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A record of atmospheric halocarbons during the twentieth century from polar firn air

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Measurements of trace gases in air trapped in polar firn (unconsolidated snow) demonstrate that natural sources of chlorofluorocarbons, halons, persistent chlorocarbon solvents and sulphur hexafluoride to the atmosphere are minimal or non-existent. Atmospheric concentrations of these gases, reconstructed back to the late nineteenth century, are consistent with atmospheric histories derived from anthropogenic emission rates and known atmospheric lifetimes. The measurements confirm the predominance of human activity in the atmospheric budget of organic chlorine, and allow the estimation of atmospheric histories of halogenated gases of combined anthropogenic and natural origin. The pre-twentieth-century burden of methyl chloride was close to that at present, while the burden of methyl bromide was probably over half of today’s value.

Chlorofluorocarbons (CFCs) and other halocarbons have been used as refrigerants, propellants and solvents since the early to middle twentieth century. Both leakage and direct emission, in combination with long atmospheric lifetimes, have resulted in a steady accumulation of these gases in the atmosphere, allowing them to increase the burden of atmospheric chlorine (Cl) from ~0.5 nmol Cl mol\(^{-1}\) (that is, 0.5 parts per billion, p.p.b.) to a peak of over 3.5 nmol Cl mol\(^{-1}\) by 1992–94.\(^{12}\) Suggestions that a build-up of CFCs and long-lived halocarbons in the atmosphere could result in the depletion of stratospheric ozone prompted the need for systematic measurements\(^1\), but only in the mid-1970s were routine atmospheric monitoring programmes begun.\(^3\) Industrial production and emission data, together with atmospheric lifetimes, have been used to estimate the atmospheric burden of CFCs before their detection and measurement.\(^6\) Until now, however, no data have been available for testing these early estimates.

Natural sources have been suggested for many of the halocarbons involved in the depletion of stratospheric ozone.\(^4\) Atmospheric methyl chloride (CH\(_3\)Cl), for example, is believed to be predominantly of natural origin, although it does have a few anthropogenic sources and there appear to be unidentified sources of this gas.\(^7\) The division of methyl bromide (CH\(_3\)Br) emissions into natural and anthropogenic components has generated considerable scientific and regulatory controversy during recent years.\(^8\)\(^11\) Some studies have suggested that natural sources may be significant for atmospheric CCL\(_4\) (ref. 12). Detection of CFCs in air sampled near volcanoes has lead to the suggestion that volcanism might be a significant source of these gases in air.\(^13\) The general absence of CFCs in the ocean’s deep waters virtually precludes this possibility, but no reliable measurements in air taken before the onset of anthropogenic emissions have been made to date. Air samples from ice cores have been too small to obtain the precision necessary to address these questions for halocarbons. Previous collections of firn air either were contaminated during sampling or extended back no more than a few years.\(^15\)

Here we use samples of air collected from firn (unconsolidated snow; Table 1) at the South Pole and Siple Dome in Antarctica and at Tunu in Greenland to obtain high-precision measurements spanning the full history of anthropogenic emission of most halocarbons (data reported here are available; see Supplementary Information). Samples of firn air from all three sites were analysed for CCL\(_2\)F\(_2\) (CFC-11), CCL\(_3\)F\(_2\) (CFC-12), CH\(_3\)CCl\(_3\), CCL\(_4\), N\(_2\)O, SF\(_6\), CBF\(_3\), (halon H-1301), CBF\(_2\)F\(_2\) (halon H-1211), CH\(_3\)Br and CH\(_3\)Cl. Newly introduced hydrofluorocarbons (for example, CF\(_3\)CH\(_2\)F or HFC-134a), hydrochlorofluorocarbons (such as CH\(_3\)CCl\(_2\)F or HCFC-141b, CH\(_3\)CCl\(_2\)F or HCFC-142), an additional CFC (CCL\(_2\)FCCl\(_2\) or CFC-113), and other partially halogenated methanes were measured in Tunu and Siple Dome samples only. (CHF\(_2\) or HCFC-22, showed significant signs of contamination in the upper samples, so have been omitted from this analysis.) Results for N\(_2\)O, CO\(_2\), CH\(_4\), O\(_2\)/N\(_2\) and \(^{15}\)N at the South Pole already have been published.\(^16\) Depth profiles from these sites have been presented in two NOAA/CMDL data reports.\(^17,18\) Owing to physical

Table 1. General properties of firn at sampling sites

| Site         | Location         | South Pole, Antarctica | Siple Dome, Antarctica | Tunu, Greenland |
|--------------|------------------|-------------------------|------------------------|-----------------|
| Elevation (m)| 2,841            | ~800                    | ~2,400                 | ~2,400          |
| Date         | Jan. 1995        | Dec. 1996               | Apr. 1996              |                 |
| Lock-in zone depth (m)| 114–122 | 48–56                  | 58–68                  |                 |
| Annual snow accumulation (cm/yr) | 8 | 15                      | 10                     |                 |
| 'CO\(_2\)' age at bottom | 1903 | 1953                   | 1929††                  |                 |

\(^*\) CO\(_2\) age is defined as the year the atmospheric CO\(_2\) value matched the CO\(_2\) concentration in the deepest sample. This is a mean age for CO\(_2\) in the bottom air, which has undergone considerable mixing. Mean ages of halocarbons are greater because of their lower diffusivities. Once in the lock-in zone, they then age at the same rate. This value is given to illustrate differences among the sampling sites; firn air at the South Pole records atmospheric history over longer time than the other two sites.

†† This value is approximate owing to the unknown evolution of the interhemispheric CO\(_2\) exchange before 1972.

†† Temperatures from measurements made at the site of the time of sampling.
effects, and in some instances chemical effects, the composition of
firm air at any given depth does not correspond exactly to the
atmospheric composition at some time in the past. Nevertheless,
because the behaviour of each gas in the firm is governed primarily
by its own diffusivity and molecular mass, we are able to estimate
histories of both anthropogenic and naturally occurring halocar-
bons during a time of rapid population, agricultural and industrial
growth.

Concentration–depth profiles of trace gases

Firm is a porous matrix in which constituent gases diffuse at rates
governed by both the structure of the firm and the nature of the
species in question. Profiles of δ15N values of N2 versus depth in the
firm (Fig. 1) reflect the processes governing transport and storage of
air18,19. Below the influence of seasonal temperature gradients and
other surface-related effects (roughly 30 m), δ15N of N2 increases
linearly with depth, owing to gravitational settling. The linearity
indicates a porous column in which transport is governed pre-
ominantly by molecular diffusion20,21. The interval of constant
δ15N of N2 at the base of the firm shows the lock-in zone23, where
dense winter layers substantially impede vertical diffusion, while
summer layers retain enough open porosity to allow sample col-
lection. Gases within the porous column atop the lock-in zone
communicate with the atmosphere through diffusion, creating a
smoothed record of atmospheric changes. In contrast, vertical
diffusion is considerably restricted within the lock-in zone, which
tends to isolate this air from the diffusive column. Thus, air in the
lock-in zone ages at approximately the same rate as the surrounding
ice. At Siple Dome and Tunu, where the diffusive column is
relatively short and smoothing is minimal, the composition of the
overlying atmosphere is recorded in the lock-in zone without
extensive diffusive mixing. At the South Pole, the deeper diffusive
column significantly smooths the atmospheric history, but also
allows for collection of very old samples24. By comparing results
from these sites with different diffusive structures, we are able to
reconstruct robust atmospheric histories.

Variations in concentration with depth reflect both long-term
trends and recent perturbations of trace gases in the atmosphere
(Figs 2–4). Concentrations of compounds known to have sig-
nificant anthropogenic sources over the past few decades (for
example, CFCs, solvents and halons) decrease considerably with
depth, where the firm air is older. Concentrations of CFC-11,
CFC-12, CFC-113, H-1301, H-1211 and SF6 all decreased to levels
that did not differ significantly from zero by the bottom of the depth
profiles (Fig. 2). This indicates that these gases were not present in
the atmosphere during the early twentieth century and confirms
their exclusively anthropogenic origin. Previously, the lowest values
reported for CFC-11 and -12, also from firm air measurements, were
16 and 18 pmol mol⁻¹ (that is, parts per trillion or p.p.t.)14. The
earliest direct measurements of atmospheric CFC-11 and -12 date
from the early to mid-1970s, with values of roughly 50 and
200 pmol mol⁻¹ (refs 12, 24–26). CFC-113 has been measured in
archived air from Cape Grim, Australia, as far back as 1978, for
which a value of 13 pmol mol⁻¹ was reported15. Systematic SF6
measurements began in 1978 at levels of 0.6 pmol mol⁻¹, or about
15% of the current atmospheric burden26, although the lowest
reported value was for 1976, at 0.24 pmol mol⁻¹ (ref. 29). Early
measurements of the halons are also available since 1976, with
amounts of the order of 0.5 pmol mol⁻¹ (ref. 30).

The concentrations of two abundant chlorocarbons, CH3CCl3
and CCl4, also decreased rapidly with depth (Fig. 3). Both of these
gases reached concentrations near the bottom of the profiles that
were at or near detection limits, suggesting that natural sources are
insignificant and that both gases were essentially absent in the pre-
twentieth-century atmosphere. The detection limit for CH3CCl3
was ~1.5 pmol mol⁻¹, although for CCl4 it was ~5 pmol mol⁻¹
because of a co-eluting peak on the gas chromatography/electro-
capture detection (GC/ECD) system (see Supplementary Informa-
tion). Thus natural sources, if they are significant at all, could not be
responsible for more than 5 pmol mol⁻¹ of CCl4 in the atmosphere.
Of course, this requires that CCl4 is stable in firm air, a question that
is raised in our attempts to reconcile an atmospheric history of CCl4

![Figure 1](image-url)

**Figure 1** Measured depth profiles of δ15N of N2. The results from the two boreholes
at the South Pole are indistinguishable from one another. Enrichments of δ15N at
shallow depths reflect thermal fractionation associated with seasonal temperature
changes at the surface. δ15N (in ‰) = ([15N]/[14N]atmospheric/[15N]/[14N]atmospheric−1)×10³;
the standard used here for all sites is contemporary tropospheric air.

![Figure 2](image-url)

**Figure 2** Measured depth profiles of anthropogenic gases with ‘known’
emissions (Tunu, Greenland). These profiles are similar to those obtained at
South Pole and Siple Dome. Depth profiles at all sites show the CFCs, halons and
SF6 penetrating deeply into the firm and dropping to zero or near-zero at the
bottom, which implies no significant sources before the introduction and use of
these gases by humans in the middle to late twentieth century. In general, gases
emitted for longer periods and with higher diffusivities penetrate most deeply. The
atmospheric increases of HCFC-141b and HFC-134a (defined in the text) are
recorded only in the diffusive zone of the firm, as these gases have not been
present long enough in the atmosphere to become locked in at depth.
from both Siple Dome and South Pole profiles. Although absolute calibration was a concern for some of the early real-time measurements of these two gases, values from the late 1970s were reported at around 60 pmol mol$^{-1}$ for CH$_3$CCl$_3$ and 90 pmol mol$^{-1}$ for CCl$_4$, after normalizing to recent calibration scales. Also apparent in the data from Siple Dome (Fig. 3) and Tunu is the 1991–93 turnaround of CH$_3$CCl$_3$ in the atmosphere that resulted from decreased anthropogenic emissions. Those HCFCs and HFCs that have been used only recently appear exclusively in the upper layers of the firm, as they have not been present in the atmosphere long enough to have been isolated in the lock-in zone at concentrations above our detection limits (Fig. 2).

Concentrations of CH$_3$Cl are significant in the deepest samples, and increase gradually toward the surface of the firm (Fig. 3). This is evidence that this gas has both natural and anthropogenic sources or at least sources that existed before the twentieth century. The concentrations of CH$_3$Cl in samples collected between 20 m and 45 m depth are similar to the mean annual concentrations at Cape Grim, Tasmania, in recent years. The decrease of 15–20 pmol mol$^{-1}$ observed in the upper 10–12 m of the firm is consistent with the seasonal variability observed for CH$_3$Cl in the Southern Hemisphere, as lower mixing ratios are observed in summer when atmospheric loss processes outweigh sources. Concentrations between 20 and 45 m depth are about 10% higher than at the bottom of the profile. If we assume that CH$_3$Cl is not being degraded slowly over time in the firm, these results indicate that the atmospheric mole fraction of CH$_3$Cl has increased by about 40 pmol mol$^{-1}$ over the past century.

The firm data for CH$_3$Br are more difficult to interpret. At the two Antarctic sites, CH$_3$Br concentrations at the top of the firm air profiles are 20–25% higher than at the bottom, implying a significant pre-twentieth-century source and an increase in the atmospheric burden of this gas over the past 50–100 years (Fig. 4). Unlike CH$_3$Cl, however, the observed difference of 5–10% between the surface samples and those below 10 m is not explained by seasonally varying mixing ratios; no significant seasonality is observed in the atmosphere at sites in the Southern Hemisphere. This anomaly remains a mystery, as it was present at both Antarctic sampling sites and appears not to be a sampling or analytical artefact. More disturbing, however, are the samples from Tunu. At this seasonally warm and coastally influenced Greenland site, the concentration of CH$_3$Br was very high near the bottom of the profile, reaching mixing ratios of nearly 50 pmol mol$^{-1}$ at the firm–ice transition (Fig. 4). We are confident that this increase in concentration at depth is not an artefact of sample collection, storage or analysis.

The depth–mixing ratio curve for CH$_3$Br was essentially identical in our two Tunu firm-air profiles, although the second profile did not extend as deeply as the first. Tests of the sampling equipment showed no evidence whatsoever of contamination by CH$_3$Br (CFCs were present in our equipment, but our sampling design and procedure still allowed for concentrations of zero or nearly zero in deep samples.) Samples in steel and glass flasks yielded similar profiles for CH$_3$Br and CH$_3$Cl, and chromatographic results, obtained by both electron-capture or mass spectrometry, were independent of analytical technique. This leads us to believe that the observed high values (up to 48 pmol mol$^{-1}$) for CH$_3$Br in the firm at Tunu are real, although not necessarily of atmospheric origin. Concentrations of other marine, biogenic gases (such as CH$_2$Br$_2$ and CH$_3$I) also increased at depth in the Tunu firm, although the anomalies were smaller than for CH$_3$Br.

**Interpreting concentration–depth data**

Obtaining a representative atmospheric history of any gas from a diffusion model and measurements of firm air requires some knowledge of the diffusivity of gases in the firm. This can be derived from
density—porosity—diffusivity relationships. These relationships, however, are poorly constrained, so we prefer to calibrate diffusivity with the measured atmospheric history of CO₂ deduced from real-time flask samples and the Law Dome ice core. We refrain from modelling the Tunu profile because of the extensive convective zone and the possibility that the firm-air CO₂ profile at that site is erroneously offset by covariance between seasonal convective mixing and seasonal variations in atmospheric CO₂ (‘rectifier’ effects). To account for the effects of diffusion in the firm on each species at the South Pole and Siple Dome, we use the simple one-dimensional firm diffusion model described in detail by Battle et al.14. As in that investigation, we infer a site-specific diffusivity—depth relationship by adjusting diffusivity until the model reproduces the observed CO₂ firm-air profile when driven by the atmospheric CO₂ history. We then calculate halocarbon—depth profiles using this adjusted diffusivity—depth profile in the diffusion model. However, we examine these as halocarbon—CO₂ rather than halocarbon—depth profiles; the former are much less sensitive to errors in the inferred profiles of diffusivity versus depth. Our results remain sensitive to errors in the diffusivities of halocarbons relative to the diffusivity of CO₂.

We apply the firm diffusion model with one of two goals, depending on the halocarbon: (1) to test an independently derived atmospheric history, or (2) to infer an atmospheric record for species with uncertain or unknown histories. The first approach is suitable for gases such as the CFCs, halons and SF₆, for which atmospheric histories have been derived from emission estimates and real-time measurements. We use these histories and the firm-air diffusion model to predict concentration—CO₂ profiles for these gases and to compare the predictions with observations in the Antarctic firm. The second approach is used for those chlorocarbons and methyl halides for which there is insufficient information to estimate or calculate complete atmospheric histories. In this approach we choose one or more suitably general mathematical descriptions of concentration as a function of time, with consideration given to recent direct atmospheric measurements as well as firm-air data. The free parameters of the mathematical expressions are then adjusted using inverse methods to optimize agreement between measured and modelled concentration—CO₂ profiles at one or both sites.

We cannot eliminate the possibility that these gases are very slowly produced or degraded in the firm. However, we have strong
CH₃CCl₃, CH₃Cl and CH₃Br are shown plotted against CO₂ in firm air (left panel) for lines). Also shown are real-time atmospheric measurements (in green) from the histories are inferred by optimizing the data–model agreement for the South Pole based on the atmospheric histories shown in the right panel (purple). These model results represent gas mole fractions (p.p.t., pmol mol⁻¹) predicted in the firm based on the atmospheric histories shown in the right panel (purple). These histories are inferred by optimizing the data–model agreement for the South Pole (blue lines) and then checking this for agreement with data from Siple Dome (red lines). Also shown are real-time atmospheric measurements (in green) from the ALE/GAGE/AGAGE network and from Khalil et al. Normalized to NOAA/OML South Pole measurements. In the inversion model, real-time atmospheric measurements have been used only to adjust the diffusivities of CH₃Br (−20%) and CH₃CCl₃ (−20%). The shapes of the inversion results are independent of these measurements. Atmospheric concentration histories shown here follow sigmoid curves, with parameters determined by the firm data. The use of other functional forms for the atmospheric histories yields indistinguishable results. Errors (shown as purple bars) correspond to a 68% confidence envelope.

Figure 6 Histories in the Southern Hemisphere of halocarbons with uncertain emission records. Modelled (lines) and measured (points) mole fractions of CO₂, CH₃CCl₃, CH₃Cl and CH₃Br are shown plotted against CO₂ in firm air (left panel) for the South Pole (blue) and Siple Dome (red) (note offset scales for each site). The model results represent gas mole fractions (p.p.t., pmol mol⁻¹) predicted in the firm based on the atmospheric histories shown in the right panel (purple). These histories are inferred by optimizing the data–model agreement for the South Pole (blue lines) and then checking this for agreement with data from Siple Dome (red lines). Also shown are real-time atmospheric measurements (in green) from the South Pole are sites sufficiently different in firm properties that any consistent histories inferred from measurements at Siple Dome and the South Pole provide additional assurance; Siple Dome and the South Pole are sites sufficiently different in firm properties that any physical, biological or chemical effects on the gas concentrations should be expressed differently at these two sites.

Tests of independently derived atmospheric histories
Concentration–CO₂ profiles predicted for CFCs, halons and SF₆ based on emission histories, real-time measurements and firm-air diffusion modelling are in good agreement with firm-air data (Fig. 5). This agreement, together with zero or near-zero concentrations in the oldest samples, is consistent with solely anthropogenic sources of these gases. It also suggests that the emission models used yield reasonably accurate estimates of the early atmospheric histories.

The one significantly inconsistent species is halon H-1211. Both modern measurements and firm results suggest either a shorter lifetime than that given solely by atmospheric chemistry models (11 compared to 20 years) or lower emissions. The atmospheric curve and model output in Fig. 5 incorporate the 11-year lifetime. For the CFCs, for which significant emissions began in the 1940s, analyses of firm air provide data for long periods where few or no real-time measurements are available. For the halons, with significant emissions beginning in the 1960s, real-time measurements span a larger fraction of their atmospheric history, although calibrations of earlier measurements are less certain. For SF₆ with significant emissions beginning in the 1970s, the concentration history is derived almost entirely from direct atmospheric measurements, and thus is insensitive to errors in estimates of emissions or lifetimes.

Inferred atmospheric records of chlorocarbons
CCL₄ appears to be derived solely from anthropogenic sources, but this conclusion must be tempered by the analytical uncertainty of ±5 pmol mol⁻¹ for the lowest-concentration samples, owing to an interfering peak in the GC/EC/CD system. This inference is based primarily upon the longer South Pole firm-air record (Fig. 6), although the concentration of CCL₄ also does not differ from zero at the bottom of the Tunu profile. The firm data do show that CCL₄ has been present in the atmosphere for a longer time than the CFCs, owing to its earlier industrial use. This earlier use also appears in the deep ocean record where CCL₄ is present in the relative absence of CFCs. Although our data from Siple Dome suggest that, before 1960, CCL₄ was substantially lower in concentration than predicted from estimated production and emissions, the data from the South Pole agree quite well with the emission prediction. Emission estimates for CCL₄, however, are much less certain than for the CFCs or halons. The lowest value at Siple Dome, corresponding to the late 1940s or early 1950s, was 4–7 pmol mol⁻¹, but the South Pole data suggest a value of about 35 pmol mol⁻¹ for 1950. In an early analysis of CCL₄ emissions, Galbally used a lifetime of 38 years to derive an expected atmospheric mixing ratio of 40 pmol mol⁻¹. More recently, and using a lifetime of 35 years, Walker et al. suggest a value of about 33 pmol mol⁻¹ for CCL₄ in the Southern Hemisphere in 1950. Though uncertainties are large, both of these estimates from emission records are reasonably consistent with our South Pole data since the 1950s, yet are lower for earlier years. Unfortunately, the inconsistency between Siple Dome and South Pole data suggests that CCL₄ is, to some extent, either consumed or absorbed in the
firms; thus, we cannot make an unambiguous reconstruction of its concentration history.

Although the derived atmospheric record of CH$_3$CCl$_3$ is consistent at the two Antarctic sites, which suggests that this gas is stable in firm air, two data points in the lower part of the South Pole record do show measurable amounts of CH$_3$CCl$_3$. These, however, are most probably caused by contamination. The lowest value at each of the three sites, representing years from the 1890s to the 1940s, was $<$2 pmol mol$^{-1}$ ($<$2% of maximum atmospheric levels). Such concentrations are very near or below our limit of detection (3–5 σ; see Supplementary Information) and probably result from low-level contamination in the sampling apparatus. Note also that, although the turnaround in atmospheric CH$_3$CCl$_3$ was recorded in the firm at Tunu (Fig. 3), this was not the case at South Pole (Fig. 6). This is because the South Pole was sampled only shortly after the turnaround. There is a time lag of about one year in transporting signals from the Northern Hemisphere to the Southern Hemisphere and wind pumping causes some mixing in the uppermost part of the firm, so the signal would be suppressed or absent in the South Pole firm in early 1995. Because the inferred temporal change in CH$_3$Cl is small relative to its variability in the firm air, a detailed history cannot be estimated reliably from these data (Fig. 6). Nevertheless, the difference of 5–10% between bottom and mid-hole samples remains significant and suggests that the atmospheric burden of CH$_3$Cl has increased by about this amount during the past century. CH$_3$Cl is the most abundant chlorine-containing gas in the atmosphere and is emitted from the ocean$^{12}$, from biomass burning$^{41}$, and by fungi$^{42}$. Its current atmospheric budget remains uncertain. Real-time measurements of atmospheric CH$_3$Cl extend back only to 1980 and show wide seasonal oscillations. The firm data represent a much longer time span, and are compatible with the real-time measurements.

**Methyl bromide**

Methyl bromide measurements from the South Pole and Siple Dome suggest a simple atmospheric history, with a rate of growth increasing from 0.01 pmol mol$^{-1}$ yr$^{-1}$ in the early 1900s to 0.05–0.06 (±0.01) pmol mol$^{-1}$ yr$^{-1}$ (90% confidence limits) during the 1970s and 1980s. These two sites differ in snow accumulation rate, firm depth and temperature (Table 1). Thus the similarity of the two CH$_3$Br–CO$_2$ profiles suggests that the record in the firm is atmospheric in origin. Taken at face value, such a record implies that the concentration of CH$_3$Br was increasing slowly in the atmosphere through the first half of the century, perhaps as a function of increased biomass burning or some other global change. The upturn in the mid-1960s coincides with the onset of CH$_3$Br use as an agricultural fumigant, which suggests that the increase since the 1960s could indicate the expected reduction, about 15–25%, from the international ban on the use of this gas as a fumigant$^{43}$. However, the response of CH$_3$Br in the atmosphere to a ban on agricultural use is also dependent upon how other sources have changed since 1960. The budget of CH$_3$Br for the modern atmosphere, calculated from what is known of sources and sinks, is grossly out of balance. Based upon current understanding$^{46,47}$, there is a large source of this gas that has not been identified. From the atmospheric concentrations implied by the deepest samples at the South Pole, it appears that this missing source was also present at the turn of the century. These results suggest that the unidentified source is separate from modern fumigation practices, or that the overall sink, calculated for CH$_3$Br from atmospheric reactions and loss to the oceans and soils, is currently overestimated.

The main problem in interpreting the CH$_3$Br data comes from the Tunu site, where concentrations of CH$_3$Br increased with depth (Fig. 4). The Tunu record does not appear to reflect past atmospheric changes, and it casts some doubt upon the utility of the Antarctic data. The simultaneous occurrence of CH$_3$Br at 50 pmol mol$^{-1}$ in the Northern Hemisphere and 5 pmol mol$^{-1}$ in the Southern Hemisphere is highly improbable, as it would require an atmospheric lifetime of 0.1 year or less for CH$_3$Br. All evidence today points to a lifetime of 0.5–1.2 years (ref. 47). Locally increased atmospheric concentrations are possible, but unlikely at these levels in remote areas. The most logical explanation is that CH$_3$Br has been injected into the firm air at Tunu, perhaps by desorption or in situ production. Tests with our firm diffusion model indicate that one can account for the anomalous enrichments only by invoking net injection of CH$_3$Br at or near the firm–ice transition (see Supplementary Information). We know of no physical, chemical or biological mechanism that could easily explain this injection. Simple adsorption followed by subsequent release during densification would have injected CH$_3$Br into the firm air at all three sites. Abiotic chemical transformation at such cold temperatures ($<$45°C) cannot be ruled out, although attempts to identify possible source materials are speculative. Tunu has significant marine influence and is located in an area affected by arctic haze, which is known to contain significant amounts of bromine$^{48}$. There is no evidence to date suggesting that organisms grow at the low temperature of the firm, but it is possible that loosely bound material could be slowly released from enzymes or cell surfaces. Whatever the source of the anomalous CH$_3$Br, we cannot prove it to be absent in Antarctica. However, if the process is driven at the firm–ice transition zone, as it most probably was at Tunu, then it could not have been significant at the South Pole or at Siple Dome, which yield observed profiles of concentration decreasing monotonically with depth to the bottom of the holes. Even a very low net production at the lock-in zone would have changed the shape of the profiles noticeably, and also would have elevated the bottom concentrations substantially. Competing, unknown production and degradation processes throughout the firm might have altered the firm-air concentrations of CH$_3$Br, but the probability is low that these processes would produce similar profiles at the two physically dissimilar Antarctic sites.

**Summary**

Antarctic and Greenland firm can provide reliable archives of many atmospheric halocarbons dating back to the late 1800s, extending records of gases that have been measured in real time only during the past two decades. Robust records of CFCs, halons and SF$_6$ extracted from the measurements of firm air agree with real-time estimates in the later parts of the profiles, corroborate emission models for some species and are useful in evaluating lifetimes and emission estimates for others. Although there are still important uncertainties, our data refine halocarbon histories and give experimental evidence about their pre- anthropogenic concentrations. It appears that for many species the cold, dry air in the firm preserves the gases. Except for CH$_3$Cl and CH$_3$Br, which have significant natural sources, all of the halocarbons studied appear to have been derived entirely from emissions during the twentieth century. CH$_3$Br and perhaps CCl$_4$ are, for unknown reasons, not always conserved in firm air, and other reactive halocarbons could conceivably behave similarly.

**Methods**

Two holes were drilled at each site. At the South Pole, both boreholes reached the firm–ice transition; at Tunu and Siple Dome the second holes ended in the diffusive zone. We only consider data from the first hole at Siple Dome for our models because of inconsistencies in the sampling protocol. Low-pressure samples (~120 kPa) were collected into duplicate, 2.5-litre glass flasks at all three sites. Higher-pressure samples (~380 kPa) were also collected into single or duplicate 2.4-litre stainless-steel flasks at Tunu and Siple Dome. Details on drilling and flask filling can be found in Battle et al.$^{40}$ Glass flasks were filled at all three sites with a pump (MB-158, Mettler Bells, Senior Flexonics, Sharon, Massachusetts) attached to nylon or Dekabon tubing, and analysed by GC/ECD for 11 trace gases. CO$_2$ and $\delta^{15}$N of N$_2$ also were measured in air from the glass flasks. Surface air was excluded from the borehole by inflating a
natural rubber bladder with stainless-steel end-caps. After the bladder was inflated, ~500–1,500 litres of firm air was extracted and pumped to waste, followed by flushing of the sample flasks with 10 volumes of firm air. Stainless-steel flasks filled with a pump (KNF Neuberger, Princeton, New Jersey) at Tunu and Siple Dome were analysed for over 20 halocarbons by GC/ECD and by gas chromatography with mass spectrometric detection (GC/MS). Measurements were calibrated with gravimetrically prepared standard gases, typically spanning a range of 20–150% of current atmospheric values. GC/MS calibration curves were linear in all cases and no zero-corrections were required; those for GC/ECD were predominantly linear. Zero air, a 20/80 mixture of purified, synthetic O2 and N2, was analysed to confirm values obtained at the bottom of the profiles and to establish detection limits for both instruments. Detection limits for the CFCs typically were within 1 or 2 pmol mol−1 of zero and, for SF6 and the halons, within 0.1 and 0.2 pmol mol−1 of zero.

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