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Extreme ^{13}C depletion of CCl_2F_2 in firn air samples from NEEM, Greenland

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Abstract

A series of 12 high volume air samples collected from the S2 firn core during the North Greenland Eemian Ice Drilling (NEEM) 2009 campaign have been measured for mixing ratio and stable carbon isotope composition of the chlorofluorocarbon CFC-12 (CCl_2F_2). While the mixing ratio measurements compare favorably to other firn air studies, the isotope results show extreme ^{13}C depletion at the deepest measurable depth (65 m), to values lower than $\delta^{13}C = -80$ ‰ vs. VPDB (the international stable carbon isotope scale), compared to present day surface tropospheric measurements near −40 ‰. Firn air modeling was used to interpret these measurements. Reconstructed atmospheric time series indicate even larger depletions (to −120 ‰) near 1950 AD, with subsequent rapid enrichment of the atmospheric reservoir of the compound to the present day value. Mass-balance calculations show that this change must have been caused by a large change in the isotopic composition of anthropogenic CFC-12 emissions, probably due to technological changes in the CFC production process over the last 80 yr. Propagating the mass-balance calculations into the future demonstrates that as emissions decrease to zero, isotopic fractionation by the stratospheric sinks will lead to continued ^{13}C enrichment in atmospheric CFC-12.

1 Introduction

Before it was banned under the Montréal protocol and subsequent amendments, the use of chlorofluorocarbon-12 (CFC-12, CCl_2F_2) as a refrigerant and aerosol propellant worldwide has resulted in significant atmospheric loading; at its peak in 2003, the mean mixing ratio of this compound in the troposphere was approximately 550 ppt (ppt = parts per trillion = pmol mol^{-1}), making it the most abundant anthropogenic halocarbon compound in the atmosphere (McCulloch et al., 2003; Forster et al., 2007). Due to the buildup of this and other anthropogenic halocarbons, total chlorine loading

in the troposphere has increased from approximately 600 ppt (1900) to nearly 3350 ppt (2008) (Forster et al., 2007; WMO 2010).

Trends in CFCs have been directly observed since the 1970s, when regular observations of atmospheric halocarbon compounds started (e.g. ALE, GAGE and AGAGE projects, AGAGE, 2011). The atmospheric mixing ratio history of CFC-12 prior to this period has been reconstructed through the measurement of firn air samples combined with firn air modeling and emissions estimates (Butler et al., 1999; Sturrock et al., 2002; McCulloch et al., 2003; Martinerie et al., 2009; Buizert et al., 2012). Firn air is extracted from compacted snow to depths above bubble close off and analyzed on-site, or captured in sample vessels for later analysis. The large volumes of air contained in compacted snow allow for the extraction of tens to hundreds of liters of ancient air (Schwander et al., 1993).

Interpretation of the measured data must be paired with firn air modeling, which takes into account the physics of trace gas transport in firn and allows the reconstruction of atmospheric histories of the compounds concerned (Trudinger et al., 1997; Witrant et al., 2011; Buizert et al., 2012). Analysis of firn air combined with firn air modeling proved that there is no natural source of CFC-12, as no trace of this compound was found in samples from Antarctica and Greenland corresponding to dates before 1930, when large-scale use began (Butler et al., 1999; McCulloch et al., 2003; Martinerie et al., 2009).

CFC-12 is a very stable compound and has its only sink in the middle and upper stratosphere, where ultraviolet radiation is energetic enough to break the C-Cl bond (reaction R1). A minor sink (3–7 %) exists through Cl abstraction by $O(^1D)$, which is produced from the photolysis of ozone in the stratosphere (reaction R2; Seinfeld and Pandis 1998; Laube et al., 2010a).

$$CCl_2F_2 + h\nu \xrightarrow{\lambda<220\,\text{nm}} CClF_2 + Cl\cdot \quad \text{(R1)}$$

$$CCl_2F_2 + O(^1D) \longrightarrow CClF_2 + ClO \quad \text{(R2)}$$

These reactions provide the initial release of chlorine, which begins the now well-known catalytic decomposition of ozone first proposed by Molina and Rowland (1974). The fact that CFC-12 can only be removed in the stratosphere leads to a long atmospheric lifetime of approximately 100 yr (Forster et al., 2007). Due to this long lifetime, the mixing ratio of CFC-12 has decreased in the atmosphere only slowly after the Montréal protocol came into effect, to approximately 530 ppt in 2010 (AGAGE, 2011).

Whereas the mixing ratio of CFC-12 has been well established by many studies, few studies of the stable isotope ratio of this compound have been completed. Stable isotope ratio studies can give insight into the budget of a compound, i.e. its sources and sinks (Goldstein and Shaw, 2003). The stable isotope composition of quantities of compounds can be altered by the mixing of molecules with differing isotope ratios, or through chemical reactions due to differences in chemical bond strengths ascribed to isotopic substitution. These cause fractionation between the different isotopologues of a given molecule (e.g. Brenninkmeijer et al., 2003). Isotope values are conveniently expressed in δ notation, in the case of ^{13}C:

$$\delta^{13}\mathrm{C}=\frac{^{13}R_{\mathrm{sample}}}{^{13}R_{\mathrm{standard}}}-1 \tag{1}$$

where ^{13}R is the ^{13}C/^{12}C ratio in a sample or standard material. The internationally accepted reference material for ^{13}C/^{12}C ratios is Vienna Pee Dee Belemnite (VPDB). The δ value is expressed in per mil (parts per thousand = ‰) for readability.

Zuiderweg et al. (2012) recently reported an unusually strong ^{13}C fractionation associated with the photolytic destruction of CFC-12 under stratospherically relevant conditions. Fractionation constants (defined as ε = $^{13}J/^{12}J$, the ratio of the photolysis rate constants of the heavy and light isotopologues and similarly expressed in per mil) in the range −50 ‰ to −70 ‰ were determined in laboratory photolysis experiments at temperatures between 288 K and 203 K. Such a strong isotope effect in the removal process should result in a continuous enrichment of the atmospheric reservoir now that

production and emissions have largely ceased (Zuiderweg et al., 2012). Air trapped in polar firn is a valuable tool to investigate whether this isotope signal is present.

Applications of stable isotope ratio studies of atmospheric compounds in firn air are diverse. δ^{15}N(N$_2$) and δ^{18}O(O$_2$) can be used for constraining ice core trapped air age (Schwander et al., 1993; Bender et al., 1994; Severinghaus et al., 2010). For methane (CH$_4$), carbon dioxide (CO$_2$), carbon monoxide (CO), and nitrous oxide (N$_2$O), historical isotope scenarios have been derived to explore trends in emissions (Trudinger et al., 1997; Etheridge et al., 1998; Francey et al., 1999; Bräunlich et al., 2001; Sowers et al., 2001; Röckmann et al., 2003; Monteil et al., 2011; Sapart et al., 2012; Wang et al., 2012). However, to date, no isotope ratio history has been reconstructed for CFC compounds, though δ^{13}C CFC measurements in urban and rural air do exist (Archbold et al., 2005; Redeker et al., 2007; Mead et al., 2008; Bahlmann et al., 2011). Here we present the first measurements and interpretation of a combined depth profile of CCl$_2$F$_2$ mixing ratio and isotopic composition from the firn air campaign at the North Greenland Eemian Ice Drilling (NEEM) site (77° 25′ 54.93″ N, 51° 03′ 19.89″ W, 2484 m a.s.l.), collected as part of the summer 2009 NEEM firn air program.

2 Method

2.1 Firn sampling

A series of 12 large volume firn air samples were obtained from the S2 firn borehole at the NEEM site to a depth of 73.6 m. Here, a firn air sampling device (FASD) constructed of a 3 m long rubber bladder, with sample lines passing through it, was lowered to the bottom of a borehole. The FASD was expanded with air to provide an airtight seal to the walls of the borehole, and air was extracted through the sampling lines from below the FASD. Once on-site CO$_2$ mixing ratio measurement confirmed that the seal of the FASD to the borehole wall was leak tight and surface air had been pumped away, air is extracted from the firn in large quantities. After sampling at each depth was completed air pressure in the firn layer was allowed to re-equilibrate to prevent surface air contamination of the firn. Following this, the FASD was deflated, extracted, and the hole was bored to the next depth to be sampled. The sampling continued downward until a depth was reached where firn porosity decreases to an extent that air can no longer be extracted from the firn using this method, due to compression from the weight of the firn above it. Further details of the sampling methods used are described by Etheridge et al. (2009).

The large air samples used for the analysis presented here were dried, and then compressed to 120 bar pressure into 5 l Luxfer aluminium cylinders using a three-stage oil free piston compressor (Mak and Brenninkmeijer, 1994).

2.2 Analytical procedure

The CFC-12 of each of the sample cylinders was measured twice, non-sequentially and on different days to detect instrument drift, for mixing ratio and δ^{13}C at the stable isotope laboratory of the Institute for Marine and Atmospheric Research Utrecht (IMAU). The isotope measurement system used is described by Zuiderweg et al. (2011). This instrument was originally designed for the measurements of stable carbon isotope ratios of non-methane hydrocarbons, and features a novel method of removing unwanted compounds that would otherwise interfere with analysis (e.g. CO_2 and CH_4) by use of a 3 m × 6.35 mm Porapak Q column. Subsequent peak separation of compounds prior to mass spectrometry is accomplished by using a 52.5 m × 0.25 mm Poraplot Q column, the effluent of which is split to (1) a HP 5970 quadrupole MS for compound identification and (2) a Thermo Finnigan Delta + XL IRMS instrument by way of a Pt-Cu-Ni combustor (for combustion to CO_2) and open split. The scale of this instrument was established by the use of two reference gases: a multicompound nonmethane hydrocarbon gas as a working standard, and a CO_2 direct reference. These were independently calibrated to VPDB by external laboratories and were consistent with each other. Further information about these calibration procedures can be found in Zuiderweg et al. (2011, 2012).

In this work, the system was extended for ^{13}C measurements of monocarbon chlorofluorocarbons. Reproducibility of the system was established with a PraxAir Inc. calibration mixture containing approximately 150 ppb ± 5 % CFC-12 among other compounds. The mean δ^{13}C of CFC-12 in this gas was established as −41.6 ‰ vs. VPDB. Testing results with various sample volumes showed that the instrument was volume independent and stable for CFC measurement, with nominal δ^{13}C instrument repeatability (1σ, 34 experiments) of 0.65 ‰ for CFC-12 above integrated peak areas of 0.5 Vs (Volt-seconds), corresponding to a carbon mass of 2 ng. The instrument is linear with peak area above this threshold (Fig. 1). Mixing ratio measurement precision is ± 5 %. Sensitivity of the instrument per mass carbon is approximately 0.25 V s ng^{-1} (Zuiderweg et al., 2012). This instrument behavior for CFC-12 is consistent in terms of stability (in δ^{13}C and mixing ratio), linearity, and sensitivity levels with other measured compounds as reported in Zuiderweg et al. (2011). Routine calibration of the instrument was accomplished by measuring the above standard before the start and after the finish of the daily measurement series. Blank measurements showed no remnant CFC or interfering peaks.

2.3 Data integration

Calculation (through peak integration) of all δ^{13}C data presented here was accomplished via raw data processing using a custom made MATLAB code as described in Bock et al. (2010) and Schmitt et al. (2011). For all firn samples, CFC-12 peaks suffer from peak interference with the preceding methyl chloride peak (shoulder overlap), prohibiting baseline-separated signals. The MATLAB routine extrapolates the peak tail of methyl chloride via an exponentially decaying function to distinguish the two gas species. This technique is not possible with the standard ISODAT software used for isotope ratio measurements. Figure 2 illustrates the background removal in chromatograms of two samples (30.2 m and 69.4 m depth, upper and lower traces, respectively). Peaks are integrated with time between the exponentially decaying background and the CFC-12 peak. Beside this shoulder overlap, all CFC-12 peaks are free of artifacts and interfering peaks. As all firn samples are treated identically, relative differences reflect the true atmospheric trend combined with firn effects.

3 Results and discussion

3.1 NEEM firn dataset

Duplicate measurements of vertical profiles of CFC-12 mixing ratio and δ^{13}C in the firn air column and their arithmetic mean with 98 % confidence intervals are shown in Figs. 3 and 4, respectively. All data are summarized in Table 1. Mixing ratio results from our instrument show the expected decrease with depth, from present values near 550 ppt in the top part of the firn to approximately 14 ppt at 71.9 m depth; at and below this depth CFC-12 peak areas were far below the limit of 0.5 Vs required for isotope measurements: at 71.9 m by at least factor of 10 less; at 73.6 m the CFC-12 peak was entirely absent.

In general, both sets of mixing ratio measurements are close together, and the series as a whole agree well (within instrument and calibration error of 10 %) with NEEM 2008 campaign CFC-12 firn air data from Buizert et al. (2012).

The δ^{13}C profile (Fig. 4) down to 63 m is relatively stable at approximately −40 to −45 ‰ , reflecting recent atmospheric values (see also Fig. 5). These values are somewhat more depleted in ^{13}C than mean values reported from Belfast, Northern Ireland (−37.0 ± 1.3) ‰ and (−37.2 ± 3.9) ‰ (Archbold et al., 2005; Redeker et al., 2007); and (−37.9 ± 1.1) ‰ in Hamburg, Germany (Bahlmann et al., 2011). However, these values were measured at urban locations where local emissions may have had an impact, as standard deviations are large. By contrast, Bahlmann et al. (2011) report (−41.2 ± 0.2) ‰ from a set of 3 samples obtained on the North Sea Coast on the Island of Sylt, Germany. Also, CARIBIC project flight 26 measurements (Male, Maldives, to Düsseldorf, Germany, 17 August 2000; Zuiderweg, 2012) give (−44.7 ± 0.6) ‰. These

aircraft samples were collected from the temperate to tropical upper troposphere region (9–11 km), well below the altitude where photolytic removal takes place (14–34 km, Laube et al., 2010a). This is corroborated by the mean mixing ratio measured of (550 ± 50) ppt, very similar to surface measurements. Therefore these values can reasonably be considered as representative of the well-mixed and undisturbed troposphere. The CARIBIC flight sample set was measured using the same instrument as for the firn samples reported here.

The relative stability of δ^{13}C in the top 30 m of the firn implies little seasonality, which is expected given the long atmospheric lifetime of CFC-12. Below 63 m (the lock-in depth at NEEM; Buizert et al., 2012), where firn diffusivity decreases rapidly and older air is found (see Fig. 5), CFC-12 becomes increasingly depleted in ^{13}C with depth. Measurements indicate a large ^{13}C/^{12}C depletion of 40 to 50 ‰ for the lowest measured sample (69.4 m) with respect to the surface. The δ^{13}C separation of the repeat measurements at the deepest point is larger than for the other sampling depths (Table 1 and Fig. 4). Both measurements at this depth had a signal above the instrument linearity threshold mentioned in section 2.2, at 0.59 and 0.55 Vs, respectively, excluding instrument nonlinearity effects. However, the neighboring methyl chloride (see Fig. 2) peaks for these samples were relatively large and therefore the uncertainties associated with shoulder overlap induce the larger error in these measurements. The observed isotope depletions are much larger in magnitude than the expected firn fractionation effects (see discussion below). Thus, they most likely reflect that real changes exist in the isotope history in the atmosphere.

3.2 Atmospheric trend reconstruction

In order to interpret these data in terms of temporal variation we use a forward model of trace gas transport in firn proposed by Witrant et al. (2011). It takes into account diffusion and gravitational fractionation, which play a significant role in the measured isotope ratio of compounds in the firn versus that observed in the atmosphere (Trudinger et al., 1997). Thermal fractionation due to varying temperature with depth is not taken into account in the model, but this is of no detriment to the results as a whole as all but one of the measured samples are from below 15 m depth. Thermal fractionation is generally considered to be important in the upper 10–15 m only due to temperature gradients (Severinghaus et al., 2001). Similarly, eddy diffusion in the upper firn should be negligible as this affects only the uppermost levels of the firn (to 20 m at NEEM), and was noted to be small in magnitude at this site and would only serve to reduce fractionation (Witrant et al., 2011; Buizert et al., 2012).

The physical parameters (e.g. diffusivity) for the NEEM firn sampling site were reconstructed from a suite of gases with known histories (Buizert et al., 2012). More specifically, two gases in particular (CO_2 and CH_4) measured at CSIRO were used for the NEEM 2009 firn air experiment to tune the diffusivity profile. Because of the relative coarseness and the magnitude of scatter of our mixing ratio data, no independent CFC-12 mixing ratio scenario was modeled from our data. Instead a best estimate CFC-12 scenario based on atmospheric measurements combined with atmospheric chemistry model results is used (Martinerie et al., 2009; Buizert et al., 2012).

Figure 5 shows the age distributions for CFC-12 calculated by the forward model: mean, 15th percentile and 85th percentile ($\pm 1\sigma$). As expected, below 60 m the mean age with depth increases rapidly. In the so-called lock in zone, the transition from firn to ice begins and further vertical diffusion slows, as firn is compacted by the weight above it. From samples collected in 2008, Buizert et al. (2012) identified the lock-in zone between 63 and 78 m at the NEEM site. At the bottom of this layer, permeability is zero, and no further trace gas transport can occur.

The recently developed scenario reconstruction method based on the separation of the effects of the major and minor isotopologues (Wang et al., 2012) is not suitable for use here as it has difficulty in reconciling large gradients in isotope ratio, leading to inconsistent results. Instead, we systematically explore scenarios with “smooth” variations of $\delta^{13}C$ (e.g. Bräunlich et al., 2001). Where both methods are suitable, they provide consistent results (Laube et al., 2010b). A large number of hypothetical scenarios are run with the forward model. Atmospheric scenarios with polynomial

parameterizations of $\delta^{13}C$ as a function of time were run in monthly time steps from 1933 (the start of CFC-12 emissions) to 2009. In detail, we use 3rd and 4th degree polynomials with coefficients varying randomly within pre-defined limits (see below).

In order to reduce computing time, modeling proceeded in two steps for each polynomial setup. First, generated polynomials were evaluated with predetermined maximum and minimum values with an intentionally large interval to exclude unfeasible scenarios: scenarios with 2009 $\delta^{13}C$ values outside the range −43 to −38 ‰ and any scenarios with $\delta^{13}C$ values outside the range −400 to −30 ‰ are excluded. Selected scenarios were subsequently tested through the forward model, which is computationally expensive. In total, 50 000 000 and 78 125 000 individual scenarios using 3rd and 4th degree polynomials were evaluated, respectively. The results of the firn modeling can be found in Fig. 6 for both the 3rd and 4th degree results. The best scenario is the one leading to the smallest root mean squared deviation (RMSD) between modeled and observed $\delta^{13}C$ (mean of two measurements at each depth) in the firn, which is shown in Fig. 7. Best RMSDs are 3.7 ‰ and 3.6 ‰ with the 3rd and 4th degree polynomial setups, respectively. The envelopes shown on Figs. 6 and 7 show the overall minimum and maximum values of all selected scenarios (6809 and 8280 selected scenarios for 3rd and 4th degree polynomials, respectively).

In Fig. 6, an increase of $\delta^{13}C$ with time is seen, at approximately 5 ‰ per year from model start to 1960, but thereafter increasing less rapidly and leveling out to 0 ‰ per year by 2000, and remaining more or less constant until model end date. The best solutions obtained with the 3rd and 4th degree polynomials are consistent. Envelopes are somewhat larger for the 4th degree as compared to the 3rd degree polynomial scenarios. This is expected, as the 4th degree polynomial has an additional degree of freedom.

To assess the magnitude of induced fractionation from diffusion and gravitational effects in the firn, we run the forward model with a constant atmospheric $\delta^{13}C$ value with time of −40 ‰ (see e.g. Trudinger et al., 1997). The results (Fig. 8) show that the fractionation with depth due to diffusion and gravitational effects is limited to less than

1 ‰. This is not unexpected as the high molecular weight of CFC-12 leads to small fractional mass differences between the two isotopologues (0.8 %), and thus reduces the magnitude of these effects. By contrast, for δ^{13}C(CH$_4$), where the fractional mass difference is much larger (6 %), diffusion and gravitational effects are more significant (Bräunlich et al., 2001; Sapart et al., 2012). Since the effect of fractionation in firn is small compared to observed variations of δ^{13}C of CFC-12 with depth, large variations of atmospheric δ^{13}C (CFC-12) must have occurred in the past.

Besides fractionation, the transport of gases through the firn also induces mixing by molecular diffusion: concentration gradients between the top of the firn and the bottom of the diffusive zone are smoothed (Bräunlich et al., 2001; Buizert et al., 2012). Therefore, the strong δ^{13}C depletion at the deepest level in the firn where mixing ratios are low implies extreme depletions in the atmosphere (to −265 and −250 ‰ for the 3rd and 4th degree best scenarios, respectively).

3.3 Isotope mass-balance interpretation

In order to aid interpretation of atmospheric trends of δ^{13}C as indicated by the scenario in terms of CFC-12 production (unknown δ^{13}C source signature) and loss (photochemical fractionation measured as enrichment), we use an isotope mass-balance calculation (Eqs. 2–5, Röckmann et al., 2003). The overall mass balance for CFC-12 is:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = P - Jn \tag{2}$$

where n is the number of moles of the compound in the atmosphere, and P is the magnitude of the emission rate of CFC-12 to the atmosphere. J, the stratospheric photolysis (first order) rate constant, is equal to $1/\tau$ where τ is the atmospheric lifetime.

Additionally, the heavy isotopologue equivalent of Eq. (2) describes the contributions of the source and the sink to the atmospheric stable isotope signature as follows

(Röckmann et al., 2003):

$$\frac{\mathrm{d}[(1+\delta)n]}{\mathrm{d}t} = P(1+\delta_P) - Jn(1+\delta)(1+\varepsilon) \tag{3}$$

where δ and δ_P are the atmospheric and emission stable carbon isotope ratios of the CFC-12, respectively; ε is the fractionation inherent in the sink.

We expand Eq. (3) to:

$$\frac{\mathrm{d}n}{\mathrm{d}t} + \delta\frac{\mathrm{d}n}{\mathrm{d}t} + n\frac{\mathrm{d}\delta}{\mathrm{d}t} = P(1+\delta_P) - Jn(1+\delta+\varepsilon+\delta\varepsilon) \tag{4}$$

Substituting Eq. (2) we derive:

$$n\frac{\mathrm{d}\delta}{\mathrm{d}t} = P(\delta_P - \delta) - Jn(1+\delta)\varepsilon \tag{5}$$

Solving for δ_P gives:

$$\delta_P = \frac{\left[n\frac{\mathrm{d}\delta}{\mathrm{d}t} + Jn(1+\delta)\varepsilon\right]}{P} + \delta \tag{6}$$

To initialize the calculation based on this equation, n is based on mean atmospheric mixing ratio reconstructed from emissions estimates verified with ALE/GAGE/AGAGE data where available (Walker et al., 2009). P is back calculated from $\mathrm{d}n/\mathrm{d}t$. J is based on an atmospheric lifetime of 100 yr (Forster et al., 2007). For δ, the 4th degree-polynomial best-fit scenario is used. $\mathrm{d}\delta/\mathrm{d}t$ is the CFC-12 atmospheric isotope ratio change per timestep.

Finally, ε is estimated at −35 ‰, approximately half of the laboratory measured isotopic fractionation at stratospheric temperatures (Zuiderweg et al., 2012). The magnitude of the fractionation directly observed in photolysis experiments is suppressed by the effect of mixing in the stratosphere. It has been shown through the stable isotope measurement of stratospheric samples that apparent (observed) fractionations in

δ^{13}C of CH_4 and δ^{15}N and δ^{18}O in N_2O (which is similarly removed through UV photolysis) are approximately half of fractionations obtained from laboratory experiments (Röckmann et al., 2003, 2011; Kaiser et al., 2006).

The parameterization was run in yearly intervals, from 1955 to 2000. The start date was chosen because it is the mean age plus 1σ of the deepest sample. Results from the mass balance calculation are shown in Fig. 9. The reconstructed stable carbon isotope ratio δ_P of the CFC-12 source changes considerably during the period concerned; it starts very depleted near 1950 and increases strongly. The increase slows down with time and during the last 10 yr of the parameterization δ_P begins to decrease. However, this decrease may not be significant given the small changes in the mixing ratio and the correspondingly large uncertainties in the net emissions.

In order to illustrate the influence of the sink fractionation effect in the model, the mass balance model was run to simulate the atmospheric δ^{13}C assuming a constant source delta, δ_P, of −45 ‰, the median value during the period 1955–2000. P, L, and ε are the same as above, and the starting (1955) δ^{13}C is set as −45 ‰. The resulting trend (Fig. 9, green trace) shows that our firn air measurements can be explained only if we assume that the isotope signature of the sources changed significantly over time. Furthermore, modeling of a hypothetical scenario with P set to 0 (thus indicating atmospheric trends in the future when atmospheric release has ceased and the sink fractionation drives CFC δ^{13}C evolution) indicated a systematic increase of only 0.29 ‰ per year.

The consistent increase in δ_P from the mass balance calculation prior to 1990 can potentially be explained by technological and industrial chemistry changes in the synthesis of CFC-12. Monocarbon chlorofluorocarbons may be synthesized by the following generalized reaction, either in the liquid, or more recently, in the gas phase at high temperatures and pressures:

$$CCl_4 + HF \xrightarrow{\text{catalyst}} CCl_3F + CClF_3 + HCl \qquad \text{(R3)}$$

The catalysts used for this reaction included $SbCl_5$ (first industrialization), or, more recently, various metallic and carbon compounds that promote chlorine-fluorine exchange. By contrast, the first CFC synthesis experiments in the 1890s used SbF_3Br_2 or SbF_3Cl_2 as a reagent (Daudt and Youker, 1935; Siegemund et al., 2003).

In addition to the above, the synthesis of the primary feedstock of CFC production, CCl_4, has changed significantly. Initially, synthesis was accomplished through the chlorination of CS_2. This was replaced within the last 50 yr by the sequential chlorination of methane, which is a less polluting, though more technically challenging, process. Despite this, the older process was still in use, though at relatively small scale, in several locations (Rossberg et al., 2003).

The release of CFC to the atmosphere undergoes variable time delays due to its diverse uses (e.g. McCulloch et al., 2003). Produced CFC was released promptly (within a short time scale, 1 to 4.5 yr) into the atmosphere through aerosol propellant use. On the other hand, the delay in CFC release to the atmosphere from non-hermetically sealed refrigeration and leakage from hermetically sealed refrigeration is difficult to quantify, with mean manufacturing to complete release times (total refrigerant release) approaching 10 yr or more. As the production (and consequently sale and usage) of CFC is now restricted, release to the atmosphere in more recent times is most likely leakage-based, which clouds the global source picture considerably due to the introduced time lag. Moreover, leakage is a continuous process unless refrigerant is released through damage, thus the aggregate effect of leakage of CFC manufactured at different times and locations (with varying δ^{13}C values) can have a long-lasting impact. This can only be resolved by refining emissions functions by directly measuring leakage rates and surveying produced CFC for δ^{13}C.

4 Conclusions

We have presented δ^{13}C (CF_2Cl_2) results from firn air collected in 2009 at the NEEM site in Greenland, the reconstructed atmospheric trend of which implies very depleted

δ^{13}C values in the middle of the last century, and a rapid enrichment (nearly 80 ‰) to the present day value near −40 ‰. Mass balance modeling indicates that changes in production processes of this compound must be responsible for most of this enrichment: indeed, process changes in the synthesis of both CFC-12 itself and the feedstock used in CFC production have occurred over the last 80 yr, due to technological advances. Furthermore, mass balance calculations indicate that in the future, when the release of the CFC to the atmosphere has ceased, the fractionation due to the photochemical sink will enrich the atmospheric reservoir continuously.

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Table 1. Firn air δ^{13}C and mixing ratio depth measurement series 1, 2 and mean.

Depth (m)	δ^{13}C Meas. 1[a]	δ^{13}C Meas. 2	δ^{13}C Mean[b]	[Meas. 1][c]	[Meas. 2]	[Mean][d]
10.5	−40.2	−41.3	−40.75	530	570	550
20.4	−42.5	−42	−42.25	536	540	538
30.2	−43.2	−43.1	−43.15	550	540	545
39.2	−43.8	−44.9	−44.35	527	527	527
50.7	−42.4	−41.2	−41.8	539	555	547
60.3	−44	−46.3	−45.15	530	527	528.5
62	−43.8	−46.4	−45.1	531	545	538
63.8	−44.4	−45.4	−44.9	460	473	466.5
66.8	−52.3	−53.3	−52.8	309	318	313.5
69.4	−78.3	−86.6	−82.45	168	169	168.5
71.9	–[e]	–	–	10	17	13.5

[a] ‰ vs. VPDB.

[b] 98 % confidence interval = 2.3 ‰.

[c] ppt = 10^{-12} mol mol^{-1}.

[d] 98 % confidence interval = 10 ppt.

[e] δ^{13}C not measurable; peak area below acceptable threshold.

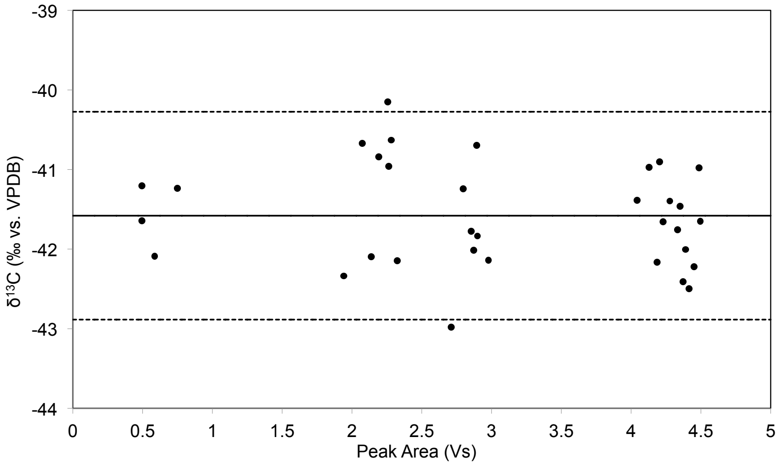

Fig. 1. Plot of δ^{13}C (CFC-12, vs. VPDB) against peak area shows sample size linearity of isotope ratio measurements of the calibration mixture (34 samples). Horizontal lines indicate mean (solid) and instrument ± 2 σ (dashed).

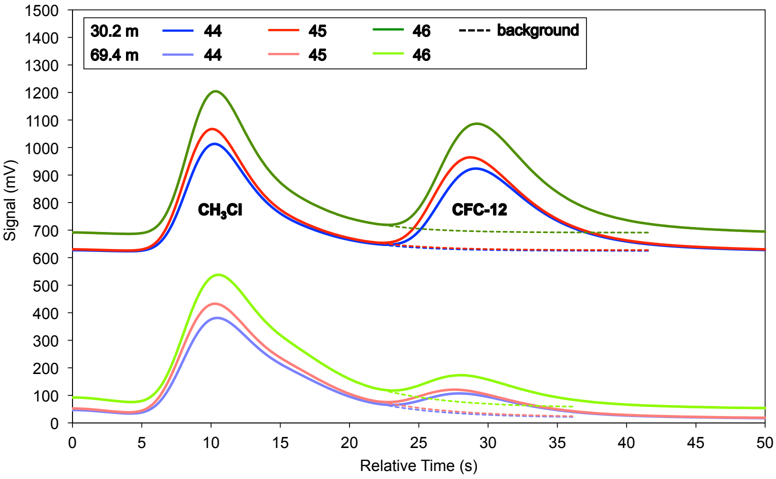

Fig. 2. Chromatograms of CH_3Cl and CFC-12 *m/z*44, 45, and 46 signals (mV) from 30.2 m (upper traces) and 69.4 m (lower traces) depth samples, showing sloping background calculation (dashed). Traces have been aligned through a +10 s time shift to the 30.2 m sample; additionally, the 30.2 m traces have been offset by 600 mV for presentation purposes.

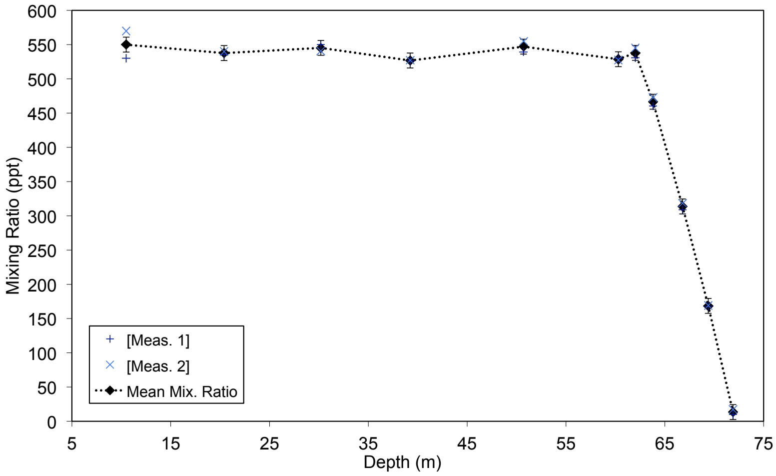

Fig. 3. Vertical profiles of CFC-12 mixing ratios (ppt) from firn air extracted from the S2 hole, NEEM, Greenland, for independent measurements 1 and 2, and mean values. Error bars represent 98 % confidence intervals with respect to the mean.

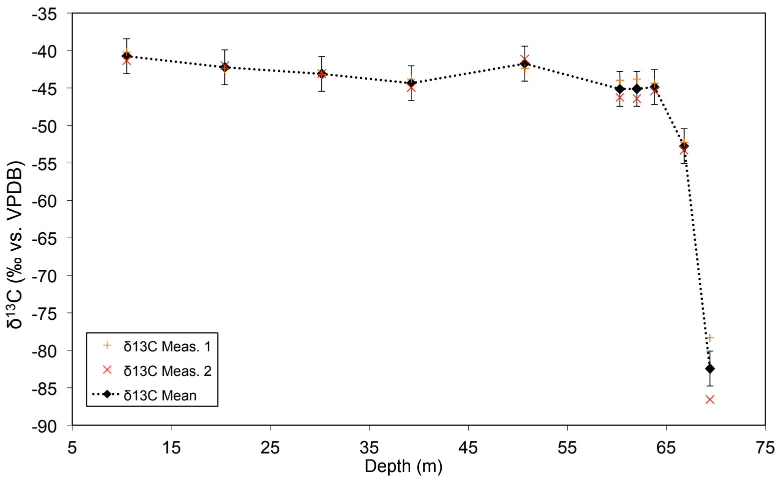

Fig. 4. Vertical profiles of δ^{13}C (CFC-12) (‰, vs. VPDB) from firn air at S2 drill site, NEEM, Greenland, for independent measurements 1 and 2 and mean values. Error bars represent 98 % confidence intervals with respect to the mean.

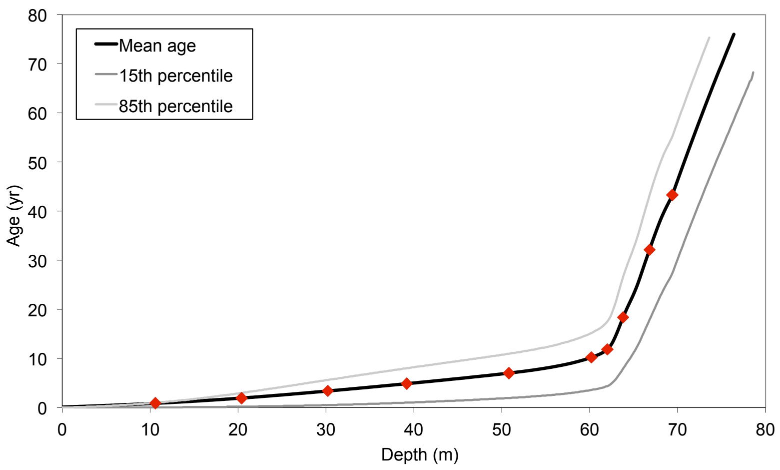

Fig. 5. Age (prior to 2009) distribution in the firn air column as a function of depth from the forward model. Red diamonds indicate sampling depths for reference.

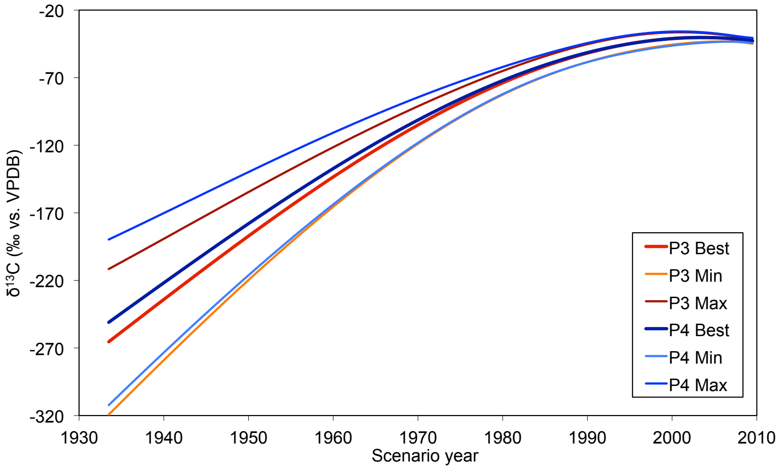

Fig. 6. Reconstructed δ^{13}C scenarios for CFC-12 from 1933 to 2009; Best scenarios, maxima, and minima. P3 and P4 indicate 3rd and 4th degree polynomial firn model results, respectively.

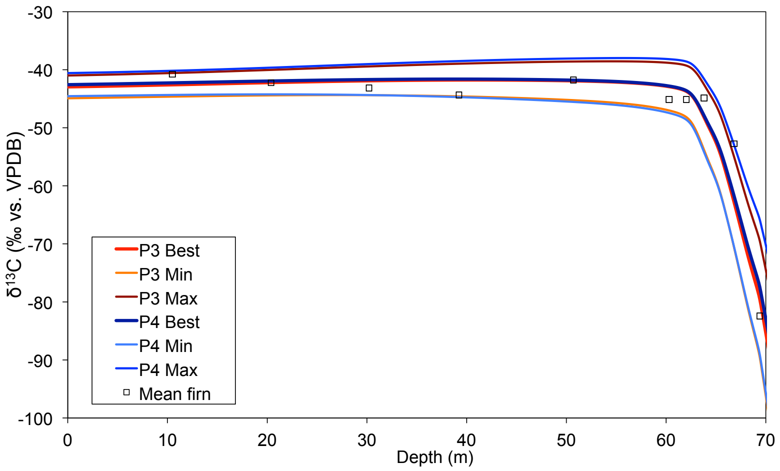

Fig. 7. 3rd and 4th degree polynomial forward model results and mean firn data with depth. The envelopes show the overall minimum and maximum values of all selected scenarios.

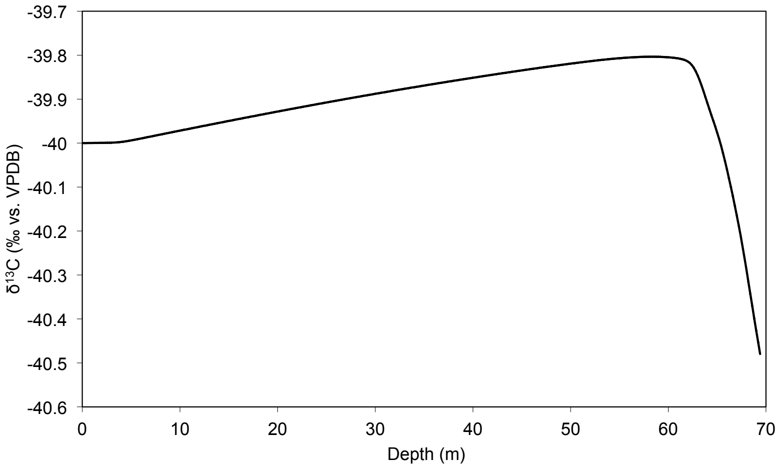

Fig. 8. Modeled fractionation effects from diffusion and gravitation based on a constant atmospheric δ^{13}C (−40 ‰) with time scenario input to the forward model.

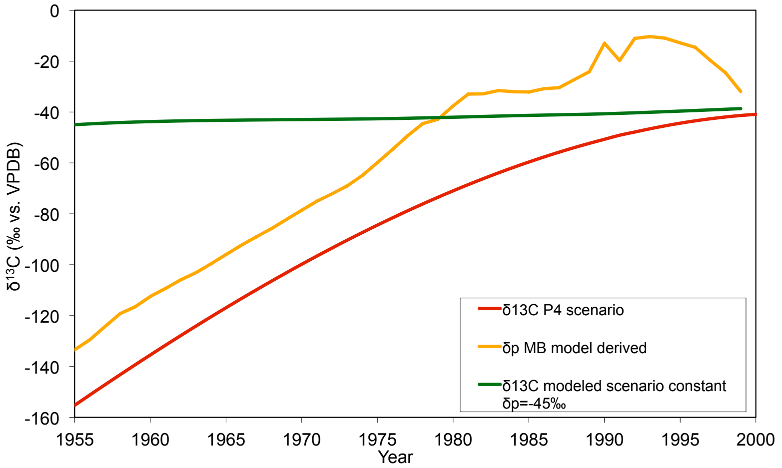

Fig. 9. Temporal evolution of reconstructed atmospheric δ^{13}C values (‰, red, best fit 4th degree polynomial from firn air modeling) which are used as mass balance model input to calculate δ^{13}C of the CFC-12 source (δ_P, orange); mass balance calculated scenario with constant δ_P = −45 ‰ and initial (1955) δ of −45 ‰ (green).