945 when the growth rate stabilised at about 5 ppbv $year^{-1}$.

1. Introduction

Methane (CH_4) in the troposphere is a greenhouse gas that has more than doubled in concentration since about 1800 AD (Craig and Chou, 1982; Rasmussen and Khalil, 1984; Stauffer et al., 1985; Pearman et al., 1986). The resulting contribution to the radiative forcing of the atmosphere is estimated to be about 30% of that caused by the increase of carbon dioxide over the same period (Shine et al., 1990).

The present rate of CH_4 increase (0.8–1.0% per year) has two possible causes: an increase in the magnitude of the total CH_4 global source, to which the relative contributions of individual CH_4 sources are not well defined, and a decrease in the magnitude of the major CH_4 sink, reaction with the hydroxyl radical (OH). Globally-representative levels of OH cannot yet be measured directly, only modelled (Spivakovsky et al., 1990) or inferred from measured distributions of methylchloroform (Prinn et al., 1987). The most comprehensive assessment of present-day CH_4 sources and sinks has been recently compiled by Fung et al. (1991). Constraints on model determinations of the present-day global CH_4 budget are imposed by measurements of the geographic distribution and seasonal variation of CH_4 concentration (Steele et al., 1987) and its isotopic

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composition (Wahlen et al., 1989; Manning et al., 1990; Quay et al., 1991).

Measurements of past CH_4 concentrations can provide further information on the CH_4 budget and how it has changed. However, reliable direct measurements (i.e., those with an appropriate level of accuracy and precision and with continuity of measurement practice, calibration and location) began only in 1978. Atmospheric CH_4 concentrations determined from measurements made before 1978 are less reliable. Sporadic gas-chromatographic measurements of atmospheric CH_4 concentration, taken during the 1960s and 1970s at various places around the globe, have been compiled by Khalil et al. (1989). These earlier gas-chromatographic measurements were sometimes subject to lower precision and calibration certainty than can now be achieved. Past CH_4 concentrations have also been inferred from solar spectra taken at two high-altitude observatories in 1951, 1975, 1981 and 1984–87 (Rinsland et al., 1985; Zander et al., 1989). The data were suitable for determining the trends in CH_4 concentration between these dates, but uncertainties were introduced in the conversion of the spectral measurements to absolute tropospheric concentration, which was necessary for comparison with the results from ground-based air sampling.

Ice cores studied to date have revealed atmospheric CH_4 variations on various time scales, from as recent as the 1960s to as long ago as 160,000 years before present (BP) (Stauffer et al., 1985; Khalil and Rasmussen, 1987; Etheridge et al., 1988; Chappellaz et al., 1990). This forms the basis of the knowledge of CH_4 levels before the middle of this century. The ice-core measurements have benefited from the use of modern, better-calibrated analytical techniques, but the nature of the air enclosure process meant that the air in any one ice-core sample covered a large range of ages and air from recent decades could not be isolated and measured. The most recent ice-core air samples previously measured for CH_4 concentration had mean ages of 1956 for the Siple ice core (Fig. 1) from West Antarctica (Stauffer et al., 1985) and 1966 for the BHD ice core (Fig. 1) from Law Dome, East Antarctica (Etheridge et al., 1988) with air-age resolutions (bubble close-off duration for 80% of the air) of 22 years and 17 years, respectively.

To determine, with better time resolution, the

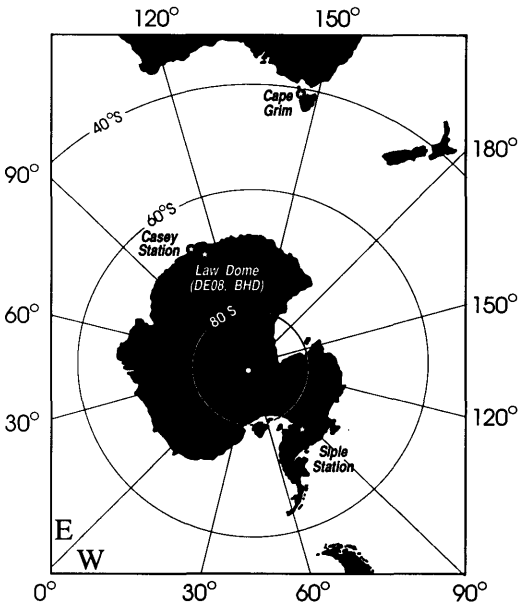

Fig. 1. Map of station locations and ice core sites.

changes in atmospheric CH_4 concentrations of the past 150 years we have investigated an Antarctic ice core, DE08, that has an extremely fine air-age resolution. This fine resolution is created by the high rate of snow-accumulation at the site (1160 kg m^{-2} $year^{-1}$, or 116 cm $year^{-1}$ of water equivalent) that encloses air into bubbles over a short time span. The air chronology was established by investigating how the age of the enclosed air is affected by three processes: bubble close-off, sealing of the firn from the atmosphere and diffusive mixing of air to the sealing level. The core contains air samples with mean air-ages ranging from pre-industrial times to 1978. For the first time, a direct comparison is made between the CH_4 concentration of ice-core measurements and direct atmospheric measurements, allowing the integrity of the ice-core record to be tested. The high quality of the core and improved air extraction and analysis techniques have enabled reconstruction of atmospheric CH_4 concentrations to a precision of ± 22 ppbv. The mean sampling interval corresponds to a spacing of about every 3 years and there are no gaps in the record longer than 10 years. The DE08 record allows analysis of the growth rates of atmospheric CH_4 at a level of detail not previously available for this period.

2. Ice core details

The DE08 ice core was drilled by the Australian Antarctic Division specifically for atmospheric studies (Etheridge and Wookey, 1989). It was drilled in 1987 on the east side of Law Dome (66°43′19″S, 113°11′58″E, 1250 m.a.s.l.) to a depth of 234 m (Fig. 1). Samples were taken essentially uncontaminated from within the core because of its large diameter (200 mm) and minimal cracking (occurring only in the bottom 15 m) and because drilling was done without the use of hydrocarbon fluid in the borehole. Refrozen ice layers from snow-surface melt events, which could adversely affect the ice-core chemistry and air enclosure, are observed only 4 times and are each less than 5 mm thick. The amount of melt is much less than expected for a site with mean annual temperature of −19°C, possibly because the short hiatus in snowfall minimizes the duration that each fresh snow surface is exposed to radiation and warm temperatures. Careful drilling and handling maintained high core quality and avoided damage to the gas record that Pearman et al. (1986) and Neftel et al. (1988) suggested could occur in ice core samples that had warmed.

3. Chronology

The ice was dated by counting the seasonal cycles observed in the oxygen isotope ratio ($\delta^{18}O$), hydrogen peroxide (H_2O_2) concentration and solid electroconductivity measurements (ECM) of the ice. $\delta^{18}O$ exhibits seasonal variations due to temperature-dependent fractionation during precipitation. The ECM technique detects total acidity in the ice which varies seasonally, partly due to the production rate in the ocean and transport to the ice sheet. H_2O_2, is produced by photochemical processes in the atmosphere and the concentrations at DE08 are 5 to 10 times higher in summer ice layers than in winter layers. These three species are well preserved throughout the DE08 ice core. Since the processes that govern their amount in the ice are quite different, ambiguities or missing data in a seasonal cycle of one species could usually be clarified upon inspection of the others. In this way, the ice was dated with an accuracy of ±3 years at 1941 AD (78 m) and ±5 years at 1805 AD (233 m). A further validation of the ice dating was made possible by the detection of a large ECM peak, most likely caused by volcanic acid deposition from the 1815 AD eruption of Tambora, which was consistent with the seasonal ice dating to within the quoted errors. A second, smaller ECM peak about 6 years earlier may coincide with the unknown eruption (Legrand and Delmas, 1987) of around 1808 AD recorded by several other Antarctic ice cores.

Air bubbles form as the deposited snow densifies into firn and then ice. About 80% of the total air content in the bubbles of an ice sample from Siple Station became closed-off as it densified from 795 to 830 kg m^{-3} (Schwander and Stauffer, 1984). The importance of the proportion closed-off before this density range is reached to the mean age of the air in different layers is discussed later. Most previous studies of ice-core air assumed that the air at the bubble close-off level had the same age as the atmosphere and the mean air age was deduced to be younger than the ice by the age of the ice at some point between these two densities. However the variability of density with the season of snow deposition means that higher density, impermeable layers can exist at mean densities of about 795 kg m^{-3}. The firn below can thus be sealed from the atmosphere before all of its pores have closed-off into bubbles (Martinerie et al., in press). The range of mean density of 795 to 800 kg m^{-3} (Schwander, 1989) better represents the mean interval at which the firn, at a location with high accumulation and no melting, becomes sealed. For DE08 this corresponds to a depth of 72–73 m and an ice age of 43 ± 3 years.

If the unsealed firn (i.e., above 72 m) presented no restriction to air mixing, the mean age of the enclosed air would be 43 years younger than the ice sample. However, air mixing throughout most of the firn is caused only by molecular diffusion. This creates a time delay and distribution width for the air at the sealing level, relative to the atmosphere. We calculated this delay, t_a, for CH_4 in air at the sealing level at DE08 from the air-age distribution of Schwander (1989) where

$$t_a = z_s^2 D^{-1} t_a^*;$$

z_s is the depth at the top of the sealing region

(72 m); D is the diffusivity of CH_4 in air at the mean temperature and pressure at the site (-19°C and 850 mb, respectively) and was calculated to be 652 m^2 $year^{-1}$ (CEH, 1973); t_a^* is the dimensionless mean of the Schwander (1989) air-age distribution. We took the age distribution of the air at the sealing level calculated by Schwander (1989) for Siple Station, West Antarctica (mean temperature -24°C and accumulation rate 500 kg m^{-2} $year^{-1}$) as being the most representative of DE08 (the similarity of the distribution for Siple Station to the distributions calculated by Schwander (1989) for other sites with significantly different temperatures and accumulation rates suggests that the distributions for DE08 and Siple Station should be very similar) and found $t_a^* = 1.05$. This gave a time delay $t_a = 8.3$ years for the air to mix down to the sealing level at DE08 and thus the difference between ice age and mean air age is about 35 ± 3 years. The uncertainty (2σ) was estimated from uncertainties in the depth and age at which the mean firn density reaches 795 kg m^{-3} and in the determination of t_a^* for DE08 from the distribution of Schwander (1989) for Siple Station. An implication of the diffusive mixing of air in the firn is that the 80% air-age distribution width is about 14 years at DE08, compared to less than 8 years if it were controlled by bubble close-off alone.

4. Experimental techniques

The techniques of air extraction and analysis were similar to our earlier work (Etheridge et al., 1988) but with several refinements. Ice samples, trimmed of the outer 20 mm or more and weighing typically 0.9 kg, were cooled to -80°C. Their length was on average 17 cm, or about 15% of a year's accumulation. They were placed in a stainless-steel vacuum flask containing a grater with many cutting edges. After evacuation, the flask was oscillated vigorously which milled the ice, opening the bubbles. This method exposed no moving parts to the ice or the extracted air which could enhance the CH_4 concentrations as described by Stauffer et al. (1985) and Pearman et al. (1986). The liberated air then passed through a vacuum line where it was dried at -100°C and condensed in a cold trap at -269°C. Improvements to the vacuum line and to the procedure of air mixing in the trap reduced the modification of the air sample during the process. The DE08 ice contains a mean of 122 cm^3 kg^{-1} of air (Martinerie et al., in press) which was extracted with an efficiency of about 80%, the rest remaining in uncrushed fragments.

The air samples were analysed for CH_4 concentration on a Carle 211-M (S series) analytical gas chromatograph (GC) using flame-ionisation detection. The GC sample loop had a fixed volume of 5 cm^3. About 20 cm^3 of sample were used to flush the loop for each analysis and up to 4 samples were analysed from each ice-core air trap and then averaged. The air was dried using a Nafion dryer (Foulger and Simmonds, 1979) before passing into the sample loop. All concentrations reported here are with respect to dry air. The outlet of the GC sample loop was open to the atmosphere (through a suitably long length of small diameter tubing) such that the volumes of the sample and bracketing calibration gas injections were equal if the barometric pressure was unchanged over the time of the 3 injections. Changes in barometric pressure typically caused no appreciable loss of precision. The CH_4 concentration of the sample was determined from the ratio of the sample peak area to the calibration peak area (interpolated to the time of sample analysis), multiplied by the CH_4 concentration assigned to the calibration gas. In previously-reported work, we used the CH_4 peak heights to determine concentrations. In this study we used peak areas which give more reliable results for samples with CH_4 concentrations largely different from the calibration gas. This situation usually results in a systematic change in peak shape which becomes more appreciable as the difference in CH_4 concentration between sample and calibration gas increases (Dyson, 1990). The linearity of CH_4 detection by this method was determined by Weeks et al. (1989) to be better than 1–2% over a range of concentrations of about 100–1400 ppbv. Estimated analytical precision (2σ) is 0.8%.

Three natural-air calibration gases were used during this study. They were collected cryogenically and stored in stainless-steel, internally electropolished, 351 tanks (Rasmussen and Lovelock, 1983). These calibration gases and the same GC system were used for measurements of atmospheric CH_4 in flask air samples collected at Cape Grim, Tasmania (Fraser et al., 1987; Fig. 1). The CH_4

concentrations determined for these calibration gases were 1582, 1588 and 1700 ppbv. This CH_4 analysis methodology and calibration scale derives from that established by Dr. R. Rasmussen of the Oregon Graduate Institute of Science and Technology (OGIST) (Rasmussen and Khalil, 1981). The OGIST CH_4 calibration scale was used at CSIRO from 1980 to 1987. A CSIRO CH_4 calibration scale, based on and consistent with the OGIST scale, has been developed and propagated, beginning in 1984. The difference between this CH_4 calibration scale and a methane-in-air standard reference material (SRM, type 1658a) provided by the U.S. National Institute of Standards and Technology (NIST), is about 25 ppb, with analysis reported in the NIST scale being higher (L. P. Steele, personal communication). Direct comparisons of these calibration gases both to each other and to additional calibration gases have shown that an extremely high degree of stability has been maintained over many years (Fraser et al., 1986 and P. J. Fraser, unpublished results). This relative stability is interpreted as indicating that there was no drift in the absolute CH_4 concentrations of these calibration gases during the period of this study.

Tests of the precision of the overall procedure involved passing samples from working air standards, with concentrations of 1588, 1805 and 1836 ppbv and with volumes comparable to the ice-core air samples, through the ice-core air extraction system. Two additional tests, made by crushing air-free ice in the presence of such air samples, were also made. During the period of this study, a total of 19 tests were performed (typically one test per 5 ice-core air extractions), returning CH_4 concentrations which were on average 6 ppbv higher than the control air samples (standard deviation 22 ppbv).

The small variability of the CH_4 concentration of ice-core air samples with the same mean age reflects the precision that this technique (including the enclosure, storage, extraction and analysis of the ice-core air) reproduces the CH_4 concentration of the atmosphere. There are 6 such sample groups in our results. The standard deviation of each of the groups is less than 23 ppbv which is very close to the precision of the overall procedure determined by the system tests. This suggests that CH_4 concentrations are homogeneous in ice layers containing air of the same mean age.

5. Results and discussion

We analysed a total of 105 DE08 ice-core samples. Results from 19 samples are not reported as they were affected either by system leaks (7 samples) or GC faults (9 samples) (usually caused by poor peak integration, unstable baselines or incorrect triggering of an internal GC valve by electrical noise). The remaining rejected samples came from ice that was contaminated because it was either brittle (1 sample) or not fully closed-off (2 samples).

Theoretical considerations and isotopic measurements of ice-core air (Craig et al., 1988; Schwander, 1989; Sowers et al., 1989) show that heavier gas species are expected to be enriched in air in the firn, relative to the atmosphere, by gravitational fractionation. For CH_4, at the depth that the firn becomes sealed from the atmosphere at the DE08 site (72 m), the maximum calculated depletion relative to the atmosphere is 0.4%. Preliminary $\delta^{15}N$ measurements of N_2 from the DE08 ice-core air (personal communication, R. J. Francey and C. E. Allison, CSIRO/DAR) suggest that this is an over-estimate, possibly because diffusive equilibrium is upset by atmospheric turbulence in surface layers. Based on the average of the $\delta^{15}N$ measurements (0.25 ± 0.05 ‰) and equation (11) of Sowers et al. (1989), we determined that gravitational fractionation lowers the CH_4 concentration of the DE08 ice-core air by 0.3%.

All reported CH_4 values from the DE08 ice core in this work have been first adjusted down by 6 ppbv to allow for the average enhancement by the extraction process and then adjusted up by 0.3% to allow for the effect of gravitational fractionation.

It was noticed for samples from the more recent part of the record that ice formed from summer-deposited snow generally had higher CH_4 concentrations than for the surrounding ice. In the DE08 ice core, the density of narrow layers of summer deposition is on average 4% lower than adjacent layers. A certain proportion of pores in an ice layer become closed-off before the layer reaches the depth where overlying layers become impermeable and seal it from the atmosphere. Since the amount of bubble formation depends on density of the layer, this proportion is lower for the low density, summer layers. This delayed bubble close-off for

summer ice layers means that more recent air is enclosed in the summer layers. For periods when atmospheric levels of CH_4 are increasing, higher concentrations will be found in the summer ice samples.

To quantify the age difference between air in summer layers and adjacent layers we did the following: we assumed that, to the first order, the difference in CH_4 concentration between air retrieved from summer layers and from adjacent layers should be proportional to the corresponding rate of increase of atmospheric CH_4. Air samples extracted from DE08 core samples were identified as having come from summer (low density) layers or otherwise and their CH_4 values denoted respectively by CH_{4s} or CH_{4o}. This identification was performed using ECM and $\delta^{18}O$ measurements of the ice as indicators of season of ice deposition and also by actual density measurements. A smoothing spline (described by Enting, 1987) was fitted to the CH_{4o} time series to find the average, $\overline{CH_{4o}}$, and its rate of change, $d\overline{CH_{4o}}/dt$, for each year. The residuals of each CH_{4s} and CH_{4o} value from the $\overline{CH_{4o}}$ value were then plotted against the corresponding $d\overline{CH_{4o}}/dt$ (Fig. 2). The slope of the linear regression fitted to the CH_{4s} residuals is thus the mean age difference between the air in summer and the air in other layers. This time delay, 1.8 ± 0.8 years, was added to the air age-ice age difference for all air samples from summer ice. As a result, the difference between ice age and mean air-age for all 23 DE08 summer ice samples is about 37 years.

We found no evidence of sample deterioration with time between coring and measurement that might be caused, for example, by selective diffusion of air species through the ice. A comparison of CH_4 concentrations of samples from the same or similar (± 1 m) depth, and not from summer ice layers, was made. No trends were detectable in the CH_4 concentrations of these samples in the time (between 3 and 46 months) between coring and measurement.

The 86 DE08 CH_4 results, including the 23 from summer ice samples, are presented in Table 1 and Fig. 3. Also shown are the annual means from the direct atmospheric measurements of CH_4 at Cape Grim (Fraser et al., 1986, 1987 and unpublished data of P. J. Fraser). The gradient of atmospheric CH_4 between the latitudes of Cape Grim and the DE08 site in Antarctica is currently very small

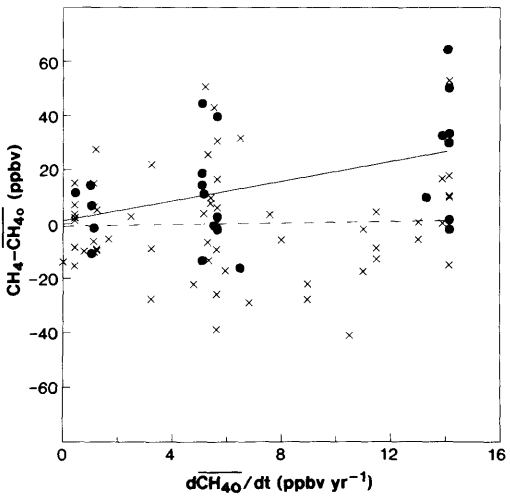

Fig. 2. The residuals of the concentrations of CH_4 in air from summer ice layers (CH_{4s}, dots) and other ice layers (CH_{4o}, crosses) from the mean, $\overline{CH_{4o}}$ (smoothing-spline fit through the CH_{4o} data) for that year, against the rate of change of $\overline{CH_{4o}}$. The gradient of the linear regression for the summer residuals (1.8 years, standard error 0.8, solid line) is the mean age difference between air in summer layers and air in other layers, due to the delayed densification and bubble close-off of the summer layers. The dashed line is the linear regression for the $CH_{4o}-\overline{CH_{4o}}$ residuals.

(less than 2 ppbv) (Fraser et al., 1986; Steele et al., 1987; Fung et al., 1991). They use the same CH_4 calibration scale.

Fitted to the 86 DE08 values in Fig. 3 is a smoothing spline with a period of 50% attenuation of 50 years. These smoothing parameters were chosen such that the spline did not appreciably follow variations in the data with periods less than about twice the air-age distribution width of 14 years. Because of the nature of the air enclosure process, real atmospheric trace gas variations on time scales of less than about twice the air enclosure duration are expected to be heavily smoothed in the trapped air bubbles (Neftel et al., 1988).

5.1. Comparison with the modern CH_4 record

An uncertainty in the interpretation of ice-core CH_4 concentrations has been whether the air composition remains unchanged during enclosure in the ice. One way to confirm this is to compare the ice-core CH_4 concentrations with the modern record of CH_4 from direct atmospheric measurements for the same year. To be meaning-

Table 1. *The concentrations of CH_4 found from the DE08 ice core*

Mean air-age (year AD)	CH_4 concentration (ppbv)		Ice depth range below January 1987 surface (m)		Ice age (year AD)	Mean air-age (year AD)	CH_4 concentration (ppbv)		Ice depth range below January 1987 surface (m)		Ice age (year AD)
	Sample:	Spline:					Sample:	Spline:			
1841	806	823	231.40	232.30	1806	1935	1111	1060	131.13	131.30	1900
1841	823		231.40	232.30	1806	1940	1094	1085	127.70	127.98	1903 S
1841	825		231.40	232.30	1806	1940	1120		127.70	127.90	1903 S
1841	829		231.40	232.30	1806	1940	1090		127.42	127.57	1903 S
1841	837		231.40	232.30	1806	1941	1067	1091	126.68	126.83	1904 S
1842	814	823	230.94	231.11	1807	1943	1095	1101	120.89	121.06	1908
1842	825		230.49	231.40	1807	1943	1127		120.89	121.06	1908
1843	825	824	229.40	229.58	1808	1944	1114	1106	119.91	120.09	1909
1846	835	826	228.98	229.17	1809 S	1944	1116		119.91	120.09	1909
1854	819	831	217.93	218.11	1819	1947	1107	1124	116.41	116.58	1912
1861	848	836	214.43	214.60	1824 S	1949	1168	1136	114.12	114.65	1914
1862	823	837	213.64	213.81	1825 S	1950	1114	1143	113.12	113.29	1915
1862	841		213.64	213.81	1825 S	1951	1120	1150	114.80	114.97	1914 S
1862	830		209.77	209.94	1827	1952	1161	1158	110.03	110.20	1917
1867	833	843	204.37	204.52	1832	1953	1159	1166	109.31	109.48	1918
1867	848		203.70	203.85	1832	1955	1155	1183	107.06	107.23	1920
1872	876	848	199.19	200.09	1837	1955	1160		107.06	107.23	1920
1875	842	851	196.16	196.31	1840	1958	1171	1212	103.84	104.01	1923
1881	874	858	190.52	190.69	1846	1959	1220	1223	101.61	101.88	1924
1882	866	859	189.04	189.97	1847	1959	1205		101.47	101.61	1924
1883	857	860	189.97	190.15	1846 S	1960	1238	1234	100.38	100.56	1925
1885	854	863	185.18	185.33	1850	1960	1221		100.07	100.97	1925
1891	866	872	178.58	178.75	1856	1960	1225		100.03	100.97	1925
1898	889	887	172.11	172.28	1863	1964	1277	1283	94.04	94.23	1929
1903	922	902	168.05	168.41	1868	1964	1284		94.04	94.23	1929
1903	873		168.05	168.41	1868	1967	1306	1324	93.55	94.48	1930 S
1903	892		168	169	1868	1968	1354	1337	88.13	88.36	1933
1913	919	942	156.03	156.20	1878	1968	1337		87.99	88.92	1933
1916	960	956	153.40	153.60	1881	1970	1370	1366	88.25	88.44	1933 S
1918	967	967	153.21	153.40	1881 S	1971	1364	1380	84.10	84.27	1936
1921	1026	983	147.70	147.87	1886	1972	1430	1394	85.95	86.13	1935 S
1923	982	994	148.40	148.57	1886 S	1972	1411		83.01	83.18	1937
1923	955		145.28	145.45	1888	1972	1403		82.33	82.40	1937
1923	984		145.28	145.45	1888	1972	1446		82.33	82.40	1937
1923	968		145.13	145.30	1888	1973	1408	1409	81.51	81.68	1938
1927	1047	1016	140.95	141.13	1892	1973	1418		81.07	81.24	1938
1927	1017		140.90	141.13	1892	1974	1427	1423	83.25	83.42	1937 S
1927	1033		140.90	141.13	1892	1974	1392		83.21	83.38	1937 S
1927	1023		140.67	140.90	1892	1974	1395		83.21	83.38	1937 S
1929	1015	1027	141.13	141.30	1892 S	1974	1408		80.13	80.30	1939
1929	1019		141.13	141.30	1892 S	1974	1449		80.13	80.30	1939
1929	1056		141.13	141.30	1892 S	1975	1438	1438	81.68	81.85	1938 S
1933	1036	1049	133.25	133.42	1898	1978	1504	1481	78.40	78.55	1941 S

Individual sample concentrations and the corresponding smoothing-spline value are given. The ice depths refer to the range of depths from which each sample was selected. The air is generally 35 years younger than the ice except in summer layers (flagged "S") where it is 37 years younger (see text).

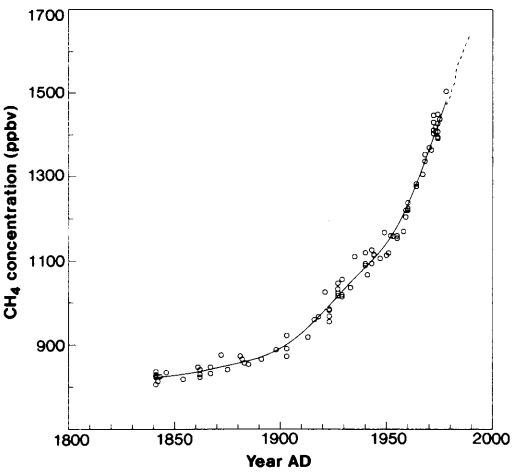

Fig. 3. CH_4 concentrations in the DE08 ice core and the smoothing-spline fit. The Cape Grim record is from the annual means of Fraser et al. (1986), Fraser et al. (1987) and unpublished data of P. J. Fraser.

ful, such a comparison requires that the air be accurately dated, as each year in error would create an apparent difference in CH_4 concentration between the two records equivalent to the annual growth rate at the time, which may have been as large as 20 ppbv per year (Fraser et al., 1981). It is also important that both records relate to the same calibration scale. Until now, such a comparison has not been possible because a gap of more than a decade separated the two types of CH_4 record. However, the mean age of the most recent air enclosed in the DE08 ice core eliminates this gap and overlaps about one year with the Cape Grim record. The individual DE08 CH_4 value for 1978 is 32 ppbv higher than the 1978 Cape Grim annual mean. The Cape Grim 1978 CH_4 annual mean was derived from three flask air samples (Fraser et al., 1986) whose mean concentration was adjusted for the average seasonal variation observed over 10 years of measurements at Cape Grim. The smoothing-spline CH_4 value, which is a better measure of the DE08 record, is only 9 ppbv higher than Cape Grim in 1978. These differences are well within the uncertainties in the DE08 CH_4 measurements (± 22 ppbv) and mean air-age (± 3 years, equivalent to up to ± 60 ppbv). We conclude that the CH_4 concentration of the DE08 ice-core air is not significantly modified when enclosed and stored, at least for a decade, in the ice.

5.2. *Comparisons with other data*

Fig. 4 presents the DE08 ice-core CH_4 concentrations together with results from some other atmospheric CH_4 measurements obtained by a variety of techniques. Comparisons with the ice-core measurements from BHD (Etheridge et al., 1988) can be made directly because the cores contain air representative of the troposphere at similar latitudes, because the air enclosure process smooths any seasonal atmospheric CH_4 variations and because they are both relative to the same calibration scale. The average of the BHD concentrations from 1796 AD to 1826 AD agrees well with the earliest DE08 results and establishes the preindustrial CH_4 level from which the DE08 results ascend. The Siple Station ice-core measurements are relative to CH_4 standards

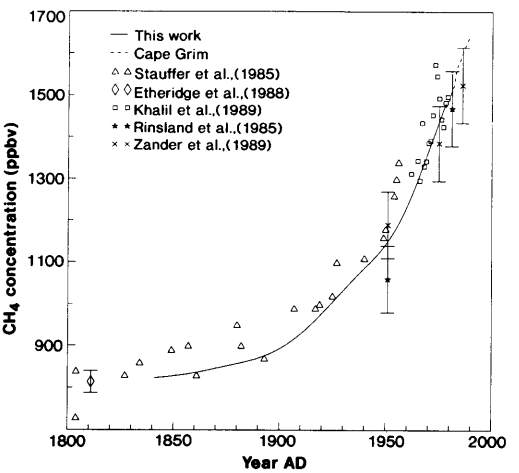

Fig. 4. Comparisons of the DE08 CH_4 record (smoothing-spline fit of Figure 3) and Cape Grim record with: *diamond*, the average CH_4 concentrations from the BHD ice core (Etheridge et al., 1988) from 1796–1826; *triangles*, results from the Siple Station ice core, using both melt and dry extraction. (Stauffer et al., 1985); *squares*, compilation by Khalil et al. (1989) of sporadic GC data, reduced by 3.1% for the latitudinal gradient between global mean and Antarctica; *stars and crosses*, CH_4 concentrations derived respectively by Rinsland et al. (1985) and Zander et al. (1989) from solar absorption spectra, reduced by 7.1% for the latitudinal gradient between the Jungfraujoch and Kitt Peak observatories and Antarctica. Error bars are quoted precisions (1σ) and where not shown (for reasons of space) vary from 23 to 180 ppbv for Khalil et al. (1989), from 60 to 90 ppbv for Stauffer et al. (1985) and are 22 ppbv for this work.

within 3% of absolute concentration (Stauffer et al., 1985). Although the exact relationship between the CH_4 calibration scale used for the Siple measurements and the one used in this work is undetermined at this stage, the differences between the CH_4 values for Siple and DE08 for the period common to both records are within the range of uncertainties in the measurements.

Comparison of the DE08 record with the compilation of sporadic gas chromatographic data for the period 1962–1979 (Khalil et al., 1989) is less direct as these data are corrected to globally averaged concentrations. Their analysis is based on the assumption that the observed 1984 latitudinal distribution of atmospheric CH_4 (Steele et al., 1987) was applicable during the 1960s and 1970s. There may also be errors of up to 2% because the Khalil et al. (1989) data are not corrected for seasonal variations of CH_4 concentration. The data are referenced to the CH_4 calibration scale established by Dr. R. Rasmussen (Rasmussen and Khalil, 1981). We have adjusted the compilation of 1962–1979 annual mean values to the concentrations expected at Antarctic latitudes assuming the observed 1984 latitudinal distribution was representative of this period. Although the uncertainties in the 1962–1979 data compilation are generally much larger than for our measurements, there is reasonable agreement with the DE08 and the Cape Grim records.

Further comparisons are made to the CH_4 concentrations derived from the atmospheric column abundances found from the analysis of solar absorption spectra. These were taken at the Jungfraujoch Station, Switzerland in 1951, 1975 and 1984–1987 and at Kitt Peak, Arizona in 1981 (Zander et al., 1989; Rinsland et al., 1985; hereinafter ZDES and RLM respectively). We have again applied the 1984 latitudinal distribution to estimate the corresponding Antarctic concentrations. With the exception of the 1951 value of ZDES, the spectrally-derived CH_4 values are lower than the DE08 and Cape Grim records. ZDES found that seasonal changes in the height of the tropopause influences the total column abundance of CH_4 and suitable adjustments were made in their derivation of CH_4 concentration from the spectra. The results of RLM did not include this adjustment which may account for their CH_4 values being low. Other likely causes for the observed differences between the CH_4 values found from the spectra and the ice core are: first, the observed 1984 latitudinal gradient may not be representative of earlier times; second, a vertical profile of CH_4 above the observation station had to be assumed by RLM and ZDES to derive the CH_4 concentration from a total column abundance, and this may have introduced uncertainties; third, the concentrations derived for the altitude of the Jungfraujoch and Kitt Peak may be considerably less because CH_4 normally decreases with height in the northern hemisphere (Fung et al., 1991). The DE08 ice-core values represent the lower-tropospheric CH_4 concentrations of the southern hemisphere because of the lower altitude of the ice-core site and the smaller vertical gradient of CH_4 in the southern hemisphere.

5.3. *Methane growth rates*

The CH_4 growth rate record corresponding to the DE08 CH_4 concentration time-series is shown in Fig. 5. It was calculated from the differences between the annual values of the smoothing spline in Fig. 3. The observed CH_4 growth rate generally increases throughout the record except between about 1920–1945 when it stabilised. The statistical uncertainty of the smoothing-spline fit is difficult to assess, but standard errors calculated for the spline at various sections suggest that the feature is qualitatively defined, if not quantitatively. The

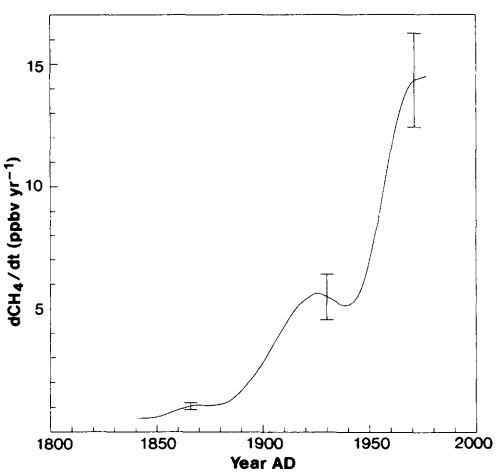

Fig. 5. The rate of change of CH_4, derived from the smoothing-spline in Fig. 3. Error bars represent the standard error of the slope for each of 3 approximately 25 year segments of the curve.

feature is retained even when splines are fitted to the CH_4 values with smoothing parameters increased to as much as twice the smoothing period of the spline in Fig. 3. Possible artifacts that could cause the feature in the record at 1920–1945 are a change in the ice-core air chronology, a systematic measurement error or a condition of the ice in this region. A change in the air chronology could occur only if there were sustained changes in the snow accumulation rate in this region of the core. Using the record of snow accumulation rate for DE08 (Morgan et al., 1991) we found that the largest changes to the air chronology from this cause would be about 1 year, too small to create the feature in the CH_4 growth-rate record. Systematic errors in the air extraction or analysis are unlikely to be concentrated in this part of the CH_4 record as the results were produced over more than three years with no chronological sequence to the sampling scheme. Finally, none of the features of the ice core (such as snow-deposition temperature, summer melt layers, ice acidity, brittleness) which could affect the CH_4 concentrations was found to be different in this region. The observed stabilisation in the CH_4 growth rate between 1920 and 1945 is then presumably a real atmospheric feature, caused by changing CH_4 sources and/or sinks.

Model simulations suggest that globally averaged OH levels may have gradually decreased since pre-industrial times (e.g., Crutzen and Zimmermann, 1991). If this is the case there would be a corresponding gradual increase in atmospheric CH_4, even if the source strengths of CH_4 remained constant. We speculate that it is unlikely that global changes in the abundance of OH could account for the stabilisation in the growth rate of CH_4 during 1920–1945 because this would require a temporary deviation from the modelled trend in OH. An adequate time-resolved simulation of atmospheric OH would address this question.

Changes in global atmospheric temperatures may increase rates of CH_4 emission from sources such as wetlands (Lashof, 1989) and CH_4 hydrates (Kvenvolden, 1988). Compilations of global average surface temperatures over the past 130 years show a steady increase of 0.5°C from about 1910 to 1940 (Jones et al., 1986). For these temperature changes to be able to account for the observed stabilisation in the growth rate from 1920–1945, there would have to be an overall negative feedback effect on atmospheric CH_4, with a delay in its onset of about 10 years. This seems a very unlikely scenario since Lashof (1989) has estimated an overall positive feedback on CH_4 emissions from a temperature increase. Also, the ice-core CH_4 results of Chappellaz et al. (1990) show that on time scales of thousands of years, warmer temperatures are strongly associated with higher levels of atmospheric CH_4.

We believe that the most likely explanation for the stabilisation of the growth rate of atmospheric CH_4 during 1920–1945 is that the global source strength grew more slowly in this period. It is very difficult to speculate in detail about such scenarios because the relative magnitudes of the source components of even the present-day budget of atmospheric CH_4 are not well known (Fung et al., 1991). Nevertheless, it seems worthwhile to address one of the likely possibilities. Currently it appears that CH_4 emissions from the utilisation of fossil fuel contribute 16–20% of the annual global CH_4 source (e.g., Quay et al., 1991). Presumably during pre-industrial times there was little, if any, CH_4 released to the atmosphere from fossil fuel reserves. Thus it seems safe to conclude that this component of the global CH_4 budget has grown substantially over the past two centuries. But it almost certainly will not have grown at a constant rate. Keeling (1973) and Marland and Rotty (1984) estimated the annual emissions of carbon dioxide to the atmosphere from fossil-fuel production. If these estimates are a proxy for the associated fossil CH_4 releases from coal gas, natural gas and oil wells and leaks in natural gas distribution systems, then a stabilisation and occasional reduction in the fossil CH_4 source may have occurred between about 1914 and 1949. This period of interruption to the growth of fossil-fuel production is attributed to World Wars I and II and the Great Depression (Elliot, 1983). Although the stabilisation of this proxy of the fossil-CH_4 source is concurrent with the observed stabilisation of the CH_4 growth rate, without more reliable data on changes to the other CH_4 sources in the past it is not possible to say whether the two are related. High-precision measurements of the $\delta^{13}C$ of the CH_4 in air from the DE08 ice core may also help identify the cause of this change to the growth rate because the fossil sources are depleted in ^{13}C compared to natural CH_4 sources and the atmospheric reservoir.

Following the 1920–1945 period, the CH_4 growth rate increased and reached an average of 14 ± 2.2 ppbv year^{-1} for the period 1965–1978. This growth rate is comparable to the values reported from direct atmospheric CH_4 measurements for periods during the 1980s at various locations (e.g., Khalil and Rasmussen, 1990; Blake and Rowland, 1988; Brunke et al., 1990; Steele et al., 1987; Fraser et al., 1986). There is some evidence in the direct atmospheric measurements that the CH_4 growth rate decreased in the 1980s (Aoki et al., this volume; Steele et al., 1987; Steele et al., in press). This may be further supported by a slowing observed in the increase of the CH_4 growth rate at the recent end of the DE08 record (i.e., from about 1970). Although it is possible that this observed slowing is simply an end effect of the smoothing spline, if real it may signal the beginning of the decrease in the CH_4 growth rate in the modern records. We look forward in anticipation to further drilling at the DE08 site in the 1992/3 austral summer, which should provide core with several years of overlap with the modern atmospheric record so that these recent trends can be further investigated.

6. Conclusions

Using the DE08 ice core we have reconstructed a detailed record of the changes in the concentration of CH_4 in the Antarctic troposphere from about 1841 to when direct atmospheric measurements began in 1978. This ice core bridges the gap between the modern direct record of atmospheric CH_4 and the paleo-records in other ice cores. The match between the DE08 record and the Cape Grim direct atmospheric measurements implies that the CH_4 concentration is not significantly modified when the air is enclosed in the ice sheet, or when it is extracted and measured. The CH_4 growth rate generally increased since pre-industrial times except during 1920–1945 when it apparently stabilised. Measurements of the $\delta^{13}CH_4$ in the DE08 ice-core air may identify whether the cause of this change in the growth rate is related to changes in fossil CH_4 emissions.

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