Responses to anonymous referee #1
General comments

Allin et al present analyses and interpretation of chlorine stable isotopes in CFC-12, CFC-11 and CFC-113 in tropospheric and stratospheric air samples, as well as in the Cape Grim air archive and in old air extracted from polar firn. This is an interesting data set in that it seems to present the first chlorine stable isotope measurements ever made on atmospheric CFC-11 and CFC-113. It also appears that the historical isotopic measurements (in the Cape Grim archive and in firn air) are a "first" for all species. The authors are to be commended for tackling such challenging measurements successfully. Because of the novelty of the measurements, this manuscript should ultimately be publishable in ACP. However, at this stage there are several major components that in my opinion are underdeveloped and/or confusing and require further work before the manuscript can be accepted.

Referee comment 1

p.31818 (Methodology) Much more detail is needed on all the samples (these could go either in the main body of the paper or in the supplement). For the stratospheric samples, were all the samples collected in the cited von Hobe et al., 2013 study measured? If not, the relevant sample subset needs to be described (collection dates, sample type, altitude, lat-long, etc).

Author response

Tables S5, S6, S7, S8 and S9 have been added to the supplement. These contain details of the stratospheric samples (sample ID, latitude, longitude, ltitude, ln [1 + *δ*] / ‰, ln [1 + uncertainty] / ‰ and ln (y/y_T)) and the tropospheric samples (sample ID, depth, air age, $\delta(^{37}\mathrm{Cl})$ and 1*σ* uncertainty).

Referee comment 2

For the Cape Grim archive, more details should be given supported by references.

Author response

Table S9 has been added to the supplement, detailing the sample ID, air age, $\delta(^{37}\mathrm{Cl})$ and 1*σ* uncertainty of the Cape Grim samples. Details of the sampling procedure have been previously reported in Langenfelds et al. (1996), which is cited in Table 2.

Referee comment 3

Have tests been performed to ensure that the species of interest are well preserved in the archive flasks over a long period of time, and are unaffected by artifacts at the times of archive creation and sub–sampling for this study?

Author response

The difference between sampling and analysis dates are highly variable, ranging from a few months to 34 years. In all cases, mole fractions for these species are consistent with previously reported time series (e.g. Martinerie et al., 2009), suggesting that they have not been altered by their storage environment.
The measured delta values from both firn air and the Cape Grim archive agree within measurement uncertainties. In this way, the Cape Grim measurements confirm that the firn measurements represent the atmospheric composition and have not been influenced by unaccounted for fractionation processes (e.g. during sampling). Also, we see delta values of 0 ‰ in 2006, meaning that measurements of samples from 2006 contain ^{37}Cl and ^{35}Cl in approximately the same ratio as the laboratory standard (air collected in 2006 at Niwot Ridge). This again suggests that our data represent reproducible measurements of the atmospheric composition. Finally, several different sampling procedures were used to collect air at Cape Grim (e.g. cryogenic trapping and direct pumping of air). There are no statistical differences between measurements made on samples collected using these different procedures.

References:
Martinerie, P., Nourtier-Mazauric, E., Barnola, J.-M., Sturges, W. T., Worton, D. R., Atlas, E., Gohar, L. K., Shine, K. P., and Brasseur, G. P.: Long-lived halocarbon trends and budgets from atmospheric chemistry modelling constrained with measurements in polar firn, Atmos. Chem. Phys., 9, 3911–3934, doi:10.5194/acp-9-3911-2009, 2009.

Referee comment 4

For the firn air samples, either a detailed description of the sampling campaigns or citations to papers containing these descriptions need to be provided.

Author response

The following description has been added to the methodology:

"Firn air was recovered from the NEEM ice core site in Greenland (NEEM Community Members, 2013) and from the Fletcher Promontory ice core site in Antarctica (Mulvaney et al., 2014). In each case, shallow ice core drills progressively penetrated the firn column, stopping every few meters to allow recovery of the firn air. The firn air extraction technique (Schwander et al., 1993) uses a bladder inflated at the bottom of the borehole to seal off ambient air from above. Gas pumps draw sample air from the firn surrounding the lowest level of the borehole through continuous Dekabon tubes (internal diameter ¼ inch) passing through the bladder and its end caps, compressing the air into sample flasks at the surface. An infrared analyser (LI-COR LI-7000) continuously monitors the sample line CO_2 and samples are only taken when the CO_2 drops to a stable reading lower than modern ambient levels, indicating that uncontaminated air is being extracted from the borehole."

References:
Mulvaney, R., Triest, J., and Alemany, O.: The James Ross Island and the Fletcher Promontory ice-core drilling projects, Ann. Glaciol., 55, 68, 179-188, doi: 10.3189/2014AoG68A044, 2014.

NEEM Community Members: Eemian interglacial reconstructed from a Greenland folded ice core, Nature, 493, 7433, 489-494, doi: 10.1038/nature11789, 2013.
Schwander, J., Barnola, J. M., Andrie, C., Leuenberger, M., Ludin, A., Raynaud, D., and Stauffer, B.: The age of the air in the firn and the ice at Summit, Greenland, J. Geophys. Res.-Atmos., 98, 2831–2838, doi:10.1029/92JD02383, 1993.

Referee comment 5

Have tests been performed to ensure that the CFCs of interest are not affected by firn air sampling artifacts?

Author response

See responses to comments 3 and 4.

Referee comment 6

p. 31819 (Sample Analysis) Is it possible that isotopic fractionation occurs during ionization and fragmentation in the MS ion source, affecting the measured values for CFC-11 and CFC-113? For both of those compounds, one of the Cl atoms is missing from the fragments that are actually measured. A discussion of this should be included.

Author response

Yes, the mass spectrometer is expected to cause isotopic fractionation. However, this fractionation is assumed to be identical for sample and standard and cancel out from the derived isotope delta since both are treated the same way (the "identical treatment principle"). This is standard practice for all relative isotope ratio measurements. The issue of delta linearity with respect to sample size is addressed in the discussion of the dilution series analysis in the supplement.

Referee comment 7

For equation 1, the authors need to justify why they use a non-standard definition of isotopic delta notation (without multiplying by the factor of 1000)

Author response

We are using the standard definition of delta (Eq. 1) and express the values in per mill, as stated in the ACPD paper. The factor of 1000 is included in the conversion to per mill, not in the definition of delta.

Referee comment 8

In equations 4 and 5, F seems to serve as both the magnitude of the trace gas flux as well as the bulk air flux – this should be clarified with subscripts.

Author response

The following definitions are now included:

“F: bulk air flux between troposphere and stratosphere and vice versa (in mol a^{-1})
F_{TS}: CFC flux from troposphere to stratosphere (in mol a^{-1})
F_{ST}: CFC flux from stratosphere to troposphere (in mol a^{-1})”

Referee comment 9

It is not clear to me that equation 8 follows from equation 7. Please present a more detailed derivation, in the supplement if necessary.

Author response

The following has been added to section 2.3:

“We have $y_T' = y_T\ (1 + \delta_T)\ R_{standard}$, $y_S' = y_S\ (1 + \delta_S)\ R_{standard}$ and $y_P' = y_P\ (1 + \delta_P)\ R_{standard}$. Substituting this into Eq. (7) gives Eq. (8)”

Referee comment 10

Same in regards to equations 9 & 10 following from 8 & 4

Author response

Eq. (4) is subtracted from Eq. (8) to give Eq. (9). Eq. (10) is derived in exactly the same fashion from Eq. (5), also using Eq. (11).

Referee comment 11

I don’t understand the purpose of equation 12. Delta(st) is a measured quantity, whereas epsilon(app) is inferred (in part from delta(st)). So why use epsilon(app) to calculate delta(st)?

Author response

The ACPD paper refers to Röckmann et al. (2003) to explain this. δ_{ST} is a representative value of the stratospheric composition at the boundary of the 2-box model (just as y_S is). It cannot be measured directly, but it is inferred from the ratio y_S/y_T and the empirically determined value for ε_{app}.

Referee comment 12

I think it would be useful to discuss the meaning and purpose of and differences between epsilon(app) and epsilon(j) in detail

Author response

The following has been added to section 2.3:

"$\varepsilon_{\mathrm{app}}$ is the apparent stratospheric isotope fractionation, which is empirically determined for the years 1999 to 2008 (reflecting the time of stratospheric sample collection and the age of stratospheric air). It depends on both chemistry and transport (Kaiser et al. 2006), which may have changed over the period of CFC emissions. ε_J is a model parameter that is tuned to give $\varepsilon_{\mathrm{app}}$ for the corresponding model years. It has no immediate physical interpretation and is only meaningful in the context of the chosen 2-box model."

Referee comment 13

After tuning J (the loss rate coefficient) in the manner described, are equations 4 – 6 then solved for Ys and P only?

Author response

Yes, that is correct.

Referee comment 14

Why is a larger suite of gases (than just CO2 and CH4) not used to constrain firn diffusivities for NEEM 2009? This should be done, unless the authors can demonstrate that this would make no significant difference to the firn modeling.

Author response

The firn modelling output has been re-calculated using SF_6, HFC-134a, CH_3CCl_3, CFC-11, CFC-12 and CFC-113 as additional constraints. This did not make a significant difference to the results, although we agree that it was worth doing. The following has been included in the supplement:

"Originally two gases (CO_2 and CH_4) were used to evaluate the firn diffusivity of the NEEM 2009 borehole (Zuiderweg et al., 2013). In the present study, SF_6, CFC-11, CFC-12, CFC-113, CH_3CCl_3 and HFC-134a have been used to update this diffusivity profile."

Referee comment 15

Table S4. The median age and age width are listed as preliminary. These need to be finalized.

Author response

This was an oversight and the numbers should not have been listed as preliminary. This has been changed. The caption now reads:

"Median air age and the width of the age distribution…"

Referee comment 16

I would recommend some chemical kinetics-based discussion of why epsilon(app) seems to be so much larger for CFC-12 than for CFC-11 and CFC-113 (and why the values appear to be similar for CFC-11 and CFC-113). To me, this seems like a somewhat surprising result.

Author response

$\varepsilon_{\mathrm{app}}$ is affected by chemistry and transport, but the influence of transport is likely to be similar for these CFCs because of their similar lifetimes. Therefore, changes in $\varepsilon_{\mathrm{app}}$ can directly be interpreted as changes in the intrinsic photochemical fractionation, which is dominated by photolysis. Theoretical quantum-chemical predictions of the photolytic isotope fractionations of these molecules are beyond the scope of this paper. However, we note that Zuiderweg et al. (2012) found that the $^{13}C/^{12}C$ fractionation during CFC-11 photolysis to be also of smaller magnitude to that of CFC-12, so the stronger fractionation of chlorine isotopes during CFC-12 photolysis is not entirely surprising.

Referee comment 17

The assumption of a constant Cl isotopic composition of the source for each of the gases is central to the box modeling. A discussion needs to be included justifying this assumption.

Author response

Without detailed information on isotopic fractionation during CFC production, changes in production processes or direct source gas measurements, this makes the fewest assumptions and is scientifically the most "economical" approach. In response to this comment, we show how the source $\delta(^{37}Cl)$ needs to change, assuming a constant tropospheric $\delta(^{37}Cl)$ (since there are no statistically significant trends in our tropospheric data). The figure and a more detailed discussion can be found in the response to comment 18.

Referee comment 18

I am not convinced by the box model interpretation of the tropospheric history data. I agree that given the relatively large measurement uncertainties, the presented interpretations (along with their relatively narrow uncertainty bands) are possible. However, many other scenarios would be just as consistent with the data and need to be explored as well. I would specifically recommend exploring more data – driven (rather than model – driven) historical scenarios and removing the assumptions of constant isotopic composition of the source and possibly of constant sink fractionation. Just visually assessing the data in figure 3, two distinct trends in the isotopes seem apparent for all species. In the early part of the record (before 1990), there seems to be a trend toward more negative isotopic values for all species, followed by an increasing trend after about 1990.

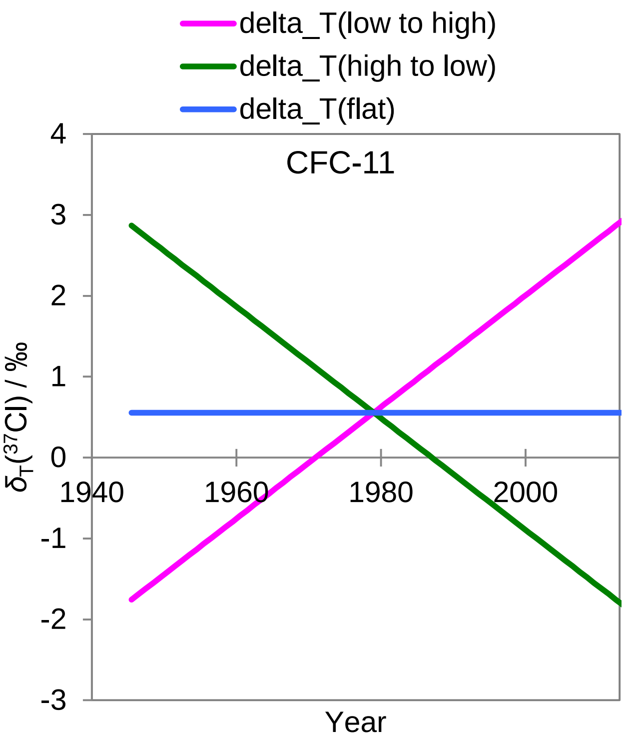
Author response

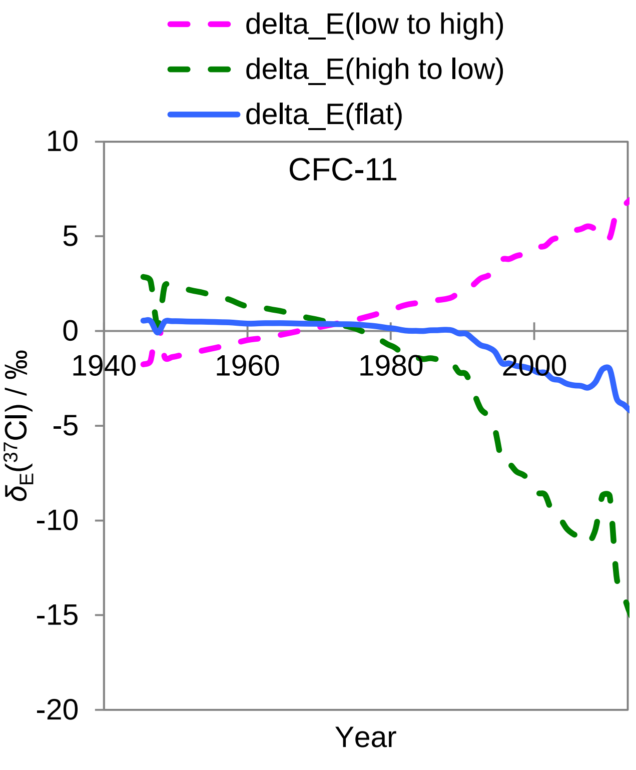
The 2-box budget equations (section 2.3) can be solved for the isotope delta of the emissions (δ_E) (Röckmann et al. 2003), using the measured tropospheric isotope delta (δ_T). However, the tropospheric measurements have large uncertainties and no statistically significant trends over time (see ‘Trends analysis’ below). Assuming a constant δ_T at the mean measured value (“delta_T(flat)” in the left hand panels below), the resultant emissions deltas are shown (“delta_E(flat)” in the right hand panels). The calculated decreases in δ_E are due to the stratospheric ^{37}Cl enrichment (Figure 1 of the ACPD paper), which would have to be balanced by a decreasing δ_E to produce a constant δ_T value. The decreasing emissions from the late 1980s (Figure 2 of the ACPD paper) make the δ_E decreases even more pronounced. These deviations from zero in the right hand panels do not indicate that the emissions have become significantly different from zero. These plots represent a cumulative effect over the whole time series, meaning that small tropospheric trends (hidden by the measurement uncertainties) would produce no change in the isotope delta of emissions (as shown in Figure 3 of the ACPD paper).

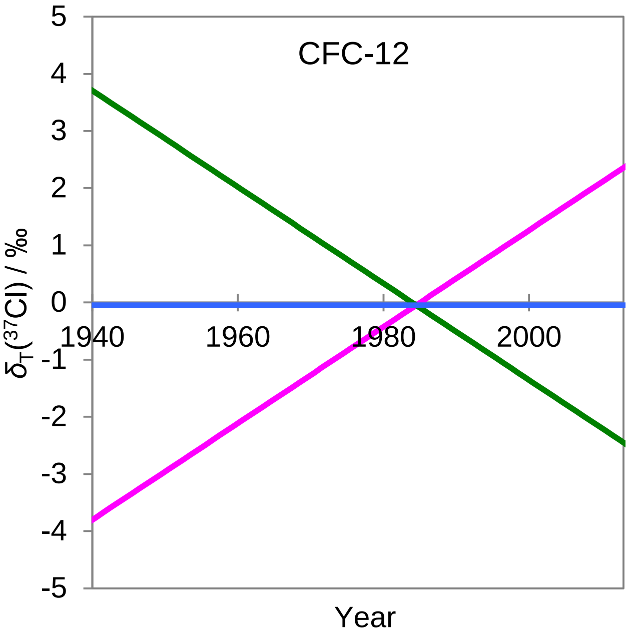
Additional atmospheric δ_T scenarios have also been investigated. The “delta_T(low to high)” scenario in the left hand panels represent a change from the mean value minus the standard deviation at the beginning of the record to the mean value plus the standard deviation at the end. The “delta_T(high to low)” represents the inverse calculation. The resultant emissions deltas in the right hand panels show the large range of δ_E histories that are possible, based on the δ_T atmospheric scenarios presented here.

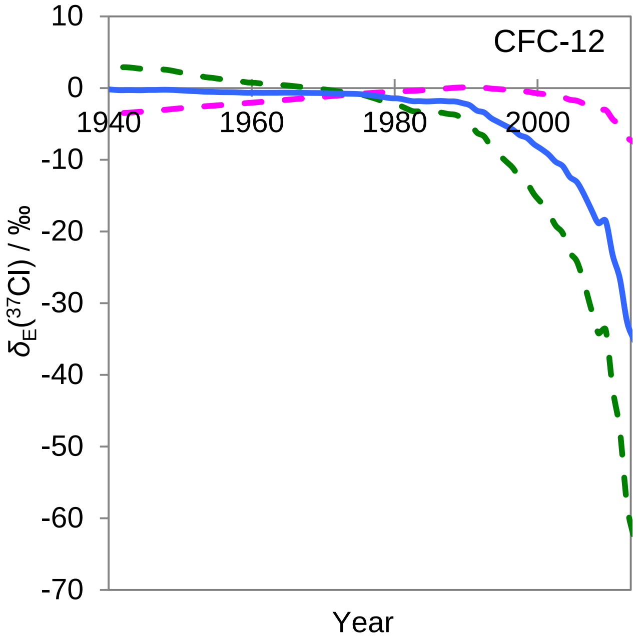
None of these trends are robust and were used to illustrate the range of δ_E histories that could have produced our δ_T measurements. At present, these trends are not thought to be realistic, because we have no evidence of a changing source composition, degradation in the environment (other than the stratosphere), or isotope fractionation during their production, storage and measurement.

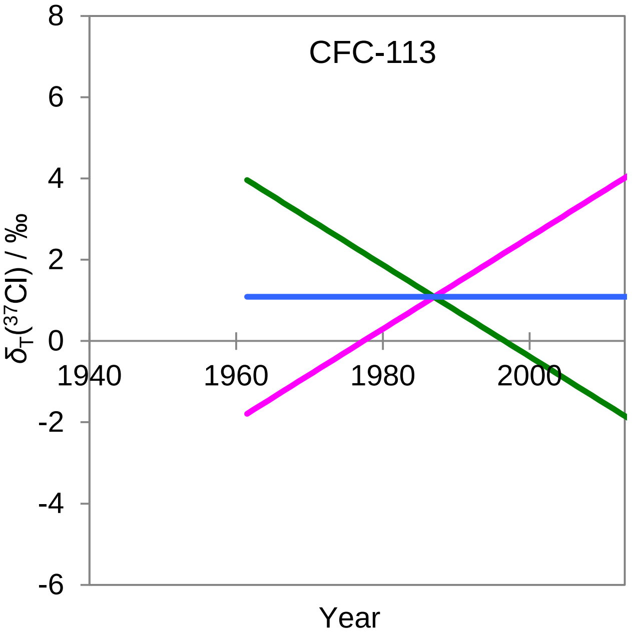
In light of this and based on the evidence that we do have, we present a constant source isotope delta scenario in the paper but point out that this is just one of a range of scenarios that would fit our tropospheric data.

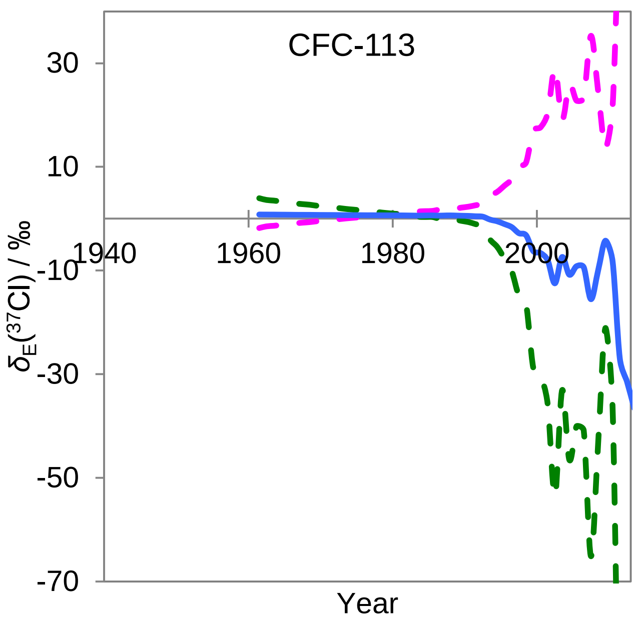












Trends analysis:

Using linear regression, we have derived the following trends for the entire data series:

CFC-11: (-0.044±0.023) ‰ a^{-1} ($p = 0.065$)
CFC-12: (-0.031±0.023) ‰ a^{-1} ($p = 0.19$)
CFC-113: (-0.063±0.030) ‰ a^{-1} ($p = 0.042$)

Except for CFC-113, these are not statistically significant at the 95 % confidence level. If the first point of the CFC-113 time series is omitted, the *p* value increases to 0.16; if the first two are omitted, the *p* value increases to 0.71.
Therefore, we do not consider any of these trends to be statistically robust.

Furthermore, as suggested by the reviewer, we have split each time series into two periods and compared the mean δ_T values for each period. This reduces the effect of individual data points that may bias linear regression analyses (see above).
We could not find any two periods with differences that were statistically significant at the 95 % confidence level. Using a *t*-test to compare the differences, the lowest *p* values were found for the following periods:

	CFC-11	CFC-12	CFC-113
Period 1	1946-1984	1955-1997	1962-1992
mean	2.1 ‰	0.7 ‰	2.4 ‰
standard deviation	3.2 ‰	3.3 ‰	3.3 ‰
standard error	1.1 ‰	0.7 ‰	0.8 ‰
number of data points *n*	9	24	15
Period 2	1985-2012	1998-2012	1993-2012
mean	0.2 ‰	–0.4 ‰	0.5 ‰
standard deviation	1.8 ‰	1.9 ‰	2.4 ‰
standard error	0.3 ‰	0.3 ‰	0.4 ‰
number of data points *n*	35	50	33
Difference period 2 minus period 1	–1.9 ‰	–1.1 ‰	–1.9 ‰
standard error	1.1 ‰	0.7 ‰	0.9 ‰
p	0.12	0.12	0.05

The following has been added to the abstract:

“From 1970 to the present-day, projected trends agree with tropospheric measurements, suggesting that within analytical uncertainties a constant average emission isotope delta is a compatible scenario. The measurement uncertainty is too high to determine whether the average emission isotope delta has been affected by changes in CFC manufacturing processes, or not.”

The following has been added to section 3.3:

“This means that for these three CFCs our observations are consistent with an isotopically invariant source signature, but the high measurement uncertainty does not allow us to preclude the possibility that it has changed over time.”

The following has been added to the conclusions:

“The predicted trends are small due to the long atmospheric lifetimes of the species and can largely be accounted for in our tropospheric measurements, although the high measurement uncertainty does not allow us to preclude the possibility that it has changed over time.”

Referee comment 19

Supplement, p.2. Please provide a reference for "the Matsunaga data series”

Author response

This has been added.

Referee comment 20

Figure S2. An equivalent plot for NEEM data should be provided for completeness

Author response

This is now included (Figure S3).

Referee comment 21

Table S3. For the caption, did you mean "median air age and the width of age distribution…”?

Author response

Yes, this has been changed.

Responses to anonymous referee #2
General comments

Allin et al provide evidence, based on measurements, of chlorine-isotope fractionations in CFC-11 and CFC-113 in the stratosphere and confirm findings of fractionation of CFC-12. Based on these fractionations and some model calculations using emissions of these CFCs they predict long-term trends of delta(37Cl) in these CFCs over the past decades. These are compared to measured delta(37Cl) in tropospheric archived air samples (firn, flasks).
The measurement-based findings of (expected) stratospheric fractionation for CFC-11 and CFC-113 is an important finding and appropriate for publication in this journal. The same is true for the tropospheric measurements despite the fact that not much can be said because of the relatively large uncertainties in the results compared to the expected signals. This paper should be published in ACP. However there are several issues that the authors need to take care of before publication. My major concern is about how the authors interpret the tropospheric results. There focus is given to the question of potential change in the delta(37Cl) in released CFCs over time and the magnitude of the change in d(37Cl) due to the stratospheric fractionation, and what the effect should be when mixed back into the troposphere. While I have no problem with the measurement results as such, as they are very convincing, the causal way these things are linked is not very convincing.

Referee comment 1

One of the major questions of this paper seems to be to understand if there had been chemical (isotope) changes in the production of the CFCs over time. I don't understand why this was not determined directly by measuring pure CFCs, which haven't cycled through the atmosphere. These CFCs must still be available in labs, old equipment etc. Obviously it would be a big task to approach this systematically but even with the analysis of a few pure CFC samples, a lot would be learnt. In fact, such samples might be readily available, for example from the group's effort to produce a primary calibration scale, which is presumably based on dilutions of pure CFCs. Often CFCs are used as boot-strap gases in the production of reference material for other compounds, and were probably already measured or readily available to be measured.

Author response

We would like to thank the reviewer for their comments, which we feel have improved our manuscript.
We agree that an investigation of source materials would make for a very useful study. Our study uses a "top-down" approach to quantify long-term global isotopic changes rather than the suggested "bottom-up" investigation of source materials. A systematic investigation of source isotope deltas would require the measurement of a large variety of source materials, which is beyond the scope of our study.

Referee comment 2

Also, I suggest that the authors write a short paragraph on how these CFCs are produced, such that the reader will understand what the source chemicals are, and if isotope changes over time might be expected, or if there are various chemical reactions to produce these CFCs etc.

Author response

The following paragraph has been added to section 3.3:

“Zuiderweg et al. (2013) describe how the manufacturing processes used to synthesise chlorofluorocarbons have altered through industrial advances in the 20th century. The most significant change occurred in the production of the main feedstock (CCl_4). Traditionally it was synthesised through the chlorination of CS_2, but in the last 50 years CH_4 has been used in this chlorination. Zuiderweg et al. (2013) cite these methodological changes as the most likely cause of the significant ^{13}C enrichment of CFC-12, but there is no direct evidence to confirm that changes in production processes have changed the isotope signature of the resultant CFCs.”

Referee comment 3

Abstract, l.2 ff. The study should referenced (probably full text citation depending on Copernicus rules).

Author response

This has been added.

Referee comment 4

Abstract, l. 13ff. This would read easier to me if you replaced ’estimate’ by ’calculate’ and ’due to’ by ’based on’.

Author response

This has been changed as suggested.

Referee comment 5

Abstract, l. 22: ’small’. Can you quantify, give a range or magnitude, is this ml or L the authors think of? This last sentence seems a bit lost anyway and I am not sure what the authors want to say with this.

Author response

This sentence highlights one of the main achievements of this work. Typically IRMS instruments use hundreds of litres of air to make measurements of isotope ratios in trace gases (e.g. Zuiderweg et al. 2013). We use approximately 200 ml of air in a single-detector system.
“(approximately 200 ml)” has been added.

Referee comment 6

Abstract, l. 19: This sentence is confusing, perphaps replace ’changes’ by ’potential changes’. It seems like the causality should be reversed, by saying ’We find no evidence of changes in CFC manufacturing processes that would have potentially lead to chlorine isotope variations...’. In general I am not convinced about this statement at all, if at all, it should be accompanied with some limitations, e.g. within the uncertainty of xxx. Obviously if there were multiple production processes each creating different isotope ratios then there could be large variations which potentially cancel out.

Author response

By reversing the causality as suggested, greater emphasis is placed on the manufacturing processes and source material isotopic composition. In structuring the causality as we have, we aimed to emphasise the measurements we have made, rather than those that we have not. However, we agree that the sentence could be improved. The following has been added:

“From 1970 to the present-day, projected trends agree with tropospheric measurements, suggesting that within analytical uncertainties a constant average emission isotope delta is a compatible scenario. The measurement uncertainty is too high to determine whether the average emission isotope delta has been affected by changes in CFC manufacturing processes, or not.”

Referee comment 7

Figures 1, 3. Tick marks on x-axes seem to be missing. Generally improve figures, they are rather small, the text is hard to read,

Author response

Figures have been improved as suggested.

Referee comment 8

p. 31817, l. 21. Can you be a bit more concrete about ’reservor’ (atmosphere?) and ’enrichement’ (of what?).

Author response

The following has replaced the original sentence:

“Zuiderweg et al. (2013) measured $\delta(^{13}\text{C}, \text{CFC-12})$ on NEEM firn air and reported a relative $^{13}\text{C}/^{12}\text{C}$ enrichment of up to 80 ‰ from 1950 to the present-day.”

Referee comment 9

p. 31820, line 11: Give a time frame for when ’all’ sample measurements were bracketed by standards. Was this by daily calibration runs? If sample and standards were alternated, then perhaps replace ’all’ by ’each’. As the sentence stands now, no information can be gained from it.

Author response

An alternating pattern was not used, so the word ‘each’ is not appropriate. We agree that this could be made clearer. The following has been added:

“Typically two sample measurements were made between standard runs, allowing instrumental drift to be quantified and corrected for.”

Referee comment 10

p. 31821 l.15 ff. Did the rejected measurements coincide with poor measurement precisions? Did the rejected measurements in one compound coincide with those in another compound? Any ideas why these were anomolous? Without having to read Laube et al., 2013, can you add a summarizing sentence on the procedure, which also explains if the ’500 samplings’ are actual measurement results. I presume that the rejected data are omitted from Fig. 1, it might be worth to mention that in the caption to Fig. 1. l. 21 Can you be more precise and say this per species?

Author response

Although some samples were rejected for multiple compounds, there is no discernible pattern. The individual measurement repeatability of rejected samples is worse than that of included samples for CFC-11 and CFC-113, but approximately the same for CFC-12. The $\varepsilon_{\mathrm{app}}$ values were the same (within 1σ) before and after the exclusion of the rejected measurements.

The following has been added to section 2.2:

“A statistical “bootstrap” analysis technique was used to determine $\varepsilon_{\mathrm{app}}$ values and their uncertainties (Volk et al., 1997). In this technique, a data pool is created by describing each sample with three values (the measured delta value and this value ± 1σ). The “bootstrap” tool draws 500 random samplings from the complete stratospheric data pool (including the possibility of drawing the same value repeatedly) to produce an overall $\varepsilon_{\mathrm{app}}$ value and a robust associated uncertainty range.”

“…rejected measurements are not included.” has been added to the caption of Figure 1 as suggested.

“21 % (CFC-11), 10 % (CFC-12) and 7 % (CFC-113) of the measurements were rejected using this method.” has been added to section 2.2 as suggested.

Referee comment 11

p. 31822, F: be more clear about the flux. Between which compartments, and which direction is positive/negative.

Author response

All fluxes are always positive. The following definitions are now included:

"F: bulk air flux between troposphere and stratosphere and vice versa (in mol a^{-1})
F_{TS}: CFC flux from troposphere to stratosphere (in mol a^{-1})
F_{ST}: CFC flux from stratosphere to troposphere (in mol a^{-1})"

Referee comment 12

P: 'trace gas production'. The term 'production' is missleading here, replace something that denotes emission to the troposphere.

Author response

We are using the term "production" for any source to the atmosphere. However, given that this term could be understood to mean anthropogenic production, we agree that "emission" would be clearer.
The "P" term has been replaced by "E" in all cases and the following definition is now included:

"E: trace gas emissions (in mol a^{-1})"

Referee comment 13

p. 31824, l. 2ff: Why are there numbers in parentheses, and do the (1) and (2) relate to the following (1) and (2). Suggest to remove and describe differently.

Author response

Altered as suggested. The following has been added to section 2.4:

"The migration of gases from the atmosphere through firn is largely controlled by diffusional and gravitational effects, such that less diffusive gases move through the firn more slowly than more diffusive gases and heavier gases and isotopologues are enriched at depth relative to lighter gases and isotopologues. Consequently, there is no unique "age-of-air" at a given depth in the firn, rather an age distribution is calculated for a specific gas or isotopologue. Also, a gas can undergo significant isotope fractionation during its movement through the firn."

Referee comment 14

p. 31824, l. 5: The wording suggests that the age of air for an individual gas or isotopologue is unique. Aren't these time distributions for individual gases?

Author response

We agree that the original wording was misleading. The following has been included:

“Consequently, there is no unique “age-of-air” at a given depth in the firn, rather an age distribution is calculated for a specific gas or isotopologue.”

Referee comment 15

p. 31824, l. 7. Is the fractionation due to only the two processes mentioned a few lines up or other processes causing fractionation in the firn?

Author response

These processes significantly affect the movement of gases in firn and are accounted for in the firn transport model. Other processes (e.g. thermal fractionation) are not thought to be significant and are therefore not included.

Referee comment 16

p. 31824, l. 26. Perhaps change to ’reconstructed scenario of the gas mole fraction (based on ...) if this is what the authors are trying to say. Can you give a rough estimate of the magnitudes of these processes for these compounds, something that lets the reader understand how important/significant these corrections are.

Author response

The following has been added:

“For within-firn isotope fractionation, a correction (of 1 – 2 ‰) is calculated using the reconstructed scenario of the gas mole fraction and assuming a constant atmospheric isotope delta.”

Referee comment 17

p. 31825, l. 14: ’sink processes prefer ....’ sounds jargon, can you rephrase.

Author response

This has been replaced with “sink reactions discriminate against heavier isotopes, in other words, the heavier isotopologue is broken down more slowly…”

Referee comment 18

Can you provide figures of dCl vs altitude similar to those in Laube et al., 2010. I find these findings of Cl isotope depletion a much stronger result than the temporal evolution of the tropospheric dCl

Author response

We chose to present the stratospheric data in Rayleigh plots (Figure 1) because this allows us to show the reader how the $\varepsilon_{\mathrm{app}}$ values where calculated (which are then used in the transport model).
In our study the samples were collected at altitudes between 10 and 20 km, whereas the study by Laube et al. sampled between 14 and 34 km. The more limited sampling altitude range in our study means that plots of $\delta(^{37}\mathrm{Cl})$ vs altitude do not provide a strong result.
Plots of $\delta(^{37}\mathrm{Cl})$ vs altitude are not used in our calculations and would not be an informative addition to our study.

Referee comment 19

p. 31841, Fig 3 caption line 6. Better say something along the lines of ’nonlinearities’ as in this context the reader does not understand ’dilution series analysis’. ’relative to 2006 standard air’. It is a bit missleading to call a single air sample ’2006 standard air’. Perhaps change to something like ’relative to an air samples collected in 2006’.

Author response

Changes made as suggested.

Referee comment 20

section 3.3 (p. 31827) is written in a rather confusing way and should be improved. The confusing parts are e.g. l. 6. ’This’, meaning the present or the referenced study? perhaps replace by ’present’. ’include two additional species’ why not name them? l. 14: ’...such as theses’. l. 15: ’slightly higher’. In delta or mole fractions. ’slightly higher’ is not very informative. I find these a lot higher. l. 19: ’... and these measurements...?’ should this say ’correction’?

Author response

Changes made as suggested:

“This” has been replaced by “The present”, “including two additional species” has been replaced by “and also includes CFC-11 and CFC-113”, “well-mixed gases such as these” has been replaced by “these well-mixed gases” and “slightly higher” has been replaced by “between 5 and 10 ‰ higher”.

Regarding the final suggestion, “correction” is not what is meant. However, we agree that the sentence could be made clearer. The following has been included:

“As the oldest samples, these 5 measurements contain the lowest CFC mole fractions, producing higher than average analytical uncertainties. Also, a small correction was applied to 4 of them, introducing an additional error (details in supplement).”

Referee comment 21

When looking at Fig 3, it does not look like good agreement between firn and CGAA for CFC-113.

Author response

In the age range covered by both firn and Cape Grim samples they have mean values of -0.1 ± 2.4 ‰ and 2.1 ± 2.3 ‰, respectively.

Referee comment 22

When eye-balling in Fig 3, there seems to be an opposite trend for CFC-12 than what one would expect, by a few permil over the decades 1950 – 2000.

Author response

There are no statistically significant trends.

Using linear regression, we have derived the following trends for the entire data series:
CFC-11: (-0.044±0.023) ‰ a^{-1} ($p = 0.065$)
CFC-12: (-0.031±0.023) ‰ a^{-1} ($p = 0.19$)
CFC-113: (-0.063±0.030) ‰ a^{-1} ($p = 0.042$)

Except for CFC-113, these are not statistically significant at the 95 % confidence level. If the first point of the CFC-113 time series is omitted, the p value increases to 0.16; if the first two are omitted, the p value increases to 0.71.

Therefore, we do not consider any of these trends to be statistically robust.

Furthermore, as suggested by the reviewer, we have split each time series into two periods and compared the mean δ_T values for each period. This reduces the effect of individual data points that may bias linear regression analyses (see above).

We could not find any two periods with differences that were statistically significant at the 95 % confidence level. Using a *t*-test to compare the differences, the lowest p values were found for the following periods:

	CFC-11	CFC-12	CFC-113
Period 1	1946-1984	1955-1997	1962-1992
mean	2.1 ‰	0.7 ‰	2.4 ‰
standard deviation	3.2 ‰	3.3 ‰	3.3 ‰
standard error	1.1 ‰	0.7 ‰	0.8 ‰
number of data points *n*	9	24	15
Period 2	1985-2012	1998-2012	1993-2012
mean	0.2 ‰	–0.4 ‰	0.5 ‰
standard deviation	1.8 ‰	1.9 ‰	2.4 ‰
standard error	0.3 ‰	0.3 ‰	0.4 ‰
number of data points *n*	35	50	33
Difference period 2 minus period 1	–1.9 ‰	–1.1 ‰	–1.9 ‰

standard error	1.1 ‰	0.7 ‰	0.9 ‰
p	0.12	0.12	0.05

Referee comment 23

l. 26. Shouldn't it be rather: '...isotopcially constant source signature based on the current understanding ....' You can't say that both (constant source and current understanding) are consistent, this could easily cancel out. Here again, if a constant source signature is consistent, then why wasn't there a single measurement done on a pure CFC sample to check if that is in agreement with the atmospheric observations?

Author response

Yes, the sentence now reads:

"This means that for these three CFCs our observations are consistent with an isotopically invariant source signature, but the high measurement uncertainty does not allow us to preclude the possibility that it has changed over time."

See response to comment 1.

Referee comment 24

p. 31828, lines 3ff. The CFC-12 system before the industrial release was very well balanced (zero). I don't think this has to do with a 'balanced' system alone, but primarily with the existance of pre-industrial N2O (and absence of CFC-12) per se.

Author response

We have already described the existence of pre-industrial N_2O as the primary factor. The word "balanced" has been removed. The passage now reads:

"Despite the noted parallels in atmospheric chemical behaviour between CFC-12 and N_2O, their atmospheric isotope delta histories differ because N_2O has been present in the atmosphere for at least 800,000 years longer than CFC-12 (Spahni et al., 2005; Schilt et al., 2010). When anthropogenic emissions began, atmospheric N_2O isotope deltas were perturbed from a near steady-state source-sink system, whereas the industrial release of CFC-12 was not preceded by any atmospheric burden. This has caused $\delta(^{15}N, N_2O)$ and $\delta(^{18}O, N_2O)$ to decrease over the last century (Röckmann et al., 2003), while $\delta(^{37}Cl, \text{CFC-12})$ is predicted to have increased slightly (Figure 3)."

Referee comment 25

p. 31828, l. 10: It might be better to replace 'cite' by 'suspect' or similar.

Author response

We disagree. In our opinion the sentence reads better as it is.

Referee comment 26

It appears that the entire Zuiderweg et al., 2013 story is based on 2 samples, were these analysed in the present study also? I am not very convinced about the line of argumentation, it appears very unlikely to have a large 13C variation without any concurrent change in Cl. Could a potential change in 13C mask/obscure some of the Cl measurements given that in the present study the measured fragments contain 'C'. Or is the 13C much less abundant in CFC-12 to affect the measured fragments?

Author response

Yes, the two samples identified from the Zuiderweg et al. study were measured in our study. They agree with our other results; our $\delta(^{37}\mathrm{Cl})$ measurements do not show any sign of the $\delta(^{13}\mathrm{C})$ changes reported by Zuiderweg et al. (2013). It is difficult to speculate whether a change in one could occur without a concurrent change in the other, although we agree that it is unlikely. Investigating the influence of changes in source materials and manufacturing processes on $\delta(^{37}\mathrm{Cl})$ and $\delta(^{13}\mathrm{C})$ would make for a very interesting and useful study. However, these measurements are beyond the scope of our study.
As stated in the ACPD paper, the instrument used for these measurements is run at a mass resolution of 1000 and we can therefore rule out interference from fragments containing ^{13}C.

Referee comment 27

Please publish the major numerical results of the measurements (e.g. those that lead to Fig. 1 or 3), in an appropriate way (e.g. in the SI).

Author response

Tables S5, S6, S7, S8 and S9 have been added to the supplement. These contain details of the stratospheric samples (sample ID, latitude, longitude, ltitude, ln [1 + δ] / ‰, ln [1 + uncertainty] / ‰ and ln (y/y_T)) and the tropospheric samples (sample ID, depth, air age, $\delta(^{37}\mathrm{Cl})$ and 1σ uncertainty).

Referee comment 28

Does ocean-atmosphere exchange play into this story particularly in the near future when CFCs are being release back to the atmosphere from the oceans, and some partical degradation (e.g. CFC-113 under suboxic conditions) might undergo large fractionations.

Author response

Oceanic sinks are negligible for the atmospheric budget of these compounds and are therefore very unlikely to alter their atmospheric isotope budgets. For this reason, we do not intend to include a discussion of ocean-atmosphere effects in this manuscript. Future studies of CFCs in the ocean interior may well want to look into processes such as degradation under suboxic conditions.

Referee comment 29

Supplement: Nonlinearity. These needs a few more information. Table S1. Is this one single sample (SX-0706077) that was diluted? What was it diluted with? What is SX-0706077, is this a real air sample or an artificial mixture? In the caption, mention that these are 'measured' mole fractions to clearly distinguish from the calculated mole fractions for this dilution series. Is there a reason why there are only mole fractions listed for this nonlinearity test, and not the delta values as well? Also, can you explain, which fragment is used for the calculation of the mole fractions. In the main text it is stated that C(35Cl)2F+ (m/z 101) and C35ClClF+ (m/z 103) and C(37Cl)2F+ are measured but it is not clear which is/are used for the mole fraction calculations. How was the nonlinearity determined, was it against calculated dilutions or only by comparing the three compounds (in which case one would be vulnerable to simultaneous changes/errors in the three compounds towards lower mole fractions.

Author response

The following has been added:

"**Table S1.** An air sample collected at Niwot Ridge in 2009 (SX-0706077) was diluted with nitrogen. Mole fractions for CFC-11, CFC-12 and CFC-113 were measured using the most abundant fragment ion (*m/z* 101). 1σ standard deviation errors are given. $\delta(^{37}\mathrm{Cl})$ measurements were also made on these samples (Figure S1 and Table S10)."

These are all measured mole fractions.

The nonlinearities were calculated relative to the undiluted 2009 air sample (SX-0706077), which was used to make the dilutions. The dilution series measurements (Table S10) were made against the 2006 air standard used for all measurements in this manuscript, to ensure internal consistency.

Chlorine isotope composition in chlorofluorocarbons CFC-11, CFC-12 and CFC-113 in firn, stratospheric and tropospheric air

S. J. Allin[1], J. C. Laube[1], E. Witrant[2], J. Kaiser[1], E. McKenna[1], P. Dennis[1], R. Mulvaney[3], E. Capron[3], P. Martinerie[4], T. Röckmann[5], T. Blunier[6], J. Schwander[7], P. J. Fraser[8], R. L. Langenfelds[8] and W. T. Sturges[1]

[1] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK

[2] Grenoble Image Parole Signal Automatique, Université Joseph Fourier/CNRS, France

[3] British Antarctic Survey, Natural Environment Research Council, Cambridge, UK

[4] CNRS/Univ. Grenoble Alpes, F-38041, Grenoble, France

[5] Max-Planck Institute for Nuclear Physics, Heidelberg, Germany

[6] Centre for Ice and Climate, University of Copenhagen, Denmark

[7] Physics Institute, University of Bern, Switzerland

[8] Centre for Australian Weather and Climate Research, Commonwealth Scientific and Industrial Research Organisation, Aspendale, Australia

1. Determination of non-linearities

A static dilution series was analysed to determine whether the measured isotope ratio of a sample is dependent on its mole fraction (i.e. whether a change in chromatographic peak size alters the measured isotope delta). Table S1 gives details of the samples analysed in the dilution series.

Figure S1 shows that delta values derived from the smallest peak areas exhibit erroneously low $\delta(^{37}\mathrm{Cl})$ values for all three species, which requires a correction. 99 % of the samples analysed have peak areas in the region where the dilution series showed no bias in the isotope delta. However, a total of 1 (CFC-11), 2 (CFC-12) and 2 (CFC-113) $\delta(^{37}Cl)$ measurements were corrected based on the instrument bias quantified by the smallest peaks in the dilution series analysis (Figure S1 insets). A linear regression line was used to track the depletion in the smallest peaks produced during the dilution series analysis. This line was then used to correct the firn measurements, based on their peak areas. An additional uncertainty was carried forward for each corrected measurement based on the uncertainty in the regression line. This uncertainty was factored such that the size of the additional uncertainty applied to a measurement is directly related to the size of the correction required.

This dilution series analysis shows an isotope delta bias which is limited to the lowest concentration samples; most samples display no bias. The unaffected samples cover a large range of mole fractions and were analysed using a variety of air volumes. Any systematic effect should be shown in these data. The absence of an effect suggests that the GC, MS and inlet system do not affect isotope deltas. It is likely that the bias shown in small peaks is introduced during data processing steps, rather than during the measurement acquisition.

2. Firn modelling

The diffusivity of firn largely determines its gas transport characteristics. The physical basis of this model is described in Witrant et al. (2012). Recent algorithm development allows the use of several reference gases to adjust the firn diffusivity, improving the quality of firn models (e.g. Buizert et al., 2012). Originally two gases (CO_2 and CH_4) were used to evaluate the firn diffusivity of the NEEM 2009 borehole (Zuiderweg et al., 2013). In the present study, SF_6, CFC-11, CFC-12, CFC-113, CH_3CCl_3 and HFC-134a have been used to update this diffusivity profile. Fletcher Promontory firn was sampled by the British Antarctic Survey in December 2011. An accumulation rate of 38 cm water equivalent per year (nearly twice the NEEM value) results in high downward advection in Fletcher firn and thus younger gas ages than at NEEM (see Tables S3 and S4). The reference gases used to estimate the firn diffusivity are: CH_4, SF_6, CFC-11, CFC-12, CFC-113, CH_3CCl_3 and HFC-134a.

Comment [S.J.A.1]: Referee 1, comment 14.

Diffusion coefficient ratios were calculated in the same way as Buizert et al. (2012). Diffusion coefficients for “major isotopologues” (including their temperature dependencies) and relative diffusion coefficients for pairs of isotopologues were calculated from Equation (6) (in the Supplement of Buizert et al., 2012). The corresponding values are shown in Table S2. Here we assumed that $C^{35}Cl_2F_2$ (the “major isotopologue”) has the same diffusion coefficient as the inclusion of all isotopologues. The diffusion coefficients of the isotopologues of a given CFC differ by less than the uncertainty on the total diffusion coefficient (~2 %).

Comment [S.J.A.2]: Referee 1, comment 19.

A correction for within-firn isotope fractionation is calculated using a reconstructed scenario for each gas and assuming a constant atmospheric isotope composition over time. Changes in fractionation with depth therefore reflect firn fractionation processes alone; they are used to correct the measured values. The corrections made to the Fletcher Promontory $\delta(^{37}Cl)$ measurements are shown in Figure S2. At the greatest depths, the corrections were around +2 ‰ for CFC-11 and CFC-12, and around +1 ‰ for CFC-113. For the NEEM data (not shown), the corrections were broadly similar.

References

Buizert, C., Martinerie, P., Petrenko, V. V., Severinghaus, J. P., Trudinger, C. M., Witrant, E., Rosen, J. L., Orsi, A. J., Rubino, M., Etheridge, D. M., Steele, L. P., Hogan, C., Laube, J. C., Sturges, W. T., Levchenko, V. A., Smith, A. M., Levin, I., Conway, T. J., Dlugokencky, E. J., Lang, P. M., Kawamura, K., Jenk, T. M., White, J.W. C., Sowers, T., Schwander, J. and Blunier, T.: Gas transport in firn: multiple-tracer characterisation and model intercomparison for NEEM, Northern Greenland, Atmos. Chem. Phys., 12, 4259–4277, doi:10.5194/acp-12-4259-2012, 2012.

CRC: CRC Handbook of Chemistry and Physics, 83rd Edition, CRC Press, Boca Raton, FL, USA, 2002.

Witrant, E., Martinerie, P., Hogan, C., Laube, J. C., Kawamura, K., Capron, E., Montzka, S. A., Dlugokencky, E. J., Etheridge, D., Blunier, T. and Sturges, W. T.: A new multi-gas constrained model of trace gas non-homogeneous transport in firn: evaluation and behaviour at eleven polar sites, Atmos. Chem. Phys., 12, 11465-11483, doi:10.5194/acp-12-11465-2012, 2012.

Zuiderweg, A., Holzinger, R., Martinerie, P., Schneider, R., Kaiser, J., Witrant, E., Etheridge, D., Petrenko, V., Blunier, T., and Röckmann, T.: Extreme ^{13}C depletion of CCl_2F_2 in firn air samples, Atmos. Chem. Phys., 13, 599-609, doi:10.5194/acp-13-599-2013, 2013.

Table S1. An air sample collected at Niwot Ridge in 2009 (SX-0706077) was diluted with nitrogen. Mole fractions for CFC-11, CFC-12 and CFC-113 were measured using the most abundant fragment ion (*m/z* 101). 1*σ* standard deviations are given. $\delta(^{37}\mathrm{Cl})$ measurements were also made on these samples (Figure S1 and Table S10).

Comment [S.J.A.3]: Referee 2, comment 29.

	Compound		
Sample ID	***y*(CFC-11) / pmol mol^{-1}**	***y*(CFC-12) / pmol mol^{-1}**	***y*(CFC-113) / pmol mol^{-1}**
SX-0706077	245.1 ± 3.6	540.0 ± 3.4	78.1 ± 0.2
K1579	164.9 ± 2.4	363.4 ± 0.7	52.7 ± 0.1
K1578	75.9 ± 0.7	167.0 ± 0.8	24.1 ± 0.1
K1583	38.5 ± 0.3	84.1 ± 0.4	12.2 ± 0.1
K1569	17.7 ± 0.2	38.8 ± 0.1	5.6 ± 0.02
K1575	2.9 ± 0.02	6.6 ± 0.1	0.9 ± 0.01
K1576	0	0.1	0

Table S2. Molecular masses and relative diffusion coefficients (with respect to the reference gas shown) used in the firn model.

Species	CFC-11	CFC-11	CFC-11	CFC-12	CFC-12	CFC-12	CFC-113	CFC-113	CFC-113
Isotopologue	$^{12}C^{35}Cl_3F$	$^{12}C^{35}Cl_2{}^{37}ClF$	$^{12}C^{35}Cl^{37}Cl_2F$	$^{12}C^{35}Cl_2F_2$	$^{12}C^{35}Cl^{37}ClF_2$	$^{12}C^{37}Cl_2F_2$	$^{12}C_2{}^{35}Cl_3F_3$	$^{12}C_2{}^{35}Cl_2{}^{37}ClF_3$	$^{12}C_2{}^{35}Cl^{37}Cl_2F_3$
Molar mass / g mol^{-1}	136.3998	138.3969	140.3939	119.9452	121.9423	123.9393	186.4073	188.4044	190.4014
Reference	CO_2	$^{12}C^{35}Cl_3F$	$^{12}C^{35}Cl_3F$	CO_2	$^{12}C^{35}Cl_2F_2$	$^{12}C^{35}Cl_2F_2$	CO_2	$^{12}C_2{}^{35}Cl_3F_3$	$^{12}C_2{}^{35}Cl_3F_3$
D/D_{ref} NEEM	0.5251	0.9987	0.9975	0.5965	0.9984	0.9969	0.4527	0.9993	0.9986
D/D_{ref} FLT	0.5250	0.9987	0.9975	0.5961	0.9984	0.9969	0.4526	0.9993	0.9986

Table S3. Median air age and the width of the age distribution (15 % to 85 % accumulated probability interval i.e. ± 1σ equivalent) for NEEM 2009. Results are given for closest model depths to measurement depths.

Comment [S.J.A.4]: Referee 1, comment 21.

Depth	CFC-11	CFC-12	CFC-113
0.00 m	0.0(0.0-0.0)	0.0(0.0-0.0)	0.0(0.0-0.0)
10.60 m	0.2(0.0-1.0)	0.2(0.0-1.0)	0.2(0.0-1.1)
20.40 m	0.7(0.2-3.3)	0.7(0.2-3.1)	0.7(0.2-3.6)
30.20 m	1.8(0.5-6.5)	1.6(0.5-5.9)	1.9(0.6-7.3)
39.20 m	3.1(1.1-9.4)	2.8(1.0-8.4)	3.5(1.3-11)
50.80 m	5.3(2.2-13)	4.8(1.9-12)	6.0(2.5-15)
60.20 m	8.3(4.0-18)	7.5(3.6-16)	9.5(4.7-20)
62.00 m	9.8(4.9-20)	8.9(4.4-19)	11(5.7-23)
63.80 m	16(8.8-30)	15(8.0-28)	18(9.8-32)
66.80 m	30(19-46)	28(18-45)	32(21-49)
69.40 m	41(29-59)	39(28-57)	43(31-61)
72.00 m	54(41-72)	52(40-70)	56(43-74)
73.60 m	61(49-79)	59(47-77)	63(51-81)

Table S4. Median air age and the width of the age distribution (15 % to 85 % accumulated probability interval i.e. ± 1σ equivalent) for Fletcher. Results are given for closest model depths to measurement depths.

Comment [S.J.A.5]: Referee 1, comment 15.

Depth	CFC-11	CFC-12	CFC-113
0.00 m	0.0(0.0-0.0)	0.0(0.0-0.0)	0.0(0.0-0.0)
3.00 m	0.1(0.0-0.5)	0.1(0.0-0.4)	0.1(0.0-0.6)
7.00 m	0.3(0.0-2.1)	0.3(0.0-1.8)	0.3(0.1-2.3)
11.00 m	0.7(0.2-4.5)	0.6(0.2-4.0)	0.8(0.2-5.2)
18.60 m	1.9(0.5-9.5)	1.7(0.4-8.4)	2.3(0.6-11)
22.00 m	2.6(0.8-11)	2.3(0.7-10)	3.0(0.8-13)
26.60 m	3.7(1.1-14)	3.2(0.9-12)	4.2(1.3-16)
38.00 m	6.3(2.2-18)	5.5(1.9-16)	7.3(2.5-21)
44.80 m	7.9(3.0-21)	7.0(2.6-18)	9.1(3.4-24)
50.20 m	9.3(3.8-23)	8.3(3.3-20)	11(4.3-26)
56.20 m	11(4.8-25)	9.8(4.3-22)	13(5.6-28)
59.20 m	12(5.5-26)	11(4.8-23)	14(6.3-30)
62.20 m	13(6.3-27)	12(5.5-24)	15(7.3-31)
65.20 m	15(7.3-29)	13(6.4-26)	17(8.3-33)
68.20 m	16(8.7-31)	15(7.7-27)	19(9.9-35)
70.20 m	20(12-34)	18(10-31)	22(13-38)
72.00 m	24(16-39)	23(14-36)	27(17-43)
74.40 m	30(21-44)	28(19-41)	32(22-49)
76.20 m	34(25-49)	32(24-46)	36(27-53)
78.20 m	39(29-53)	37(28-50)	41(31-58)
79.20 m	41(32-56)	39(30-52)	43(33-60)
80.60 m	44(35-59)	42(33-56)	46(36-63)

Table S5. The CFC-11 stratospheric data used in Figure 1. The ID code, latitude, longitude and altitude of each sample are also included.

Comment [S.J.A.6]: Referee 1, comment 1 and 2. Referee 2, comment 27.

Sample ID	Latitude / ° N	Longitude / ° E	Altitude / km	ln [1+ δ] / ‰	ln [1+ uncertainty] / ‰	ln (y/y_T)
Mid-latitude samples:						
F2-18 (N5)	48.47	10.29	10.00	0.04	1.88	-0.01
F1-18 (B1/9)	48.08	10.44	10.05	2.37	1.65	-0.02
F1-17 (B1/12)	48.43	10.13	12.96	2.00	1.65	-0.01
F1-0 (81)	48.34	10.24	13.97	0.06	2.78	-0.01
F2-8 (R3/16)	53.14	10.28	14.69	0.11	1.61	-0.08
F2-17 (707)(R2/6)	48.93	9.26	15.03	-0.96	1.88	-0.07
F1-16 (R2/3)	48.21	10.79	15.58	0.45	1.65	-0.07
F2-7 (N4)	53.36	8.89	16.76	0.46	1.88	-0.25
F1-1 (B1/3)	48.29	10.58	16.85	0.81	1.65	-0.24
F1-15 (102)	48.44	10.17	17.57	0.53	3.43	-0.30
F2-3 (R3/9)	50.02	8.86	17.86	0.68	2.49	-0.82
F1-5 (S1/14)	51.54	11.46	17.99	1.45	3.43	-0.33
F1-4 (T3/15)	50.69	10.93	18.01	1.22	1.65	-0.40
F1-3 (S3/18)	49.83	10.46	18.02	3.32	3.43	-0.40
F2-6 (N3)	52.89	8.42	18.29	1.12	2.49	-0.73
F2-5 (B1/18)	51.93	8.55	18.30	2.35	1.88	-0.93
F2-16 (R3/3)	49.27	8.28	18.40	2.83	1.88	-0.87
F1-6 (R2/19)	51.76	12.02	18.50	3.55	3.43	-0.55
F2-10 (R3/4)	52.50	11.35	18.58	4.02	1.88	-0.94
F1-7 (B1/2)	50.75	11.63	18.60	2.49	2.78	-0.62
F1-8 (R1/2)	49.77	11.28	18.63	2.86	3.43	-0.49
F1-9 (S2/5)	48.85	10.69	18.65	3.96	1.65	-0.61
F1-11 (B1/13)	49.93	10.57	18.68	1.57	2.49	-0.69
F1-10 (R2/13)	49.03	10.09	18.69	2.15	3.43	-0.42
F1-12 (N1)	50.80	11.16	18.73	0.91	3.43	-0.49
F2-11 (B1/7)	52.26	10.29	18.77	5.18	1.61	-1.13
F2-14 (R3/13)	51.27	7.66	18.78	2.69	1.88	-1.46
F2-13 (R3/18)	52.19	7.67	18.79	3.65	1.88	-1.37
F2-15 (R3/17)	50.33	7.80	19.26	5.49	1.61	-1.24
F1-13(R2/4)	50.38	11.37	19.52	1.53	2.78	-0.79
F1-14 (N2)	49.46	10.81	19.82	1.11	1.65	-0.91
High-latitude samples:						
Kiruna_U133	67.72	20.50	9.27	0.59	0.74	0.00
Kiruna_U174	67.90	20.28	10.95	0.15	2.47	-0.08
Kiruna_F1_U112	68.21	20.81	13.00	-0.78	4.02	-0.13
Kiruna_U160	67.24	18.93	13.55	2.49	0.85	-0.31
Kiruna_U128	68.71	20.42	14.33	0.39	0.74	-0.32
Kiruna_U140	67.04	20.75	14.51	1.92	0.74	-0.33
Kiruna_U134	70.98	23.06	15.45	0.91	2.47	-0.53

Kiruna_U137	71.78	24.44	15.92	2.11	2.47	-0.55
Kiruna_F1_U239	71.17	20.74	16.17	3.32	4.10	-0.76
Kiruna_F1_U113	68.99	21.60	16.28	0.94	4.02	-0.69
Kiruna_F1_U237	69.49	20.68	16.61	1.74	4.02	-0.86
Kiruna_U176	67.67	16.16	17.30	4.81	2.53	-1.56
Kiruna_U130	72.53	25.87	17.33	4.12	0.74	-0.87
Kiruna_U182	68.85	21.83	17.45	2.45	0.74	-0.91
Kiruna_F1_U104	76.24	20.10	17.66	4.84	4.10	-1.36
Kiruna_F1_U101	73.69	20.48	17.67	3.51	4.10	-1.31
Kiruna_F1_U109	75.84	21.62	17.69	1.83	4.06	-1.25
Kiruna_U253	67.15	9.48	17.70	4.57	2.53	-1.57
Kiruna_F1_U103	75.45	20.22	17.71	1.33	4.06	-1.20
Kiruna_U249	66.83	8.09	17.73	3.26	0.85	-1.71
Kiruna_U254	66.85	10.35	17.74	4.93	0.85	-1.55
Kiruna_U132	73.33	27.25	18.09	4.34	0.85	-1.43
Kiruna_U155	66.27	10.88	18.20	4.11	2.53	-1.30
Kiruna_F1_U106	73.30	23.08	18.34	3.08	4.06	-1.47
Kiruna_U170	67.75	16.11	18.35	3.30	2.53	-1.63
Kiruna_F1_U105	72.39	22.77	18.50	3.15	4.06	-1.54
Kiruna_U145	69.50	24.23	18.55	3.99	0.85	-1.63
Kiruna_U135	68.68	23.31	18.64	4.90	0.74	-1.70

Table S6. The CFC-12 stratospheric data used in Figure 1. The ID code, latitude, longitude and altitude of each sample are also included.

Comment [S.J.A.7]: Referee 1, comments 1 and 2. Referee 2, comment 27.

Sample ID	Latitude / ° N	Longitude / ° E	Altitude / km	ln [1+ δ] / ‰	ln [1+ uncertainty] / ‰	ln (y/y_T)
Mid-latitude samples:						
F2-18 (N5)	48.47	10.29	10.00	-3.54	3.33	0.00
F1-18 (B1/9)	48.08	10.44	10.05	0.57	1.72	0.00
F1-17 (B1/12)	48.43	10.13	12.96	-0.80	1.72	0.00
F2-0 (R2/16)	48.16	10.15	13.61	-2.30	3.65	0.01
F1-0 (81)	48.34	10.24	13.97	-1.93	1.78	0.00
F2-8 (R3/16)	53.14	10.28	14.69	-1.57	3.20	-0.04
F2-17 (707)(R2/6)	48.93	9.26	15.03	0.19	3.33	-0.03
F1-16 (R2/3)	48.21	10.79	15.58	0.07	1.72	-0.02
F2-7 (N4)	53.36	8.89	16.76	-0.06	3.33	-0.13
F1-1 (B1/3)	48.29	10.58	16.85	-1.13	1.72	-0.12
F2-9 (R3/5)	53.33	11.28	17.03	0.67	3.33	-0.14
F1-15 (102)	48.44	10.17	17.57	0.06	4.58	-0.14

F2-2 (R3/15)	49.08	8.97	17.77	2.75	3.65	-0.38
F2-3 (R3/9)	50.02	8.86	17.86	5.37	3.65	-0.38
F1-5 (S1/14)	51.54	11.46	17.99	1.03	4.58	-0.15
F1-4 (T3/15)	50.69	10.93	18.01	-0.39	1.72	-0.19
F1-3 (S3/18)	49.83	10.46	18.02	1.68	4.58	-0.20
F2-6 (N3)	52.89	8.42	18.29	0.98	3.65	-0.34
F2-5 (B1/18)	51.93	8.55	18.30	6.32	3.33	-0.43
F2-4 (R3/7)	50.97	8.68	18.30	6.81	3.65	-0.57
F1-6 (R2/19)	51.76	12.02	18.50	-1.26	4.58	-0.25
F2-10 (R3/4)	52.50	11.35	18.58	6.29	3.33	-0.43
F1-7 (B1/2)	50.75	11.63	18.60	2.60	1.78	-0.29
F1-8 (R1/2)	49.77	11.28	18.63	4.14	4.58	-0.24
F1-9 (S2/5)	48.85	10.69	18.65	1.19	1.72	-0.29
F1-11 (B1/13)	49.93	10.57	18.68	1.26	3.65	-0.32
F1-10 (R2/13)	49.03	10.09	18.69	1.63	4.58	-0.20
F1-12 (N1)	50.80	11.16	18.73	0.14	4.58	-0.23
F2-11 (B1/7)	52.26	10.29	18.77	5.50	3.20	-0.50
F2-14 (R3/13)	51.27	7.66	18.78	4.48	3.33	-0.61
F2-13 (R3/18)	52.19	7.67	18.79	3.35	3.33	-0.58
F2-15 (R3/17)	50.33	7.80	19.26	3.94	3.20	-0.54
F1-13(R2/4)	50.38	11.37	19.52	5.60	1.78	-0.36
High-latitude samples:						
Kiruna_U133	67.72	20.50	9.27	1.52	2.68	0.00
Kiruna_U174	67.90	20.28	10.95	-0.21	1.78	-0.02
Kiruna_F1_U112	68.21	20.81	13.00	-1.58	1.32	-0.07
Kiruna_U160	67.24	18.93	13.55	0.87	1.12	-0.15
Kiruna_F1_U240	71.99	20.66	14.16	1.59	1.32	-0.09
Kiruna_F1_U236	68.58	20.36	14.21	-1.42	1.32	-0.13
Kiruna_U128	68.71	20.42	14.33	0.35	2.68	-0.17
Kiruna_U140	67.04	20.75	14.51	1.15	2.68	-0.17
Kiruna_U183	67.74	18.05	14.73	-1.25	1.94	-0.29
Kiruna_U180	68.19	20.89	14.98	-1.15	1.94	-0.20
Kiruna_U134	70.98	23.06	15.45	3.27	1.78	-0.24
Kiruna_U137	71.78	24.44	15.92	2.51	1.78	-0.27
Kiruna_F1_U239	71.17	20.74	16.17	3.11	3.60	-0.37
Kiruna_F1_U113	68.99	21.60	16.28	0.54	1.32	-0.34
Kiruna_F1_U241	72.81	20.59	16.50	4.07	1.32	-0.31
Kiruna_F1_U237	69.49	20.68	16.61	2.74	1.32	-0.42
Kiruna_F1_U238	70.34	20.83	16.79	2.57	1.95	-0.39
Kiruna_U131	70.31	22.04	17.10	1.05	2.16	-0.47
Kiruna_U176	67.67	16.16	17.30	4.33	1.50	-0.70
Kiruna_U130	72.53	25.87	17.33	5.26	2.68	-0.41
Kiruna_U149	66.52	21.21	17.43	3.22	1.88	-0.55
Kiruna_U182	68.85	21.83	17.45	3.06	2.68	-0.44
Kiruna_F1_U104	76.24	20.10	17.66	1.21	3.60	-0.62
Kiruna_F1_U101	73.69	20.48	17.67	4.89	3.60	-0.60
Kiruna_U177	66.87	12.61	17.68	2.56	1.94	-0.70

Kiruna_F1_U109	75.84	21.62	17.69	4.53	1.95	-0.59
Kiruna_U253	67.15	9.48	17.70	6.54	1.50	-0.69
Kiruna_U246	67.13	7.08	17.71	6.23	1.94	-0.83
Kiruna_F1_U103	75.45	20.22	17.71	4.66	1.95	-0.55
Kiruna_F1_U108	75.05	23.40	17.72	5.75	1.95	-0.56
Kiruna_U150	67.09	4.68	17.73	1.32	1.12	-0.66
Kiruna_U243	66.81	3.60	17.74	2.11	1.94	-0.68
Kiruna_U254	66.85	10.35	17.74	6.62	1.12	-0.66
Kiruna_F1_U102	74.59	20.43	17.74	4.84	1.32	-0.58
Kiruna_U226	67.00	-0.73	17.77	3.27	1.94	-0.83
Kiruna_F1_U107	74.19	23.39	18.07	6.10	1.95	-0.64
Kiruna_U184	67.13	14.53	18.09	5.06	1.94	-0.80
Kiruna_U132	73.33	27.25	18.09	5.22	1.12	-0.65
Kiruna_U129	74.06	27.88	18.15	2.48	1.88	-0.68
Kiruna_U141	73.65	27.62	18.16	6.35	2.16	-0.67
Kiruna_U178	72.62	27.89	18.20	5.25	2.16	-0.56
Kiruna_U155	66.27	10.88	18.20	4.63	1.50	-0.56
Kiruna_U125	72.26	27.54	18.25	3.52	1.94	-0.51
Kiruna_U143	72.74	28.10	18.28	3.35	2.16	-0.71
Kiruna_U173	71.90	27.69	18.31	4.67	2.16	-0.52
Kiruna_F1_U106	73.30	23.08	18.34	5.28	1.95	-0.66
Kiruna_U170	67.75	16.11	18.35	4.36	1.50	-0.69
Kiruna_U144	71.90	27.34	18.37	4.14	2.16	-0.70
Kiruna_F1_U114	69.75	22.01	18.47	5.08	1.32	-0.71
Kiruna_U153	70.31	25.17	18.52	2.57	2.16	-0.69
Kiruna_U145	69.50	24.23	18.55	3.81	1.12	-0.72
Kiruna_F1_U110	71.51	22.45	18.67	7.50	1.95	-0.66
Kiruna_U142	66.97	22.03	18.81	4.02	1.94	-0.82
Kiruna_F1_U111	70.62	22.20	18.83	6.13	1.95	-0.68

Table S7. The CFC-113 stratospheric data used in Figure 1. The ID code, latitude, longitude and altitude of each sample are also included.

Comment [S.J.A.8]: Referee 1, comments 1 and 2. Referee 2, comment 27.

Sample ID	**Latitude / ° N**	**Longitude / ° E**	**Altitude / km**	**ln [1+ δ] / ‰**	**ln [1+ uncertainty] / ‰**	**ln (y/y_T)**
Mid-latitude samples:						
F2-18 (N5)	48.47	10.29	10.00	-0.06	3.27	0.00
F1-18 (B1/9)	48.08	10.44	10.05	-2.31	2.89	-0.01
F1-17 (B1/12)	48.43	10.13	12.96	-2.22	2.89	0.01
F2-0 (R2/16)	48.16	10.15	13.61	0.09	3.70	-0.02

F1-0 (81)	48.34	10.24	13.97	3.17	1.81	0.00
F2-8 (R3/16)	53.14	10.28	14.69	2.66	2.54	-0.04
F2-17 (707)(R2/6)	48.93	9.26	15.03	-0.54	3.27	-0.03
F1-16 (R2/3)	48.21	10.79	15.58	-4.19	2.89	-0.04
F2-1 (R3/19)	48.24	9.31	16.26	-0.29	3.70	-0.18
F2-7 (N4)	53.36	8.89	16.76	-0.58	3.27	-0.18
F1-1 (B1/3)	48.29	10.58	16.85	-0.48	2.89	-0.14
F2-9 (R3/5)	53.33	11.28	17.03	2.02	3.27	-0.17
F1-15 (102)	48.44	10.17	17.57	-0.49	3.56	-0.17
F2-2 (R3/15)	49.08	8.97	17.77	0.97	3.70	-0.48
F2-3 (R3/9)	50.02	8.86	17.86	-1.43	3.70	-0.46
F1-5 (S1/14)	51.54	11.46	17.99	2.21	3.56	-0.18
F1-4 (T3/15)	50.69	10.93	18.01	-1.97	2.89	-0.23
F1-3 (S3/18)	49.83	10.46	18.02	1.94	3.56	-0.23
F2-6 (N3)	52.89	8.42	18.29	-3.70	3.70	-0.40
F2-5 (B1/18)	51.93	8.55	18.30	2.92	3.27	-0.51
F2-4 (R3/7)	50.97	8.68	18.30	0.05	3.70	-0.70
F2-16 (R3/3)	49.27	8.28	18.40	0.44	3.27	-0.49
F1-6 (R2/19)	51.76	12.02	18.50	-1.66	3.56	-0.31
F2-10 (R3/4)	52.50	11.35	18.58	-0.87	3.27	-0.51
F1-7 (B1/2)	50.75	11.63	18.60	-1.74	1.81	-0.32
F1-8 (R1/2)	49.77	11.28	18.63	-1.94	3.56	-0.28
F1-9 (S2/5)	48.85	10.69	18.65	-1.31	2.89	-0.35
F1-11 (B1/13)	49.93	10.57	18.68	-1.32	3.70	-0.38
F1-10 (R2/13)	49.03	10.09	18.69	1.66	3.56	-0.24
F1-12 (N1)	50.80	11.16	18.73	2.66	3.56	-0.28
F2-11 (B1/7)	52.26	10.29	18.77	5.41	2.54	-0.60
F2-14 (R3/13)	51.27	7.66	18.78	2.80	3.27	-0.75
F2-13 (R3/18)	52.19	7.67	18.79	3.62	3.27	-0.71
F2-15 (R3/17)	50.33	7.80	19.26	3.96	2.54	-0.66
F1-13(R2/4)	50.38	11.37	19.52	-1.80	1.81	-0.43
F1-14 (N2)	49.46	10.81	19.82	1.27	2.89	-0.49
High-latitude samples:						
Kiruna_U133	67.72	20.50	9.27	-0.28	3.44	0.00
Kiruna_U174	67.90	20.28	10.95	-0.51	1.33	-0.04
Kiruna_F1_U112	68.21	20.81	13.00	1.66	4.84	-0.08
Kiruna_U160	67.24	18.93	13.55	-2.51	2.87	-0.20
Kiruna_F1_U240	71.99	20.66	14.16	4.71	4.84	-0.10
Kiruna_F1_U236	68.58	20.36	14.21	3.75	4.84	-0.14
Kiruna_U128	68.71	20.42	14.33	2.46	3.44	-0.20
Kiruna_U140	67.04	20.75	14.51	-1.66	3.44	-0.19
Kiruna_U180	68.19	20.89	14.98	-2.66	4.93	-0.23
Kiruna_U134	70.98	23.06	15.45	-3.06	1.33	-0.30
Kiruna_F1_U239	71.17	20.74	16.17	2.33	3.62	-0.45
Kiruna_F1_U113	68.99	21.60	16.28	0.29	4.84	-0.41
Kiruna_F1_U241	72.81	20.59	16.50	6.18	4.84	-0.37
Kiruna_F1_U237	69.49	20.68	16.61	-0.16	4.84	-0.51

Kiruna_F1_U238	70.34	20.83	16.79	6.09	3.89	-0.44
Kiruna_U131	70.31	22.04	17.10	6.57	10.73	-0.59
Kiruna_U176	67.67	16.16	17.30	3.90	3.64	-0.86
Kiruna_U130	72.53	25.87	17.33	-1.71	3.44	-0.50
Kiruna_U149	66.52	21.21	17.43	7.47	2.60	-0.68
Kiruna_U182	68.85	21.83	17.45	7.75	3.44	-0.52
Kiruna_F1_U104	76.24	20.10	17.66	0.06	3.62	-0.76
Kiruna_F1_U101	73.69	20.48	17.67	4.52	3.62	-0.73
Kiruna_U177	66.87	12.61	17.68	0.79	4.93	-0.87
Kiruna_F1_U109	75.84	21.62	17.69	4.20	3.89	-0.70
Kiruna_U253	67.15	9.48	17.70	2.63	3.64	-0.85
Kiruna_F1_U103	75.45	20.22	17.71	0.50	3.89	-0.67
Kiruna_F1_U108	75.05	23.40	17.72	0.97	3.89	-0.67
Kiruna_U249	66.83	8.09	17.73	-1.09	2.87	-0.91
Kiruna_U150	67.09	4.68	17.73	3.31	2.87	-0.84
Kiruna_U243	66.81	3.60	17.74	3.09	4.93	-0.83
Kiruna_U254	66.85	10.35	17.74	2.31	2.87	-0.84
Kiruna_F1_U102	74.59	20.43	17.74	5.72	4.84	-0.71
Kiruna_U226	67.00	-0.73	17.77	5.77	4.93	-1.01
Kiruna_F1_U107	74.19	23.39	18.07	7.26	3.89	-0.79
Kiruna_U132	73.33	27.25	18.09	2.29	2.87	-0.78
Kiruna_U129	74.06	27.88	18.15	1.25	2.60	-0.82
Kiruna_U141	73.65	27.62	18.16	0.96	10.73	-0.83
Kiruna_U178	72.62	27.89	18.20	1.82	10.73	-0.66
Kiruna_U155	66.27	10.88	18.20	5.82	3.64	-0.70
Kiruna_U125	72.26	27.54	18.25	-0.41	4.93	-0.62
Kiruna_U173	71.90	27.69	18.31	4.20	10.73	-0.63
Kiruna_F1_U106	73.30	23.08	18.34	4.44	3.89	-0.80
Kiruna_U170	67.75	16.11	18.35	0.14	3.64	-0.84
Kiruna_F1_U114	69.75	22.01	18.47	4.07	4.84	-0.87
Kiruna_U139	71.11	26.13	18.47	1.78	2.60	-0.85
Kiruna_F1_U105	72.39	22.77	18.50	3.59	3.89	-0.84
Kiruna_U153	70.31	25.17	18.52	4.07	10.73	-0.85
Kiruna_U145	69.50	24.23	18.55	3.06	2.87	-0.89
Kiruna_U135	68.68	23.31	18.64	4.13	3.44	-0.91
Kiruna_F1_U110	71.51	22.45	18.67	8.32	3.89	-0.80
Kiruna_U136	67.82	22.65	18.71	7.67	2.60	-0.95
Kiruna_U142	66.97	22.03	18.81	3.37	4.93	-0.99
Kiruna_U179	69.63	23.11	18.82	-1.66	4.93	-0.70
Kiruna_F1_U111	70.62	22.20	18.83	-1.64	3.89	-0.84

Table S8. The firn air data used in Figure 3.

Comment [S.J.A.9]: Referee 1, comments 1 and 2. Referee 2, comment 27.

		CFC-11			CFC-12			CFC-113		
Sample ID	**Depth / m**	**Age / years AD**	**$\delta(^{37}Cl)$ / ‰**	**1σ uncertainty / ‰**	**Age / years AD**	**$\delta(^{37}Cl)$ / ‰**	**1σ uncertainty / ‰**	**Age / years AD**	**$\delta(^{37}Cl)$ / ‰**	**1σ uncertainty / ‰**
NEEM 2009 firn air:										
1, 14 and 15	0	2009.54	-0.997	1.71	2009.54	-0.331	2.515	2009.54	0.05	2.151
2	10.5	2009.46	0.89	1.512	2009.46	-0.591	1.687	2009.46	2.082	1.908
3	20.4	2008.96	3.026	1.847	2008.96	0.557	3.748	2008.87	-2.252	1.453
4	30.2	2007.46	-0.877	2.718	2007.71	-3.253	0.927	2007.21	0.026	4.546
5	39.23	2005.71	-1.045	2.886	2006.12	-0.185	3.192	2005.12	0.934	3.798
6	50.7	2003.37	0.608	1.293	2004.04	-1.297	1.132	2002.46	-2.72	1.512
7	60.3	1999.79	-0.224	2.765	2000.79	1.042	1.866	1998.37	-0.375	1.145
8	62.02	1998.12	-0.705	0.734	1999.29	1.645	2.326	1996.62	0.753	3.378
9	63.8	1991.46	-2.292	1.702	1992.96	0.257	2.793	1989.62	1.472	4.6
10	66.8	1977.54	-0.56	2.247	1979.29	-0.029	1.728	1975.37	2.181	1.637
11	69.4	1965.29	-0.822	1.815	1967.21	0.914	1.915	1962.96	6.647	2.900
12	71.9				1955.62	5.342	3.197			
13	73.6	1946.37	7.814	2.032						
Fletcher Promontory firn air:										
12 and 25	0	2011.96	1.626	4.837	2011.96	-0.009	4.99	2011.96	1.319	5.58
28	3.035	2011.88	-2.093	3.219	2011.88	2.693	2.983	2011.88	1.037	4.459
22	6.905	2011.71	3.681	3.458	2011.71	3.162	2.227	2011.63	-2.588	4.78
18	10.985	2011.29	0.783	2.923	2011.38	1.378	1.472	2011.21	2.393	4.582
30	18.58	2010.04	0.673	4.932	2010.29	-1.7	3.048	2009.71	-1.747	3.602
14	21.925	2009.38	1.153	3.282	2009.63	-0.466	3.555	2008.96	0.05	5.464
20	26.57	2008.29	-0.334	2.923	2008.79	-2.109	1.472	2007.79	-0.592	4.582
8	38.06	2005.71	2.607	3.713	2006.46	1.919	6.138	2004.71	4.116	6.688
16	44.7	2004.04	-0.821	0.365	2004.96	-1.491	2.129	2002.88	2.509	3.008
24	50.19	2002.63	0.172	0.365	2003.71	-0.629	2.129	2001.21	-3.63	3.008
13	56.245	2000.88	1.364	2.267	2002.13	-3.699	4.53	1999.13	-1.153	2.201
E	59.23	1999.88	-1.76	0.365	2001.21	-4.736	2.129	1998.04	-2.636	3.008
G	62.17	1998.79	1.022	4.837	2000.21	-4.444	3.351	1996.79	0.845	3.827
K	65.18	1997.38	-4.301	4.932	1999.04	-4.646	3.048	1995.29	-2.958	3.602
D	68.15	1995.63	3.879	4.415	1997.38	2.674	3.916	1993.38	-0.142	6.721
J	70.15	1992.21	-1.965	3.933	1994.04	0.278	2.816	1989.88	5.064	6.456
C	71.98	1987.63	0.318	2.923	1989.46	-0.827	1.472	1985.21	-0.642	4.582
B	74.33	1982.38	-0.714	4.932	1984.29	-7.528	3.048	1979.88	-5.107	3.602
23	76.13	1978.04	0.599	4.715	1979.96	-3.242	4.085	1975.63	3.089	6.391
27	80.57	1968.13	6.576	1.545	1970.04	2.043	4.910	1965.63	8.317	5.412

Table S9. The Cape Grim data used in Figure 3.

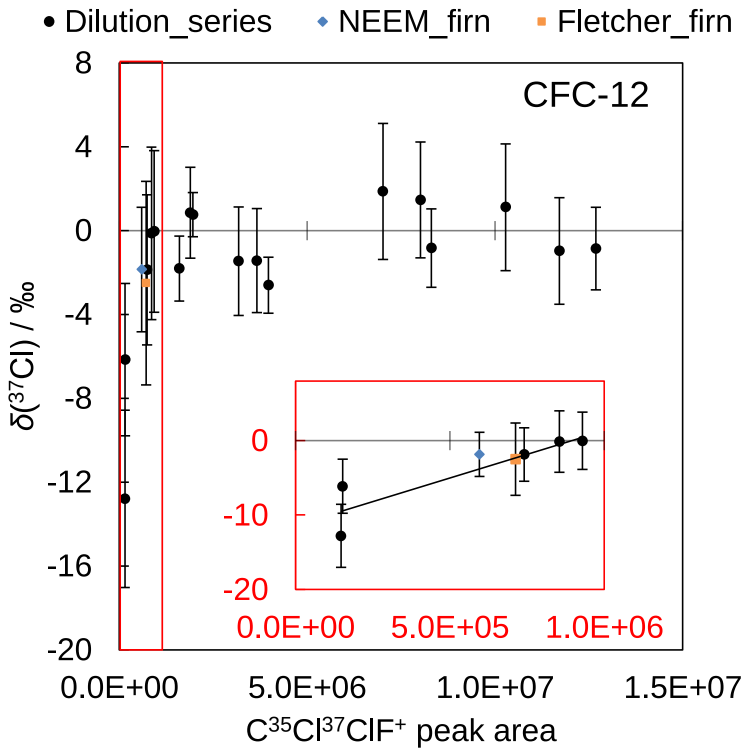
Comment [S.J.A.10]: Referee 1, comments 1 and 2. Referee 2, comment 27.

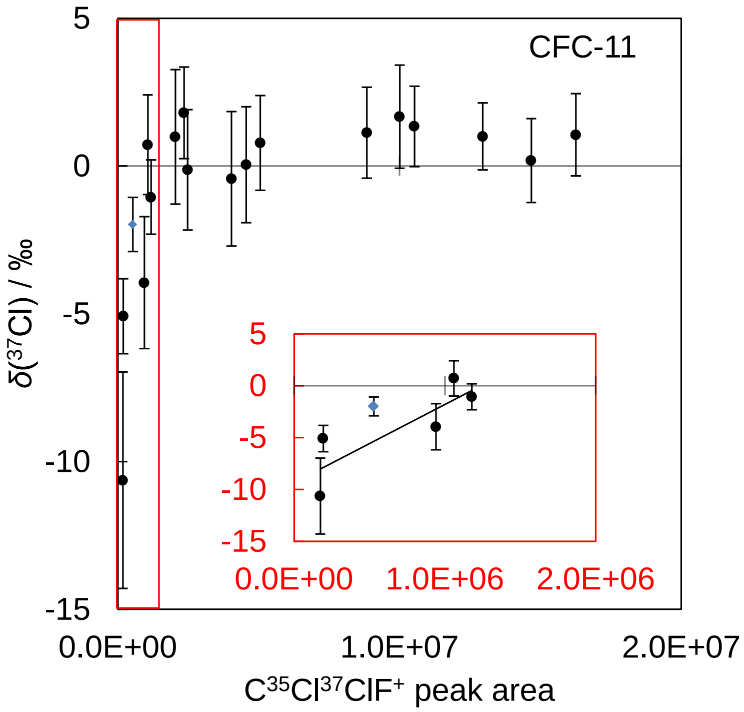
CFC-11				CFC-12				CFC-113			
Sample ID	**Age / years AD**	**$\delta(^{37}\text{Cl})$ / ‰**	**1σ uncertainty / ‰**	**Sample ID**	**Age / years AD**	**$\delta(^{37}\text{Cl})$ / ‰**	**1σ uncertainty / ‰**	**Sample ID**	**Age / years AD**	**$\delta(^{37}\text{Cl})$ / ‰**	**1σ uncertainty / ‰**
SIL-K1514	2010.94	2.744	1.954	K1511	2012.93	0.244	1.749	SIL-K1524	2011.47	3.951	2.950
SIL-K1517	2009.57	2.029	1.770	K1509	2012.66	0.437	1.749	SIL-K1523	2011.40	4.219	3.332
SIL-K1525	2009.18	-1.046	1.823	K1508	2012.32	1.059	1.749	SIL-1522	2011.30	-0.823	3.522
S320-U105	1995.45	1.774	2.793	SIL-K1524	2011.47	0.842	2.552	SIL-K1516	2011.21	6.759	3.332
S320-U32	1993.43	-0.531	2.793	SIL-K1523	2011.40	0.443	2.532	SIL-K1515	2011.11	-0.706	3.571
S320-U19	1991.20	0.818	3.469	SIL-1522	2011.30	0.015	2.228	SIL-K1514	2010.94	3.825	3.869
S320-U06	1989.32	-0.890	2.793	SIL-K1516	2011.21	-1.261	2.310	SIL-K1517	2009.57	-0.273	2.930
S320-U05	1987.41	-2.161	2.793	SIL-K1515	2011.11	-2.708	3.069	SIL-K1525	2009.18	0.204	3.386
S320-U13	1985.60	-1.316	2.793	SIL-K1514	2010.94	-1.280	2.370	S320-U105	1995.45	1.905	3.671
S320-U09	1983.58	1.016	2.783	SIL-K1517	2009.57	-1.883	1.074	S320-U32	1993.43	1.437	3.671
S320-U12	1980.65	3.084	2.793	SIL-K1525	2009.18	-1.209	4.592	S320-U19	1991.20	0.905	4.809
S320-U29	1978.52	1.670	2.234	SIL-1146B	2008.45	2.675	3.467	S320-U06	1989.32	0.304	3.671
				SIL-1141	2007.51	2.390	2.684	S320-U05	1987.41	6.030	3.671
				SIL-1175	2006.64	0.382	3.467	S320-U13	1985.60	3.088	3.671
				1148	2005.76	1.233	2.480	S320-U09	1983.58	0.909	2.222
				SIL-1127	2005.26	1.259	3.784	S320-U12	1980.65	1.578	3.671
				SIL-1155	2005.11	1.253	1.749	S320-U29	1978.52	2.455	4.356
				1128	2004.96	-0.641	2.480				
				SIL-1138	2004.67	-1.641	3.383				
				1135	2004.50	-0.144	2.480				
				1146	2003.39	-1.068	2.882				
				SIL-1144	2002.47	-0.302	3.467				
				1295	2001.95	-2.240	2.480				
				1276	2001.32	0.077	2.720				
				SIL-1129	2000.75	-0.953	3.467				
				S320-U203	2000.15	0.081	2.480				
				S320-U216	1999.47	1.113	3.081				
				#213	1998.29	-1.720	1.969				
				UEA97	1997.02	-2.622	4.709				
				S320-U105	1995.45	5.955	1.719				
				S320-111	1994.12	3.541	3.553				
				S320-U33	1993.49	-2.149	1.969				
				S320-U32	1993.43	1.434	1.719				
				S320-U19	1991.20	0.472	1.564				
				S320-U06	1989.32	3.962	1.719				
				S320-U05	1987.41	-1.453	3.341				
				S320-U13	1985.60	6.704	1.719				
				S320-U09	1983.58	1.211	2.235				
				S320-U12	1980.65	2.103	1.719				
				S320-U17	1979.10	-2.604	1.969				
				S320-U29	1978.52	3.103	1.863				
				S320-U23	1978.32	-2.208	1.969				

Table S10. The data used in Figure S1. The sample IDs refer to the diluted air samples detailed in Table S1.

Sample ID	CFC-11			CFC-12			CFC-113		
	C^{35}Cl^{37}ClF^{+} peak area	δ(^{37}Cl) / ‰	1σ uncertainty / ‰	C^{35}Cl^{37}ClF^{+} peak area	δ(^{37}Cl) / ‰	1σ uncertainty / ‰	C^{35}Cl^{37}ClF^{+} peak area	δ(^{37}Cl) / ‰	1σ uncertainty / ‰
SX-0706077	16253338.5	1.05782	1.39632	12686959.5	-0.8629	1.97051	17441913	-2.8783	2.11851
	14672027	0.1872	1.42331	11717824	-0.9739	2.53866	17202522	-0.8435	2.19575
	12951190	1.00753	1.13404	10285792	1.1173	3.02452	12920942.5	2.47961	2.25934
K1579	10527296	1.34422	1.35948	8308076	-0.834	1.86769	12179131.67	0.88014	4.60998
	10001930	1.6686	1.74426	8019910	1.46511	2.76813	11666651	1.24218	3.55465
	8836375.5	1.12902	1.5406	7017476	1.86524	3.24583	8797107	1.01759	4.88259
K1578	5056587.5	0.78529	1.60417	3969374.5	-2.6067	1.33767	5413831	1.3018	1.66084
	4556389	0.04723	1.96261	3661516	-1.4332	2.48087	5326372	-3.2186	2.08051
	4032314.5	-0.4322	2.2791	3174294	-1.4598	2.58697	3958446	1.58713	1.59149
K1583	2478613	-0.1251	2.03851	1959719	0.75495	1.05459	2847635	1.21639	5.15792
	2345094.5	1.80598	1.54955	1889938.5	0.8507	2.16988	2716815.5	3.23799	2.0351
	2041025	0.98848	2.2754	1596358	-1.8126	1.54831	2000064.5	0.69131	1.74905
K1569	1178474.5	-1.0532	1.25676	929655	-0.0425	3.85089	1262753	-3.0363	2.09579
	1059251	0.71974	1.68739	854573	-0.1272	4.11566	1243590	2.7468	2.56427
	940497	-3.9446	2.23401	740710.5	-1.8695	3.5773	923461	1.46313	2.34042
K1575	193281.5	-5.0797	1.26942	152500.5	-6.1505	3.63347	220193	-1.9928	4.39585
	173429	-10.633	3.6622	147147	-12.798	4.23373	207857.5	-13.201	3.54046

Figure S1. Dilution series measured for $\delta(^{37}\mathrm{Cl})$, plotted against the integrated peak area of the $\mathrm{C^{35}Cl^{37}ClF^{+}}$ fragment ion (*m/z* 103). 1σ standard deviation error bars are shown. Insets highlight the firn air measurements that fall within the depleted region of the dilution series analysis (red highlighted regions on the left). Linear regression lines are used to adjust the firn samples, based on the observed dilution series depletion. Unaffected samples are not displayed. All delta values are relative to 2006 standard air.




CFC-11
5
0
-5
-10
-15
δ(³⁷Cl) / ‰
0.0E+00
1.0E+07
2.0E+07
C³⁵Cl³⁷ClF⁺ peak area
5
0
-5
-10
-15
0.0E+00
1.0E+06
2.0E+06

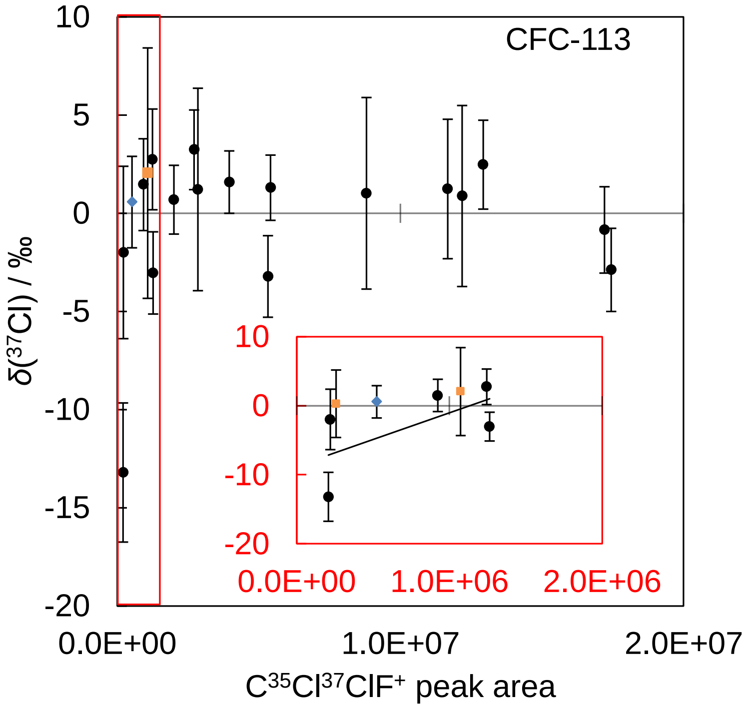
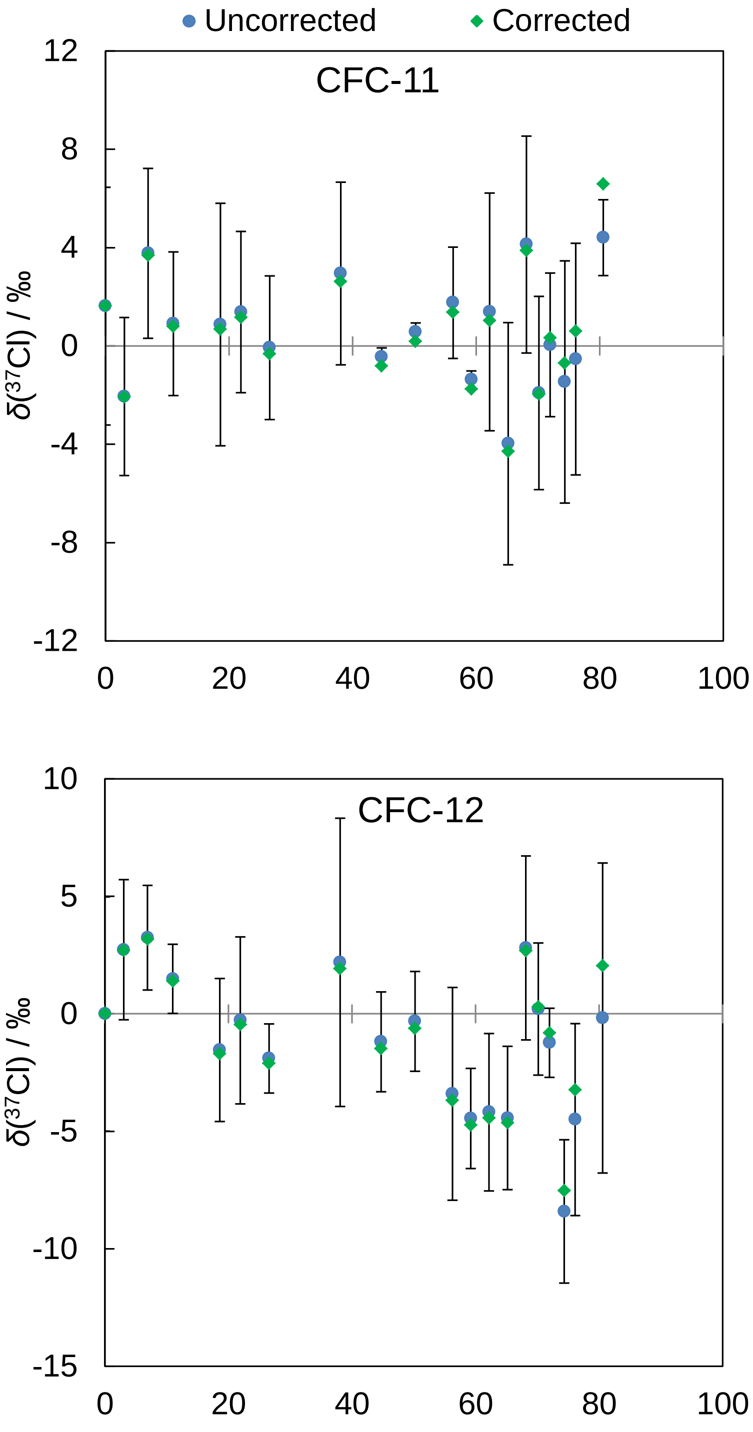

CFC-113
10
5
0
-5
-10
-15
-20
δ(³⁷Cl) / ‰
0.0E+00
1.0E+07
2.0E+07
C³⁵Cl³⁷ClF⁺ peak area
10
0
-10
-20
0.0E+00
1.0E+06
2.0E+06

Figure S2. Measured $\delta(^{37}\text{Cl})$ values (blue circles, with 1σ standard deviation error bars), and the same after correcting for gravitational and diffusional fractionations (green diamonds, error bars not included), as a function of firn depth at Fletcher Promontory.



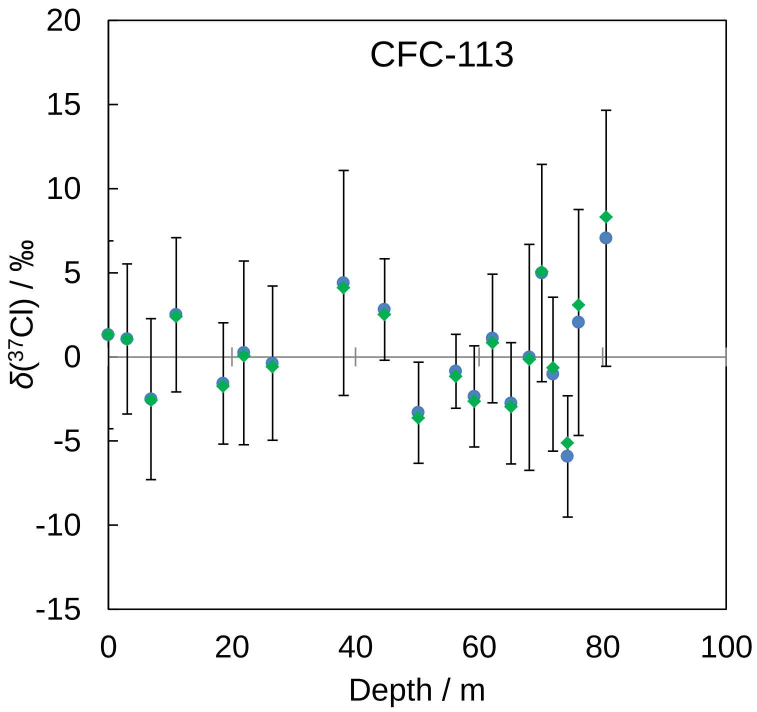
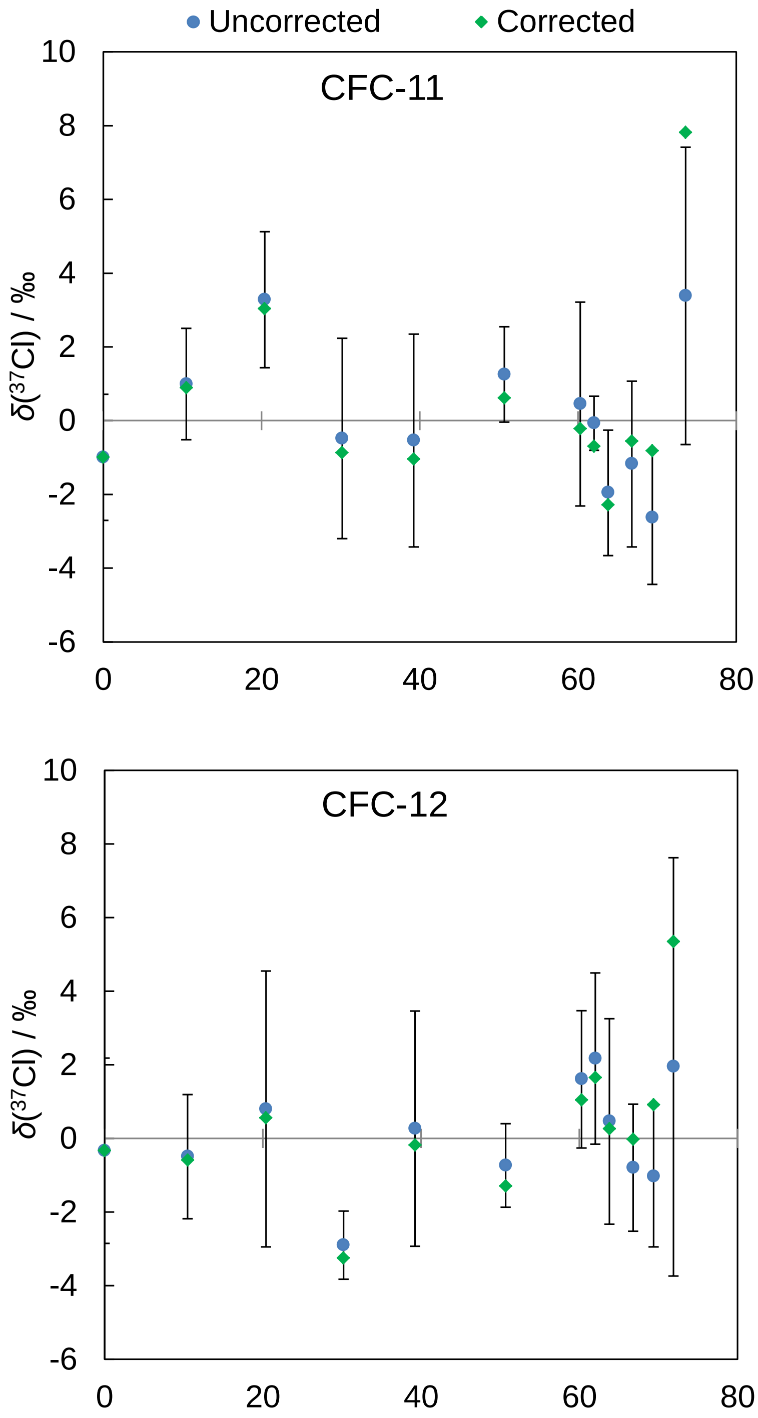
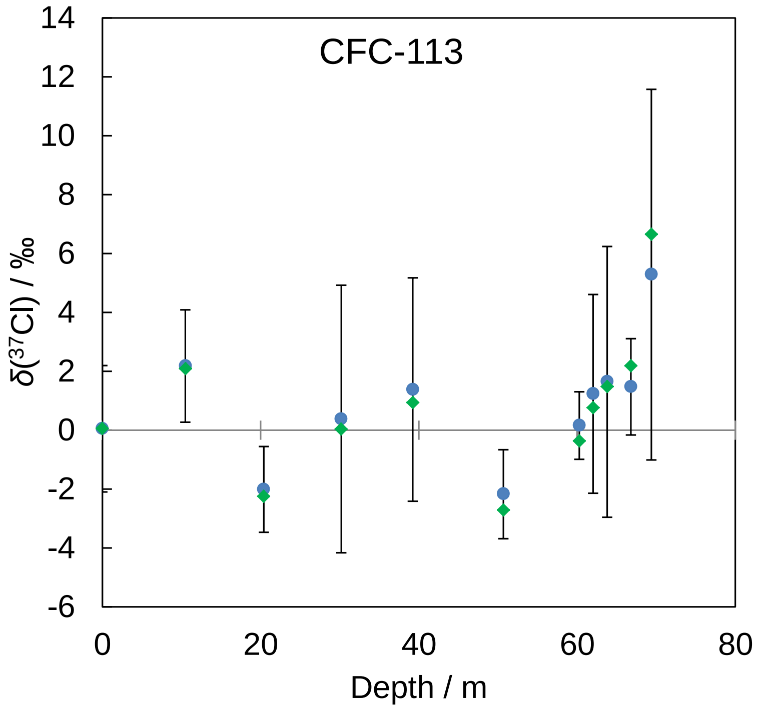

CFC-113
δ(37Cl) / ‰
20
15
10
5
0
-5
-10
-15
0
20
40
60
80
100
Depth / m

Figure S3. Measured $\delta(^{37}\text{Cl})$ values (blue circles, with 1σ standard deviation error bars), and the same after correcting for gravitational and diffusional fractionations (green diamonds, error bars not included), as a function of firn depth at NEEM.

Comment [S.J.A.11]: Referee 1, comment 20.




CFC-113
δ(37Cl) / ‰
14
12
10
8
6
4
2
0
-2
-4
-6
0
20
40
60
80
Depth / m