A 1000-year high precision record of $\delta^{13}C$ in atmospheric CO_2

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ABSTRACT

We present measurements of the stable carbon isotope ratio in air extracted from Antarctic ice core and firn samples. The same samples were previously used by Etheridge and co-workers to construct a high precision 1000-year record of atmospheric CO_2 concentration, featuring a close link between the ice and modern records and high-time resolution. Here, we start by confirming the trend in the Cape Grim in situ $\delta^{13}C$ record from 1982 to 1996, and extend it back to 1978 using the Cape Grim Air Archive. The firn air $\delta^{13}C$ agrees with the Cape Grim record, but only after correction for gravitational separation at depth, for diffusion effects associated with disequilibrium between the atmosphere and firn, and allowance for a latidudinal gradient in $\delta^{13}C$ between Cape Grim and the Antarctic coast. Complex calibration strategies are required to cope with several additional systematic influences on the ice core $\delta^{13}C$ record. Errors are assigned to each ice core value to reflect statistical and systematic biases (between $\pm 0.025‰$ and $\pm 0.07‰$); uncertainties (of up to $\pm 0.05‰$) between core-versus-core, ice-versus-firn and firn-versus-troposphere are described separately. An almost continuous atmospheric history of $\delta^{13}C$ over 1000 years results, exhibiting significant decadal-to-century scale variability unlike that from earlier proxy records. The decrease in $\delta^{13}C$ from 1860 to 1960 involves a series of steps confirming enhanced sensitivity of $\delta^{13}C$ to decadal timescale-forcing, compared to the CO_2 record. Synchronous with a "Little Ice Age" CO_2 decrease, an enhancement of $\delta^{13}C$ implies a terrestrial response to cooler temperatures. Between 1200 AD and 1600 AD, the atmospheric $\delta^{13}C$ appear stable.

1. Introduction

The most striking change in the modern and ice core records of atmospheric CO_2 over recent centuries is the increase attributed to industrial, mainly fossil fuel, emissions (Keeling et al., 1989a; Etheridge et al., 1996). Significant CO_2 perturbations can also be expected from land-use change (Houghton et al., 1983). Both perturbations influ-

ence the atmospheric stable carbon isotope ratio $^{13}C/^{12}C$. The majority of land plants employ the C3 photosynthetic pathway which results in stored carbon approximately 18‰ depleted in ^{13}C with respect to the atmosphere (Farquhar et al., 1982). Around 21% of carbon uptake by modern plants is via C4 photosynthesis, so that the global mean discrimination is marginally less, around 15‰ (Lloyd and Farquhar, 1994). Fossil fuel releases involve the combustion of ancient, mainly C3 photosynthate, slightly isotopically modified over

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time by fractionating processes depending on fuel type (Tans, 1981; Andres et al., 1998). Since the fractionation that occurs in combustion and respiration of fossil, plant and soil carbon is small, both industrial and land-use changes impose similar changes in the ^{13}C/^{12}C ratio of the global atmosphere. In contrast, the fractionation associated with diffusion across the air-sea interface is an order of magnitude smaller (Mook et al., 1974) and the dissolved CO$_2$ is generally assumed to be in isotopic equilibrium with dissolved inorganic carbon (DIC) which contributes the bulk ($\sim$99%) of the mixed layer carbon. Since the DIC is not significantly disturbed by marine photosynthesis at typical open ocean primary production rates (Francois et al., 1993), marine photosynthesis has minimal impact, globally, on atmospheric values. Thus atmospheric ^{13}C/^{12}C records can be used to partition the uptake of fossil fuel carbon between oceanic and terrestrial reservoirs (Pearman and Hyson, 1986). They can also be used in studies of natural variability in the carbon cycle (Keeling et al., 1989b) and in calibrating global carbon budget models (Siegenthaler and Oeschger, 1987; Heimann and Maier-Reimer, 1996).

The detection of the fossil fuel signature in the stable carbon isotope ratio of atmospheric CO$_2$ was first reported by Keeling et al. (1979, 1980). This work compared early clean-air monitoring results in 1977 and 1978 at La Jolla (33°N), Fanning Island (4°N) and South Pole (90°S) with measurements taken 22 years earlier at a variety of US land and marine sites. Significant calibration problems exist in relating measurements 22 years apart, never-the-less a change in δ^{13}C of -0.65 ± 0.13‰ was reported. The same team has reported a similar overall decrease rate in δ^{13}C since 1977 (Whorf et al., 1993; Keeling et al., 1995). Recently, Francey et al. (1995a) report an independent set of atmospheric δ^{13}C measurements from 1982, again with a similar overall rate of decline in the relative ^{13}C/^{12}C ratio, but with considerably smaller inter-annual variability. Shorter records are also available from Nakazawa et al. (1993a, 1997) since 1984, and Trolier et al. (1996) since 1990.

There have been several attempts to detect the fossil fuel signal on century time-scales via the ^{13}C/^{12}C ratio in organic material, primarily using tree rings (Stuiver, 1978). The advantage of using tree rings for this purpose is the excellent

dating and yearly time resolution over century to millennium time-scales. However, Francey and Farquhar (1982) argued that the past CO$_2$ could not be inferred via isotopic measurements of tree rings without independent evidence of historical changes in tree physiology ("vital effects"), since the kinetics of carbon assimilation control the photosynthetic fractionation factor (Farquhar et al., 1982). Stuiver et al. (1984) used a correlation between ring-width and δ^{13}C to argue that the ring widths reflect assimilation rate (when in fact they record the cumulative seasonal assimilation). While qualitatively useful, the different averaging times and possible non-linear processes make the potential errors appreciable and there is considerable block-to-block (10 yr) variation in their ring-area-normalised average δ^{13}C record.

A theoretical study on C4 plants by Farquhar (1983) suggested that the different carbon assimilation pathway would reduce kinetic effects. This idea was explored by Francey (1986) using historic sugar samples but the results were scattered and inconclusive. Marino and McElroy (1991) employed catalogued samples of maize cobs and kernels (*Zea mays*) to obtain a trend over the 1950–1990 period similar to the Keeling et al. (1980) atmospheric results, however the year-to-year scatter is very large ($\sim$0.5‰) post 1978, compared to the overlapping atmospheric record. The high time resolution and long sequence advantages of the C3 tree rings are not generally shared by C4 plants. With a similar rationale, White et al. (1994) exploit the stomata-less properties of mosses and peat in a sediment core to obtain a 14 000 year record of atmospheric δ^{13}C, however the last 1000 years of relevance here is not well resolved in this record (4 points). The δ^{13}C precision on all of these methods has been limited by the preparation, combustion and analysis error of around 0.1‰ or more, over and above possible vital effect contributions.

Druffel and Benavides (1986) selected a Jamaican slow-growing marine sponge, which accretes aragonite close to equilibrium with the surrounding dissolved inorganic carbon (DIC) system, aiming to suppress kinetic effects associated with photosynthesis. Druffel and Benavides measured an ocean surface-layer δ^{13}C change of -0.5 ± 0.15‰ from 1800 to 1972 (similar to the change measured in more scattered data from a Bermuda coral, Nozaki et al., 1978). Most of this

decline occurs between 1920 and 1960, which is interpreted as a peak in CO_2 production from forest/soil sources around this time. Using the modelled surface-ocean response, Druffel and Benavides point out similarities during this period to the ring-area-normalised tree ring record of Stuiver et al. (1984). Although Keeling (1993) reports very large inter-annual variation in direct measurements of surface ocean $\delta^{13}C$ since 1983, Böhm et al. (1996) measured a smooth high precision record of $\delta^{13}C$ in DIC from sponges in the Caribbean and Coral seas from 1800 AD to the present. Dating of the material back to 1960 is confirmed by bomb ^{14}C measurements, but prior to that it is estimated from assumed growth rates and is uncertain by around 50 years in 1900 AD, and 100 years in 1800 AD. Apart from smaller scatter, the Böhm et al. data have much less decline over the 1900 to 1960 period than that implied by the Druffel and Benavides data. Baksaran and Krishnamurthy (1993) report a $\delta^{13}C$ decrease in speleothems. Again the complex processes involved in carbon precipitation limit applicability, and the dating is not precise.

There have been several $\delta^{13}C$ records measured from the air enclosed in ice cores. The ice core records avoid "vital effects", but there is modification of trace gas composition during the entrapment and storage of air in ice. Two $\delta^{13}C$ ice core studies relate to air prior to the industrial period, Siegenthaler et al. (1988) report a $\delta^{13}C$ change in the 13th century using a South Pole core, and Leuenberger et al. (1992) discuss glacial/Holocene differences in $\delta^{13}C$ from an ice core drilled at Byrd Station, Antarctica. The studies covering the industrial period include the cores Siple (Friedli et al., 1986) and H15 (Nakazawa et al., 1993b) from Antarctica, and Dye 3 (Leuenberger, 1992) from Greenland. The major drawback with all of these records is that the most recent trapped air is prior to the 1960s, with unresolved calibration problems in precisely relating to the post 1978 modern record. The scatter, relative to the overall measured $\delta^{13}C$ trend prior to 1960, is also significant. In addition, the published records generally have not been corrected for diffusion effects and gravitational settling in the firn prior to bubble close-off in the ice (Craig et al., 1988; Schwander, 1989). For example, Siegenthaler and Oeschger (1987) deconvolve combined Siple ice core and direct atmospheric $\delta^{13}C$ measurements without allowing for the significant fractionation in the ice samples as the importance of these effects was not appreciated at the time. This is an important omission for applications relying on the total change in $\delta^{13}C$ over the industrial period, but does not explain the significant flattening of the $\delta^{13}C$ record between 1920 and 1950 (the end of their ice core record) reported by Siegenthaler and Oeschger. The 1920–50 flattening is quite unlike the trend in the Druffel and Bernavides DIC record and Stuiver normalised tree ring records, but not unlike that measured in the DIC record of Böhm et al. (1996).

We use 3 ice cores from 2 sites at Law Dome, Antarctica, firn air pumped from the highest accumulation site, and air from the Cape Grim Air Archive, to overcome many of the problems encountered in studies by other workers. Preliminary $\delta^{13}C$ results over the industrial period from these samples have been previously presented by Leuenberger et al. (1993) and interpreted by Joos et al. (1994). The results presented here are more comprehensive and now include rigorous correction for several effects not included in the preliminary studies. These include continuity between the modern and ice core record, and a consistent calibration strategy for the various measurements of archived air and the contemporary global network. Reference is also made to ship-board cruise data linking the relevant sites.

2. Site and sample collection details

The ice and firn samples were collected from coastal Antarctica, near the summit of Law Dome, 1390 m above sea level at 66°44′S, 112°50′E. Site information, and general drilling and dating strategies, are given by Morgan et al. (1997). Information specific to the drilling and sample collection for study of the composition of entrapped air is detailed by Etheridge et al. (1996). Drilling sites were at DE08 in 1987 (providing ice ranging in age 1820–1939, DE08-2 in 1993 (ice spanning 1802–1948, and firn air) and DSS, drilled over the period 1988 and 1993 to bedrock (spanning the Holocene and beyond, with trace gas analyses so far completed for 948 to 1901 AD). Ice dating accuracy is ± 2 yr at 1850 in all three cores and ± 10 yr at 1350 AD in DSS. Etheridge et al. (1996) establish the air age difference between

ice and entrapped air as 30 ± 1 years for the two DE08 sites and 58 ± 2 years for DSS, with the DE08-2 result subsequently accurately and independently confirmed by Levchenko et al. (1996, 1997) using the 1960s atmospheric ^{14}C bomb spike. Levchenko et al. also confirm the very high time resolution in the DE08-2 core of 12.5 ± 1.5 years, resulting from the large accumulation of 1100 kg m^{-2} yr^{-1} at the site.

Low mean temperatures ($< -19°$C at DE08 and colder at DSS) largely avoid summer melt on the surface, and this coupled with low impurity levels, minimise trace gas modification. The uniform accumulation at the sites, and small temperature gradients in the firn, suggest that thermal fractionation effects (Severinghaus et al., 1998) will be small. Different drilling techniques, thermal, electromechanical and fluid immersed electrochemical, were employed at DE08, DE08-2 and DSS respectively. However no systematic influence associated with drill type has been detected in trace gas results.

At DE08-2 in 1993, firn air sampling devices (FASDs) were employed to collect air samples from the porous firn between the surface and impermeable ice at around 90 m depth. Air pumped from the surface, and from 12 layers at 5 m intervals from 10 m, was collected in flasks after drying with anhydrous magnesium perchlorate. A variety of FASDs materials, pump types and flask containers was employed. No systematic influence of FASD or pump was detected, while some flask types contributed scatter in the results for some species. High precision trace gas data were obtained using a CSIRO pump unit and pressurized 0.5 litre glass flasks with PFA O-ring taps (Francey et al., 1996a), and only these results are considered here.

The primary comparison of the Law Dome δ^{13}C records is with the Cape Grim δ^{13}C monitoring program (Francey et al., 1995), and with measurements on archived air collected at Cape Grim.

3. Laboratory details

The Ice Core Extraction Laboratory (ICELAB) was established in CSIRO for the extraction of dry air from bubbles trapped in ice, using a "cheese-grater" technique (Etheridge et al., 1988,

1989, 1992). Typically, 1 kg sub-samples are selected and trimmed for processing. After evacuation, then grating, an ice sample yields 50–150 standard ml of air, which is cryogenically dried at $-100°$C and collected in electro-polished and preconditioned stainless steel traps at around $-255°$C (Etheridge et al., 1996). On thawing, trap pressure is typically 10 bar. The traps used to transfer the samples to the trace gas analysing laboratory have no welds in the condensation volume and use all-metal valves with non-rotating stems.

The Global Atmospheric Sampling Laboratory (GASLAB) provides multi-species, high precision analysis of air samples for CO$_2$, CH$_4$, CO, H$_2$, and N$_2$O, by gas chromatography (GC) and δ^{13}C and δ^{18}O of CO$_2$ by mass spectrometery (MS). Typically 20 standard ml of air is employed per GC injection and 30 standard ml (STP) of air provides a precise MS analysis. The mass spectrometer techniques central to the study are described in more detail in the next section. The GC measurements of most relevance involved a Carle Series 400 GC, which catalytically converts CO$_2$ (after separation) to CH$_4$ for detection with a Flame Ionisation Detector, and a Shimadzu GC with Electron Capture Detector for the measurement of N$_2$O. The N$_2$O/CO$_2$ ratio is used in the correction of MS data (Mook and Van der Hoek, 1983), and the CO$_2$ data, described in detail by Etheridge et al. (1996), are also fundamental to the biogeochemical interpretation of the isotope data.

4. Mass spectrometry

The stable isotope ratios of CO$_2$ in the air samples are determined using a MAT 252 mass spectrometer (Finnigan MAT GmbH, Bremen). Cape Grim in situ extracted CO$_2$, routine whole air samples from flasks, and the small, high pressure, whole air samples from ICELAB require three different methods of introducing samples to the mass spectrometer, creating opportunities for systematic differences between the records. The three strategies are summarised in Fig. 1.

1. The Cape Grim in situ extraction of CO$_2$ provides samples that are admitted through the conventional bellows input of the CO$_2$ multiport.
2. Air samples from global network flasks (includ-
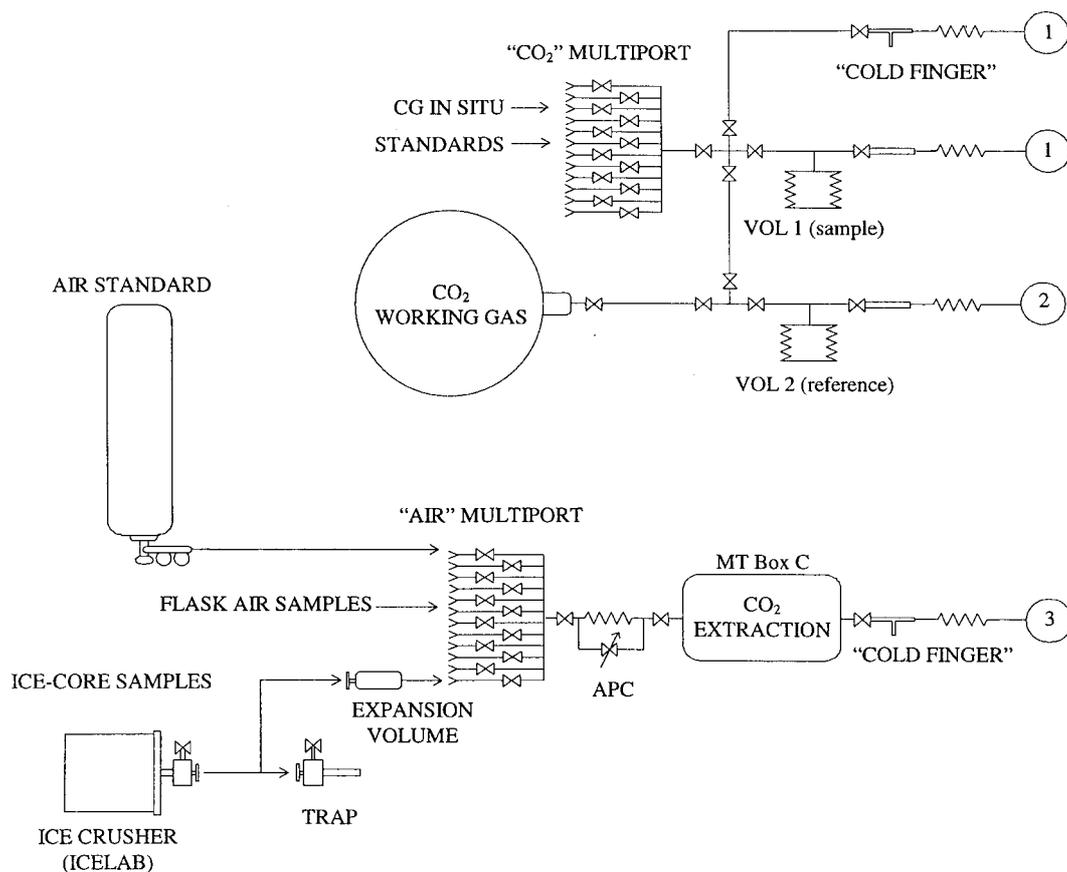
Fig. 1. Inlet strategies for analysing $\delta^{13}C$ of CO_2 using: (a) pure CO_2 samples through the "CO_2" multiport (the Cape Grim in situ record and international CO_2 standards analysed with respect to reference CO_2 in VOL 2), (b) large volume air samples via the MT Box-C (routine flasks, CG Archive and firn samples analysed w.r.t. VOL2, but expressed relative to bracketing AIR STANDARD), (c) small volume air samples via a modified MT Box-C system (ice core samples analysed and expressed w.r.t. reference CO_2 in VOL 2, see text). Numbers on the right hand side refer to inlet connections to the change-over valve of the MAT252 mass spectrometer.

ing firn samples and the Cape Grim Air Archive) are admitted via a separate "air" (MT Box-C) multiport which feeds through an initial capillary to drop air pressure in the series of cryogenic traps. The pressure typically varies between 100 and 200 mbar in the traps. The cryogenic traps retain water vapour and other condensables, and extract CO_2 (plus N_2O) for injection into the MAT252 via a dedicated micro-volume and crimped capillary.

3. For the smaller volume and higher initial pressure ice core air samples, expansion volumes are connected to the MT Box-C multi-port to drop the initial pressure to less than ∼4 bar to

avoid incorrect valve operation. In addition, an automatic pressure controller (Granville-Phillips 216 APC) in parallel with the MT Box-C capillary, is switched in for small ice core samples to maintain viscous flow as the sample pressure drops. The CO_2 extraction (98%) occurs at pressures above 15 mbar.

The assessment of differences between strategies 1 and 2 comes from a comparison of 5 years of data from parallel in situ and flask sampling at Cape Grim (see next section). In later sections, we also assess the differences between strategies 2 and 3 by a series of "blank" tests via the expansion

volumes with strategy 3, using air standards characterised and monitored using strategy 2. For reasons related to a subtle malfunction in the MT Box-C, the 2 versus 3 comparison proved the most difficult to quantify and delayed final publication of these data until now.

High precision isotopic ratios are determined by alternating sample CO$_2$ and reference CO$_2$ injected via matched crimped capillaries. The carbon isotopic ratio of the sample (S) is expressed relative to the reference (R) as:

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_S}{(^{13}C/^{12}C)_R} - 1 \right] 1000‰ \qquad (1)$$

The MAT252 simultaneously measures ion beam intensities at mass/charge (m/e) ratios of 44, 45 and 46, with primary interest in the ratio of $^{13}C^{16}O^{16}O$ to $^{12}C^{16}O^{16}O$; results are initially reported as δ45 and δ46. Here we have derived $^{13}C/^{12}C$ values from the δ45 and δ46 values by correcting for the interfering N$_2$O ions at m/e 44 (using GC determined N$_2$O and CO$_2$ values) and due to $^{12}C^{16}O^{17}O$ at m/e 45 (using the m/e 46 ratio) using assumptions and algorithms given by Allison et al. (1995). The reference CO$_2$ used in this study is the high purity CO$_2$ working standard HC453 with isotopic ratios relative to the international standard V-PDB(CO$_2$) on the "1987 HC453 scale" taken as:

$$\delta^{13}C_{PDB} = -6.396‰, \qquad \delta^{18}O_{PDB} = -13.176‰. \qquad (2)$$

Correction for possible minor modification of the working gas stored in the reference reservoir, and conversion of δ^{13}C measured relative to HC453 to values relative to V-PDB, also follow procedures and assumptions described by Allison et al. (1995).

The direct determination of the HC453 δ^{13}C on the V-PDB scale relies on relatively infrequent and low precision ($\pm 0.05‰$) preparations of CO$_2$ from the NBS-19 carbonate standard. Even if the value of HC453 were determined against NBS-19 with more precision, systematic offsets associated with the extraction of CO$_2$ from air samples have often exceeded 0.05‰ (see below). In the application of these measurements we are interested in the changes of isotopic ratio rather than absolute values, so that the precision of ice core δ^{13}C relative to values in the firn and to the direct atmospheric measurements (in situ and flask pro-

grams), is of more relevance. An as yet unattained objective for this work was to reduce systematic errors to better than the external precision for routine flasks of $\sim 0.015‰$ (e.g., the mean and standard deviation of the difference between 77 flask pairs collected at Cape Grim during the two years including the ice core analyses was $-0.002 \pm 0.015‰$).

5. The Cape Grim δ^{13}C record

A detailed assessment of possible systematic differences between two pre-treatment and sample loading methods is possible from the parallel Cape Grim operations of the in situ cryogenic extraction program and the routine GASLAB collection of chemically dried air in 0.5 litre flasks for CO$_2$ extraction using the MT Box-C. The in situ and flask δ^{13}C, when expressed relative to the same pure CO$_2$ working gas, HC453, exhibit large and variable differences over the period 1992–1996. The [flask-in situ] differences are similar in amplitude and timing to variations in δ^{13}C of CO$_2$ extracted via the conventional MT Box-C, from high-pressure cylinders of clean, dry ambient air used as standards. The air standard δ^{13}C are shown against analysis date in Fig. 2, adapted from Allison and Francey (1999), to include the timing of measurement sessions and "events" of relevance to this paper.

Several potentially serious systematic variations are evident in Fig. 2, including the step increase of around 0.07‰ in April 1993 ("APC in") and corresponding drop in February 1996 ("APC out"), discontinuities of order 0.05‰ at other significant hardware modifications (e.g., "MEMCO", "HV"), and increasing δ^{13}C over the weeks following gaps in the record which mostly indicate admission of whole air (rather than pure CO$_2$) to the source region of the mass spectrometer. The last are more evident after commencement of routine O$_2$/N$_2$ observations in January 1995, when the system was regularly switched between CO$_2$ and air modes on time-scales of months.

The "APC" event is of direct relevance here since "APC in" refers to installation of the APC so that ice core samples could be measured. Both ice core and Archive samples were measured between "APC in", and "APC out" when the cause of the problem (not the APC but a faulty pressure
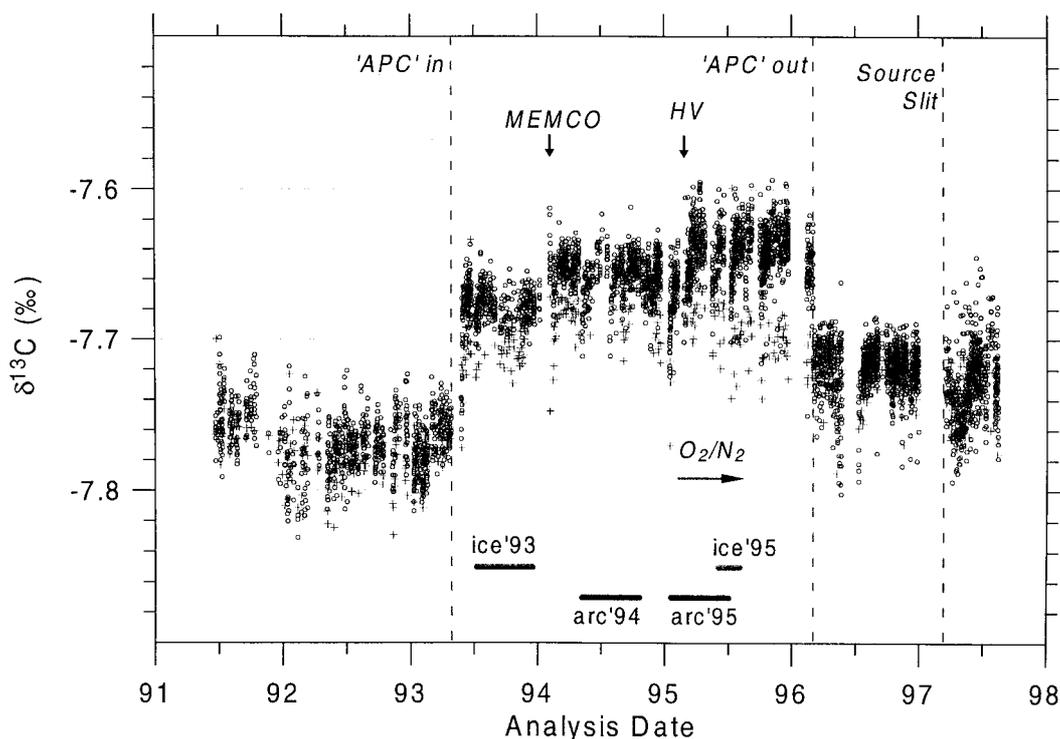
Fig. 2. Systematic biases in $\delta^{13}C$ in standard air from high-pressure cylinders. Plus symbols (+) represent the first standard analysis of a session, circles are the average of other (typically 5) standard analyses in the session. A typical session is an overnight, automated sequence of samples and standards extracted and analysed on the MT Box-C and MAT252 mass spectrometer system. Mean differences between cylinder standards, determined by multiple overlap comparisons, have been removed (thus in the absence of systematic effects, no trend or discontinuity is anticipated in this plot). Times of analysis of ice core (ice'YY) and CGAA archived air (arc'YY) used in this paper are indicated. Significant events (e.g., "APC in") are identified in the text.

transducer installed with the APC) was correctly identified. Note that during this period, the first cylinder analysis in a session (marked by a cross in Fig. 2) is systematically lower than the mean of other standard analyses in the session. This is mentioned further in the ice core analysis section below.

Allison and Francey (1999) provide more detail on the various systematic effects of Fig. 2, and describe the calibration strategy, based on the air standards, which overcomes the influence of all of these effects on the $\delta^{13}C$ value of flask samples pre-treated via the MT Box-C and analysed during automated sequences. All samples analysed via the MT Box-C are reported relative to the average of air standard determinations in a session (excluding the first). An air standards calibrations scale, CG92, was determined by 163 measurements of

the primary reference tank (UAN900001) over a 2-month period in 1992. During this time the mean difference between 8 in situ and 14 flask samples from Cape Grim was 0.008 ± 0.010‰, not significantly different from zero. We generally assume no difference between the CG92 air standard scale and the "in situ" or the 1987 HC453 CO_2 scale. The effectiveness of the calibration strategy is dramatically illustrated in a comparison between the in situ and flask values adjusted onto the CG92 scale over the full period of 1992–1996 by Allison and Francey; the differences in the annual average of in situ and flask values reduce to 0.001, 0.001, 0.010, 0.019 and 0.002‰ respectively, which is close to our target precision for comparing different sampling strategies.

There is an inherent implication here that the in situ record is correct. The implication should

be questioned. Large inter-annually varying differences (up to 0.1‰) through the 1980s between the Cape Grim in situ δ^{13}C record (Francey et al., 1995b) and comparable results from the Scripps Institution of Oceanography record (Keeling et al., 1995) are well documented. Since 1991, the possibility of error in the Cape Grim in situ δ^{13}C record is substantially diminished (but not totally excluded) by a close on-going "operational inter-comparison" with a totally independent extraction and analysis mass spectrometer system (Francey et al., 1994; Masarie et al., personal communication). The full Cape Grim in situ record, and the flask record from 1991, are available from CDIAC (http:\\www.cdiac.ornl.gov) or directly via ftp: ftp atmos.dar.csiro.au; login: anonymous, password: your e-mail address; cd GASLAB\c13co2.

6. The Cape Grim Air Archive (CGAA)

Prior to 1991, we have obtained additional information on the Cape Grim δ^{13}C record from the Cape Grim Air Archive. The CGAA has proven useful for reconstructing the atmospheric histories of a large range of species back to 1978, including species for which no measurement methodology existed until recently, and species for which inadequate calibration existed over the last 2-decades (Langenfelds et al., 1996). In this case we were able to measure 40 suitable CGAA tanks on two separate occasions, mostly over 6 months in 1994, with a subset spanning the whole period repeated in early 1995 (see "arc'95" in Fig. 2). The relative precision of routine samples analysed and confirmed over such short periods is close to the external precision of ± 0.015‰.

The CGAA is stored in metal containers, mainly electropolished 35 litre stainless steel tanks. To collect the air samples, the tanks were pressurised to around 10 bar with Cape Grim baseline air using immersion in liquid nitrogen assisted by a metal bellows diaphragm pump. For approximately half of the tanks, the air was dried cryogenically using an ethanol bath at $\sim -80°$C; for the remainder, air was not dried, however after collection, tanks were thawed for 1–2 days in an inverted position (with the valve at the bottom) and the valve momentarily opened to blow out collected water. In Fig. 3, the two filling strategies (dry and wet) are identified by symbol and there

is a clear tendency for the wet filled tanks to fall below the Cape Grim in situ δ^{13}C record.

We also observed that the wet tanks exhibited large depletions in δ^{18}O of CO$_2$ compared to atmospheric values. Fig. 4 shows the "δ^{13}C anomaly" in the tanks, defined as the difference of "deseasonalized" archive tank data from a 2.5-year smoothing spline through the in situ record, plotted against measured δ^{18}O (the seasonal correction uses a harmonic fit to the in situ data). The wet and dry tanks are clearly distinguished and there is a significant empirical relationship—the exact mechanism for the anomaly in δ^{13}C is not understood, but is possibly related to disequilibrium generated by the blowing out of the excess cold water.

The Fig. 4 regression is used to correct all points in Fig. 3 (insignificant in the case of dry tanks). The remaining apparent scatter in the Archive record is now seen to generally correspond to seasonal features of the in situ record. Three points extend the Cape Grim record back to 1978. The 1978 point is a dry tank, well behaved in all species analysed; the other two are wet tanks exhibiting anomalous δ^{15}N, but retained here because of the sparsity of data in this period. δ^{15}N has proven to be a good diagnostic for effusive leakage from some tanks. The direction of the δ^{15}N correction is indicated in Fig. 4 for the 1980 and 1982 points; based on the timing of δ^{15}N versus δ^{13}C measurements, upper limits to the corrections are 0.048‰, 0.024‰ respectively bringing the points back close to the plotted symbols for wet tanks (note: a more accurate δ^{13}C from these tanks may result from further tests to establish the relative δ^{13}C and δ^{15}N drift rates). The CGAA record supports the long-term calibration stability in the Cape Grim in situ record and provides a reliable 1978 point to extend the record.

7. Firn air samples

The flask samples collected from the Law Dome firn are treated identically to routine Cape Grim flasks in terms of analysis and conversion to the CG92 scale. However, the composition of air in the firn is modified by gravity and diffusion which become appreciable effects at the 1 part in 10^5 precision attempted here. The effect of gravity can
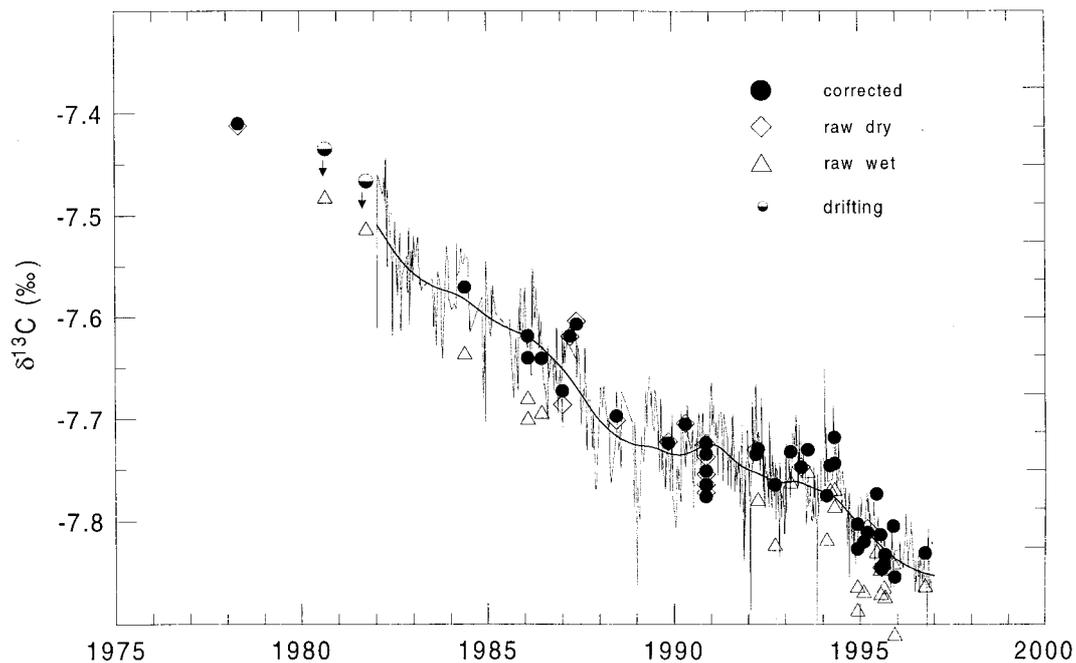
Fig. 3. The δ^{13}C of CO_2 in the Cape Grim Air Archive (CGAA). The diamonds (generally obscured) and triangles show measured values for tanks filled dry and wet respectively (see text). Filled circles are all values, corrected using an empirical relationship (see Fig. 4). Corrected values are significantly different only for the wet tanks. The half-filled circles represent two tanks in which values (in particular δ^{15}N) are drifting, but retained in this plot because they predate the in situ record and may be refined by future drift rate measurements (see text). The in situ record is shown by fine grey lines between points (exhibiting a seasonal variation of around 0.05‰), and a dark line representing a 2.5 year smoothing spline.

be independently estimated via measurement of δ^{15}N in the firn since the stability of N_2 concentration in the atmosphere means that an equilibrium depth profile for this isotope is established in the firn. The increasing CO_2 in the atmosphere means that an equilibrium situation is not established for δ^{13}C, so that the slightly faster diffusion rate of ^{12}C compared to ^{13}C becomes important. The resulting influence, which depends on relative diffusion coefficients and the atmospheric growth rate, is more fully explored by Trudinger et al. (1997) using a firn-diffusion model. Note however, that at the very high accumulation Law Dome sites, the model produces different changes in δ^{13}C and δ^{15}N even for assumed constant atmospheric CO_2. This is because vertical advection also limits the degree to which gravitational separation is established. The modelled δ^{13}C/δ^{15}N changes of 0.94 for DE08 and 0.97 for DSS can be used to

scale measured δ^{15}N changes to predict the relative δ^{13}C gravitational corrections for the two sites.

The effects of gravity and the growth-rate-related effect of diffusion in the firn are shown to be effectively additive, a fact used in Fig. 5 to illustrate the magnitude of both influences on δ^{13}C of CO_2 at the Law Dome DE08 site. The gravitational correction is shown both for measured δ^{15}N, and from the model in which the correction is effectively determined by tuning the model against atmospheric CO_2 and SF_6 profiles (and checking with CH_4). The measured δ^{15}N at the surface of the firn (1993 point) does not agree well with Cape Grim, and the firn δ^{15}N generally exhibit more scatter than is expected. In order to avoid introducing δ^{15}N measurement scatter to the δ^{13}C from the gravitational correction, and to obtain consistent corrections for firn and ice (see below), we use the model values here. Trudinger et al.
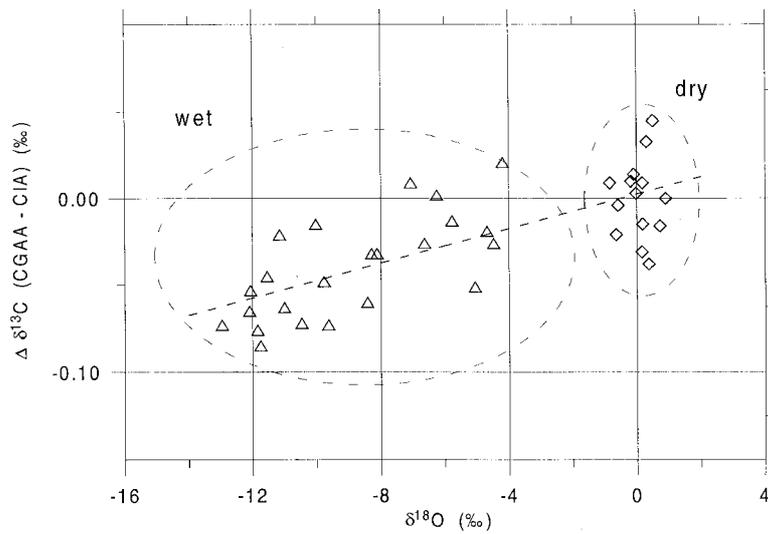
Fig. 4. The empirical relationship between δ^{13}C anomaly (difference from the smoothed Cape Grim in situ record, CIA) and measured δ^{18}O of the CO$_2$ in the CGAA tanks. The "wet" filled tanks have depleted ^{18}O. The linear regression through the points has the equation: $\Delta\delta^{13}$C $= 0.0050(\pm 0.0007)\delta^{18}$O $+ 0.003(\pm 0.006)$‰.
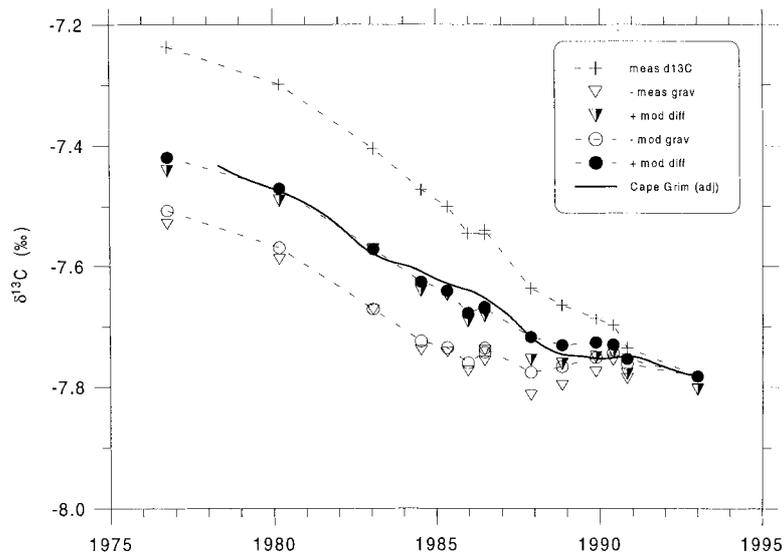
Fig. 5. The effects on δ^{13}C values with depth in the firn at DE08, Law Dome, of gravity and of diffusion in the firn. The effects of gravitational settling are first applied to the measured δ^{13}C (+ symbols) using both measured δ^{15}N (scaled by a factor of 0.94, open triangles) and the modelled δ^{13}C gravitational correction (open circles). The model of firn diffusion (Trudinger et al., 1997) predicts the degree to which gravitational settling is offset by carbon isotope diffusion in the non-equilibrium situation of rising CO$_2$ levels (leading to half-filled triangles and filled circles after application to the measured and modelled gravitational correction cases, respectively). The final corrected values are compared to a spline fit through the Cape Grim record (solid line, adjusted by -0.015‰ to agree in 1993, a difference consistent with the latitudinal gradient).

(1997) show that the model diffusion correction at DE08 survives a critical test when applied to $\delta^{13}CH_4$ (where the "growth-rate" correction dominates the gravitational correction). The trends in the corrected firn $\delta^{13}C$ curve in Fig. 5 bear a close resemblance to the Cape Grim record (adjusted by −0.015‰ to agree with the firn in 1993, see the discussion section below).

8. Ice core samples

8.1. Gravity and atmospheric growth-rate related diffusion corrections

The air trapped in ice bubbles has already undergone modification in the firn. The firn diffusion and trapping model of Trudinger et al. (1997) provides a framework for predicting the magnitude of these effects in the bubbles. Assuming constant snow accumulation at each drilling site, the record of CO_2 in the atmosphere of Etheridge et al. (1996) was used with the firn model to estimate the diffusion correction in the firn at the DE08, which has been applied to both DE08 and DSS sites. The diffusion correction for $\delta^{13}C$ is large for recently trapped air ($\sim 0.1‰$ for 1970) but becomes insignificant ($< 0.01‰$) prior to industrialisation when atmospheric changes are small.

The deepest DE08-2 firn samples had measured $\delta^{15}N = 0.31‰$, corresponding to a $\delta^{13}C$ gravitational correction of 0.29‰ (this is considered an upper limit to the value trapped in ice, which comprises bubbles sealed over a range of depths). A few isolated measurements of $\delta^{15}N$ in air extracted from DE08 ice suggested a $\delta^{13}C$ gravitational separation correction of $0.22 \pm 0.04‰$, and even more preliminary measurements in DSS ice give $\sim 0.22‰$. Because of the preliminary and scattered nature of the ice core $\delta^{15}N$ measurements, we have chosen to use the firn model result of 0.26‰ for $\delta^{13}C$ in DE08-2 and DE08. Assuming a similar relationship between diffusivity, porosity and density for the lower accumulation and colder DSS site also provides a 0.26‰ gravitational correction.

8.2. Extraction details

Two extraction processes are involved for ice core samples, : air from ice, and CO_2 from the air. The extraction of air from ice is described in detail by Etheridge et al. (1996). In a typical crushing of 1 kg of ice, pressure in the sample trap can be as high as 1 Mpa. Even after analyses on two gas chromatographs for trace gas concentrations, remaining pressure can conceivably exceed 450 kPa on occasions, above which there will be incorrect operation of the MT Box-C pneumatic inlet valves (Francey et al., 1996a). For this reason, ice core air samples are admitted to the MT Box-C via a small stainless steel expansion volume to halve the pressure. All of the air from the expansion volume is then processed to extract the CO_2.

8.3. Blank corrections

Blank tests have been carried out aimed at measuring the combined effect of air and CO_2 extractions, as well as various intermediate steps, including the transfer of air to the MT Box-C and the final CO_2 extraction. The tests involve using high-pressure cylinder air with isotopic composition established by direct extractions on the MT Box-C via a pressure regulator. Regulators have the potential to influence $\delta^{13}C$, but the influences can be demonstrated as insignificant in the present case as a result of careful regulator selection, preconditioning and dedication to the cylinder for its lifetime. For the blank tests, we have used two high-pressure cylinders of natural air, filled using an oil-free Rix compressor with phosphorous pentoxide drying (Francey et al., 1996a). The cylinders were filled at Cape Schanck (38.5°S, 144.9°E) in conditions of strong winds from the south-west (Southern Ocean) sector. Cylinder air was introduced via the regulator, at various stages into the sequence involving the ice crushing container, sometimes with "bubble-free" laboratory ice, the full crushing and air extraction step, transfer via the trap, and the CO_2 extraction sequence. A total of 46 such blank tests were conducted.

These tests included specific comparisons of 8 individual traps using sample sizes indicated by a mass spectrometer mass 44 collector voltage output of 3.8 ± 0.5 volts. Of the 7 traps used for ice core analyses the standard deviation of the mean value of 25 analyses of air from cylinder CC was 0.017‰. The traps are not distinguished in what follows, and thus ice core analyses are expected to have scatter at least at the 0.017‰ level.

Two full "bubble-free" ice crushing tests yielded differences of −0.053 and −0.062‰ from the tank

value established directly through a regulator. In tests in which the full crushing sequence was carried out, but only the bubble-free ice was omitted, the results were $\Delta\delta^{13}C = -0.053 \pm 0.019‰$ ($n = 11$), suggesting no additional influence of the ice crushing.

We initially interpreted the results as requiring an ice core "blank" correction of $\sim +0.05‰$ (Francey et al., 1996b). However, this assumes that the conversion onto the CG92 scale will be the same when air is extracted directly from the regulator, compared to the same air extracted from the various containers (crushing volume, trap, expansion volume) involved in transferring ice core air. A number of pieces of evidence have emerged which suggest this is not the case.

We now argue that the analyses involving the transfer containers, like the Cape Grim in situ analyses, should not be normalised against the air standards, rather, should be expressed against the pure CO$_2$ HC453 standard. Thus, the true "blank" for ice core samples is the difference of $\sim -0.11 \pm 0.03‰$ ($n = 46$) between cylinder air measured via the transfer container relative to HC453, and the same air determined directly through the regulator and normalised onto the CG92 air standard scale. The physical basis for the argument relates to the parameters of the cryogenic CO$_2$ extraction from air. Using factory settings and normal flask or cylinder samples, typically 1.5 bar is maintained at the multiport air inlet throughout the extraction in the MT Box-C, with cryogenic trap pressure rising to around 200 mbar during a 5-min extraction. For ice cores, and blank tests using the expansion volumes, pressure at the multiport inlet quickly falls to less than 1 bar and the pressure in the cryogenic traps is maintained for as long as possible at 15 mbar during a 5-min trap. In this regard, the expansion volume extractions have a similarity to the in situ CO$_2$, extracted at a constant 20 mbar at Cape Grim, and measured through the variable volume inlet (Fig. 1), and we treat them similarly. The circumstantial evidence supporting the argument are significant increases in scatter in the ice core record if the results are normalised onto the CG92 scale, and significant inconsistency between ice core and firn results. If the ice core data are corrected onto the CG92 scale as for the cylinder standards, they fall more than 0.1‰ below the firn data in the 1970s. Further circumstantial support comes from the lack of a

difference between the 1st-of-a-sequence, and later extractions of a session in the measurements from the transfer volumes, unlike the case for analyses directly from cylinders (Allison and Francey, in press). Our basic hypothesis implies that all routine extractions through the MT Box-C are in a marginal operating zone for complete extraction of CO$_2$ (shorter molecular mean free paths at the higher pressure do not guarantee a collision of every CO$_2$ molecule onto a cold surface) and/or removal of possible contaminants. The combination of fixed automated timing between extractions, of relatively constant CO$_2$ sample size (measured by a mass spectrometer sample voltage of ~ 4 V) and normalising onto the CG92 scale with the bracketing air standards effectively overcomes problems caused by the marginal operation, as demonstrated for the Cape Grim programs. The in situ and ice core samples are extracted in a pressure regime ensuring full CO$_2$ extraction and/or removal of contaminants. We proceed on the basis that the ice core samples should not be normalised, but corrected for the $-0.11‰$ blank.

8.4. Ethanol contamination

The mass spectrometer typically compares 4–8 alternating integrations of the sample and reference ion ratios to determine an average $\delta 45$ for the sample. A "preliminary $\delta 45$" can be calculated for each sample/reference pair. Some initial ice core measurements sampled in 1993, after initial stable "preliminary $\delta 45$", exhibited a rapid increase suggesting contamination. This phenomenon was tentatively identified with a contaminant with delayed passage through the mass spectrometer capillary reaching the ion source. Ethanol was a prime suspect, since it produces m/e 46, 45 and 44, and it was inadvertently stored in the ICELAB cold room. The delay is consistent with the higher melting point of ethanol compared to the sublimation temperature of CO$_2$. The combined measures of removal of the ethanol from the cold room and reprogramming of the MT Box-C vapour trap temperatures of the extraction line from $-80°C$ to $-100°C$ effectively eliminated the problem. At least two successive "preliminary $\delta 45$" differing by less than 0.2‰ were required to avoid rejection. We have rejected 10 DSS sample ratios on this criterion and accepted 13 with less than 4 cycles. These are identified in the tabulation of data below, and allocated a larger uncertainty.

8.5. Sample size effects

Compared to routine flasks, cylinder analyses and the blank tests, the ice core samples experienced a very wide range of sample mass 44 voltage outputs (V_{SA}), from 1.5 to 6 volts. An initial program study was undertaken to investigate the sample size limitations for ice core air analyses (Lang, 1991). This study (with $\delta 45 \sim -1.5‰$) documented at least 3 processes contributing to a variation of $\delta^{13}C$ with sample size.

(a) In very small samples, $V_{SA} < 1$ volt, even with balanced capillary flows, $\delta 45$ increased with increasing sample size, attributed to unstable operation as flow in the capillaries enters a non-viscous regime at low pressures.

(b) Increasing $\delta 45$ with increasing sample size was also documented for sample pressures (indicated by V_{SA}) less than reference gas pressure (V_{ST}) and vice-versa. In typical operation the reported V_{SA}/V_{ST} ratio (determined on the second of 4–8 cycles of reference-sample) in our MAT252 is around 0.9, and is accompanied by slightly different depletion rates for sample and reference gas. For constant V_{SA}/V_{ST} ratios, Lang (1991) used a second-order polynomial to describe the increase in $\delta 45$ with increasing V_{SA} (smaller changes at higher V_{SA}); the effect is larger for lower V_{SA}/V_{ST}.

(c) A competing effect, decreasing $\delta 45$ with increasing V_{SA}, which was subsequently attributed to a mixing between reference and sample gas in the source region of our MAT252 mass spectrometer (Francey and Allison, 1994). Subsequent to (and at least in part as a result of) these experiments, Finnigan-MAT GmbH modified the source region of the MAT252 in a way which substantially reduced this effect. Symptoms of the working gas effect are a bias in values towards the reference gas isotopic ratio, the size of which depends on the flushing time ("idle time") between reference and sample integrations, and the capillary flow ("sample size"). In this context, the $\delta^{13}C$ of the working gas given in eqn. (2) is extremely fortuitous, being, at $-6.4‰$, very close to the measured pre-industrial CO_2 isotope ratio ($\delta 45$ differences range from $-1‰$ in modern larger samples to around $-0.1‰$ in the older, and smaller, samples, which result in relatively uniform corrections over the whole range). Thus, the potentially large corrections are negligible in this case.

With the range of ice core sample sizes pro-cessed, (b) is of most concern. Because the relative importance and magnitude of the sample size influences are sensitive, to not-well-documented-fine adjustments to capillaries for example, we adopt an empirical approach. The residuals of a weighted smooth spline (through the otherwise fully corrected ice core samples) are examined for a sample size dependency consistent with the described influences. Only results after 1800 AD are considered, because low sample density prior to this time means that the spline fits most points by definition. The results are shown in Fig. 6 and a trend (significant at the 1% level) is evident. The trend is represented by a polynomial fit of the form used by Lang (1991), (which results in a marginally higher correlation than a linear regression, $r^2 = 0.16$ c.f. 0.12). The polynomial is close to zero above 3.8 volts, which is the mean sample size for the blank tests, and reflects the general features of a pressure imbalance effect, in particular, larger corrections at smaller sample sizes. In these data, V_{SA} is always $< V_{ST}$, and data are rejected for $V_{SA}/V_{ST} < 0.8$ (4 samples). The remaining data are corrected using the polynomial, adjusted to be zero at 4 volts which is the nominal sample size for routine flask samples and air standard analyses.
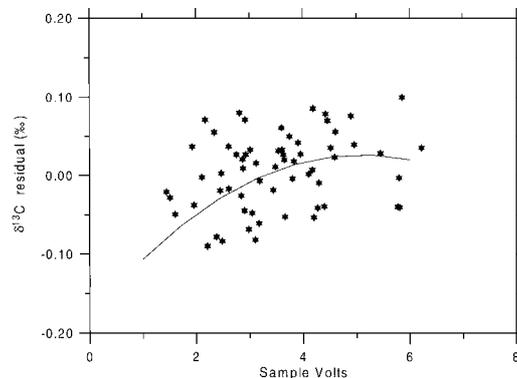
Fig. 6. Sample size dependency in the residuals of the initially obtained Law Dome ice core $\delta^{13}C$ record from a smoothing spline fit to the data. The spline fit is weighted according to data density and has an effective smoothing with half-width around 25 years, after 1800 AD. The polynomial fit ($y = -0.008x^2 + 0.081x - 0.180$) adequately represents the capillary imbalance process thought to be the main contributor to the sample size effect.

8.6. Summary of data selections and corrections

We distinguish here between the uncertainty associated with an individual measurement, and that associated with systematic biases between one group of measurements and another (specifically between ice cores, between ice cores and firn, and between these and global tropospheric measurements). Individual uncertainties are estimated from statistical scatter in measurements, except for documented anomalies, which are assigned (somewhat arbitrarily) larger uncertainties. These are used to weight points when obtaining smoothed curves for inversion studies (the relative weights being more important than the actual weights). The systematic biases between sets of data are not included in smoothing processes but are estimated and referred to in the discussion.

Of the 84 Law Dome ice core CO_2 values reported by Etheridge et al. (1996), 11 samples were not analysed for $\delta^{13}C$; and 58 provided reasonable $\delta^{13}C$ values. The 15 rejected values included:

- 1 failed analysis attempt;
- 4 samples were rejected on the basis of sample-reference capillary imbalance of $V_{SA}/V_{ST} < 0.8$,
- of 23 analyses influenced by ethanol contamination, 10 (including 1 $V_{SA}/V_{ST} < 0.8$) consisted of only 1 acceptable cycle of sample-reference comparison and have an estimated statistical uncertainty of around $\pm 0.1‰$.

(These points are not tabulated or used, but for perspective, are included as background points in Fig. 9, below).

Three other ethanol-affected samples provided 2 acceptable sample-reference comparisons, and 10 provided 3 comparisons. These have been allocated statistical uncertainties of $\pm 0.07‰$ and $\pm 0.05‰$, respectively.

For the remaining accepted ice core samples, we allocate a minimum measurement uncertainty of $\pm 0.025‰$. The mass spectrometer assigns a standard deviation, σ_n, where n is the number of sample-reference comparisons (for the accepted ice core samples, the mean σ_n is $\pm 0.016‰$). The $\pm 0.025‰$ value allows for the additional standard deviation of $\pm 0.017‰$ measured in the blank tests on the trap volumes. Where the $|\sigma_n| > 0.025$, the actual σ_n is used (3 samples). For the firn and archive samples, a conservative $\pm 0.02‰$ uncer-

tainty is appropriate for all samples. In fitting the data to obtain a Law Dome curve (firn and ice) we have allowed slightly larger uncertainties of $\pm 0.05‰$ on the shallowest ice core sample (DE08-2 012) and deepest firn sample (85 m depth) reflecting the difficulties in extracting air from the respective media in the transition region.

Errors in the systematic corrections necessary to obtain $\delta^{13}C$ of the ice core air from measured $\delta 45$ are more complicated. The maximum corrections are often large compared to the scatter in the record provided here. The magnitudes of the successive additive corrections are summarised in Fig. 7, and are briefly assessed for importance here in the order that they have been applied:

- The average sample size correction in the selected ice core data is 0.032 ± 0.023, 0.004 ± 0.015, $0.017 \pm 0.021‰$ for DSS, DE08, DE08-2, respectively. The standard deviations represent the range of sample sizes measured, which is larger for the generally smaller DSS samples (which also have the largest mean correction). We assume that errors in the correction are included in the estimates of uncertainty in Table 3, below. The corrections are relative to a 4 volt signal which is very similar to that for firn and other routine flask samples, adding no additional uncertainty between ice and other samples.
- The bleed correction of $-0.009 \pm 0.006‰$ overall is similar for all three cores, and flask samples and introduces no further uncertainty.
- The ^{17}O correction, not shown in Fig. 7, is large and variable, $0.031 \pm 0.088‰$. However, this is solely determined by the mass 46 ion current and a fixed tropospheric $^{17}O/^{18}O$ relationship and does not introduce significant uncertainty.
- The blank correction, taken as a constant $-0.11‰$, was determined to a precision of $\sim 0.025‰$. This is an additional uncertainty in the overall value of ice core samples relative to firn and CGAA samples The overall magnitude is dependent on our hypothesis of a pressure dependent fractionation during sample extraction in the MAT252 MT trapping box.
- The N_2O correction of $+0.238 \pm 0.007‰$ is determined by the measured N_2O/CO_2 values and is well determined with negligible scatter.
- The mean gravitational correction of $-0.26‰$, is uncertain due to the difficulty in identifying exactly when diffusion ceases and trapping
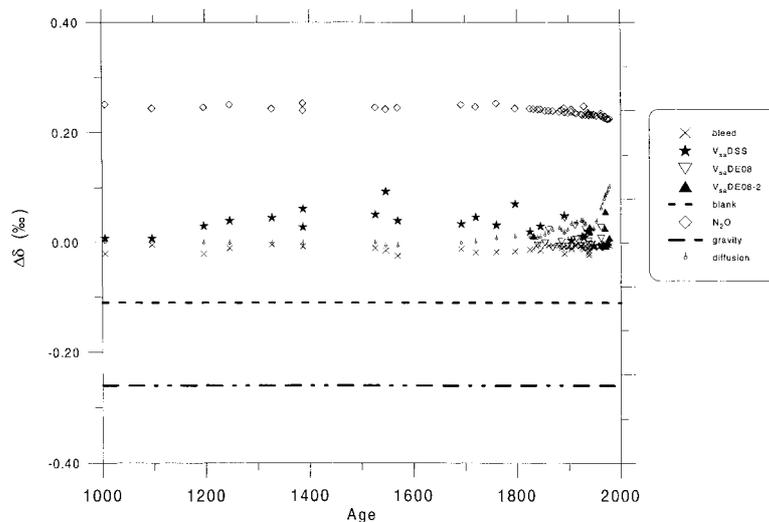
Fig. 7. The magnitude and sign of corrections made to measurements of ice core air $\delta 45$ to get $\delta^{13}C$, plotted as a function of CO_2 age of the sample. The ion correction for ^{17}O is not shown (see text).

occurs, and in this case, by the conflicting measurements derived from $\delta^{15}N$ at the deepest firn layers ($\sim 0.31‰$) compared to $\delta^{15}N$ measured in DSS ice bubbles ($\sim 0.22‰$). We note the very preliminary nature of our $\delta^{15}N$ measurement techniques, compared to $\delta^{13}C$. However, by using model values for both firn and ice we estimate the firn versus ice uncertainty at $<0.03‰$, and the DE08 versus DSS uncertainty at something less than this. The sample-to-sample scatter in one core is not known but assumed small due to the relatively constant accumulation at the Law Dome site. The uncertainty of Law Dome measurements relative to the troposphere from this correction is also estimated at $<0.03‰$.

- The diffusion correction varies from near zero pre-industrially (average $0.009 \pm 0.014‰$ in DSS) to around $0.1‰$ in the shallowest ice (0.037 ± 0.021, $0.065 \pm 0.038‰$ in DE08, DE08-2 respectively), Trudinger et al. (1997). The percentage uncertainty in the diffusion correction is mainly determined by uncertainty in the CO_2 growth rate in the atmosphere, and overall, the uncertainty is estimated here to be small, $<0.02\%$. There are similar considerations concerning firn-to-ice transition as for the gravitational correction, but the uncertainty is proportionately less.

- Empirical checks for dependence of $\delta^{13}C$ on analysis date or on "anomalous" carbon monoxide measured in the samples, which can be sensitive to contamination, yielded no significant dependency.

While the blank and gravitational corrections add uncertainty to the relative values between cores and the firn, we note that in Fig. 8 below, there is no evidence of offset between the 3 ice-cores in the period of overlap. The comparison of the Law Dome results with measurements at other sites is limited to a few hundredths of a per mil by knowledge of spatial gradients. The comparison of any GASLAB $\delta^{13}C$ analysis with those from other laboratories is limited by intercalibration uncertainties which are $<0.04‰$ with NOAA/CMDL (Masarie et al., in preparation) but maybe as large as $0.1‰$ with other laboratories.

9. Results

A tabulation of the fully corrected results for the Cape Grim Air Archive, the DE08-2 firn and the DE08, DE08-2 and DSS ice cores is given in Tables 1–3. Fig. 8 focuses on the comparison of the various records since 1800 AD. The full Law Dome isotopic record is plotted in Fig. 9. Error bars reflect the statistical errors discussed above.
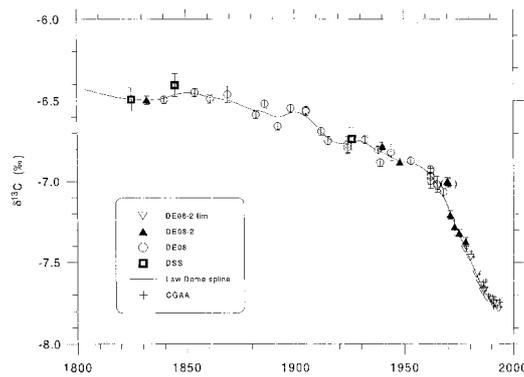
Fig. 8. The overlap between δ^{13}C in atmospheric CO$_2$ from, the Cape Grim Air Archive, firn at DE08-2 and ice cores DE08, DE08-2 and DSS, Law Dome, Antarctica. The smoothing spline is weighted by the statistical error in, and density of, data; effective smoothing is 25 years after 1800 AD and ~130 years before 1800 AD. Two points (bracketed), corresponding to the only 1995 DE08-2 analyses, are considered outliers and do not contribute to the spline.

A smoothing spline is shown (Enting et al., 1987) in which the degree of smoothing is determined by weighting with the allocated errors in Table 3. Prior to 1800 AD, when data density is ~2/century (compared to ~20/century after 1800 AD) the weighting is reduced by a factor of 10. Typical smoothing periods are 130 years and 25 years, respectively. We also note here that the spline fit through the data in Fig. 8 has ignored two DE08-2 points, bracketed. These two points are the only DE08-2 points measured in 1995 and are the most significant outliers. While there is no evidence for 1993 versus 1995 analysis differences in DE08 and DSS cores, we discount the 1995 DE08-2 points in the following discussion.

Note that the ice core CO$_2$ concentrations reported here are a constant 0.2 ppm less than those of Etheridge et al. (1996), reflecting adjustment of all CSIRO GASLAB measurements onto the WMO X93 mole fraction calibration scale.

10. Discussion

The Cape Grim records from the in situ program and the Cape Grim Air Archive are in excellent agreement with each other in Fig. 3, and closely agree in trend with the DE08-2 firn data

Table 1. *δ^{13}C in atmospheric CO$_2$ from the Cape Grim Air Archive*

Sample	Air age (dec. year)	CO$_2$ (ppm)	δ^{13}C (‰)	Comment
780001	1978.318	333.8	−7.41	d
800003	1980.672	336.2	−7.43	w
810002	1981.761	336.9	−7.47	w
840004	1984.393	341.7	−7.57	w
860001	1986.097	344.2	−7.64	w
860002	1986.097	344.5	−7.62	w
860003	1986.466	344.3	−7.64	w
870002	1987.019	345.3	−7.67	d
870004	1987.229	346.4	−7.62	d
870006	1987.407	346.2	−7.61	d
880002	1988.471	348.5	−7.70	d
890005	1989.852	350.8	−7.72	d
900048	1990.318	351.4	−7.70	d
900001	1990.869	352.4	−7.78	d
900006	1990.869	352.2	−7.72	d
900050	1990.871	351.6	−7.76	d
900005	1990.871	352.0	−7.75	d
900051	1990.871	351.8	−7.73	d
920469	1992.213	353.5	−7.73	d
920408	1992.269	353.9	−7.73	w
920655	1992.727	354.1	−7.76	w
930278	1993.146	354.6	−7.73	w
930620	1993.433	354.9	−7.75	d
931007	1993.611	354.5	−7.73	w
940378	1994.111	355.7	−7.77	w
940379	1994.205	356.0	−7.75	w
940679	1994.321	355.8	−7.74	w
940678	1994.321	355.9	−7.72	w
941413	1994.933	357.7	−7.83	w
941412	1994.933	357.8	−7.80	w
950242	1995.102	357.1	−7.82	w
950527	1995.199	357.6	−7.81	d
950789	1995.449	358.2	−7.77	w
950890	1995.546	357.9	−7.81	w
950891	1995.563	357.6	−7.84	w
950894	1995.586	358.5	−7.85	d
951018	1995.643	358.6	−7.84	w
951019	1995.667	358.6	−7.83	w
960050	1995.893	358.5	−7.80	w
960051	1995.925	358.6	−7.85	w
961409	1996.755	359.8	−7.83	w

The data have been deseasonalised using a seasonality determined from a harmonic fit to flask records; the comment column indicates whether the air was dried on filling (d) or the tank was filled "wet" (w). The uncertainty on data points is conservatively estimated at ±0.02‰. The CO$_2$ mixing ratios are expressed on the WMO X93 mole fraction calibration scale.

Table 2. $\delta^{13}C$ in atmospheric CO_2 from the Law Dome firn at DE08-2

Sample	Air age (dec. year)	CO_2 (ppm)	$\delta^{13}C$ (‰)	Comment
930349	1976.77	332.6	−7.42*	85
930341	1980.18	335.5	−7.46	80
930337	1983.07	339.9	−7.57	75
930336	1984.53	342.9	−7.63	70
930335	1985.34	344.0	−7.64	65
930348	1985.97	344.6	−7.67	60
930347	1986.48	345.3	−7.67	55
930346	1986.48	345.5	−7.66	55
930343	1987.89	347.8	−7.73	40
930342	1988.85	349.8	−7.74	30
930340	1989.88	351.4	−7.75	20
930339	1990.41	352.2	−7.74	15
930338	1990.84	352.8	−7.76	10
930345	1993.08	354.6	−7.80	0

The firn CO_2 age has been determined from a firn diffusion model calibrated against several species measured in the firn (Trudinger et al., 1997). The uncertainty on data points is conservatively estimated at ±0.02‰, except for the deepest value (asterisked) which is assigned ±0.05‰. The CO_2 mixing ratios are expressed on the WMO X93 mole fraction calibration scale.

(Fig. 5). We note that the age spread of air in the firn increases from <1 year at the surface to 12.5±1.5 years at the deepest layers in DE08-2 (Levchenko et al., 1997). Thus, while the $\delta^{13}C$ flattening in the 1990s is evident in the firn record, possible large inter-annual variability around 1984 (such as that reported in the atmosphere by Keeling et al., 1995) will be smoothed by diffusion and mixing at deeper layers. The firn profile is therefore not able to distinguish between the Keeling et al. and the Cape Grim in situ versions of the atmospheric record in the early 1980s. The Air Archive supports the Cape Grim in situ record through this period, but does not conclusively resolve the main conflict with Keeling et al. since the CGAA record basically depends on one tank in 1984.

Though the trends agree well, the Cape Grim data are, on average, 0.015‰ higher than the fully corrected firn record. We note however, that there is no significant difference between Cape Grim and South Pole data as measured by the CSIRO program (not shown). The difference between Cape Grim and the firn is in the direction of a latitudinal

gradient of ∼0.04‰ observed between Tasmania and the coast of Antarctica on a number of (mainly summer) ship transects (Beggs, 1996). The lower coastal Antarctica ship values are attributed to a ^{13}C disequilibrium flux with the oceans which varies due to the temperature dependence in the air-sea fractionation factor (Mook et al., 1974); the sea surface temperatures on the coast of Antarctica are >10°C lower than at Cape Grim. Keeling et al. (1989b), using a 3D model of atmospheric transport, estimate a difference of ∼0.04‰, but their assumption of constant mixed layer $\delta^{13}C$ means this is an upper limit. Rayner and Law (personal communication) estimate a difference of ∼0.024‰, also using a 3D model with prescribed sources. There are quantitative uncertainties associated with each of these approaches, including the degree to which the Law Dome sites, some 150 km inland, reflect the oceanic draw down. Uncertainties in the mean gravitational correction have a similar influence. In the present context we conclude that the observed difference between firn and Cape Grim is consistent with expectation (sampling at Casey station at 66°S, 110°E, has commenced to verify this result).

While the main purpose of this paper is to present and document the 1000 year $\delta^{13}C$ record, preliminary comment is made on major features. The 1000-year $\delta^{13}C$ record in Fig. 9 exhibits systematic variability on several time-scales. The overall decrease during the last 1–2 centuries is attributed to anthropogenic emissions. Maximum $\delta^{13}C$ occur during a 1600–1800 AD period, reported by Etheridge et al. (1996) as a ∼6 ppm CO_2 decrease and linked to "the little ice age" (LIA). The $\delta^{13}C$ enhancement during this period provides a clear example of the additional constraints on the carbon cycle provided by the $\delta^{13}C$ measurements. Trudinger et al. (1999) use a box diffusion model constrained by these data to demonstrate that a global CO_2 response resulting from the influence of decreased temperature (∼1°C) on terrestrial biota (influencing both respiration and photosynthesis) adequately explains both the CO_2 and $\delta^{13}C$ ice core records. In contrast the response to similar oceanic surface cooling is to give a CO_2 decrease but also decreased $\delta^{13}C$. This result isolates global cooling during the LIA, which would be expected in the sea-surface temperatures, instead preferring regional cooling over the land

Table 3. *δ^{13}C in atmospheric CO$_2$ from the Antarctic ice cores DE08, DE08-2 and DSS*

Sample	CO$_2$ air age (dec. year)	CO$_2$ (ppm)	δ^{13}C (‰)	Error (‰)	Comment
DE08-2 012	1978	331.8	−7.37	0.050	
DE08-2 003	1975	331.0	−7.32	0.025	
DE08-2 002	1973	327.9	−7.28	0.050	3c, CO
DE08-2 005	1971	323.9	−7.21	0.025	
DE08-2 015	1970.2	325.0	−7.01	0.025	95
DE08-2 016	1969.7	324.5	−7.00	0.025	95
DE08 235	1968	323.5	−7.07	0.025	
DE08 226	1965	318.6	−7.02	0.050	3c
DE08 225	1965	319.3	−7.02	0.025	
DE08 214	1962	319.2	−6.96	0.050	3c
DE08 215	1962	316.8	−6.99	0.050	3c
DE08 212	1962	318.5	−6.93	0.025	CO
DE08 213	1962	316.8	−6.97	0.050	3c
DE08 236	1953	312.5	−6.87	0.025	CO
DE08-2 009	1948	309.7	−6.88	0.025	
DSS 029	1948	311.2	−6.90	0.025	CO
DE08 227	1944	309.5	−6.82	0.050	3c
DE08-2 007	1940	310.3	−6.78	0.025	
DE08 243	1939	310.8	−6.88	0.025	
DSS 037	1939	309.0	−6.77	0.027	95
DE08 240	1938	310.3	−6.80	0.025	
DSS 027	1936	307.7	−6.83	0.025	
DE08 238	1932	307.6	−6.74	0.025	
DSS 041	1929	305.0	−6.72	0.025	95, CO
DSS 008	1926	304.8	−6.74	0.070	2c
DE08 231	1924	304.6	−6.79	0.040	
DE08 237	1924	303.9	−6.77	0.050	3c, CO
DE08 233	1915	301.1	−6.75	0.025	
DE08 239	1912	300.5	−6.69	0.025	
DE08 253	1905	297.1	−6.56	0.025	95
DE08 254	1905	298.3	−6.56	0.025	95
DSS 033	1905	298.8	−6.65	0.025	95
DE08 230	1898	294.5	−6.55	0.025	
DE08 241	1892	294.4	−6.66	0.025	
DSS 030	1891	294.5	−6.61	0.050	3c, CO, bal
DE08 252	1886	293.9	−6.52	0.025	
DE08 229	1882	291.7	−6.59	0.025	95, CO
DE08 228	1869	287.2	−6.46	0.050	3c
DE08 232	1861	286.4	−6.49	0.025	CO
DE08 234	1854	284.7	−6.45	0.025	
DSS 009	1845	285.9	−6.40	0.070	2c
DE08 222	1840	282.8	−6.49	0.025	
DE08-2 006	1832	284.3	−6.50	0.025	CO
DSS 010	1825	284.9	−6.49	0.070	2c
DSS 015	1796	283.5	−6.33	0.050	3c, CO, bal
DSS 031	1760	276.5	−6.28	0.025	95
DSS 019	1720	277.3	−6.31	0.025	CO
DSS 011	1692	276.3	−6.25	0.025	
DSS 032	1570	281.7	−6.32	0.025	95
DSS 018	1547	282.6	−6.32	0.031	
DSS 035	1527	283.0	−6.33	0.025	95
DSS 024	1387	279.8	−6.36	0.025	
DSS 026	1387	280.2	−6.36	0.025	

Table 3. *(Cont'd.)*

Sample	CO$_2$ air age (dec. year)	CO$_2$ (ppm)	$\delta^{13}C$ (‰)	Error (‰)	Comment
DSS 034	1327	283.2	−6.36	0.025	95
DSS 039	1246	281.5	−6.36	0.025	95, CO
DSS 036	1196	283.7	−6.36	0.025	95, CO
DSS 042	1096	282.2	−6.41	0.025	95, CO
DSS 038	1006	279.2	−6.44	0.025	95, CO

Ice $\delta^{13}C$ errors have been estimated as described in the text. Comments on the ice core $\delta^{13}C$ refer to the number of sample-reference integrations (2c, 3c), analysis in the 1995 session (all others 1993), suspect pressure imbalance through sample and reference capillaries (bal, $0.8 < V_{SA}/V_{ST} < 0.9$), or enhanced carbon monoxide in the sample (>75 ppb). Note: no influence of enhanced CO or analyis year on $\delta^{13}C$ is evident.
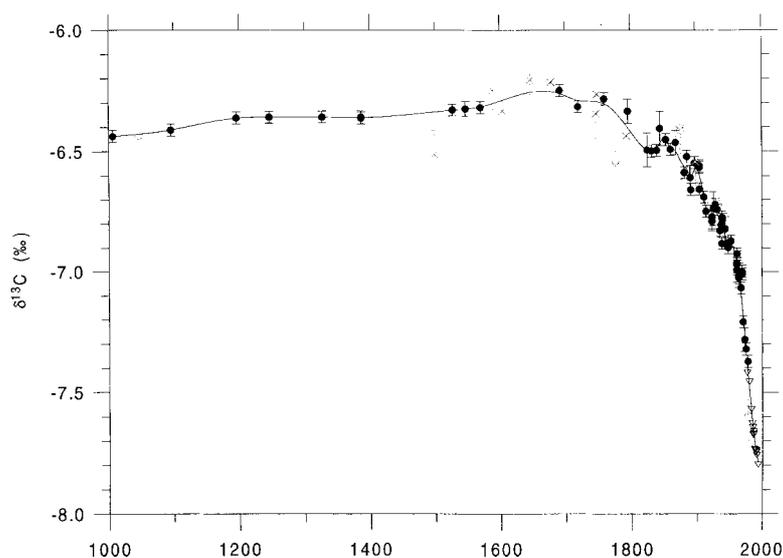
Fig. 9. The complete record of CO$_2$ and $\delta^{13}C$ from the Law Dome ice cores and firn. The smoothing spline is weighted by the statistical error in, and density of, data; effective smoothing is 25 years after 1800 AD and ~ 130 years before 1800 AD. (Light grey symbols are rejected points from the section "Summary of data selections and corrections" and are included here only to provide a perspective on the selection processes. Crosses indicate ethanol contaminated samples, open circles are other rejections).

masses of the northern hemisphere, a result consistent with reported European and Asian historical records, as well as a high precision CH$_4$ record from these ice cores (Etheridge et al., 1998).

It is apparent that the ice core results presented here are not compatible with trends reported from tree ring and coral records. They are more consistent with early, less precise, ice core determinations reported by Friedli et al. (1986), see Fig. 10a. The only century-scale record with comparable small scatter to our data are the recent ocean DIC data of Böhm et al. (1996). These are compared in Fig. 10b

via the mixed layer DIC $\delta^{13}C$ provided by the Trudinger et al. box diffusion model (which is tuned primarily to ^{14}C data but also gives good agreement with $\delta^{13}C$ atmospheric record from this study).

The comparison between the model tropospheric $\delta^{13}C$ (derived from the Etheridge et al. CO$_2$ data) and model global DIC variations shows the marked suppression of temporal variation in the ocean mixed layer due to the different buffering of the ^{12}C signal compared to ^{13}C, discussed further below. The Böhm et al. (1996) DIC curve gives slightly more overall change (~ 0.1‰) in
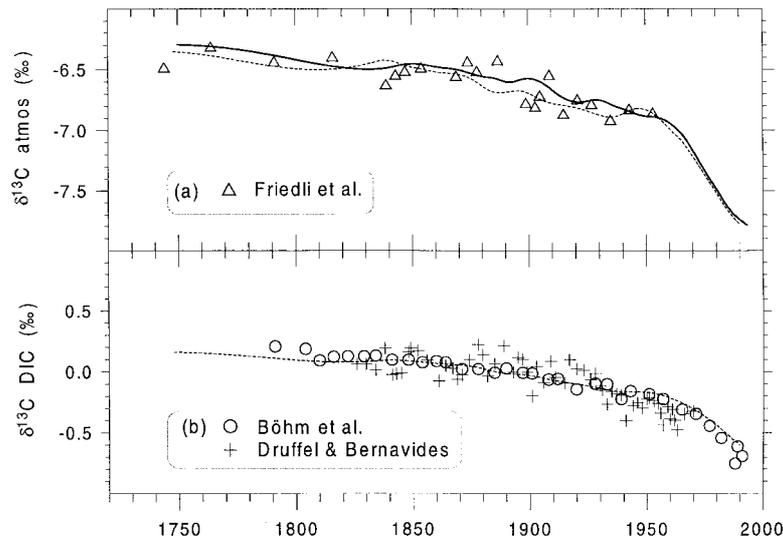
Fig. 10. Comparisons with other published records. (1) The ice core δ^{13}C data of Friedli et al. (1986, triangles) are compared to the Law Dome ice cores and firn using the spline of Figs. 8, 9 (solid line), and to model troposphere δ^{13}C derived from the Law Dome CO$_2$ record (dashed line, Trudinger et al., this volume). (2) The proxy DIC δ^{13}C data of Böhm et al., 1996 (circles, +4.674) and Druffel and Bernavides, 1986 (crosses, −0.193) are compared to the model mixed layer DIC (dashed line, +2.294) from the same model run used in (a). The numbers in brackets above are values, averaged over the 1820–1940 period, used to normalise each record to zero over this period to aid comparison of the temporal behaviour.

δ^{13}C than our model value, by an amount which is most likely accommodated by different tuning of key exchange parameters in the respective models. There is reasonable support for similar multi-decadal behaviour through the 19th century in both the sponge and ice core CO$_2$ data. The large mean decline in the more scattered sponge data of Druffel and Bernavides (1986) between 1900 and 1950 is not supported by the newer data.

Multi-decadal time-scale features are evident in Fig. 8 as a much larger contribution to variance compared to the fossil fuel signature, than is the case for CO$_2$ concentration of Etheridge et al. (1996). In fact, the δ^{13}C decrease appears to have proceeded via a series of "steps", the most recent of which is in the 1990s. This is illustrated more clearly in Fig. 11, which plots the δ^{13}C versus CO$_2$ concentration, and compares the result to the single deconvolution of the Etheridge et al. CO$_2$ record using the box diffusion model (Trudinger et al., this volume). Some extra variance in the δ^{13}C record is anticipated from the different response times of ^{12}C and ^{13}C in exchange between atmosphere and ocean (Siegenthaler and Oeschger, 1987), however the

effects seem more marked in this record. Whether the extra variability in the δ^{13}C record reflects changes in the net partition of uptake between land and ocean (changes a single deconvolution is unlikely to capture) or changes in the isotope disequilibrium fluxes (e.g., due to ocean circulation or biology related mixed layer δ^{13}C changes), is the subject of ongoing study.

Apart from providing new information on natural variability, a prime application of the δ^{13}C data is in constraining global carbon cycle models, in particular those attempting to predict the global response to increasing atmospheric burdens of CO$_2$. The δ^{13}C trend presented here is quite different from the exponential decrease assumed by Heimann and Maier-Reimer (1996) in order to "dynamically constrain" ocean uptake. Though their overall conclusion is not sensitive to small deviations from the assumed trend, clearly conclusions on less than century timescales will require the more detailed information. Preliminary box-diffusion model tuning using these data is presented by Trudinger et al. (this volume).

Future work on this record is planned and will
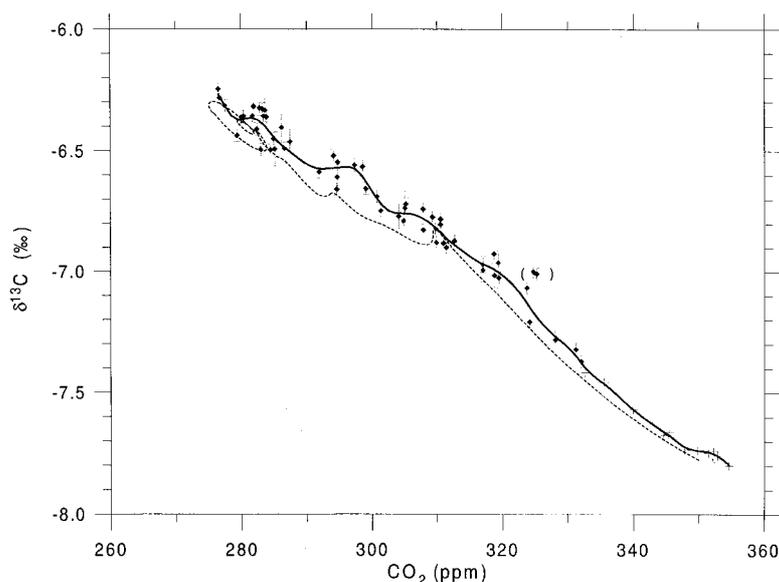
Fig. 11. The complete record of $\delta^{13}C$ from the Law Dome ice cores and firn plotted against the measured CO_2 concentration. A smoothing spline (solid line) through the data is weighted by the statistical error in, and density of, data. Two points (bracketed) corresponding to the only 1995 DE08-2 analyses are considered outliers and do not contribute to the spline. The dashed curve is a single deconvolution of the CO_2 data using the box diffusion model described by Trudinger et al. (this volume).

focus on significantly improved data density, particularly prior to 1800 AD. At the same time, a number of opportunities to improve precision have been identified, including the more accurate determination of the relative gravitational corrections between ice cores, and cores versus firn (via improved $\delta^{15}N$ measurements), and reduced sensitivity to blank and sample size biases.

11. Acknowledgements

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