Thanks to both reviewers for their time, their comments on this manuscript, and for expressing interest in the topic. We have already responded to several points made by Reviewer 1 in an author response (https://acp.copernicus.org/preprints/acp-2020-843/acp-2020-843-SC1-supplement.pdf) and here address their comments point by point, referring back to our author response where appropriate. We address the comments of Reviewer 2 for the first time.

Throughout, our response is in green, the reviewer comments are in black, deletions from our manuscript are in red, and insertions to our manuscript are in blue.

Please see the track changes document at the end of this response which highlights all changes.

Response to Reviewer 2

R2 asked that we make fuller use of our data and analysis. We have addressed their specific points through changes to the text of the results, discussion, and conclusion of our manuscript.

R2 comment

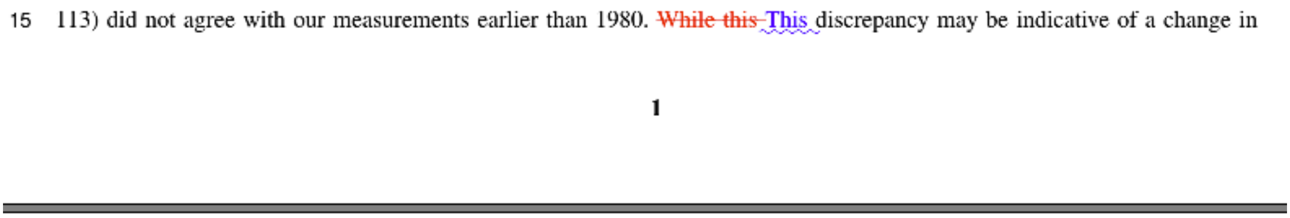
1) More work should be performed in order to put the results of the analysis and modelling into context. 1. The reader is left themselves to try to make sense of the discrepancy in the delta_T(13C, CFC-113) data before 1980. The authors write provocatively, 'While this discrepancy may be indicative of a change in d_E(13C, CFC-113), it is premature to assign one.' I believe the discrepancy could also be indicative of faults with the sampling, analysis, and modelling and that either it is premature or it is not. The authors should decide if they have confidence in the conclusion and wish to defend it, or perhaps, based on statistics, model validation and so on, they would decide to withdraw. If they support the conclusion I would suggest doing more work to investigate what this change would be, for example change in manufacturer or process.

Author response

As stated in the manuscript, the discrepancy between our measurements and modelling for $\delta_T(^{13}C$, CFC-113) highlights a possible change in $\delta_E(^{13}C$, CFC-113). This discrepancy is based on measurements of one sample with a low mole fraction (mole fractions are now given in the supplement) and box modelling of $\delta_T(^{13}C$, CFC-113). The discrepancy is only marginally significant, with the 95 % bounds on the measured and modelled trend a maximum of 1.9 ‰. We find no reason to exclude these data, having found no chromatographic interferences on the ions used, and no evidence for any artefacts from sampling or firn modelling as evidenced by the histories of multiple gases reconstructed from samples collected during those campaigns, including the chlorine isotopologues of the three CFCs presented here (e.g., Buizert et al., 2012; Witrant et al., 2012; Allin et al., 2015). However, we acknowledge that there are potential unknown unknowns, particularly at the low mole fraction of this sample. We stand by our conclusion: our analysis suggests a change in source signature but more work would be needed to definitively ascribe one.

According to Kirk-Othmer (1994) the two main feedstock materials for manufacturing CFC-113 have been hexachloroethane and tetrachloroethene. However, there are multiple processes that use CFC-113 as an intermediate or where it is a byproduct (Adcock et al., 2018), some of which were only introduced in the 1990s. In comparison to CFC-11 or CFC-12 there is therefore much greater scope for a change in isotopic signature of CFC-113 over the last decades. We compared the change in δ_E(^{13}C, CFC-113) required to bring our modelled confidence bounds into line with the range of previously reported δ_E(^{13}C, CFC-113) – with a range of nearly 5 ‰ – in the discussion.

To address R2’s concerns, we have:
changed the abstract



113) did not agree with our measurements earlier than 1980. ~~While this~~ This discrepancy may be indicative of a change in

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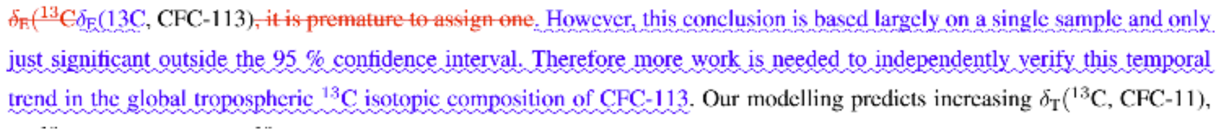
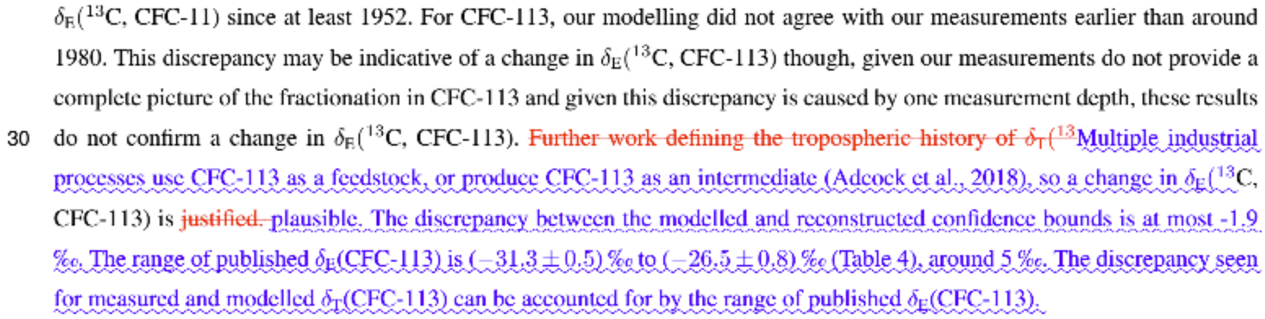


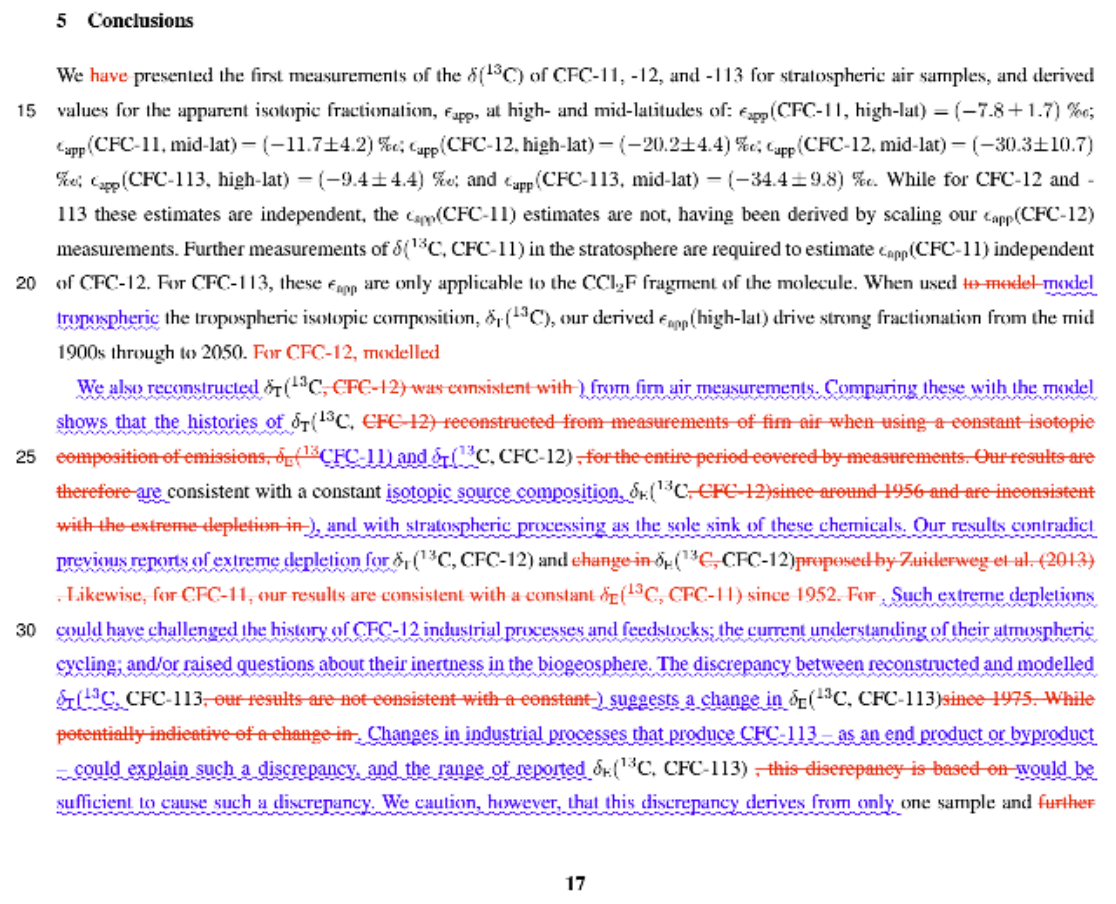
~~δ_E(^{13}C~~δ_E(13C, CFC-113)~~, it is premature to assign one~~. However, this conclusion is based largely on a single sample and only just significant outside the 95 % confidence interval. Therefore more work is needed to independently verify this temporal trend in the global tropospheric ^{13}C isotopic composition of CFC-113. Our modelling predicts increasing δ_T(^{13}C, CFC-11),

changed the discussion



δ_E(^{13}C, CFC-11) since at least 1952. For CFC-113, our modelling did not agree with our measurements earlier than around 1980. This discrepancy may be indicative of a change in δ_E(^{13}C, CFC-113) though, given our measurements do not provide a complete picture of the fractionation in CFC-113 and given this discrepancy is caused by one measurement depth, these results do not confirm a change in δ_E(^{13}C, CFC-113). ~~Further work defining the tropospheric history of δ_T(^{13}~~Multiple industrial processes use CFC-113 as a feedstock, or produce CFC-113 as an intermediate (Adcock et al., 2018), so a change in δ_E(^{13}C, CFC-113) is ~~justified.~~ plausible. The discrepancy between the modelled and reconstructed confidence bounds is at most -1.9 ‰. The range of published δ_E(CFC-113) is (-31.3 ± 0.5) ‰ to (-26.5 ± 0.8) ‰ (Table 4), around 5 ‰. The discrepancy seen for measured and modelled δ_T(CFC-113) can be accounted for by the range of published δ_E(CFC-113).

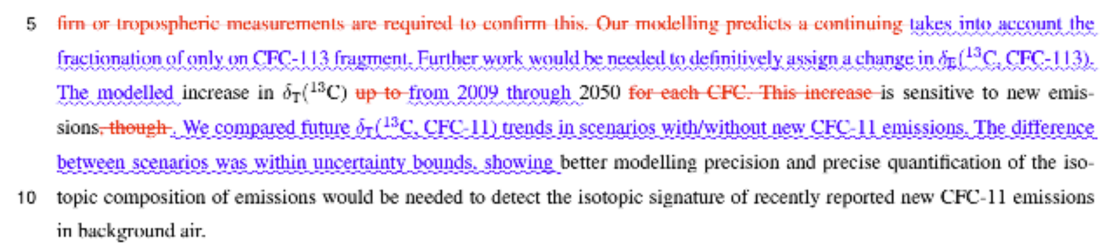
changed the conclusions



5 Conclusions

We have presented the first measurements of the $\delta(^{13}C)$ of CFC-11, -12, and -113 for stratospheric air samples, and derived values for the apparent isotopic fractionation, ϵ_{app}, at high- and mid-latitudes of: ϵ_{app}(CFC-11, high-lat) = (-7.8 ± 1.7) ‰; ϵ_{app}(CFC-11, mid-lat) = (-11.7 ± 4.2) ‰; ϵ_{app}(CFC-12, high-lat) = (-20.2 ± 4.4) ‰; ϵ_{app}(CFC-12, mid-lat) = (-30.3 ± 10.7) ‰; ϵ_{app}(CFC-113, high-lat) = (-9.4 ± 4.4) ‰; and ϵ_{app}(CFC-113, mid-lat) = (-34.4 ± 9.8) ‰. While for CFC-12 and -113 these estimates are independent, the ϵ_{app}(CFC-11) estimates are not, having been derived by scaling our ϵ_{app}(CFC-12) measurements. Further measurements of $\delta(^{13}C$, CFC-11) in the stratosphere are required to estimate ϵ_{app}(CFC-11) independent of CFC-12. For CFC-113, these ϵ_{app} are only applicable to the CCl_2F fragment of the molecule. When used ~~to model~~ model tropospheric the tropospheric isotopic composition, $\delta_T(^{13}C)$, our derived ϵ_{app}(high-lat) drive strong fractionation from the mid 1900s through to 2050. For CFC-12, modelled

We also reconstructed $\delta_T(^{13}C$~~, CFC-12) was consistent with~~) from firn air measurements. Comparing these with the model shows that the histories of $\delta_T(^{13}C$, ~~CFC-12) reconstructed from measurements of firn air when using a constant isotopic composition of emissions, $\delta_E(^{13}$~~CFC-11) and $\delta_T(^{13}C$, CFC-12) ~~, for the entire period covered by measurements. Our results are therefore~~ are consistent with a constant isotopic source composition, $\delta_E(^{13}C$~~, CFC-12)since around 1956 and are inconsistent with the extreme depletion in~~), and with stratospheric processing as the sole sink of these chemicals. Our results contradict previous reports of extreme depletion for $\delta_T(^{13}C$, CFC-12) and ~~change in~~ $\delta_E(^{13}$~~C,~~ CFC-12)~~proposed by Zuiderweg et al. (2013)~~ ~~. Likewise, for CFC-11, our results are consistent with a constant $\delta_E(^{13}C$, CFC-11) since 1952. For~~ . Such extreme depletions could have challenged the history of CFC-12 industrial processes and feedstocks; the current understanding of their atmospheric cycling; and/or raised questions about their inertness in the biogeosphere. The discrepancy between reconstructed and modelled $\delta_T(^{13}C$, CFC-113~~, our results are not consistent with a constant~~) suggests a change in $\delta_E(^{13}C$, CFC-113)~~since 1975. While potentially indicative of a change in~~ . Changes in industrial processes that produce CFC-113 – as an end product or byproduct – could explain such a discrepancy, and the range of reported $\delta_E(^{13}C$, CFC-113) ~~, this discrepancy is based on~~ would be sufficient to cause such a discrepancy. We caution, however, that this discrepancy derives from only one sample and ~~further~~



~~firn or tropospheric measurements are required to confirm this. Our modelling predicts a continuing~~ takes into account the fractionation of only on CFC-113 fragment. Further work would be needed to definitively assign a change in $\delta_E(^{13}C$, CFC-113). The modelled increase in $\delta_T(^{13}C)$ ~~up to~~ from 2009 through 2050 ~~for each CFC. This increase~~ is sensitive to new emissions~~, though~~. We compared future $\delta_T(^{13}C$, CFC-11) trends in scenarios with/without new CFC-11 emissions. The difference between scenarios was within uncertainty bounds, showing better modelling precision and precise quantification of the isotopic composition of emissions would be needed to detect the isotopic signature of recently reported new CFC-11 emissions in background air.

2) More work is needed to put the results into perspective. What is known now that was not known before? How will the results be used? Were the CFC budgets under-constrained, or will these results provide additional insight into stratospheric changes or processes in firn, or ?

We have reconstructed tropospheric histories of the ^{13}C isotopologues of CFC-11, and CFC-12 over several decades and have shown that these are consistent with changes expected from stratospheric processing alone. This is important independent evidence as large isotopic changes (such as the one inferred by Zuiderweg et al. (2013)) would have challenged the current understanding of their atmospheric cycling and raised questions about their inertness in the biogeosphere. For $\delta_E(^{13}C$, CFC-113), we find tentative evidence for significant changes before 1980, hinting at changes in production procedures and/or materials, though we cannot exclude other measurement artefacts. We also show the potential of our measurements to ascertain adherence to the Montreal Protocol, as the ^{13}C content of all three species should increase in the future – though, as we point out, better precision for ε_{app}, and δ_E would be required to use this technique in background air.

Our stratospheric measurements provide the estimates of ε_{app}(CFC-11), ε_{app}(CFC-12), and ε_{app}(CFC-113). Our ε_{app}(CFC-12) measurement allows calculating δ_T(^{13}C, CFC-12), and hence to infer that δ_E(^{13}C, CFC-12) has probably not undergone a large change, unlike previously reported. Similarly, δ_E(^{13}C, CFC-11) is unlikely to have undergone a significant change, whereas our results hint at a possible change in δ_E(^{13}C, CFC-113). These are direct uses of our results, made clearer by adding:

We have made this clearer by revising the conclusions (please see full conclusions in response to previous comment).

3) Does the derived stratospheric photolytic fractionation factor match the predictions of theory and experiment?

For CFC-12, our measured apparent isotopic fractionation, ε_{app}, is in semi-quantitative agreement with previously reported photolytic fractionation, ε_p (Zuiderweg et al. 2012). The agreement is semi-quantitative because atmospheric processes tend to reduce ε_{app} by a factor of 2-3 relative to ε_p (Kaiser et al. 2006), in the lower stratosphere. The ε_p(CFC-12) presented by Zuiderweg et al. (2012) is 2-3 times ε_{app}(CFC-12).

Our best estimate of ε_{app}(CFC-11) is based on the measurements of ε_{app}(CFC-12), rescaled using ε_p values for CFC-11 and CFC-12 measured by Zuiderweg et al. (2012). We hence have no independent point of comparison for ε_{app}(CFC-11).

Our best estimate of ε_{app}(CFC-113) is, to the best of our knowledge, the only value present in the literature, and we are not aware of any measurements or theoretical predictions of ε_p(CFC-113).

Given the lack of points of comparison, we believe the text in the first paragraph of the discussion is sufficient.

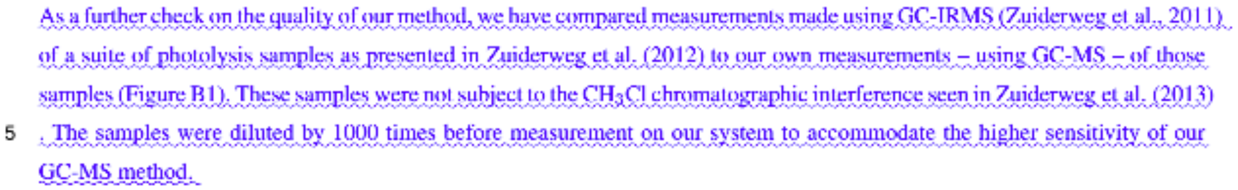
4) There are a number of technical issues listed by another reviewer which should be addressed.

We refer R2 to our response to R1 (below).

Response to Reviewer 1

R1 had concerns about the quality of the data presented. These concerns were laid out in R1's preamble, and some were followed up with specific comments. We first respond to their preamble, referring often to our previous author comment dealing with these concerns (https://acp.copernicus.org/preprints/acp-2020-843/acp-2020-843-SC1-supplement.pdf). To translate the points made in the author comment to the manuscript we made many changes. The biggest and most important change is the addition of a new Appendix (see below), where we validate our methods.

New appendix: Appendix B: Comparison of GC-MS with GC-IRMS measurements



As a further check on the quality of our method, we have compared measurements made using GC-IRMS (Zuiderweg et al., 2011) of a suite of photolysis samples as presented in Zuiderweg et al. (2012) to our own measurements – using GC-MS – of those samples (Figure B1). These samples were not subject to the CH_3Cl chromatographic interference seen in Zuiderweg et al. (2013). The samples were diluted by 1000 times before measurement on our system to accommodate the higher sensitivity of our GC-MS method.

The agreement between the methods is good (Figure B1). Linear regression gives a high regression coefficient ($r^2 = 0.92$) and a gradient consistent with unity (1.0 ± 0.1). This agreement holds over a range of δ spanning almost 60 ‰. The intercept is (46.3 ± 2.7) ‰. This intercept results in a δ value for CFC-12 in AAL-071170 on the VPDB scale of (-44.2 ± 2.5) ‰ — consistent with the (43.0 ± 2.3) ‰ derived using Equation 3.

New appendix figure, showing good agreement between methods

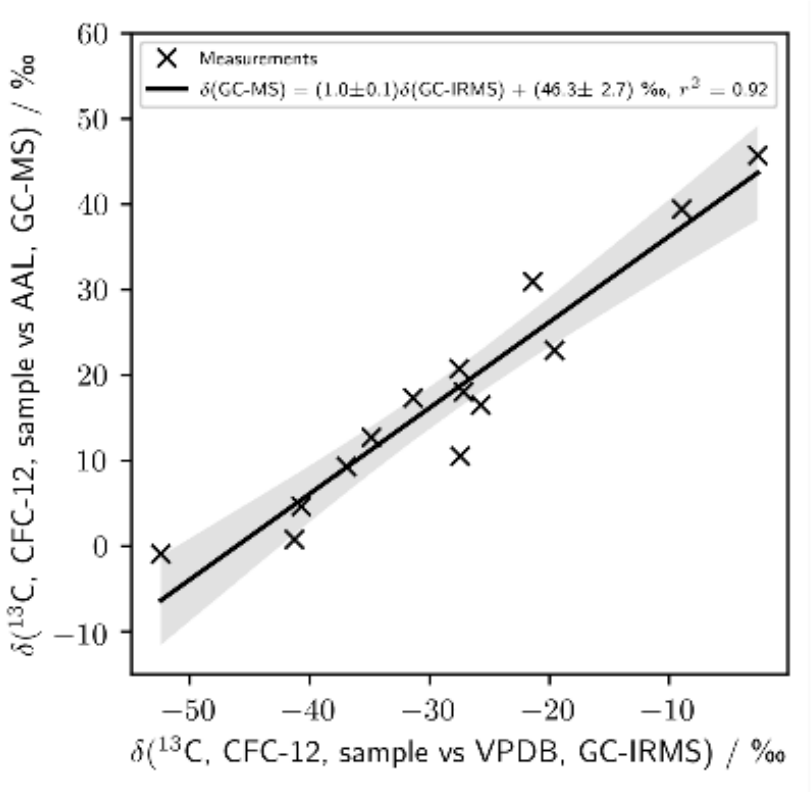


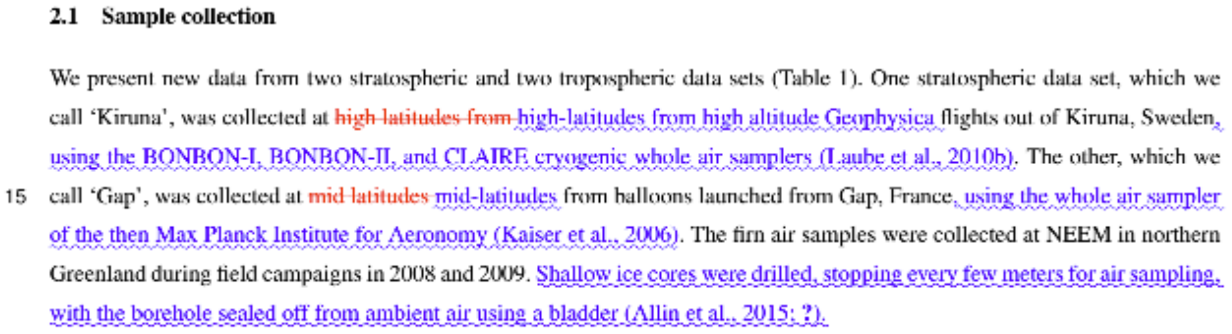
Figure B1. Comparison of measurements presented by Zuiderweg et al. (2012) using GC-IRMS (Zuiderweg et al., 2011) to our own measurements of those same samples.

Response to preamble

Our overarching message when responding to the preamble is that the concerns raised have no significant bearing on the results we present, and no bearing on the conclusions we draw.

Preamble 1) there is no information about the sampling procedures in this manuscript. This should be provided, at least in brief, in the appendix. It is not accept- able that the reader has to read several other papers in order to find information that is highly relevant to the current study. Furthermore, the used method, measurement of delta13C by GC-MS with a single detector, is completely new to me and I also did not find any published GC-MS method successfully demonstrating delta13C analysis at natural isotope abundance levels. Such methods need to be ground truthed, that is, important parameters such as analytical precision, reproducibility, accuracy etc have to be evaluated and reported. The submitted manuscript contains no such information apart from a linearity check.

We have added the following to Section 2.1 to give the reader an overview of the sampling methods:



2.1 Sample collection

We present new data from two stratospheric and two tropospheric data sets (Table 1). One stratospheric data set, which we call 'Kiruna', was collected at ~~high latitudes from~~ high-latitudes from high altitude Geophysica flights out of Kiruna, Sweden, using the BONBON-I, BONBON-II, and CLAIRE cryogenic whole air samplers (Laube et al., 2010b). The other, which we call 'Gap', was collected at ~~mid latitudes~~ mid-latitudes from balloons launched from Gap, France, using the whole air sampler of the then Max Planck Institute for Aeronomy (Kaiser et al., 2006). The firn air samples were collected at NEEM in northern Greenland during field campaigns in 2008 and 2009. Shallow ice cores were drilled, stopping every few meters for air sampling, with the borehole sealed off from ambient air using a bladder (Allin et al., 2015; ?).

There are several references using single detector GC-MS measuring natural abundance $\delta(^{13}C)$ (please see also our author response):
Eiler et al., 2017; Hauri et al., 2002; Schutten et al., 1957; and Nier, 1940

For method A, an estimate of the precision of the methodology is given in Figures 3 and C1. We have added some explanation to the caption of Figure C1 so that it is consistent with Figure 3. In the original manuscript, the error bars for CFC-12 and CFC-11 were switched. We have amended that error in the plots. For method B we take the uncertainty from the loess regression of the firn profile to be our best estimate of the precision of our reconstructed firn profile. These are given in Section 3.1. Updated stratospheric plots are shown below.

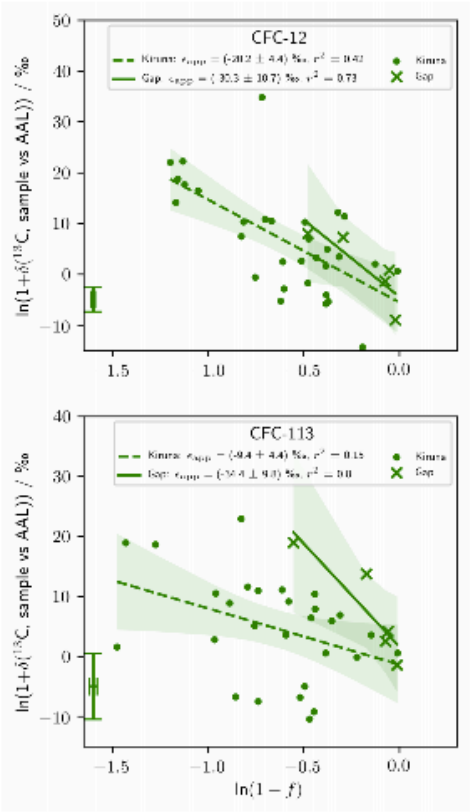


Figure 3. Rayleigh plots of our stratospheric measurements. The linear regression (lines) and 95 % confidence bounds on the regression (shading) are shown for the high-latitude (Kiruna) and mid-latitude (Gap) data sets. The gradients of these regressions, corresponding to ϵ_{app}, are given in the legend with one standard error. The errorbar in the bottom left corner of each graph shows the median repeatability of the reference gas measurements over the measurement days and the median error deriving from the fractional release factor. CFC-11 data are presented in Appendix D.

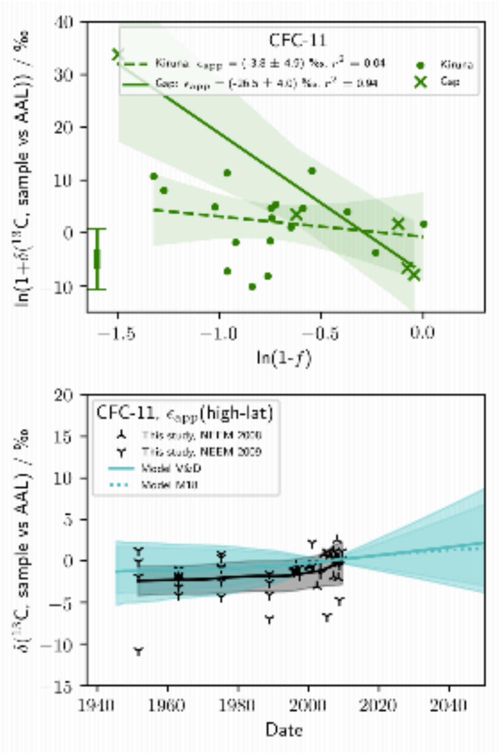


Figure D1. Rayleigh plot showing observations of δ^{13}(C, CFC-11), and derived ϵ_{app}(CFC-11, high-lat) and ϵ_{app}(CFC-11, mid-lat) (top). Also shown is measured and modelled δ_T(CFC-11) (see Figure 4 and Section 2.5 for a description of the model). The model was forced with ϵ_{app}(CFC-11, high-lat). The errorbar in the bottom left corner of each graph shows the median repeatability of the reference gas measurements over the measurement days and the median error deriving from the fractional release factor.

Preamble 2) It is also concerning that basic principles of stable isotope analysis are disregarded such as the use of several reference materials which are directly linked to the isotope-delta zero-point and realization of a two-point calibration in order to correct for scale contraction effects. This means, that the delta13C and epsilons are not comparable with other published values because the scale measured by this mass spec may differ from the official scale. Without a referencing procedure and two-point calibration, the uncertainty of the data can be considered substantially larger than presented (see also specific comments). A two-point calibration should be carried out in a sequence with the samples because the measured scale may even change from day to day. Therefore, unfortunately, a retrospective correction is not possible and the data would have to be re-measured using the appropriate reference materials and methods

We provided an in depth response to this comment previously, which we reproduce here (https://acp.copernicus.org/preprints/acp-2020-843/acp-2020-843-SC1-supplement.pdf).

We measure and report our δ(^{13}C) values against a reference tank containing dried tropospheric air (AAL-071170) at high pressure (collected at a northern hemisphere background site at Niwot Ridge, Colorado, USA, in summer 2005). From comparisons with similar tanks, we know that the CFC mole fractions and isotope ratios in this tank were stable over years, including the period of the measurements reported in the manuscript. Similarly, the samples (some of which were stored for more than 17 years before they were analysed by us) showed no significant long-term changes in their CFC mole fractions compared with measurements made nearer the time when they were collected.

A tropospheric air tank is an ideal reference material for our purposes because it is homogeneous, stable, widely available and comprises the same air matrix as the unknown sample. This tank (AAL-071170) defines the zero point of our isotope delta scale. The availability is not restricted to similar tanks of background air filled around the same time; actually, the troposphere as a whole can be used because of the long atmospheric lifetimes of the three CFC gases studied (52 to 100 years).

The focus of the manuscript is on relative variations in δ(^{13}C) over time (firn) and space (stratosphere) with respect to modern tropospheric air (chosen to be represented by the AAL071170 tank). The detection and quantification of such changes do not require calibration against other reference materials (such as the virtual VPDB standard), which – as the reviewer correctly points out – would only lead to higher uncertainties in the reported δ(^{13}C) values.

The absence of a calibration against VDPB, or indeed the lack of SI traceability, is no impediment for the study of relative changes in gas or isotope ratios, as evidenced – for example – by atmospheric O_2/N_2 ratio measurements, which have been carried out and exploited successfully for more than 30 years' of carbon cycle research before an absolute calibration scale with an accuracy similar to the achievable measurement precision was developed (Aoki et al., 2019).

Similarly, variations in N_2O isotopocule ratios in firn air and the stratosphere have been reported against uncalibrated in-house standards, without loss of relevance or credibility (Röckmann et al., 2003; Röckmann et al., 2001).

In particular, the apparent stratospheric isotope fractionations (ε_{app}) are entirely independent of the chosen isotope delta scale. Other than claimed in the review, they would therefore be easily comparable with other published stratospheric isotope fractionations, should additional measurements become available in the future. We are not aware of any measurements besides the ones we report.

Contrary to the reviewer's assertion, we can compare our $\delta(^{13}C)$ values with other measurements. In the manuscript, we have indeed compared our CFC-12 isotopologue ratio measurements in firn air (on the AAL-071170 scale) against analyses of the same samples using a GCcombustion-IRMS system, reported on the VPDB scale (Zuiderweg et al., 2013). This allowed determining the $\delta(^{13}C)$ value of CFC-12 in AAL-071170 on the VPDB scale as (–43.0±2.3) ‰ (Eq. 3 of the manuscript). A similar approach could be taken for CFC-11 and CFC-113 in AAL071170 and at that time a retrospective correction be applied.

The reviewer also criticised the lack of scale normalisation. Such scale normalisations are required where there is cross-contamination between samples, isotope exchange or blank effects (Kaiser, 2008), which generally lead to a delta scale contraction. Such corrections are usually of the order of <10 % of the delta differences. We cannot exclude the possibility that our method experiences scale contraction, but even a 10 % scale correction would be irrelevant, given the analytical precision we can achieve with our method. For example, the uncertainties in the firn air δ changes are between 30 and 60 % of the δ changes: (2.9±1.6) ‰ for CFC-11, (5.3±2.2) ‰ for CFC-12 and (9.3±2.7) ‰ for CFC-113. Having said that, we are confident that our analytical system does not suffer from memory effects, significant blanks or isotope exchange. The inlet is evacuated to < 0.1 mbar between runs and we have found no memory effects for our analytical species. All blank signals are well below 0.1 % of the reference tank peak area. Isotope exchange is unlikely to play a significant role due to the chemical inertness of the CFCs. This is reflected by their long-term stability in our tanks and canisters.

It is worth noting that the air volume of between 200 and 600 ml (20 ºC, 1bar) used to achieve this level of precision only yields 2 pmol for CFC-113, 12 pmol for CFC-12 and 6 pmol for CFC11 at their modern tropospheric mole fractions. This low sample volume is a limitation imposed by the nature of the highly valuable firn and stratospheric samples. For comparison, the CFC amounts our method requires are a factor of 10^4 to 10^5 less than what Horst et al. (2015) have used to achieve a precision of 0.5 ‰ for $\delta(^{13}C)$. The CFC amounts stated here are for reference gas extractions; they are lower at stratospheric altitudes and the lower firn depths.

We have checked our method against measurements made using GC-IRMS (Zuiderweg et al. 2012). The agreement is good over a range of 60 ‰, validating our methodology. We have added an appendix (B) showing this validation, and also a new figure B1 (please see start of response to R1).

Specific comments:
Page 3 line 3-5: Strictly speaking, the Rayleigh model requires a first-order or pseudo first order reaction. Two reactions (photolysis and O1D) and transport and mixing altogether would give an epsilon that will differ constantly depending on sampling height, temperature, mixing pattern (etc). Epsilon app is, for example, applied in microbiology to describe enrichment factors that are smaller due to a rate limitation. A constantly changing mixture of different processes will yield enrichment factors that are not reproducible. It will be difficult to quantify degradation rates with these kind of

epsilons. How do the authors make sure that a specific sample is not just the result of mixing/ dilution?

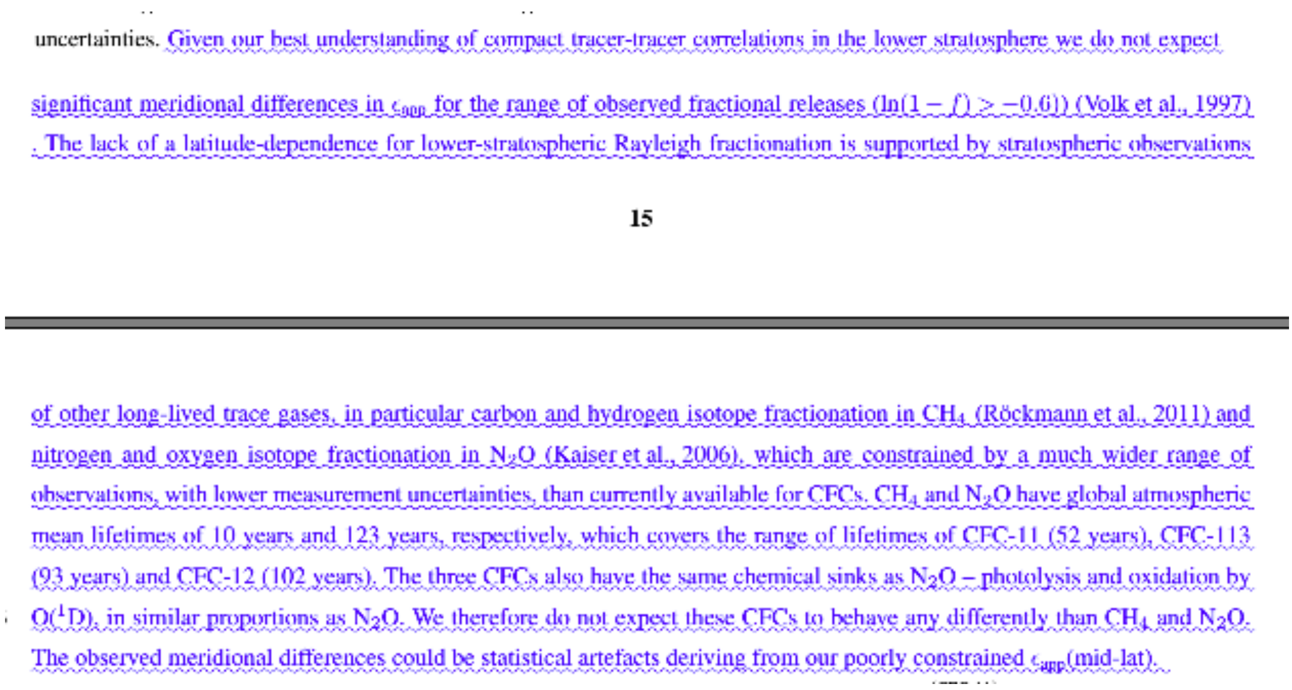
Rayleigh fractionation has been used as a model to define ε_{app} from a range of stratospheric data sets (Kaiser et al., 2006). As stated in the paper, ε_{app} is an empirical value, affected by photolysis, reaction with O(^{1}D), plus transport, mixing, and dilution. ε_{app} is therefore an appropriate value for box modelling the influence of stratosphere-troposphere exchange on the tropospheric isotope signature where these stratospheric processes are not individually resolved. The Rayleigh model is independent of the reaction order. It applies for any process, for which the relationship $dc(^{13}C)/dc(^{12}C) / [c(^{13}C) / c(^{12}C)] = 1 + \varepsilon = \text{const.}$ holds.

Page 3 line 6-12: I'm not sure if these chlorine isotope measurements are of big help. Photolysis cleaves the C-Cl bond and therefore fractionation should occur at a similar rate for the isotopes of both C and Cl. It seems contradictory to me that there is no difference in fractionation between mid and high latitude samples for chlorine isotopes (Allin et al 2015) whereas for carbon a distinct difference is reported. One would expect that there is a latitudinal dependence of both C and Cl or no dependence for the both of them.

We agree with the reviewer on this point. Based on what is known about compact tracer-tracer correlations in the lower stratosphere (e.g., Volk et al. 1997), we would not expect to find any significant latitude-dependence in the apparent stratospheric isotope fractionations for the range of fractional release factors our observations cover. As the reviewer mentions, Allin et al. (2015) did not find a significant latitude-dependence for $\varepsilon_{app}(^{37}Cl)$ in in CFC-11 and CFC-113. The differences seen for $\varepsilon_{app}(^{37}Cl)$ in CFC-12 at mid-latitudes and high-altitudes (Allin et al. 2015) are possibly down to statistical artefacts or, less likely, a decrease of $\varepsilon_{app}(^{37}Cl)$ with altitude. This is illustrated by re-analysing the high-latitude data of Allin et al. (2015), but restricting the analysis to a subset of the data for which $\ln(y/y_T) \geq -0.6$. This gives $\varepsilon_{app}(^{37}Cl) = (-9.1\pm1.4)$ ‰ instead of (6.8±0.8) ‰ as reported by Allin et al. (2015). The value of (–9.1±1.4) ‰ agrees, to within 2σ, with the mid-latitude $\varepsilon_{app}(^{37}Cl)$ value of (–12.2±1.6) ‰.

The lack of a latitude-dependence for lower-stratospheric Rayleigh fractionation is supported by stratospheric observations of other long-lived trace gases, in particular carbon and hydrogen isotope fractionation in CH_4 (Röckmann et al. 2011) and nitrogen and oxygen isotope fractionation in N2O (Kaiser et al. 2006), which are constrained by a much wider range of observations, with lower measurement uncertainties, than currently available for CFCs. CH_4 and N_2O have global atmospheric mean lifetimes of 10 years and 123 years, respectively, which covers the range of lifetimes of CFC-11 (52 years), CFC-113 (93 years) and CFC-12 (102 years). The three CFCs also have the same chemical sinks as N_2O – photolysis and oxidation by O(^{1}D), in similar proportions as N_2O. We therefore do not expect these CFCs to behave any differently than CH_4 and N_2O.

We have removed the comparison between out measurements and Allin et al. from the results, and we have added the following text to the discussion.

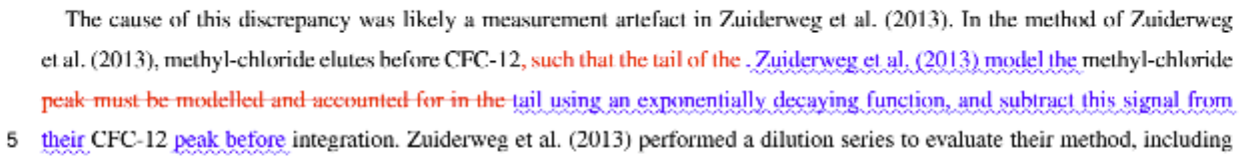


uncertainties. Given our best understanding of compact tracer-tracer correlations in the lower stratosphere we do not expect significant meridional differences in ϵ_{app} for the range of observed fractional releases ($\ln(1-f) > -0.6$)) (Volk et al., 1997). The lack of a latitude-dependence for lower-stratospheric Rayleigh fractionation is supported by stratospheric observations of other long-lived trace gases, in particular carbon and hydrogen isotope fractionation in CH_4 (Röckmann et al., 2011) and nitrogen and oxygen isotope fractionation in N_2O (Kaiser et al., 2006), which are constrained by a much wider range of observations, with lower measurement uncertainties, than currently available for CFCs. CH_4 and N_2O have global atmospheric mean lifetimes of 10 years and 123 years, respectively, which covers the range of lifetimes of CFC-11 (52 years), CFC-113 (93 years) and CFC-12 (102 years). The three CFCs also have the same chemical sinks as N_2O – photolysis and oxidation by $O(^1D)$, in similar proportions as N_2O. We therefore do not expect these CFCs to behave any differently than CH_4 and N_2O. The observed meridional differences could be statistical artefacts deriving from our poorly constrained ϵ_{app}(mid-lat).

Page 3 line 32-34: to be sure that the integration method in Zuiderweg et al (2013) works, one would have to show that different CFC-12 amounts/ peaksizes after the CH3Cl peak (which does not change much) would leave the CFC-12 signature unchanged. The baseline calculation used by Zuiderweg cuts away the front part of the peak and the smaller the CFC-12 peak, the more (relative to total peak area) is cut away. The frontpart is always heavier compared to the tail (e.g. Matucha et al 1991 Doi 10.1016/0021-9673(91)85030-J). This could be the reason for the very depleted values for firn air samples at 67m and 69m. This is partly also discussed in Appendix B but how the correction was carried out does not become clear. Please also define gamma(CH3Cl) and gamma (CFC-12) in Appendix B

We have defined those gamma terms

We agree that this is a plausible mechanism for the artefact. We have added the following to clarify the correction performed



The cause of this discrepancy was likely a measurement artefact in Zuiderweg et al. (2013). In the method of Zuiderweg et al. (2013), methyl-chloride elutes before CFC-12, such that the tail of the . Zuiderweg et al. (2013) model the methyl-chloride ~~peak must be modelled and accounted for in the~~ tail using an exponentially decaying function, and subtract this signal from their CFC-12 peak before integration. Zuiderweg et al. (2013) performed a dilution series to evaluate their method, including

Page 4 line 15-18: What kind of MS is used? Stable carbon isotope measurements are usually carried out by isotope ratio mass spectrometers with several detectors (Faraday type) to allow for the simultaneous measurement of the masses. As far as I could find out, the tri-sector has only one detector which means switching between masses and thus less precise measurements. I'm aware that stable chlorine isotopes can be measured in this way but precision is considerably worse compared to standard methods (DI/GC-IRMS, GC-MC-ICPMS). For stable carbon isotopes I did not find a published method for single detector MS being able to measure d13C at natural abundance and no information is given about the performance of this method (analytical precision, reproducibility, accuracy etc). A citation of the corresponding methods paper should be given and the most important parameters mentioned in the manuscript or much more information is required which could be given in the Appendix

Allin et al. (2015) detail the bulk of the methodology used in this paper. All changes to their method are detailed in Section 2.3 and 2.3. There is no difference in the fundamental principles of the method for carbon and chlorine isotopes, other than natural abundance ratios being a factor of 29 lower for ^{13}C/^{12}C than for ^{37}Cl/^{35}Cl, but the resulting loss on signal-to-noise ratio is partly offset by the relative isotope effects being larger for ^{13}C/^{12}C.

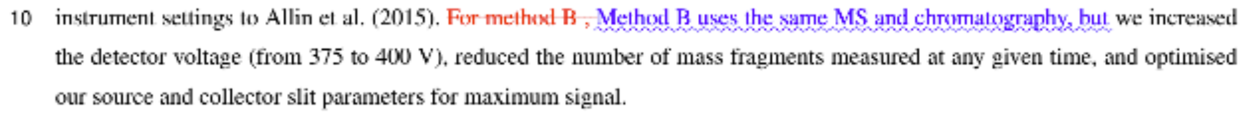
For additional references of single-detector carbon isotope mass spectrometry, see Eiler et al., 2017; Hauri et al., 2002; Schutten et al., 1957; and Nier, 1940

Please see the additional appendix (B) with method validation.

Page 5 line 5-8: Are these the only differences between method A and Method B? If the same instrument was used and only these few parameters were changed this brief description is sufficient. Calling it method A and B is confusing because the reader might think of different methods such as GC-IRMS, laser etc.

Yes, those were the only differences.

We have added some clarification that each method uses the same instrument.



instrument settings to Allin et al. (2015). ~~For method B ,~~ Method B uses the same MS and chromatography, but we increased the detector voltage (from 375 to 400 V), reduced the number of mass fragments measured at any given time, and optimised our source and collector slit parameters for maximum signal.

Page 5 Line 9-11: It is quite concerning that only one standard was used on a regular MS system not being an isotope ratio mass spectrometer. The usual way would be to use three reference materials which were cross-calibrated against secondary (or at least tertiary reference materials) thus allowing to put the samples's isotopic values in relation to the 0-point of the scale (e.g. VPDB). Even if another zero-point is chosen, such as the mentioned air standard AAL, this two-point calibration procedure is necessary because the scales measured by each mass spec may be contracted or expanded. This means that, for example, 12 ‰ difference between two samples measured with one mass spec may be 10 or 13 with another. This effect of scale compression is relatively small for d13C measured with GC-IRMS but it can be quite large for GC-MS. For instance, Bernstein et al (2011, doi: 10.1021/ac200516c) showed that for chlorine the scales of different GCMS varied by plus/minus 30%. Since the abundance difference of the heavy (99% 12C) and the light carbon isotope (1% 13C) is much larger than for chlorine (76% for 35Cl, 24% for 37Cl) I would expect even larger uncertainties here and these uncertainties add to the already quite large analytical uncertainties shown in the paper.

We refer back to our previous response to R1, and our response earlier in this document to a similar comment in the preamble. Scale normalisations are required where there is cross-contamination between samples, isotope exchange or blank effects (Kaiser, 2008), which generally lead to a delta scale contraction. Such corrections are usually of the order of <10 % of the delta differences. We cannot exclude the possibility that our method experiences scale contraction, but even a 10 % scale correction would be irrelevant, given the analytical precision we can achieve with our method. For example, the uncertainties in the firn air δ changes are between 30 and 60 % of the δ changes: (2.9±1.6) ‰ for CFC-11, (5.3±2.2) ‰ for CFC-12 and (9.3±2.7) ‰ for CFC-113 s (p. 8, l. 18). Having said that, we are confident that our analytical system does not suffer from memory effects, significant blanks or isotope exchange. The inlet is evacuated to < 0.1 mbar between runs and we have found no memory effects for our analytical species. All blank signals are well below 0.1 % of the reference tank peak area. Isotope exchange is unlikely to play a significant role due to the chemical inertness of the CFCs. This is reflected by their long-term stability in our tanks and canisters.

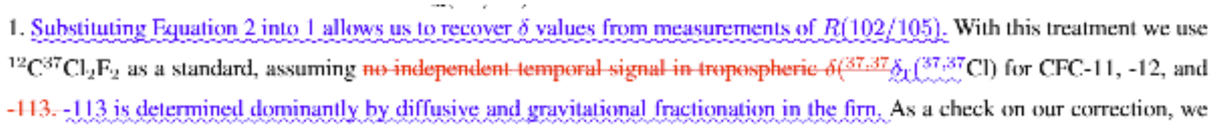
It is worth noting that the air volume of between 200 and 600 ml (20 ºC, 1bar) used to achieve this level of precision only yields 2 pmol for CFC-113, 12 pmol for CFC-12 and 6 pmol for CFC11 at their modern tropospheric mole fractions. This low sample volume is a limitation imposed by the nature of the highly valuable firn and stratospheric samples. For comparison, the CFC amounts our method requires are a factor of 104 to 105 less than what Horst et al. (2015) have used to achieve a precision of 0.5 ‰ for δ(13 C). The CFC amounts stated here are for reference gas extractions; they are lower at stratospheric altitudes and the lower firn depths.

Our method has been validated over a wide range of δ values by comparing to measurements of the same samples made by Zuiderweg et al. (2012), showing scale effects have little effect on our results and none one our conclusions. Please see additional appendix (B) with method validation.

Page 5 Line 20: deriving the isotope ratio from the regression of the raw intensities is quite handy but from own experience I know that it does not work well for all methods. If the mass spec has only one detector (switching between the masses), the outcome is not a straight line but a hysteresis curve which produces a higher uncertainty than the usual integration approach (integrating the area under the peaks). There is also no information in the cited papers about the quality of this approach (e.g. R2 of the regression line).
We used the regression method because it gave better precision than the peak area method (Allin, 2015).

- Figure 1: It is not clear to me, what the authors are correcting for. Transport is corrected in section 2.4 as far as I could understand. Also, given the spread of the d37Cl values, does this correction provide any improvement to the data?
This correction allows us to use measurements of R(102/105) rather than R(102/101) for method B samples. By predicting R(105/101) using the firn model, we can use Equation 2 to recover R(102/101), which is our desired ratio. The correction is small and within the uncertainty bounds on our firn reconstructions shallow in the firn. Deeper in the firn, the correction reached around 4 ‰, which is significant.

We have clarified the purpose of this correction by adding



1. Substituting Equation 2 into 1 allows us to recover δ values from measurements of $R(102/105)$. With this treatment we use ${}^{12}C^{37}Cl_2F_2$ as a standard, assuming ~~no independent temporal signal in tropospheric $\delta($~~$^{37,37}\delta_t({}^{37,37}Cl)$ for CFC-11, -12, and -113. -113 is determined dominantly by diffusive and gravitational fractionation in the firn. As a check on our correction, we

- Page 7 line 12: Isn't the concentration of CFCs in firn air directly related to the "age"? Wouldn't that provide an independent tool to check modelling results? Or is it assumed that CFCs diffuse downward due to lower concentrations there? This would be a mixing problem again.
The concentration of CFCs, and the isotopologues of them, is related to their age in the firn, plus gravitational and diffusive mixing, which is what the model calculates. This model has been

previously demonstrated to work well for multiple trace gases with different concentration gradients and physico-chemical properties (Buizert et al. 2012, Witrant et al. 2012).

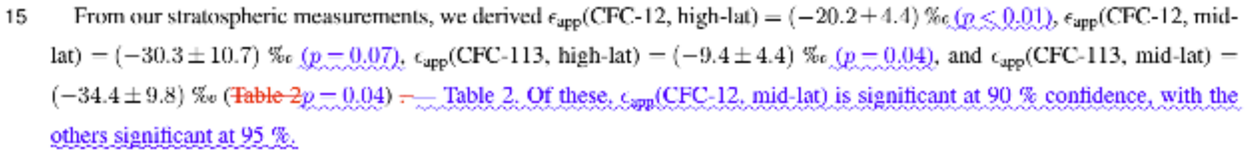
- Page 8 Line 3-10: As stated above, there is no certainty about the d13C scale because no cross calibration against international reference material was carried out. Re-measuring two samples does not give more certainty in this case because Zuiderweg et al do also not provide any details about two-point calibration, reference material etc. All data can only be treated as a rough approximation.

We refer back to our previous response to R1, and our response earlier in this document to a similar comment in the preamble.

- Figure 3: Did the authors carry out a regression analysis? For instance for CFC-113 (Kiruna) the data is so scattered that I would assume they are not even correlated. Please provide R2 in the plots. Preferably also provide p-values of a statistical test or, if the authors prefer, use another measure of the effect size to show whether the data is correlated or not. There must also be something wrong with the confidence bounds given in the plots. 95% confidence interval means that it contains 95% of the data points (which they do not).

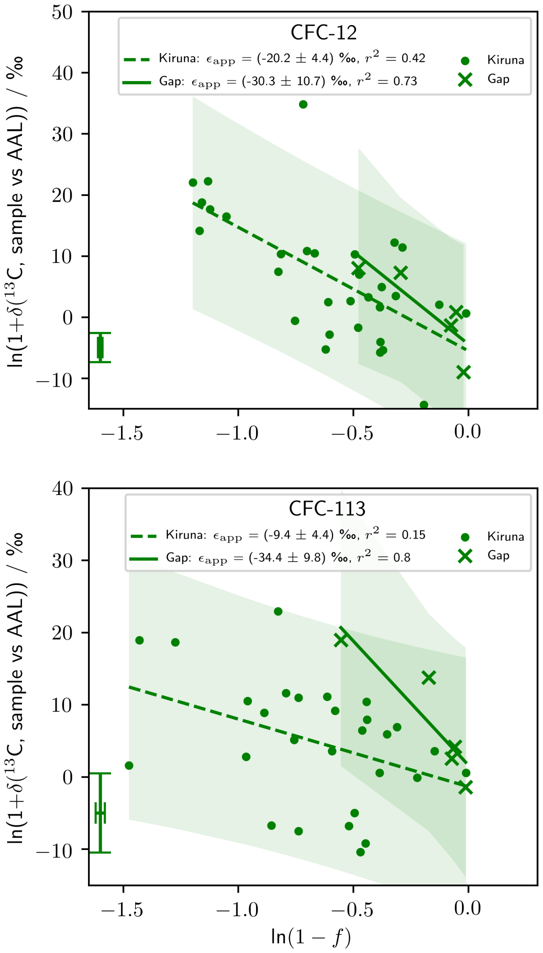
We have added r^2 to the legends of the stratospheric plots (Figures 3 and D1).

We have added p values for the gradient of each of the regressions. Note that, for CFC-12 and -113, each gradient and hence ε_{app}, is significant with at least 90 % confidence. Each high latitude ε_{app} is significant at 95 % confidence. We acknowledge that the mid-latitude ε_{app} are poorly constrained and only use our high latitude ε_{app} values for the stratosphere-troposphere box model calculations.



From our stratospheric measurements, we derived ϵ_{app}(CFC-12, high-lat) = $(-20.2+4.4)$ ‰ ($p \leq 0.01$), ϵ_{app}(CFC-12, mid-lat) = (-30.3 ± 10.7) ‰ ($p = 0.07$), ϵ_{app}(CFC-113, high-lat) = (-9.4 ± 4.4) ‰ ($p = 0.04$), and ϵ_{app}(CFC-113, mid-lat) = (-34.4 ± 9.8) ‰ (~~Table 2~~$p = 0.04$) ~~.~~ — Table 2. Of these, ϵ_{app}(CFC-12, mid-lat) is significant at 90 % confidence, with the others significant at 95 %.

The confidence bounds give the 95 % confidence interval for the regression model. These are different to the 95 % prediction intervals, which would encompass 95 % of the data. Here is Figure 3 with 95 % prediction intervals, which are much larger than the 95 % confidence bounds.



- Page 12 Line 31-32: How can values of about -60‰ (Zuiderweg) be consistent with about -20‰ This is a comparison of apples and oranges. With an assumed scale factor eventually all data will be “consistent”

In this case the scale factor is based on previous comparisons of photolytic and apparent fractionation for δ(^{15}N, N_2O) and δ(^{18}O, N_2O) reported in Kaiser et al. (2006). This scale factor is roughly 2 to 3, and hence our values of around -20‰ are consistent with a range from -40 to -60 ‰. This is not a quantitative comparison but is the only point of comparison available.

This comparison is particularly useful for CFC-11, where it allowed us to identify our $\varepsilon_{\mathrm{app}}$(^{13}C, CFC-11) as biased high. In this case, $\varepsilon_{\mathrm{app}}$(^{13}C, CFC-11, mid-lat) ≈ ε_{p}(^{13}C, CFC-11) which is inconsistent with previously reported scale factors. Combined with the small sample size (n=5), this comparison highlighted our calculated $\varepsilon_{\mathrm{app}}$(^{13}C, CFC-11, mid-lat) as spurious.

- Page 12 Line 33: I doubt that diffusion in the open atmosphere changes the isotopic composition in a way that would be relevant to this study. It is much slower than advection which does not cause fractionation.

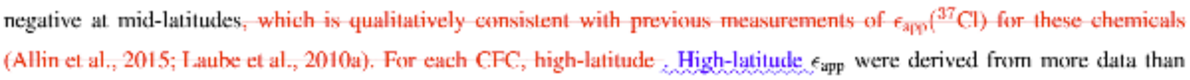
In fact, diffusion is responsible for the attenuation of the intrinsic photochemical fractionation to the observed apparent isotope fractionation, which is a factor of 2 to 3 times lower (Kaiser et al. 2006).

- Page 13 Figure 4: Are the symbols at each time point indicating measurements of the same sample (replicates) or are they actually individual samples? Overall this comparison does not provide much information. The spread of the data is very large.

The individual points show replicates. This figure shows that our reconstructed trends are consistent with our model (CFC-11 and CFC-12), that there is a discrepancy between our reconstructed CFC-113 trend and our model, and that the reconstructed trend of Zuiderweg et al. (2013) is inconsistent with our reconstructed trend and our modelling. The uncertainties, though admittedly rather large, are sufficient to draw these conclusions.

- Page 13 Line 2: Allin et al did not report a meridional difference. That was stated further above.

In fact, Allin et al. did report a meridional difference for CFC-12. We do not expect to find significant meridional differences in ε_{app} over the range of fractional release factors covered by our mid-latitude ε_{app}. We have removed this comparison in the results.



negative at mid-latitudes~~, which is qualitatively consistent with previous measurements of $\epsilon_{app}(^{37}Cl)$ for these chemicals (Allin et al., 2015; Laube et al., 2010a). For each CFC, high-latitude~~ . High-latitude ϵ_{app} were derived from more data than

- Page 14 Table 4: There is more emission data out there in the literature. Phillips et al 2020 (DOI: 10.1021/acs.est.9b05746) reported Dual Inlet IRMS measurements of CFCs (and HCFCs) which are very precise and properly linked to the V-PDB scale

Thanks for this useful reference. We've added the compositions from Phillips et al. (2019) and Horst et al. (2015) that were missing to Table 4
and have changed the text of Section 3.3

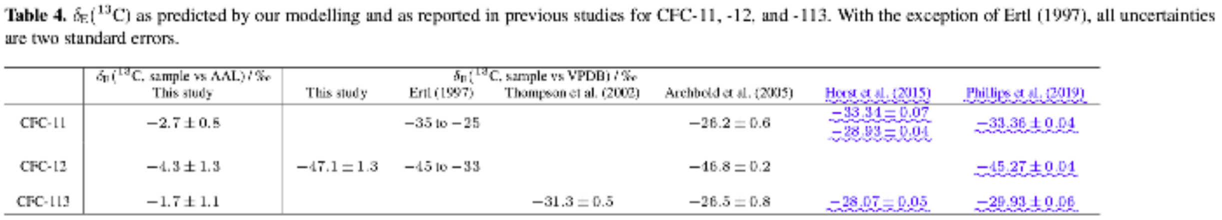
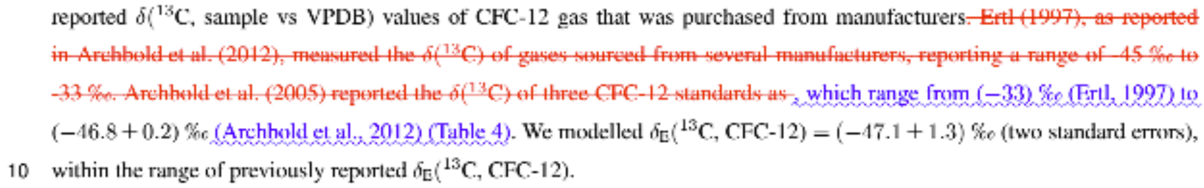


Table 4. $\delta_E(^{13}C)$ as predicted by our modelling and as reported in previous studies for CFC-11, -12, and -113. With the exception of Ertl (1997), all uncertainties are two standard errors.

	$\delta_E(^{13}C$, sample vs AAL) / ‰	$\delta_E(^{13}C$, sample vs VPDB) / ‰					
	This study	This study	Ertl (1997)	Thompson et al. (2002)	Archbold et al. (2005)	Horst et al. (2015)	Phillips et al. (2019)
CFC-11	-2.7 ± 0.8		-35 to -25		-26.2 ± 0.6	-33.34 ± 0.07 -28.93 ± 0.04	-33.36 ± 0.04
CFC-12	-4.3 ± 1.3	-47.1 ± 1.3	-45 to -33		-46.8 ± 0.2		-45.27 ± 0.04
CFC-113	-1.7 ± 1.1			-31.3 ± 0.5	-26.5 ± 0.8	-28.07 ± 0.05	-29.93 ± 0.06



reported $\delta(^{13}C$, sample vs VPDB) values of CFC-12 gas that was purchased from manufacturers~~. Ertl (1997), as reported in Archbold et al. (2012), measured the $\delta(^{13}C)$ of gases sourced from several manufacturers, reporting a range of -45 ‰ to -33 ‰. Archbold et al. (2005) reported the $\delta(^{13}C)$ of three CFC-12 standards as~~ , which range from (−33) ‰ (Ertl, 1997) to (−46.8 ± 0.2) ‰ (Archbold et al., 2012) (Table 4). We modelled $\delta_E(^{13}C$, CFC-12) = (−47.1 ± 1.3) ‰ (two standard errors), within the range of previously reported $\delta_E(^{13}C$, CFC-12).

- Page 14 Line 6 This can only provide a very rough estimate because the errors for epsilon-CFC-12 are also scaled

The uncertainties on ε_{app}(CFC-11) were calculated by propagating the errors on our measurements of ε_{app}(CFC-12) and the errors on ε_p(CFC-11) and ε_p(CFC-12) as measured by Zuiderweg et al. (2012). We disagree that this is a rough estimate – rather, it is an estimate with quantified uncertainty.

- Page 14 Line 10-13 Does it mean that the modelling is based only on high latitude measurements taken above the polar circle (Kiruna)? These epsilons are smaller than those at mid latitudes. So the model would only make sense if one assumes that only in the high latitudes CFCs mix with the troposphere. Otherwise I would think that a weighted mean of the mid and high latitude epsilons should be calculated. This would still ignore low latitude fractionation for which no epsilons are known yet. Does the model account for mixing of stratospheric CFC (high and mid latitude) before they mix back into the troposphere? If not, would the model still fit the data if mid latitude epsilons are used? Maybe I missed it but this should be made clear.

From our understanding of compact tracer-tracer relationships in the lower stratosphere in general and Rayleigh-type fractionation of long-lived trace gases and their isotopologues in particular, we do not expect to see latitude-dependent differences in ε_{app}. See also our reply to another comment above. We have therefore used the statistically best-constrained high-latitude ε_{app} values because they were derived from more data and we therefore have more confidence in them. The mid-latitude ε_{app} are poorly constrained, and we therefore have less confidence in them and modelling resulting from them.

R1 also had some technical corrections:

C6- Page 1 Line 10: delta is expressed in an unusual way: δ(13C). What is the rational of using parentheses? There are multiple good practice guides on how to properly report delta and epsilon (e.g. https://www.forensic-isotopes.org/gpg.html or Coplen 2011, DOI: 10.1002/rcm.5129)

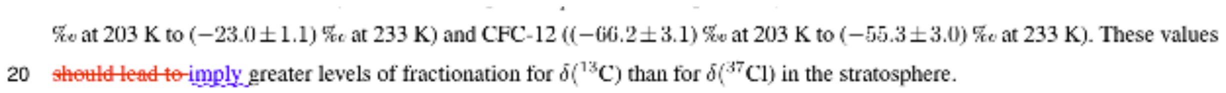
This notation follows long-standing international conventions on the notation of physical quantity symbols and any associated labels, see, for example, the recommendations in the IUPAC Green Book (https://iupac.org/what-we-do/books/greenbook). Coplen (2011) recognizes the correct notation in a footnote, but expressed a personal preference for the incongruent notation without parentheses.

- Page 3 line 15: please define epsilon p

Done

- Page 3 line 17-18: The cause and effect relationship is mixed up here. It is not the values that lead to larger fractionation but the process (having shown large values in the laboratory).

We have reworded:



‰ at 203 K to (−23.0 ± 1.1) ‰ at 233 K) and CFC-12 ((−66.2 ± 3.1) ‰ at 203 K to (−55.3 ± 3.0) ‰ at 233 K). These values ~~should lead to~~ imply greater levels of fractionation for $\delta(^{13}C)$ than for $\delta(^{37}Cl)$ in the stratosphere.

- Page 5 line 16-17: Only every forth measurement was a reference. So samples are therefore not “bracketed” by reference measurements because this would require every second measurement to be a reference.

We have reworded:

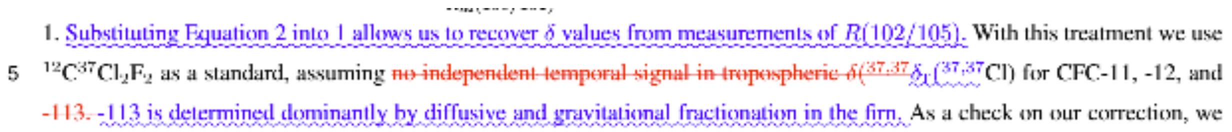
100.9 ≈ 101) ion fragments for the sample and the ~~standard~~reference gas, respectively. R_{std} was taken to be the weighted mean ratio of two ~~bracketing standards~~preceding and subsequent reference gases. Measured $\delta(^{13}C$, CFC-11) and $\delta(^{13}C$, CFC-12)

- Page 5 line 19 was AAL used as “bracketing standard”?

We have replaced ‘standard’ with ‘reference gas’, which we believe clears this up (please see response to previous comment).

- Page 5 line 29: what is the meaning of temporal signal? The change of the isotopic signature over time? Please clarify here and further below.

We have clarified:



1. Substituting Equation 2 into 1 allows us to recover δ values from measurements of $R(102/105)$. With this treatment we use $^{12}C^{37}Cl_2F_2$ as a standard, assuming ~~no independent temporal signal in tropospheric $\delta(^{37,37}$~~ $\delta_1(^{37,37}Cl)$ for CFC-11, -12, and -113. -113 is determined dominantly by diffusive and gravitational fractionation in the firn. As a check on our correction, we

- Page 5 line 26-30:It is not clear for what the correction is applied

We have clarified (please see response to previous comment).

- Page 8 line 26: Please define what the fractional release factor is. How is it calculated? Error bars for 1-f should be provided in Figure 3 and C1 (x-axis)

We have clarified. Please note, the reference gives the method of calculation.

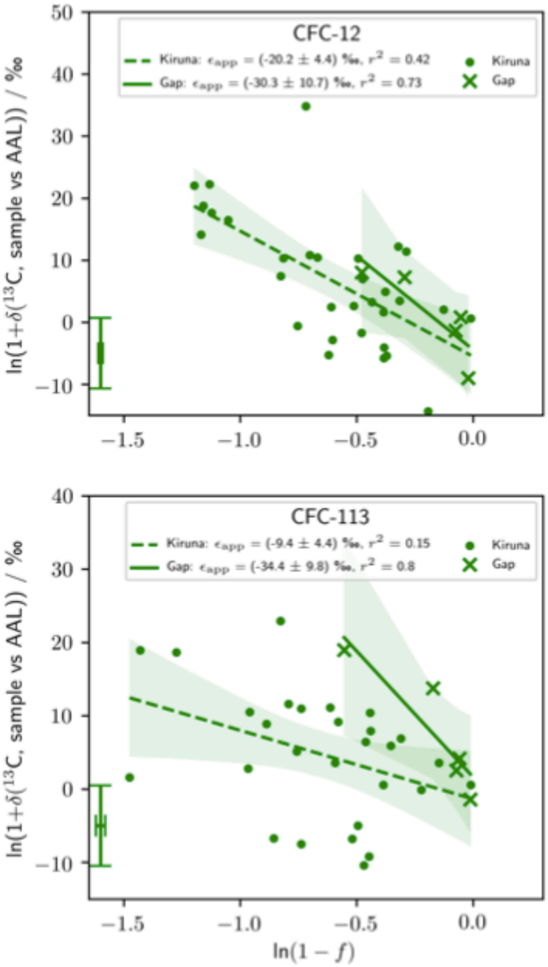


Figure 3. Rayleigh plots of our stratospheric measurements. The linear regression (lines) and 95 % confidence bounds on the regression (shading) are shown for the high-latitude (Kiruna) and mid-latitude (Gap) data sets. The gradients of these regressions, corresponding to ϵ_{app}, are given in the legend with one standard error. The errorbar in the bottom left corner of each graph shows the median repeatability of the reference gas measurements over the measurement days and the median error deriving from the fractional release factor. CFC-11 data are presented in Appendix D.

A horizontal errorbar has been added to Figures 3 and D1 to show the error in ln(1-f). This error is small (1-2 %).

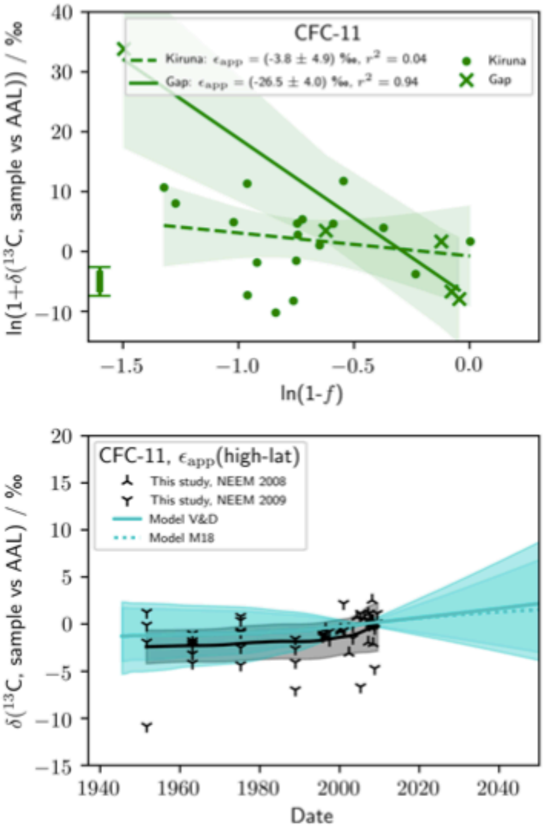
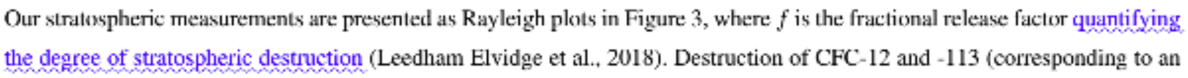


Figure D1. Rayleigh plot showing observations of δ^{13}(C, CFC-11), and derived ϵ_{app}(CFC-11, high-lat) and ϵ_{app}(CFC-11, mid-lat) (top). Also shown is measured and modelled δ_T(CFC-11) (see Figure 4 and Section 2.5 for a description of the model). The model was forced with ϵ_{app}(CFC-11, high-lat). The errorbar in the bottom left corner of each graph shows the median repeatability of the reference gas measurements over the measurement days and the median error deriving from the fractional release factor.


Our stratospheric measurements are presented as Rayleigh plots in Figure 3, where f is the fractional release factor quantifying the degree of stratospheric destruction (Leedham Elvidge et al., 2018). Destruction of CFC-12 and -113 (corresponding to an

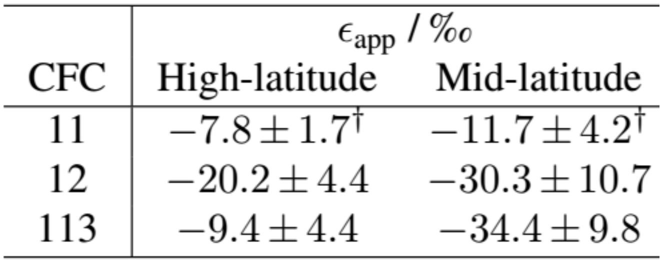
- Page 11 line 6: one could write "larger" because it is a larger isotope effect. The minus just means it is a normal isotope effect

We have stuck with more negative as we feel this terminology is totally unambiguous.

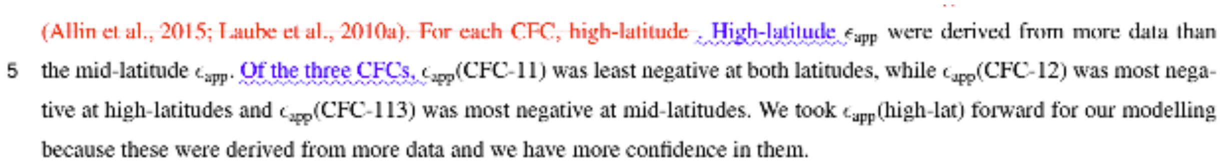
- Page 11 line 9: “while epsilonapp(CFC-12) was most negative at high-latitudes” this is not consistent with table 2

This statement is consistent with table 2. Note that we are comparing the different CFCs a high-latitudes, not CFC-12 at high-latitude with CFC-12 at mid-latitude, which we have clarified by adding:

?!



CFC	ϵ_{app} / ‰ High-latitude	Mid-latitude
11	$-7.8 \pm 1.7^{\dagger}$	$-11.7 \pm 4.2^{\dagger}$
12	-20.2 ± 4.4	-30.3 ± 10.7
113	-9.4 ± 4.4	-34.4 ± 9.8



(Allin et al., 2015; Laube et al., 2010a). For each CFC, high-latitude . High-latitude ϵ_{app} were derived from more data than the mid-latitude ϵ_{app}. Of the three CFCs, ϵ_{app}(CFC-11) was least negative at both latitudes, while ϵ_{app}(CFC-12) was most negative at high-latitudes and ϵ_{app}(CFC-113) was most negative at mid-latitudes. We took ϵ_{app}(high-lat) forward for our modelling because these were derived from more data and we have more confidence in them.

- All Figures: It would be very helpful to see the error bars for each data point. If the same uncertainty is assumed for each sample the error bar can be presented as in Figure 3 (± 6‰. Please also give the uncertainty for (1-f) and the calculated ages.

We have added the 1-f uncertainty to Figures 3 and C1 (see above). This uncertainty encompasses, among other important uncertainties, the error on the calculated ages.

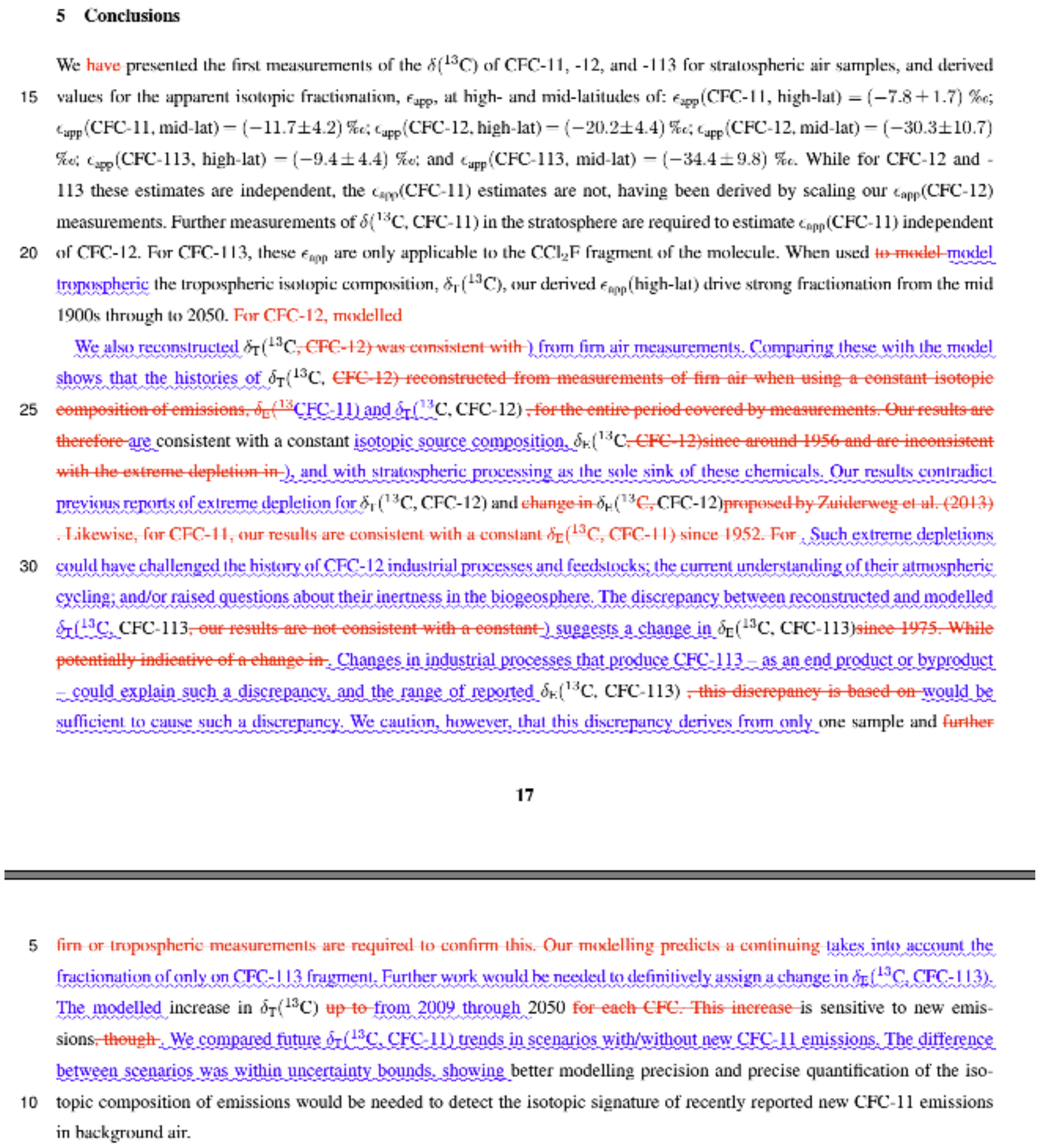
For the Figures 2 and 4 we feel the error on the loess regression is the best estimate of the uncertainty and have retained these figures as is.

- Page 15 line 9: “caused by one measurement depth”. What are the authors trying to say?

We have done some more work on the CFC-113 discrepancy in response to R2 (please see above). Please see the additional qualifications in the abstract and discussion.

- Page 15-16 Conclusion section: This is just again a summary of the results. What are the implications of this study? Does it remove any uncertainty mentioned in the introductions?

We have revised the conclusions in response to both reviewers, please see below.



5 Conclusions

We have presented the first measurements of the $\delta(^{13}\mathrm{C})$ of CFC-11, -12, and -113 for stratospheric air samples, and derived values for the apparent isotopic fractionation, ϵ_{app}, at high- and mid-latitudes of: ϵ_{app}(CFC-11, high-lat) = $(-7.8 + 1.7)$ ‰; ϵ_{app}(CFC-11, mid-lat) = (-11.7 ± 4.2) ‰; ϵ_{app}(CFC-12, high-lat) = (-20.2 ± 4.4) ‰; ϵ_{app}(CFC-12, mid-lat) = (-30.3 ± 10.7) ‰; ϵ_{app}(CFC-113, high-lat) = (-9.4 ± 4.4) ‰; and ϵ_{app}(CFC-113, mid-lat) = (-34.4 ± 9.8) ‰. While for CFC-12 and -113 these estimates are independent, the ϵ_{app}(CFC-11) estimates are not, having been derived by scaling our ϵ_{app}(CFC-12) measurements. Further measurements of $\delta(^{13}\mathrm{C}$, CFC-11) in the stratosphere are required to estimate ϵ_{app}(CFC-11) independent of CFC-12. For CFC-113, these ϵ_{app} are only applicable to the $\mathrm{CCl_2F}$ fragment of the molecule. When used ~~to model~~ model tropospheric the tropospheric isotopic composition, $\delta_{\mathrm{T}}(^{13}\mathrm{C})$, our derived ϵ_{app}(high-lat) drive strong fractionation from the mid 1900s through to 2050. For CFC-12, modelled

We also reconstructed $\delta_{\mathrm{T}}(^{13}$C~~, CFC-12) was consistent with~~) from firn air measurements. Comparing these with the model shows that the histories of $\delta_{\mathrm{T}}(^{13}$C, ~~CFC-12) reconstructed from measurements of firn air when using a constant isotopic composition of emissions, $\delta_{\mathrm{E}}(^{13}$~~CFC-11) and $\delta_{\mathrm{T}}(^{13}$C, CFC-12) ~~, for the entire period covered by measurements. Our results are therefore~~ are consistent with a constant isotopic source composition, $\delta_{\mathrm{E}}(^{13}$C~~, CFC-12)since around 1956 and are inconsistent with the extreme depletion in~~), and with stratospheric processing as the sole sink of these chemicals. Our results contradict previous reports of extreme depletion for $\delta_{\mathrm{T}}(^{13}$C, CFC-12) and ~~change in $\delta_{\mathrm{E}}(^{13}$C,~~ CFC-12)~~proposed by Zuiderweg et al. (2013). Likewise, for CFC-11, our results are consistent with a constant $\delta_{\mathrm{E}}(^{13}$C, CFC-11) since 1952. For~~ . Such extreme depletions could have challenged the history of CFC-12 industrial processes and feedstocks; the current understanding of their atmospheric cycling; and/or raised questions about their inertness in the biogeosphere. The discrepancy between reconstructed and modelled $\delta_{\mathrm{T}}(^{13}$C, CFC-113~~, our results are not consistent with a constant~~) suggests a change in $\delta_{\mathrm{E}}(^{13}$C, CFC-113)~~since 1975. While potentially indicative of a change in~~ . Changes in industrial processes that produce CFC-113 – as an end product or byproduct – could explain such a discrepancy, and the range of reported $\delta_{\mathrm{E}}(^{13}$C, CFC-113) ~~, this discrepancy is based on~~ would be sufficient to cause such a discrepancy. We caution, however, that this discrepancy derives from only one sample and ~~further~~

~~firn or tropospheric measurements are required to confirm this. Our modelling predicts a continuing~~ takes into account the fractionation of only on CFC-113 fragment. Further work would be needed to definitively assign a change in $\delta_{\mathrm{E}}(^{13}$C, CFC-113). The modelled increase in $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ ~~up to~~ from 2009 through 2050 ~~for each CFC. This increase~~ is sensitive to new emissions~~, though~~ . We compared future $\delta_{\mathrm{T}}(^{13}$C, CFC-11) trends in scenarios with/without new CFC-11 emissions. The difference between scenarios was within uncertainty bounds, showing better modelling precision and precise quantification of the isotopic composition of emissions would be needed to detect the isotopic signature of recently reported new CFC-11 emissions in background air.

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Stratospheric carbon isotope fractionation and tropospheric histories of CFC-11, CFC-12 and CFC-113 isotopologues

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Abstract. We present novel measurements of the carbon isotope composition of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CFC-113 ($CF_2ClCFCl_2$), three atmospheric trace gases that are important for both stratospheric ozone depletion and global warming. These measurements were carried out on air samples collected in the stratosphere – the main sink region for these gases – and on air extracted from deep polar firn snow. We quantify, for the first time, the apparent isotopic fractionation, $\epsilon_{\text{app}}(^{13}\text{C})$, for these gases as they are destroyed in the high- and mid-latitude stratosphere: ϵ_{app}(CFC-12, high-lat) = (-20.2 ± 4.4) ‰ and ϵ_{app}(CFC-113, high-lat) = (-9.4 ± 4.4) ‰, ϵ_{app}(CFC-12, mid-lat) = (-30.3 ± 10.7) ‰ , and ϵ_{app}(CFC-113, mid-lat) = (-34.4 ± 9.8) ‰. Our CFC-11 measurements were not sufficient to calculate ϵ_{app}(CFC-11) so we instead used previously reported photolytic fractionation for CFC-11 and CFC-12 to scale our ϵ_{app}(CFC-12), resulting in ϵ_{app}(CFC-11, high-lat) = (-7.8 ± 1.7) ‰ and ϵ_{app}(CFC-11, mid-lat) = (-11.7 ± 4.2) ‰. Measurements of firn air were used to construct histories of the tropospheric isotopic composition, $\delta_{\text{T}}(^{13}\text{C})$, for CFC-11 (1950s to 2009), CFC-12 (1950s to 2009), and CFC-113 (1970s to 2009) — with $\delta_{\text{T}}(^{13}\text{C})$ increasing for each gas. We used ϵ_{app}(high-lat), which were derived from more data, and a constant isotopic composition of emissions, $\delta_{\text{E}}(^{13}\text{C})$, to model $\delta_{\text{T}}(^{13}\text{C}$, CFC-11), $\delta_{\text{T}}(^{13}\text{C}$, CFC-12), and $\delta_{\text{T}}(^{13}\text{C}$, CFC-113). For CFC-11 and CFC-12, modelled $\delta_{\text{T}}(^{13}\text{C})$ was consistent with measured $\delta_{\text{T}}(^{13}\text{C})$ for the entire period covered by the measurements, suggesting no dramatic change in $\delta_{\text{E}}(^{13}\text{C}$, CFC-11) or $\delta_{\text{E}}(^{13}\text{C}$, CFC-12) has occurred since the 1950s. For CFC-113, our modelled $\delta_{\text{T}}(^{13}\text{C}$, CFC-113) did not agree with our measurements earlier than 1980. ~~While this~~ This discrepancy may be indicative of a change in

~~δ_{E}(^{13}C~~δ_{E}(13C, CFC-113)~~, it is premature to assign one~~. However, this conclusion is based largely on a single sample and only just significant outside the 95 % confidence interval. Therefore more work is needed to independently verify this temporal trend in the global tropospheric ^{13}C isotopic composition of CFC-113. Our modelling predicts increasing δ_{T}(^{13}C, CFC-11), δ_{T}(^{13}C, CFC-12), and δ_{T}(^{13}C, CFC-113) into the future. We investigated the effect of recently reported new CFC-11 emissions on background δ_{T}(^{13}C, CFC-11) by fixing model emissions after 2012, and comparing δ_{T}(^{13}C, CFC-11) in this scenario to the model base case. The difference in δ_{T}(^{13}C, CFC-11) between these scenarios was 1.4 ‰ in 2050. This difference is smaller than our model uncertainty envelope and would therefore require improved modelling and measurement precision, as well as better quantified isotopic source compositions, to detect.

1 Introduction

Chlorofluorocarbons (CFCs) have been produced since the 1940s for multiple uses, such as refrigerant gases, aerosol propellants, and in foam blowing. Since their role in ozone depletion was discovered (Molina and Rowland, 1974; Farman et al., 1985), there has been a global effort to phase out the production and use of CFCs, culminating in the essentially complete elimination of their production in 2015 under the Montreal protocol. Long-term monitoring shows that the atmospheric mole fractions of the three most abundant CFCs (CFC-11, -12 and -113) have been declining as a result (Carpenter et al., 2014). However, recent studies highlight the need for continued, careful monitoring of CFCs. Montzka et al. (2018) found evidence for a recently emerged source of atmospheric CFC-11, with subsequent studies tracing these emissions largely to north-east China (Rigby et al., 2019; Adcock et al., 2020). In addition, Adcock et al. (2018) found increasing mole fractions of CFC-113a. Isotopic measurements could provide additional constraints when identifying sources and sinks of CFCs.

CFCs are released to the troposphere by industrial processes and emission from existing banks (Lickley et al., 2020). Once in the troposphere, CFCs are transported to the stratosphere where they are subject to UV photolysis and reaction with O(^{1}D). Loss by photolysis is dominant, with loss by O(^{1}D) contributing around 2 %, 6 %, and 6% for CFC-11, -12, and -113, respectively (Burkholder et al., 2013). The balance of these sources and sinks, and the transport processes between them, determines the atmospheric lifetime of a CFC and its tropospheric concentration.

These processes also influence the isotopic signature of CFCs. Breakdown in the stratosphere preferentially destroys light isotopologues, causing a fractionation that leaves the un-photolysed stratospheric CFC pool enriched in heavy isotopes – ^{13}C and ^{37}Cl – relative to the troposphere. Such behaviour has been observed for δ(^{37}Cl, CFC-11), δ(^{37}Cl, CFC-12), and δ(^{37}Cl, CFC-113) (Allin et al., 2015; Laube et al., 2010a), and for other gases, such as N_2O (Griffith et al., 2000; Rahn and Wahlen, 1997; Röckmann et al., 2001; Kaiser et al., 2006; Toyoda et al., 2018), CH_4 and H_2 (Röckmann et al., 2003b; Rahn et al., 2003; Rhee et al., 2006; Röckmann et al., 2011). Heavy isotopologues of CFCs are enriched in the troposphere when this stratospheric pool mixes with the troposphere. There is a good conceptual understanding of isotopic budgets of CFCs, but significant uncertainties remain that hinder the use of isotopic methods to study CFC emissions, sources, and sinks.

One such uncertainty is the degree to which CFCs fractionate in the stratosphere. To date, few studies have been carried out to quantify the apparent isotopic fractionation, ϵ_{app}, in CFCs. ϵ_{app} relates the change in isotopic signature of a chemical to the degree of destruction observed in the atmosphere using a Rayleigh fractionation model. It is an empirical value that is affected by intrinsic photochemical fractionation, destruction by $O(^1D)$, and transport and mixing (Kaiser et al., 2006). In the dominant stratospheric sink region, photochemical loss dominates loss from reaction with $O(^1D)$ for CFC-11 and -12 (Minschwaner et al., 2013). Laube et al. (2010b) measured vertical profiles of $\delta(^{37}\text{Cl, CFC-12})$ in stratospheric air from tropical latitudes, calculating $\epsilon_{\text{app}}(^{37}\text{Cl, CFC-12}) = (-12.1 \pm 1.7)$ ‰. Using similar methodology, Allin et al. (2015) calculated $\epsilon_{\text{app}}(^{37}\text{Cl, CFC-12}) = (-12.2 \pm 1.6)$ ‰ at mid- and (-6.8 ± 0.8) ‰ high-latitudes. This decrease in the magnitude of $\epsilon_{\text{app}}(^{37}\text{Cl})$ with increasing latitude is qualitatively consistent with observations of $\delta(^{15}\text{N}, N_2O)$ and $\delta(^{18}\text{O}, N_2O)$ (Kaiser et al., 2006), though the decrease is larger for CFC-12. Allin et al. (2015) observed no latitude dependence for $\epsilon_{\text{app}}(^{37}\text{Cl, CFC-11})$ (mid: (-2.4±0.5) ‰, high: (-2.3±0.4) ‰) and $\epsilon_{\text{app}}(^{37}\text{Cl, CFC-113})$ (mid: (-3.5±1.5) ‰, high: (-3.3±1.2) ‰), though they speculated that some latitude dependence could be obscured by their uncertainties.

For CFCs, the only study of $\epsilon_{\text{app}}(^{13}\text{C})$ – from here, ϵ_{app} – under conditions representative of the stratosphere was the laboratory photolysis experiment of Zuiderweg et al. (2012). Laboratory experiments exclude the effects of atmospheric transport and mixing, which tend to dilute observed fractionations such that ϵ_{app} tends to be less than intrinsic photolytic fractionations, ϵ_{p}, (Kaiser et al., 2006). Zuiderweg et al. (2012) reported ϵ_{p} under stratospherically relevant conditions for CFC-11 ((-23.8 ± 0.9) ‰ at 203 K to (-23.0 ± 1.1) ‰ at 233 K) and CFC-12 ((-66.2 ± 3.1) ‰ at 203 K to (-55.3 ± 3.0) ‰ at 233 K). These values ~~should lead to~~ imply greater levels of fractionation for $\delta(^{13}\text{C})$ than for $\delta(^{37}\text{Cl})$ in the stratosphere.

Another uncertainty in our understanding of CFC isotopologues is the isotopic signature of their sources. Allin et al. (2015) used their measured ϵ_{app} for CFC-11, CFC-12, and CFC-113 to model a tropospheric history of $\delta(^{37}\text{Cl})$ in these chemicals, following the approach of Röckmann et al. (2003a). Allin et al. (2015) constructed a tropospheric history of the isotopic composition of these chemicals from measurements of tropospheric and firn air — deep, compacted snow containing an archive of tropospheric air going back decades (e.g. Buizert et al., 2012). When a constant isotopic source signature was assumed, the model agreed well with measurements of $\delta(^{37}\text{Cl})$ representative of tropospheric air from around 1970 onwards. Five pre-1970 air samples had $\delta(^{37}\text{Cl})$ values that were inconsistent with the model. However, no clear trend was observable for these five samples and, in addition, the disagreement was not significant to 2σ. The authors concluded that a constant source signature is likely consistent with measured $\delta(^{37}\text{Cl})$ since 1970, and that, with current measurement precisions, it is premature to assign a source change to CFC-11, -12, and -113 in the period before this.

In contrast, Zuiderweg et al. (2013) presented evidence for a past change in $\delta(^{13}\text{C, CFC-12})$. Large depletions, around -40 ‰ relative to the present day troposphere, were measured in one deep firn air sample that corresponded to a mean age of around 1965. A significant change in the source signature of CFC-12 is required to explain this observation, and Zuiderweg et al. (2013) suggest that a change in feedstock during CFC production is the most promising explanation. But the results

Table 1. Samples analysed in this study.

Sample type	Sampling location	Sampling date	Time period covered by samples	Analytical method
High latitude stratosphere	Aircraft flights out of Kiruna†	December 2011	December 2011	A
Mid latitude stratosphere	Balloon launched out of Gap*	June 1999	June 1999	A
Firn air	Northern Greenland+	21–30 July 2008	≈1997 to 2008††	B
Firn air	Northern Greenland§	15–24 July 2009	≈1955 to 2009††	B

† 62 to 72 °N, 2 °W to 24 °E; 9–19 km; Laube et al. (2010b)
* 44.4 to 44.8 °N, 3.1 to 6.3 °E; 8–34 km; Kaiser et al. (2006)
+ 77.45 °N, 51.06 °W; Buizert et al. (2012)
§ 77.45 °N, 51.06 °W; Zuiderweg et al. (2013)
†† Mean ages of the age distributions of the firn air samples

of Zuiderweg et al. (2013) rely heavily on one firn air sample that was potentially biased due to interference from a nearby chromatographic peak (see below and Appendix C). The tropospheric history of $\delta(^{13}\text{C, CFC-12})$ remains uncertain.

We re-measured the firn profile analysed by Zuiderweg et al. (2013) using a different method to better constrain and independently assess the history of $\delta(^{13}\text{C, CFC-12})$. Together with $\delta(^{13}\text{C, CFC-12})$, we also measured $\delta(^{13}\text{C, CFC-11})$ and $\delta(^{13}\text{C, CFC-113})$ in firn and stratospheric air samples. For the first time, stratospheric measurements were used to calculate $\epsilon_{\text{app}}(^{13}\text{C})$ for CFC-11, -12, and -113. We then used these ϵ_{app} values to quantify the isotope effect associated with the stratospheric removal in a two box model, using a constant isotopic source signature, and calculated the temporal evolution of tropospheric $\delta(^{13}\text{C})$ for these chemicals since 1937 (CFC-12), 1946 (CFC-11), and 1962 (CFC-113). Model results were compared to the firn measurements to investigate whether changes in isotopic source composition are required to explain the $\delta(^{13}\text{C})$ history of these chemicals.

2 Methodology

2.1 Sample collection

We present new data from two stratospheric and two tropospheric data sets (Table 1). One stratospheric data set, which we call ‘Kiruna’, was collected at ~~high latitudes from~~ high-latitudes from high altitude Geophysica flights out of Kiruna, Sweden, using the BONBON-I, BONBON-II, and CLAIRE cryogenic whole air samplers (Laube et al., 2010b). The other, which we call ‘Gap’, was collected at ~~mid latitudes~~ mid-latitudes from balloons launched from Gap, France, using the whole air sampler of the then Max Planck Institute for Aeronomy (Kaiser et al., 2006). The firn air samples were collected at NEEM in northern Greenland during field campaigns in 2008 and 2009. Shallow ice cores were drilled, stopping every few meters for air sampling, with the borehole sealed off from ambient air using a bladder (Allin et al., 2015; ?).

2.2 Sample preparation and analysis

All of the samples were analysed using a gas chromatography (GC)/mass spectrometry (MS) system that has been used successfully to measure trace gas isotopologues in previous studies (Laube et al., 2010b; Allin et al., 2015). In short, an Agilent 6890 GC was coupled to a VG/Waters tri-sector mass spectrometer. Air samples were dried by passing them through magnesium perchlorate granules, before being concentrated onto a Hayesep D 80/100 mesh held at -78 ^{o}C in a sample loop using a dry-ice/ethanol mixture. Desorption from the Hayesep D was achieved by heating the sample loop to around 95 ^{o}C using hot water. A high purity helium stream transferred the sample to a 0.32 mm internal diameter, GS-GasPro (30 m) or KCl-passivated CP-PLOT Al_2O_3 (50 m) column held at -10 ^{o}C. The column was heated at 10 ^{o}C min^{-1} to 200 ^{o}C to release the chemicals of interest, separated by their retention strength, and pass them to the MS. Every 4th injection was a standard. While the above method was used for every sample analysed, different volumes were trapped for the stratospheric samples (200 ml at 20 °C and 1 bar, method A) and the NEEM 2008/09 firn samples (600 ml at 20 °C and 1 bar, method B). Also, method A used similar instrument settings to Allin et al. (2015). ~~For method B ,~~Method B uses the same MS and chromatography, but we increased the detector voltage (from 375 to 400 V), reduced the number of mass fragments measured at any given time, and optimised our source and collector slit parameters for maximum signal.

Our method allows measurements of $\delta(^{37}\mathrm{Cl})$ (Allin et al., 2015) and $\delta(^{13}\mathrm{C})$ (this study) for CFCs with main isotopologues in the pmol/mol range. An advantage of our method is that we can make these measurements using only a few hundred millilitres of air, which is important when measuring typical stratospheric and firn air samples where sample volumes are restricted.

2.3 Data processing

$\delta(^{13}\mathrm{C})$ was calculated using

$$\delta(^{13}\mathrm{C}) = \frac{R_{\mathrm{samp}}(102/101)}{R_{\mathrm{std}}(102/101)} - 1, \tag{1}$$

where $R_{\mathrm{samp}}(102/101)$ and $R_{\mathrm{std}}(102/101)$ are the ratios of the $^{13}\mathrm{C}^{35}\mathrm{Cl}_2\mathrm{F}^+$ $(m/z = 101.9 \approx 102)$ to $^{12}\mathrm{C}^{35}\mathrm{Cl}_2\mathrm{F}^+$ $(m/z = 100.9 \approx 101)$ ion fragments for the sample and the ~~standard~~reference gas, respectively. R_{std} was taken to be the weighted mean ratio of two ~~bracketing standards~~preceding and subsequent reference gases. Measured $\delta(^{13}\mathrm{C}$, CFC-11) and $\delta(^{13}\mathrm{C}$, CFC-12) reflect the total fractionation of each gas whereas $\delta(^{13}\mathrm{C}$, CFC-113) only reflects the fractionation on the $\mathrm{CCl_2F}$ fragment, neglecting fractionation on the $\mathrm{CClF_2}$ fragment. The reference used for all measurements was 2005 Northern Hemisphere background air, AAL-071170 — from here referred to as ‘AAL’. For the stratospheric samples (method A), $R(102/101)$ was calculated by regressing separate raw intensities for each ion fragment against each other (Laube et al., 2010a; Allin et al., 2015). For the firn samples (method B, using a larger air volume) the intensity of the $m/z101$ fragment saturated the detector and we instead used the $^{12}\mathrm{C}^{37}\mathrm{Cl}_2\mathrm{F}^+$ $(m/z = 104.9 \approx 105)$ fragment to calculate $R(102/105)$, again by the regression of the separate raw intensities for each fragment. To recover $R(102/101)$, we applied a correction to the measured $R(102/105)$ based on the expected $R(105/101)$ using the relation

$$\frac{R_{\text{samp}}(102/101)}{R_{\text{std}}(102/101)} = \frac{R_{\text{samp}}(102/105)}{R_{\text{std}}(102/105)} \cdot \frac{R_{\text{samp}}(105/101)}{R_{\text{std}}(105/101)}. \tag{2}$$

The expected $R(105/101)$ values correspond to $^{12}C^{37}Cl_2F_2/^{12}C^{35}Cl_2F_2$ isotopologue ratios (relative mass difference of 4) and were calculated based on the modelling of diffusive/gravitational fractionation in firn (Section 2.4), assuming a constant isotopic source composition. In this case, $\frac{R_{\text{samp}}(105/101)}{R_{\text{std}}(105/101)} = 1 + 4c$, with c being the correction for a relative mass difference of 1. Substituting Equation 2 into 1 allows us to recover δ values from measurements of $R(102/105)$. With this treatment we use $^{12}C^{37}Cl_2F_2$ as a standard, assuming ~~no independent temporal signal in tropospheric $\delta(^{37,37}$~~$\delta_{\mathrm{T}}(^{37,37}\mathrm{Cl})$ for CFC-11, -12, and ~~-113.~~ -113 is determined dominantly by diffusive and gravitational fractionation in the firn. As a check on our correction, we plot depth profiles of $2c$ and $\delta(^{37}\mathrm{Cl})$ measurements of the NEEM 2009 firn profile presented in Allin et al. (2015) (Figure 1). $2c$ is similar to $\delta(^{37}\mathrm{Cl})$, within the precision of the data, as expected considering Allin et al. (2015) did not observe temporal signals in $\delta(^{37}\mathrm{Cl})$. Given the lack of temporal signals in $\delta(^{37}\mathrm{Cl})$, we do not expect large temporal changes in tropospheric $\delta(^{37,37}\mathrm{Cl})$. The median magnitude of the effect of this correction on our $\delta(^{13}\mathrm{C})$ is 0.8 ‰ (CFC-11), 0.7 ‰ (CFC-12), and 0.5 ‰ (CFC-113). The impact of the correction on $\delta(^{13}\mathrm{C})$ increases with depth in the firn, reaching maximum magnitudes of 4.2 ‰ (CFC-11), 4.3 ‰ (CFC-12), and 0.9 ‰ (CFC-113).

To ascertain the linearity of the response of our analytical system, we performed dilution series for both methods, as described in Appendix A and shown in Figure A1. For method A, the dilution series showed that below a certain threshold (minimum peak area) there are systematic deviations in our measurement methods. Based on these results, a number of stratospheric samples, for which the peak area fell blow this threshold, were excluded. From a total of 38 measurements of each CFC, we rejected 22 (CFC-11), 9 (CFC-12), and 12 (CFC-113) measurements because they fell outside of the linearity limit of our method. For method B, we did not reject any of the 56 measurements performed based on the dilution series. We did, however, exclude the 69.4 m and 71.9 m NEEM 2009 samples (10 measurements) for CFC-113 because, for the corresponding mean ages, there was too little CFC-113 in the atmosphere (Adcock et al., 2018) to reliably determine $\delta(^{13}\mathrm{C})$ values. These 10 measurements are shown in Figure A1 but did not contribute to our analysis.

2.4 Modelling firn air transport

Differing masses and diffusivities cause gases, and isotopologues of a given gas, to move through firn at different rates. Here, a model of gas transport in firn air (Witrant et al., 2012) was used to predict both the age distribution for CFC-11, -12, and -113 at each firn sampling depth, and the gravitational and diffusive fractionation of each of these CFCs, using a constant isotopic source composition. The gravitational/diffusive corrections for a relative mass difference of 1 (c in Section 2.3 and Figure 1) range from -1.0 ‰ to 0.2 ‰ (CFC-11); -1.1 ‰ to 0.2 ‰ (CFC-12); and -0.2 ‰ to 0.2 ‰ (CFC-113). In the upper firn, enrichment due to gravitational fractionation gives positive c; while in the deeper firn, c is negative as diffusive fractionation overwhelms the gravitational fractionation. Once measurements of firn air are corrected for this fractionation, any change in $\delta(^{13}\mathrm{C})$ is indicative of changes in the tropospheric isotopic composition, $\delta_{\mathrm{T}}(^{13}\mathrm{C})$.

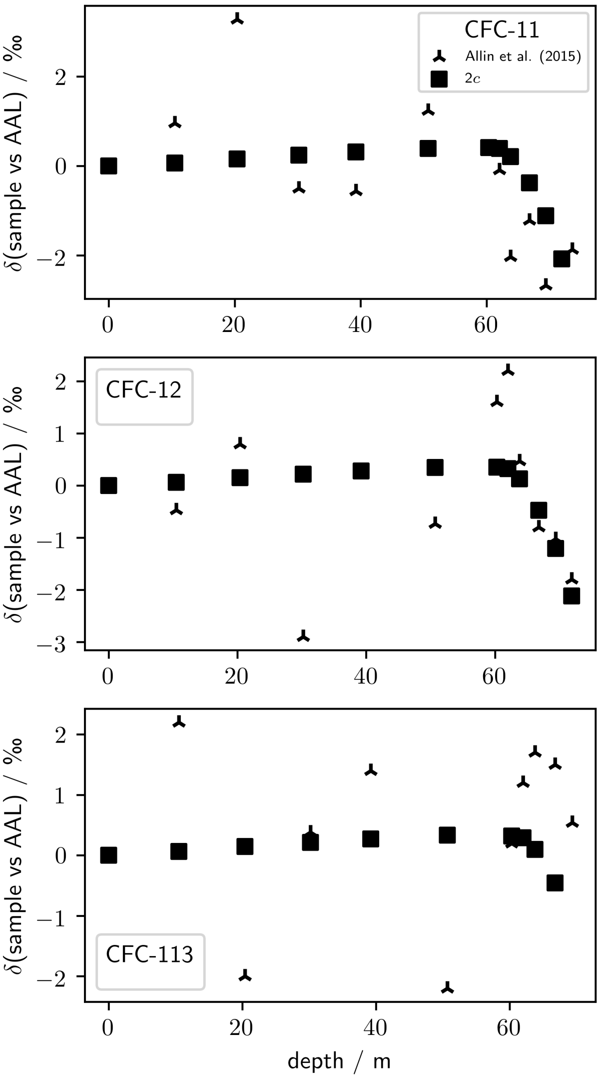

Figure 1. $\delta(^{37}\mathrm{Cl})$ as measured by Allin et al. (2015) against depth in NEEM 2009 firn air samples. Also shown is the correction factor, c, used in this work to convert $R(102/105)$ to $R(102/101)$ (Equation 2), multiplied by 2. c gives the fractionation for a relative mass difference of 1 and, assuming no change in $\delta(^{37}\mathrm{Cl})$ – which has a relative mass difference of 2 – $2c$ should be consistent with $\delta(^{37}\mathrm{Cl})$.

2.5 Modelling the tropospheric isotopic composition

We modelled $\delta_\mathrm{T}(^{13}\mathrm{C}$, CFC-11), $\delta_\mathrm{T}(^{13}\mathrm{C}$, CFC-12), and $\delta_\mathrm{T}(^{13}\mathrm{C}$, CFC-113) from 1937 to 2050 using a two box model. The model was used by Röckmann et al. (2003a), Bernard et al. (2006), and Prokopiou et al. (2017) for N_2O isotopologue budget calculations, and was adopted by Allin et al. (2015) to model the evolution of chlorine isotopes in CFC-11, -12, and -113. This model is detailed in Allin et al. (2015) so we only present a brief overview. The model boxes represent the troposphere and stratosphere. CFCs are emitted to the tropospheric box with a constant isotopic composition, $\delta_\mathrm{E}(^{13}\mathrm{C})$. Some portion of the tropospheric CFC load is transported to the stratospheric box, where CFCs are destroyed and fractionated according to ϵ_{app}. As these fractionated CFCs are exchanged with the troposphere, they alter the tropospheric isotopic composition — our desired variable. Troposphere/stratosphere exchange is parametrised according to Holton (1990) and Appenzeller et al. (1996). The dominant uncertainties in the model are the uncertainty in ϵ_{app} and the magnitude of the bulk air troposphere/stratosphere exchange flux, both of which are accounted for in the model uncertainty envelope. We offset modelled $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ such that it is 0 ‰ in 2005. This treatment ensures that the modelled $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ is relative to the tropospheric composition in 2005, consistent with our data, which are referenced to a 2005 air standard (AAL). We also shift the uncertainty envelope such that it is 0 ‰ in 2005 and increases backwards and forwards in time, reflecting the fact that in 2005 $\delta_{\mathrm{T}}(^{13}\mathrm{C}) = 0$ ‰ by definition. Our only change to the modelling of Allin et al. (2015) is to the value of ϵ_{app} such that it reflects ^{13}C rather than ^{37}Cl fractionation.

3 Results

3.1 Measurements of $\delta(^{13}\mathrm{C})$ in firn air

Measurements of firn air from NEEM 2008/09, plotted against mean age of air, are shown in Figure 2. In the absence of a calibration of our AAL standard against the international standard VPDB, we present $\delta(^{13}\mathrm{C}$, CFC-11) and $\delta(^{13}\mathrm{C}$, CFC-113) relative to our 2005 background air reference gas (AAL). For CFC-12, there were measurements of the same samples on the VPDB scale (Zuiderweg et al., 2013), allowing us to re-scale our measurements. Taking the mean of the NEEM 2009 samples from 50.7 m to 10.5 m gave $\delta(^{13}\mathrm{C}$, sample vs VPDB) $= (-42.4 \pm 1.4)$ ‰ and $\delta(^{13}\mathrm{C}$, sample vs AAL) $= (0.6 \pm 1.9)$ ‰, resulting in

$$\begin{aligned} \delta(^{13}\mathrm{C}, \mathrm{AAL\ vs\ VPDB}) &= \\ \frac{\delta(^{13}\mathrm{C}, \mathrm{sample\ vs\ AAL}) - \delta(^{13}\mathrm{C}, \mathrm{sample\ vs\ VPDB})}{1 + \delta(^{13}\mathrm{C}, \mathrm{sample\ vs\ AAL})} &= \\ (43.0 \pm 2.3)\ ‰&, \end{aligned} \quad (3)$$

which we used to re-scale our $\delta(^{13}\mathrm{C}$, CFC-12, sample vs AAL) measurements to VPDB. A smooth $\delta(^{13}\mathrm{C})$ trend and uncertainty envelope was calculated using the non-parametric LOESS (locally weighted scatter plot smoothing) technique. Uncertainty in the trend derives from measurement uncertainty and the width of the age distribution at each depth. To account for the age uncertainty, we sub-sampled the relevant probability-weighted age distribution 200 times for each measurement and calculated the LOESS using the resulting measurement pairs. All further details are supplied in the Supplementary Information. The mean standard error on the LOESS was 1.0 ‰ (CFC-11), 1.3 ‰ (CFC-12), and 1.6 ‰ (CFC-113).

We calculated trends in $\delta(^{13}\mathrm{C})$ using the LOESS. For each CFC we saw an increase in $\delta(^{13}\mathrm{C})$ from the oldest to the youngest air: $\delta(^{13}\mathrm{C}$, CFC-11) increased by (2.9 ± 1.6) ‰ between 1952 and 2009; $\delta(^{13}\mathrm{C}$, CFC-12) increased by (5.3 ± 2.2) ‰ between 1954 and 2009; and $\delta(^{13}\mathrm{C}$, CFC-113) increased by (9.3 ± 2.7) ‰ between 1973 and 2009 (standard error and mean age). The observed trends had large relative uncertainty and were similar in magnitude to our *m/z*105 to *m/z*101 correction.

For CFC-12, there was general agreement between our measured firn profile and the measurements of Zuiderweg et al. (2013) after around 1990. However, in the oldest two samples measured by Zuiderweg et al. (2013) – corresponding to mean ages of 1965 and 1977 – there was a significant difference between our measurements of the NEEM 2009 profile and those presented by Zuiderweg et al. (2013). For the 1965 sample, the measurements of Zuiderweg et al. (2013) were around 40 ‰ outside of our 95 % confidence intervals, an order of magnitude larger than our *m/z*105 to *m/z*101 correction.

3.2 Calculating ϵ_{app} from stratospheric measurements

Our stratospheric measurements are presented as Rayleigh plots in Figure 3, where f is the fractional release factor quantifying the degree of stratospheric destruction (Leedham Elvidge et al., 2018). Destruction of CFC-12 and -113 (corresponding to an increase in fractional release factor and decreasing $\ln(1-f)$) was concurrent with an increase in $\delta(^{13}\text{C})$ for the remaining stratospheric pool (Figure 3). The gradient of the linear regression of $\ln(1+\delta(^{13}\text{C}))$ with ~~f~~ $\ln(1-f))$ gives ϵ_{app}, which was negative for CFC-12 and -113 in both latitude regions. CFC-11 is omitted from Figure 3 because we do not take ϵ_{app}(CFC-11) forward for our modelling or analysis. We present stratospheric CFC-11 data and justify their omission from our analysis in Appendix D.

From our stratospheric measurements, we derived ϵ_{app}(CFC-12, high-lat) $= (-20.2 \pm 4.4)$ ‰ ($p < 0.01$), ϵ_{app}(CFC-12, mid-lat) $= (-30.3 \pm 10.7)$ ‰ ($p = 0.07$), ϵ_{app}(CFC-113, high-lat) $= (-9.4 \pm 4.4)$ ‰ ($p = 0.04$), and ϵ_{app}(CFC-113, mid-lat) $= (-34.4 \pm 9.8)$ ‰ (~~Table 2~~$p = 0.04$) ~~.~~ — Table 2. Of these, ϵ_{app}(CFC-12, mid-lat) is significant at 90 % confidence, with the others significant at 95 %.

We derived ϵ_{app}(CFC-11) by scaling our measured ϵ_{app}(CFC-12) based on previous laboratory measurements of photolytic carbon isotope fractionation, ϵ_{p} (Zuiderweg et al., 2012). ϵ_{app} is less than ϵ_{p} because atmospheric mixing dilutes the isotopic effect of photolytic fractionation (Kaiser et al., 2006). Atmospheric mixing affects CFC-11 and -12 similarly so we expect

$$\epsilon_{\text{app}}(\text{CFC-11}) \approx \epsilon_{\text{app}}(\text{CFC-12}) \frac{\epsilon_{\text{p}}(\text{CFC-11})}{\epsilon_{\text{p}}(\text{CFC-12})}. \tag{4}$$

Taking the mean of ϵ_{p} measured at stratospherically relevant temperatures (203 K and 233 K) gives $\epsilon_{\text{p}}(^{13}\text{C, CFC-11}) = (-23.4 \pm 0.7)$ ‰ and $\epsilon_{\text{p}}(^{13}\text{C, CFC-12}) = (-60.8 \pm 2.2)$ ‰, such that $\frac{\epsilon_{\text{p}}(\text{CFC-11})}{\epsilon_{\text{p}}(\text{CFC-12})} = 0.39 \pm 0.02$. Scaling our measured ϵ_{app}(CFC-12) by this factor gives $\epsilon_{\text{app}}(^{13}\text{C, CFC-11, high-lat}) = (-7.8 \pm 1.7)$ ‰ and $\epsilon_{\text{app}}(^{13}\text{C, CFC-11, mid-lat}) = (-11.7 \pm 4.2)$ ‰. These are the best estimates of $\epsilon_{\text{app}}(^{13}\text{C, CFC-11})$ possible using our measurements. For each CFC, ϵ_{app} was more negative at mid-latitudes~~, which is qualitatively consistent with previous measurements of $\epsilon_{\text{app}}(^{37}\text{Cl})$ for these chemicals (Allin et al., 2015; Laube et al., 2010a). For each CFC, high-latitude~~ . High-latitude ϵ_{app} were derived from more data than the mid-latitude ϵ_{app}. Of the three CFCs, ϵ_{app}(CFC-11) was least negative at both latitudes, while ϵ_{app}(CFC-12) was most negative at high-latitudes and ϵ_{app}(CFC-113) was most negative at mid-latitudes. We took ϵ_{app}(high-lat) forward for our modelling because these were derived from more data and we have more confidence in them.

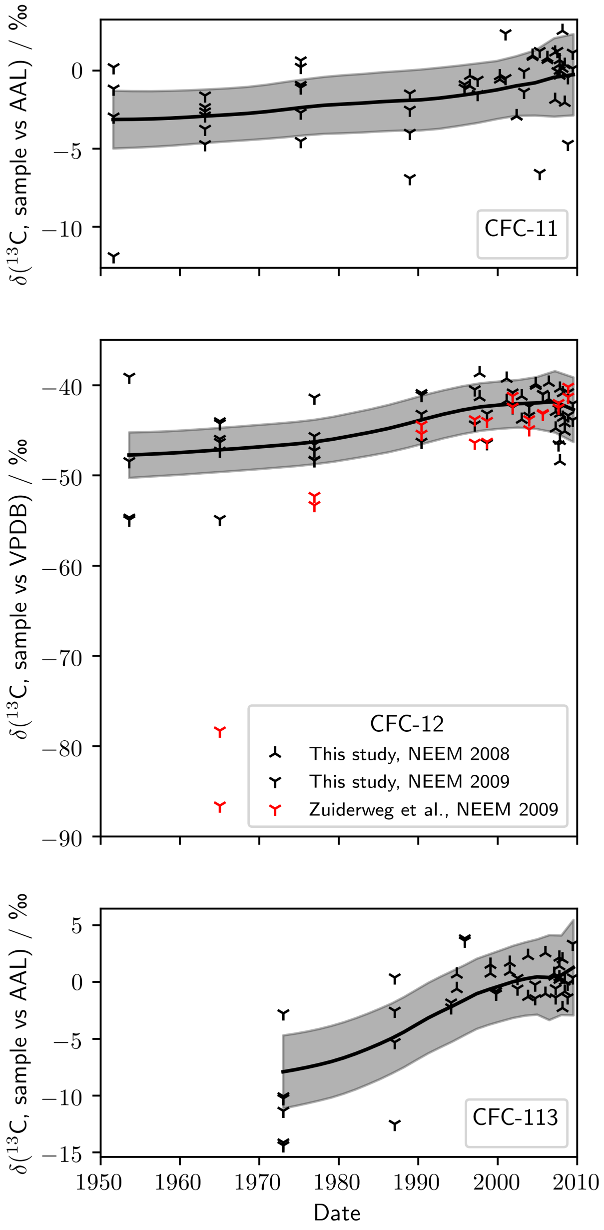

Figure 2. Measured $\delta(^{13}\text{C}$, CFC-11) [top], $\delta(^{13}\text{C}$, CFC-12) [middle], and $\delta(^{13}\text{C}$, CFC-113) [bottom] in NEEM 2008 and 2009 firn air. Also shown is $\delta(^{13}\text{C}$, CFC-12) as measured by Zuiderweg et al. (2013) in the same NEEM 2009 firn air samples. The smoothed trend (black line) and 95% confidence bounds (grey shading) were generated using a LOESS regression.

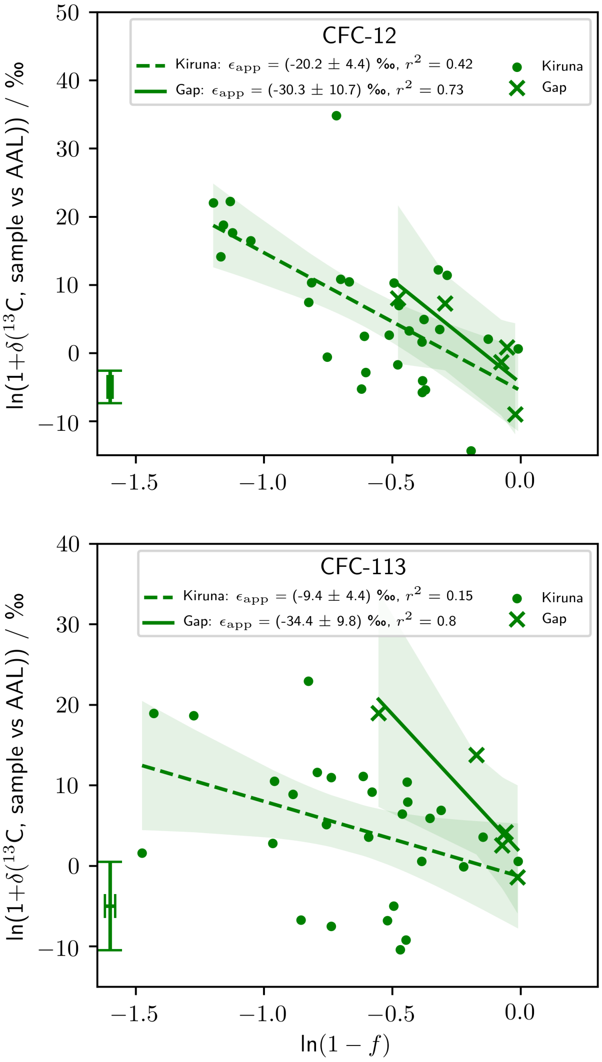

Figure 3. Rayleigh plots of our stratospheric measurements. The linear regression (lines) and 95 % confidence bounds on the regression (shading) are shown for the high-latitude (Kiruna) and mid-latitude (Gap) data sets. The gradients of these regressions, corresponding to ϵ_{app}, are given in the legend with one standard error. The errorbar in the bottom left corner of each graph shows the median repeatability of the reference gas measurements over the measurement days and the median error deriving from the fractional release factor. CFC-11 data are presented in Appendix D.

3.3 Reconstructed tropospheric isotopic composition

We now turn to our measured and modelled $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ (Figure 4). Our firn measurements have been corrected for gravitational and diffusive fractionation. The smoothed trend and 95 % confidence interval were, similar to the firn profiles, based on LOESS regression on these corrected data. The standard error on the $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ reconstruction was equal to that of the firn profile to within 0.1 ‰ for each CFC. Modelled $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ is presented with 95 % confidence intervals. The model was forced with

Table 2. The apparent isotopic fractionation, ϵ_{app}, derived from our stratospheric measurements and the photolytic isotopic fractionation, ϵ_{p}, measured by Zuiderweg et al. (2012). All uncertainties are one standard error.

	ϵ_{app} / ‰		ϵ_{p} / ‰	
CFC	High-latitude	Mid-latitude	203 K	233 K
11	$-7.8 \pm 1.7^{\dagger}$	$-11.7 \pm 4.2^{\dagger}$	-23.8 ± 0.9	-23.0 ± 1.1
12	-20.2 ± 4.4	-30.3 ± 10.7	-66.2 ± 3.1	-55.3 ± 3.0
113	-9.4 ± 4.4	-34.4 ± 9.8		

†Calculated using Equation 4. Taking the mean of the 203 K and 233 K measurements gives $\frac{\epsilon_{\text{p(CFC-11)}}}{\epsilon_{\text{p(CFC-12)}}} = 0.39 \pm 0.02$.

our derived ϵ_{app}(high-lat), prescribed CFC emissions, and a constant isotopic composition of emissions. For CFC-12, we also show the polynomial presented by Zuiderweg et al. (2013) representing the tropospheric trend that best captured their firn measurements.

As with the firn profile, we calculated trends in measured $\delta_{\text{T}}(^{13}\text{C})$ using a LOESS. For each CFC, measured $\delta_{\text{T}}(^{13}\text{C})$ increased through time: $\delta_{\text{T}}(^{13}\text{C}$, CFC-11) increased by (2.1 ± 1.6) ‰ between 1952 and 2009; $\delta_{\text{T}}(^{13}\text{C}$, CFC-12) increased by (4.8 ± 2.2) ‰ between 1956 and 2009; and $\delta_{\text{T}}(^{13}\text{C}$, CFC-113) increased by (9.0 ± 2.7) ‰ between 1975 and 2009 (standard error and mean age). These trends are similar to, and slightly smaller than, the trends in the firn because of the gravitational/diffusive correction. The polynomial of Zuiderweg et al. (2013) only agreed with our reconstructed $\delta_{\text{T}}(^{13}\text{C}$, CFC-12) after around 1995. Our measurements are compared to previously published $\delta_{\text{T}}(^{13}\text{C}$, CFC-11), $\delta_{\text{T}}(^{13}\text{C}$, CFC-12), and $\delta_{\text{T}}(^{13}\text{C}$, CFC-113) in Table 3. Our $\delta_{\text{T}}(^{13}\text{C}$, CFC-12) measurements were re-scaled to Zuiderweg et al. (2013) using 50.7 m and shallower samples representative of mean ages of around 2000 to 2009. In this period, our measured $\delta_{\text{T}}(^{13}\text{C}$, CFC-12) is therefore consistent with Zuiderweg et al. (2013) by definition. These measurements were consistent with Bahlmann et al. (2011) (-41.2 ± 0.2) ‰ and with Redeker et al. (2007) (-40.3 ± 2.6) ‰ to within one standard deviation. For each CFC, our $\delta_{\text{T}}(^{13}\text{C}$, sample vs AAL) for this period was consistent with 0 ‰, as expected given our AAL reference was collected in 2005. For CFC-11 and -113, a quantitative comparison of our data to previous measurements (Thompson et al., 2002; Redeker et al., 2007; Bahlmann et al., 2011) was not possible due to our data being on a different scale.

We take the mean of the $\delta_{\text{T}}(^{13}\text{C})$ as predicted using the Appenzeller et al. (1996) and Holton (1990) stratosphere/troposphere exchange parametrisations for a given emissions scenario and ϵ_{app} to be one model scenario. Hence, four model scenarios are shown in Figure 4: one for each CFC using Velders and Daniel (2014) emissions (three scenarios, labelled V&D); plus an additional scenario for CFC-11 that differs from V&D by fixing emissions after 2012 (one scenario, labelled M18). The model uncertainty for a scenario is taken to be the full $\delta_{\text{T}}(^{13}\text{C})$ envelope as predicted using the two stratosphere/troposphere exchange parametrisations. The dominant uncertainty was from ϵ_{app}, as shown by the strong overlap between the uncertainty envelopes of the two stratosphere/troposphere exchange parametrisations. Each model run predicted an increase in $\delta_{\text{T}}(^{13}\text{C})$ through time. This behaviour is qualitatively consistent with our measurements for each CFC. There was quantitative agreement between our measurements and modelling for CFC-11 and CFC-12 for the entire period covered by the measurements. For CFC-113,

Table 3. Comparison of $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ measurements for CFC-11, -12, and -113 from various studies. Only measurements from background, rural, or coastal sites are included as these are most representative of the remote firn measurements presented here. The uncertainties are one standard deviation and the number in brackets gives the number of observations.

	$\delta_{\mathrm{T}}(^{13}\mathrm{C}$, sample vs VPDB) / ‰					$\delta_{\mathrm{T}}(^{13}\mathrm{C}$, sample vs AAL) / ‰
	Thompson et al. (2002)[†]	Redeker et al. (2007)[*]	Bahlmann et al. (2011)[+]	Zuiderweg et al. (2013)[‡]	This study[§]	This study[§]
CFC-11		-26.8 ± 4.4 (9)	-31.5 ± 2.6 (3)			-0.5 ± 1.9 (31)
CFC-12		-40.3 ± 2.6 (9)	-41.2 ± 0.2 (3)	-42.5 ± 1.4 (10)	-42.5 ± 2.2 (31)	0.5 ± 2.3 (31)
CFC-113	-23.3 ± 9.6 (38)	-12.6 ± 6.8 (1)	-25.4 ± 1.1 (3)			0.2 ± 1.4 (31)

[†] Thompson et al. (2002), sampled July 1999 to March 2001 background northern (Alert, Canada (82.5 °N, 62.3 °W)) and southern hemisphere (Baring Head, New Zealand (41.4 °S, 174.9 °E)) air

[*] Redeker et al. (2007), sampled August to November 2004, Crossgar (54.40 °N, 5.76 °W), Hillsborough (54.46 °N, -6.08 °W), and Mace Head (53.20 °N, 9.54 °W)

[+] Bahlmann et al. (2011), marine influenced air, Wadden Sea Station in List/Sylt (55.02 °N, 8.44 °E), August to September 2010

[‡] Zuiderweg et al. (2013), firn air samples representing, depths 50.7 m and shallower, representing 2002 to 2009; NEEM 2009 campaign

[§] This study, firn air samples corrected for gravitational and diffusive fractionation, depths 50.7 m and shallower, representing: 2001 to 2009 (CFC-11), 2002 to 2009 (CFC-12), 2000 to 2009 (CFC-113); NEEM 2008/09 campaigns

the model is consistent with the measurements after around 1980, but predicts too little fractionation to capture the observed $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ depletion measured in the sample with a mean age of 1975.

Our model returned a value for the isotopic composition of emissions, $\delta_{\mathrm{E}}(^{13}\mathrm{C})$, such that modelled $\delta_{\mathrm{T}}(^{13}\mathrm{C}) = 0$ ‰ in 2005 (Table 4). Hence, more negative ϵ_{app}, which drive greater fractionation up to 2005, produce more negative $\delta_{\mathrm{E}}(^{13}\mathrm{C})$. We take $\delta_{\mathrm{E}}(^{13}\mathrm{C})$ as the mean of the predictions using the Appenzeller et al. (1996) and Holton (1990) stratosphere/troposphere exchange parameterisations. For each CFC, $\delta_{\mathrm{E}}(^{13}\mathrm{C})$ was negative and significantly different from 0 ‰, relatively depleted in $^{13}\mathrm{C}$ compared to 2005 tropospheric air. For CFC-12, we can perform a quantitative comparison with previously reported $\delta(^{13}\mathrm{C}$, sample vs VPDB) values of CFC-12 gas that was purchased from manufacturers~~. Ertl (1997), as reported in Archbold et al. (2012), measured the $\delta(^{13}\mathrm{C})$ of gases sourced from several manufacturers, reporting a range of -45 ‰ to -33 ‰. Archbold et al. (2005) reported the $\delta(^{13}\mathrm{C})$ of three CFC-12 standards as~~, which range from (-33) ‰ (Ertl, 1997) to (-46.8 ± 0.2) ‰ (Archbold et al., 2012) (Table 4). We modelled $\delta_{\mathrm{E}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}12}) = (-47.1 \pm 1.3)$ ‰ (two standard errors), within the range of previously reported $\delta_{\mathrm{E}}(^{13}\mathrm{C}$, CFC-12).

4 Discussion

Our measurements provide the first observational constraints on $\epsilon_{\mathrm{app}}(^{13}\mathrm{C})$ for CFC-12 and -113. Our derived $\epsilon_{\mathrm{app}}(^{13}\mathrm{C}$, CFC-12) are consistent with previously reported $\epsilon_{\mathrm{p}}(^{13}\mathrm{C}$, CFC-12) (Zuiderweg et al., 2012), being a factor of 2 to 3 lower than $\epsilon_{\mathrm{p}}(^{13}\mathrm{C}$, CFC-12), as expected given the effect of mixing and diffusion in the atmosphere (Kaiser et al., 2006). The meridional differences observed in ϵ_{app}(CFC-12) are qualitatively consistent with previously reported isotopic fractionation patterns of other elements in long-lived trace gases, such as $\delta(^{37}\mathrm{Cl}$, CFC-12) (Allin et al., 2015; Laube et al., 2010b) and $\mathrm{N_2O}$ isotopologues (Kaiser et al., 2006). For CFC-113, we have only measured the $\delta(^{13}\mathrm{C})$ of the $\mathrm{CCl_2F}$ fragment and our results do not provide information on the $\mathrm{CClF_2}$ fragment or for the molecule as a whole. Our derived ϵ_{app}(CFC-113) are internally consistent with our firn air measurements, with both data sets being measured on the same fragment. Allin et al. (2015) do not observe meridional differences for $\epsilon_{\mathrm{app}}(^{37}\mathrm{Cl}$, CFC-113) – as we observe for $\epsilon_{\mathrm{app}}(^{13}\mathrm{C}$, CFC-113) – but speculate that differences could be masked by their uncertainties. Given our best understanding of compact tracer-tracer correlations in the lower stratosphere we do not expect

Table 4. $\delta_{\mathrm{E}}(^{13}\mathrm{C})$ as predicted by our modelling and as reported in previous studies for CFC-11, -12, and -113. With the exception of Ertl (1997), all uncertainties are two standard errors.

	$\delta_{\mathrm{E}}(^{13}\mathrm{C}$, sample vs AAL) / ‰	$\delta_{\mathrm{E}}(^{13}\mathrm{C}$, sample vs VPDB) / ‰					
	This study	This study	Ertl (1997)	Thompson et al. (2002)	Archbold et al. (2005)	Horst et al. (2015)	Phillips et al. (2019)
CFC-11	-2.7 ± 0.8		-35 to -25		-26.2 ± 0.6	-33.34 ± 0.07 -28.93 ± 0.04	-33.36 ± 0.04
CFC-12	-4.3 ± 1.3	-47.1 ± 1.3	-45 to -33		-46.8 ± 0.2		-45.27 ± 0.04
CFC-113	-1.7 ± 1.1			-31.3 ± 0.5	-26.5 ± 0.8	-28.07 ± 0.05	-29.93 ± 0.06

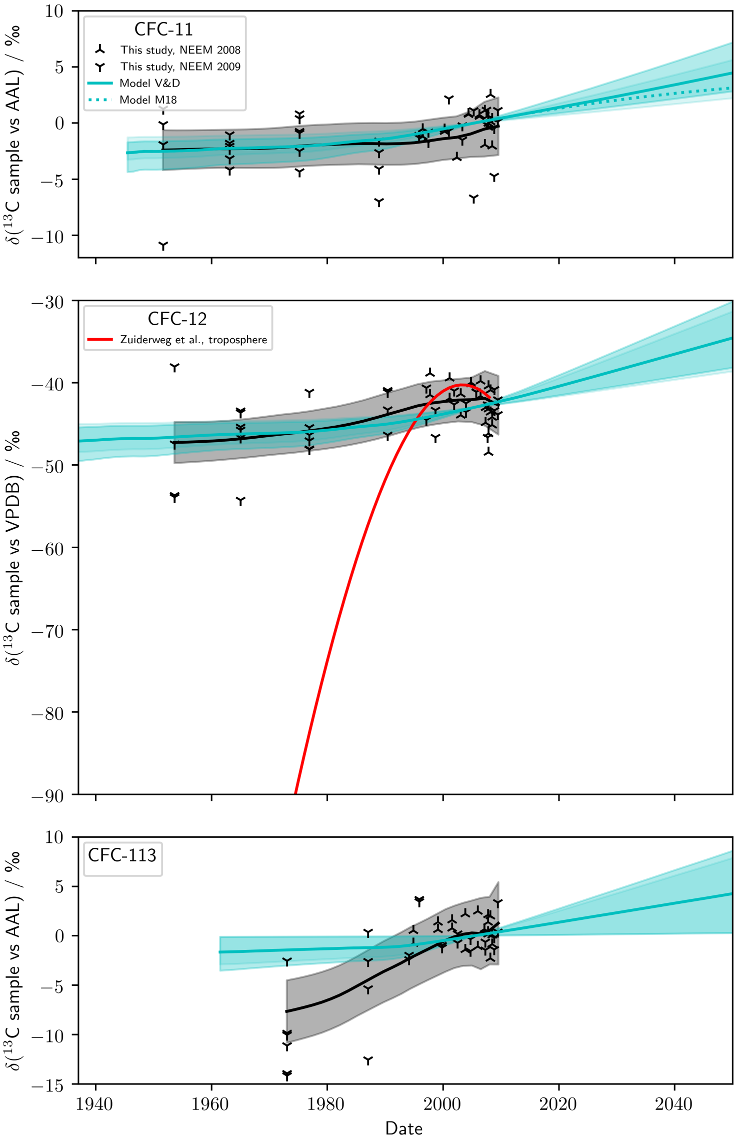

Figure 4. Measured and modelled $\delta_\text{T}(^{13}\text{C}$, CFC-11), $\delta_\text{T}(^{13}\text{C}$, CFC-12), and $\delta_\text{T}(^{13}\text{C}$, CFC-113). The smoothed trend and 95 % confidence intervals for measured $\delta_\text{T}(^{13}\text{C})$ are shown by the solid black line and grey shading, respectively. The solid blue line shows the mean modelled $\delta_\text{T}(^{13}\text{C})$ for the Velders and Daniel (2014) scenario (V&D) and the two stratosphere/troposphere exchange parameterisations (Holton, 1990; Appenzeller et al., 1996). ϵ_app(high-lat) was used for each CFC. Blue shading shows the 95 % uncertainty envelope for the Holton (1990) and Appenzeller et al. (1996) parameterisations. For CFC-11 only, the dotted blue line shows the mean modelled $\delta_\text{T}(^{13}\text{C})$ for the M18 scenario, with the uncertainty envelope omitted for clarity. For CFC-12, the red line shows $\delta_\text{T}(^{13}\text{C})$ as predicted by Zuiderweg et al. (2013) [amending a typo in the coefficients presented by Zuiderweg et al. (2013), $\delta_\text{T}(^{13}\text{C}, \text{CFC-12}) = -265.4280 + 4.8315x + (7.8555\times10^{-5})x^2 - (3.3070\times10^{-4})x^3$, where $x = t - 1933.5$ and t gives the date].

significant meridional differences in ϵ_app for the range of observed fractional releases ($\ln(1-f) > -0.6$)) (Volk et al., 1997) . The lack of a latitude-dependence for lower-stratospheric Rayleigh fractionation is supported by stratospheric observations of other long-lived trace gases, in particular carbon and hydrogen isotope fractionation in CH_4 (Röckmann et al., 2011) and nitrogen and oxygen isotope fractionation in N_2O (Kaiser et al., 2006), which are constrained by a much wider range of observations, with lower measurement uncertainties, than currently available for CFCs. CH_4 and N_2O have global atmospheric mean lifetimes of 10 years and 123 years, respectively, which covers the range of lifetimes of CFC-11 (52 years), CFC-113 (93 years) and CFC-12 (102 years). The three CFCs also have the same chemical sinks as N_2O – photolysis and oxidation by $O(^1D)$, in similar proportions as N_2O. We therefore do not expect these CFCs to behave any differently than CH_4 and N_2O. The observed meridional differences could be statistical artefacts deriving from our poorly constrained ϵ_{app}(mid-lat).

We derived ϵ_{app}(CFC-11) by scaling our measured ϵ_{app}(CFC-12) to previously reported $\frac{\epsilon_{\text{p}}(\text{CFC-11})}{\epsilon_{\text{p}}(\text{CFC-12})}$ (Zuiderweg et al., 2012). While our presented ϵ_{app}(CFC-11) are our best estimates, they are dependent on our ϵ_{app}(CFC-12) estimates, ϵ_{p}(CFC-11), and ϵ_{p}(CFC-12). Our re-scaled ϵ_{app}(CFC-11) also omit the effect of fractionation by $O(^1D)$, though given the around 2 % contribution of $O(^1D)$ to stratospheric CFC-11 loss (Burkholder et al., 2013), we expect this omission to have little effect. Appendix D gives technical details on why we do not use our CFC-11 measurements in our analysis and modelling. For all three CFCs, our ϵ_{app}(high-lat) were derived from more data than our ϵ_{app}(mid-lat) so we have more confidence in our ϵ_{app}(high-lat). For each CFC, $\epsilon_{\text{app}}(^{13}\text{C})$ is larger than previously reported $\epsilon_{\text{app}}(^{37}\text{Cl})$ (Allin et al., 2015), causing more negative fractionation during stratospheric destruction.

Our tropospheric reconstructions and modelling (Figure 4) allow us to investigate changes in $\delta_{\text{E}}(^{13}\text{C})$. Our model was run using a constant $\delta_{\text{E}}(^{13}\text{C})$ and agreement between our reconstructed and modelled $\delta_{\text{T}}(^{13}\text{C})$ is therefore evidence that no large change in $\delta_{\text{E}}(^{13}\text{C})$ has occurred over the time period spanned by the measurements. For CFC-12, there was agreement between our reconstructed $\delta_{\text{T}}(^{13}\text{C})$ and comparable previous measurements (Table 3). This agreement reflects the calibration of Zuiderweg et al. (2013), to which our measurements were re-scaled, but is still a check on the quality of our reconstruction. Our modelled and measured $\delta_{\text{T}}(^{13}\text{C}$, CFC-12) were in agreement for the entire period covered by the measurements (Figure 4). Our results are therefore consistent with a constant $\delta_{\text{E}}(^{13}\text{C}$, CFC-12). Furthermore, $\delta_{\text{E}}(^{13}\text{C}$, CFC-12) as predicted by our model was within the range of previously reported isotopic source compositions for CFC-12 (Table 4). While some variation in $\delta_{\text{E}}(^{13}\text{C}$, CFC-12) is possible within our uncertainties, these confluent lines of evidence suggest that no dramatic change in $\delta_{\text{E}}(^{13}\text{C}$, CFC-12), as proposed by Zuiderweg et al. (2013), has occurred since around 1956. The cause of this discrepancy was likely an analytical artefact in Zuiderweg et al. (2013), discussed further in Appendix C. Our measurements and modelling of $\delta_{\text{T}}(^{13}\text{C}$, CFC-11) are in agreement for the entire period covered by measurements and are therefore consistent with a constant $\delta_{\text{E}}(^{13}\text{C}$, CFC-11) since at least 1952. For CFC-113, our modelling did not agree with our measurements earlier than around 1980. This discrepancy may be indicative of a change in $\delta_{\text{E}}(^{13}\text{C}$, CFC-113) though, given our measurements do not provide a complete picture of the fractionation in CFC-113 and given this discrepancy is caused by one measurement depth, these results do not confirm a change in $\delta_{\text{E}}(^{13}\text{C}$, CFC-113). ~~Further work defining the tropospheric history of $\delta_{\text{T}}(^{13}$~~Multiple industrial processes use CFC-113 as a feedstock, or produce CFC-113 as an intermediate (Adcock et al., 2018), so a change in $\delta_{\text{E}}(^{13}\text{C}$, CFC-113) is ~~justified.~~ plausible. The discrepancy between the modelled and reconstructed confidence bounds is at most -1.9 ‰. The range of published δ_{E}(CFC-113) is (-31.3 ± 0.5) ‰ to (-26.5 ± 0.8) ‰ (Table 4), around 5 ‰. The discrepancy seen for measured and modelled δ_{T}(CFC-113) can be accounted for by the range of published δ_{E}(CFC-113).

Our modelling predicts increasing $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ for CFC-11, -12, and -113, as lighter isotopologues are preferentially destroyed in the stratosphere and the remaining stratospheric CFC pool, enriched in ^{13}C, is mixed with tropospheric air. An acceleration in the rate of increase of $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ was modelled for each CFC, starting in around 1990. This acceleration is caused by reduced emissions, with relatively depleted $\delta_{\mathrm{E}}(^{13}\mathrm{C})$, as emissions mitigate stratospheric ^{13}C enrichment. Therefore, the new CFC-11 emissions identified by Montzka et al. (2018) have the potential to decrease the rate of increase in $\delta_{\mathrm{T}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}11})$. We estimated the potential effect of these new emissions by comparing the V&D and M18 scenarios. As expected, in M18, $\delta_{\mathrm{T}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}11})$ was lower than V&D after 2012. Using ϵ_{app}(CFC-11, high-lat), the difference was 1.4 ‰ in 2050 — well within our uncertainty envelope. Improved modelling precision and more precise knowledge of $\delta_{\mathrm{E}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}11})$ would be needed if $\delta_{\mathrm{T}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}11})$ measurements were to be used as a tool for monitoring global CFC-11 emissions, though the isotopic signal from emissions may be more pronounced on regional scales.

5 Conclusions

We ~~have~~ presented the first measurements of the $\delta(^{13}\mathrm{C})$ of CFC-11, -12, and -113 for stratospheric air samples, and derived values for the apparent isotopic fractionation, ϵ_{app}, at high- and mid-latitudes of: $\epsilon_{\mathrm{app}}(\mathrm{CFC\text{-}11, high\text{-}lat}) = (-7.8 \pm 1.7)$ ‰; $\epsilon_{\mathrm{app}}(\mathrm{CFC\text{-}11, mid\text{-}lat}) = (-11.7 \pm 4.2)$ ‰; $\epsilon_{\mathrm{app}}(\mathrm{CFC\text{-}12, high\text{-}lat}) = (-20.2 \pm 4.4)$ ‰; $\epsilon_{\mathrm{app}}(\mathrm{CFC\text{-}12, mid\text{-}lat}) = (-30.3 \pm 10.7)$ ‰; $\epsilon_{\mathrm{app}}(\mathrm{CFC\text{-}113, high\text{-}lat}) = (-9.4 \pm 4.4)$ ‰; and $\epsilon_{\mathrm{app}}(\mathrm{CFC\text{-}113, mid\text{-}lat}) = (-34.4 \pm 9.8)$ ‰. While for CFC-12 and -113 these estimates are independent, the ϵ_{app}(CFC-11) estimates are not, having been derived by scaling our ϵ_{app}(CFC-12) measurements. Further measurements of $\delta(^{13}\mathrm{C}, \mathrm{CFC\text{-}11})$ in the stratosphere are required to estimate ϵ_{app}(CFC-11) independent of CFC-12. For CFC-113, these ϵ_{app} are only applicable to the $\mathrm{CCl_2F}$ fragment of the molecule. When used ~~to model~~ model tropospheric the tropospheric isotopic composition, $\delta_{\mathrm{T}}(^{13}\mathrm{C})$, our derived ϵ_{app}(high-lat) drive strong fractionation from the mid 1900s through to 2050. ~~For CFC-12, modelled~~

We also reconstructed $\delta_{\mathrm{T}}(^{13}$C~~, CFC-12) was consistent with~~) from firn air measurements. Comparing these with the model shows that the histories of $\delta_{\mathrm{T}}(^{13}$C, ~~CFC-12) reconstructed from measurements of firn air when using a constant isotopic composition of emissions, $\delta_{\mathrm{E}}(^{13}$~~CFC-11) and $\delta_{\mathrm{T}}(^{13}$C, CFC-12) ~~, for the entire period covered by measurements. Our results are therefore~~ are consistent with a constant isotopic source composition, $\delta_{\mathrm{E}}(^{13}$C~~, CFC-12)since around 1956 and are inconsistent with the extreme depletion in~~), and with stratospheric processing as the sole sink of these chemicals. Our results contradict previous reports of extreme depletion for $\delta_{\mathrm{T}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}12})$ and ~~change in~~ $\delta_{\mathrm{E}}(^{13}$~~C,~~CFC-12)~~proposed by Zuiderweg et al. (2013). Likewise, for CFC-11, our results are consistent with a constant $\delta_{\mathrm{E}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}11})$ since 1952. For~~. Such extreme depletions could have challenged the history of CFC-12 industrial processes and feedstocks; the current understanding of their atmospheric cycling; and/or raised questions about their inertness in the biogeosphere. The discrepancy between reconstructed and modelled $\delta_{\mathrm{T}}(^{13}$C, CFC-113~~, our results are not consistent with a constant~~) suggests a change in $\delta_{\mathrm{E}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}113})$~~since 1975. While potentially indicative of a change in~~. Changes in industrial processes that produce CFC-113 – as an end product or byproduct – could explain such a discrepancy, and the range of reported $\delta_{\mathrm{E}}(^{13}\mathrm{C}, \mathrm{CFC\text{-}113})$ ~~, this discrepancy is based on~~ would be sufficient to cause such a discrepancy. We caution, however, that this discrepancy derives from only one sample and ~~further~~

~~firn or tropospheric measurements are required to confirm this. Our modelling predicts a continuing~~ takes into account the fractionation of only on CFC-113 fragment. Further work would be needed to definitively assign a change in $\delta_{\mathrm{E}}(^{13}\mathrm{C}$, CFC-113). The modelled increase in $\delta_{\mathrm{T}}(^{13}\mathrm{C})$ ~~up to~~ from 2009 through 2050 ~~for each CFC. This increase~~ is sensitive to new emissions~~, though~~. We compared future $\delta_{\mathrm{T}}(^{13}\mathrm{C}$, CFC-11) trends in scenarios with/without new CFC-11 emissions. The difference between scenarios was within uncertainty bounds, showing better modelling precision and precise quantification of the isotopic composition of emissions would be needed to detect the isotopic signature of recently reported new CFC-11 emissions in background air.

Code and data availability. All data and plot scripts used in this study are given as supplementary information.

Appendix A: Dilution series and quality control

We measured two dilution series to account for any errors or biases that may be introduced by the low concentrations of CFCs in some samples (Figure A1). The first dilution series was produced using method A, and is therefore applicable to measurements of the Kiruna and Gap samples. The second dilution series was produced using method B, and is therefore applicable to measurements of the NEEM 2008/09 firn samples. Each dilution series included repeat measurements of a reference gas (unpolluted tropospheric air collected in 2009; SX-0706077) at five concentrations ranging from: (2.9 ± 0.02) pmol/mol to (245.1 ± 3.6) pmol/mol (CFC-11); (6.6 ± 0.1) pmol/mol to (540.0 ± 3.4) pmol/mol (CFC-12); and (0.9 ± 0.01) pmol/mol to (78.1 ± 0.2) pmol/mol (CFC-113). Measurements of this dilution series were previously reported by Allin et al. (2015, SI). The m/z102 peak area was used as an indicator of the level of dilution in the sample. Noting that the true $\delta(^{13}\mathrm{C}$, sample vs SX-0706077) value of each measurement is 0 ‰, we assessed the performance of our method by plotting peak area against measured $\delta(^{13}\mathrm{C}$, sample vs SX-0706077) for each sample.

For method A, the measured $\delta(^{13}\mathrm{C})$ was negative for the samples with the lowest m/z102 peak area. We have therefore taken the lowest dilution series m/z102 peak area where we do not see this behaviour to be the lower m/z102 peak area limit for method A, above which we have reliable data. This limit was 39000 (CFC-11), 57000 (CFC-12), and 44000 (CFC-113), and is shown in Figure A1 by the red dotted line. Kiruna and Gap measurements with m/z102 peak areas below this threshold were excluded from our results but are provided in the Supplementary Information. For method B, the measured $\delta(^{13}\mathrm{C})$ showed no bias for lower peak areas and we therefore retained all data. We have excluded the 69.4 m and 71.9 m NEEM 2009 samples for CFC-113 because, for the corresponding mean ages, there was too little CFC-113 in the atmosphere (Adcock et al., 2018) to reliably determine $\delta(^{13}\mathrm{C})$.

Appendix B: Comparison of GC-MS with GC-IRMS measurements

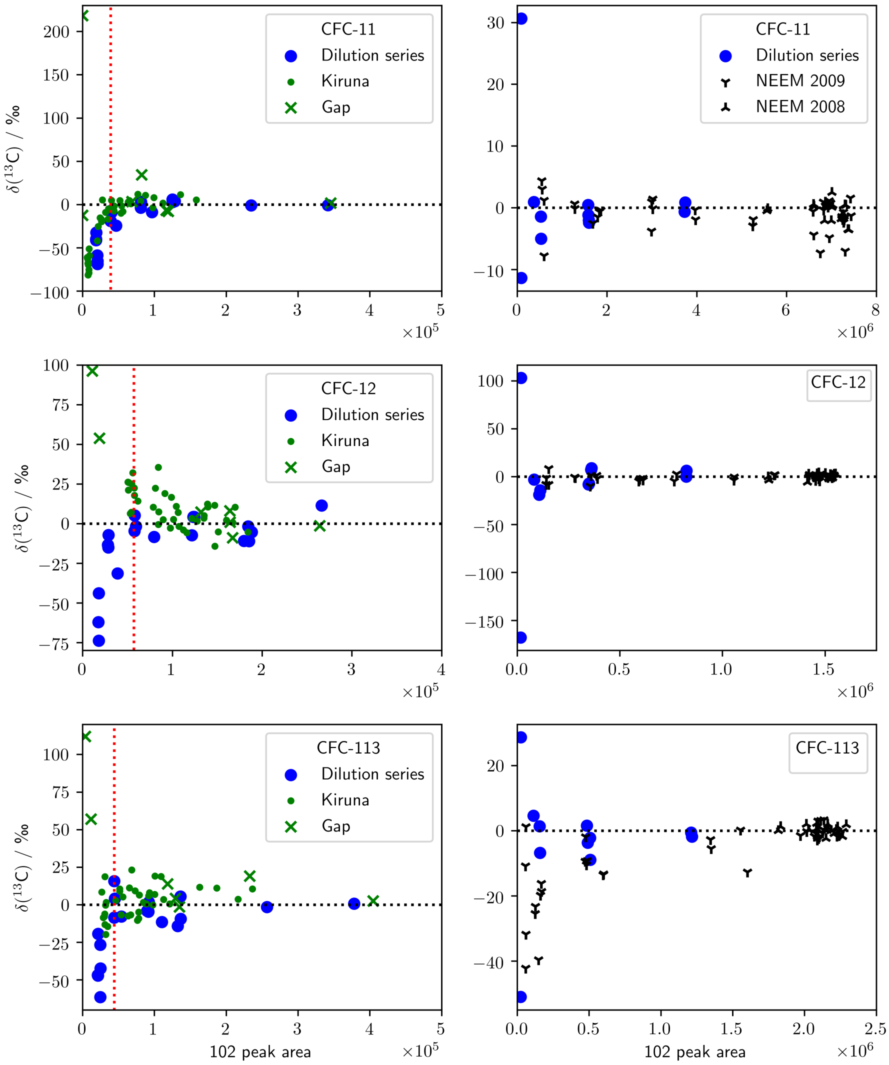

Figure A1. Dilution series for the analytical methodologies used in this work. Left: Method A, which was used to measure stratospheric samples. The red dotted line shows the lower limit of m/z102 peak areas that were retained. Right: Method B, which was used to measure firn air. Dilution series measurements are relative to SX-0706077 (2009 air) and stratospheric and firn air measurements are relative to AAL (2005 air).

As a further check on the quality of our method, we have compared measurements made using GC-IRMS (Zuiderweg et al., 2011) of a suite of photolysis samples as presented in Zuiderweg et al. (2012) to our own measurements – using GC-MS – of those samples (Figure B1). These samples were not subject to the CH_3Cl chromatographic interference seen in Zuiderweg et al. (2013) . The samples were diluted by 1000 times before measurement on our system to accommodate the higher sensitivity of our GC-MS method.

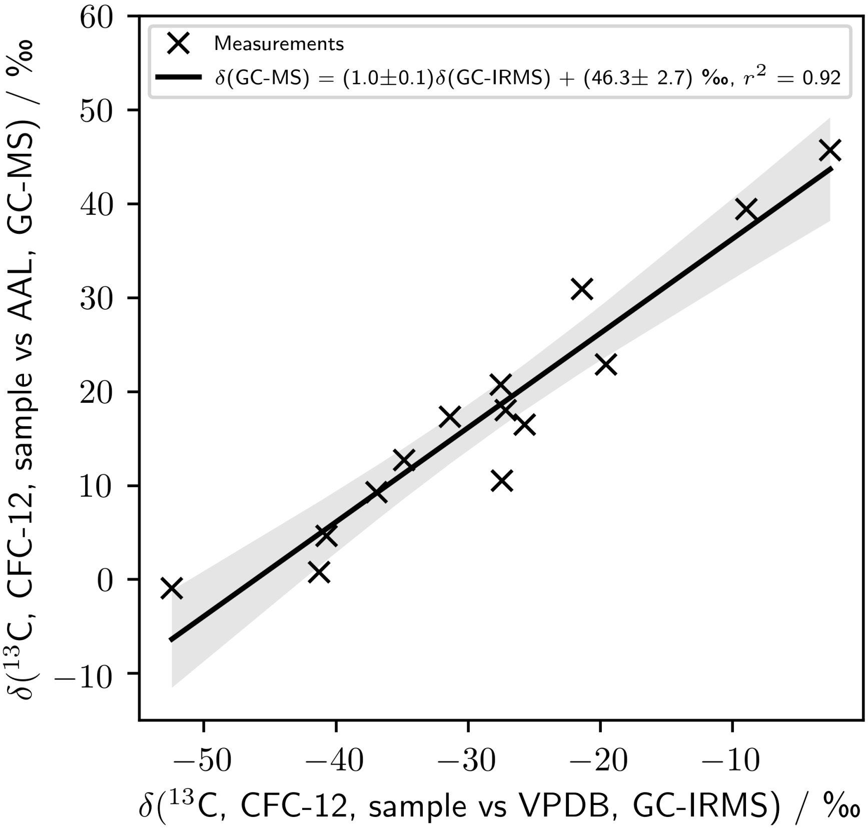

Figure B1. Comparison of measurements presented by Zuiderweg et al. (2012) using GC-IRMS (Zuiderweg et al., 2011) to our own measurements of those same samples.

The agreement between the methods is good (Figure B1). Linear regression gives a high regression coefficient ($r^2 = 0.92$) and a gradient consistent with unity (1.0 ± 0.1). This agreement holds over a range of δ spanning almost 60 ‰. The intercept is (46.3 ± 2.7) ‰. This intercept results in a δ value for CFC-12 in AAL-071170 on the VPDB scale of (-44.2 ± 2.5) ‰ — consistent with the (43.0 ± 2.3) ‰ derived using Equation 3.

Appendix C: Reason for NEEM 2009 discrepancy

We measured $\delta(^{13}$C, CFC-12) in the same NEEM 2009 flask samples as Zuiderweg et al. (2013) and linked our measurements to the VPDB calibration scale used by Zuiderweg et al. (2013). The measurements in these two studies were consistent, except for the samples at 66.8 and 69.4 m, corresponding to mean ages of 1977 and 1965, respectively (Figure 2). For the sample corresponding to a mean age of 1965, the discrepancy between data sets is around 40 ‰, an order of magnitude larger than our 95 % confidence intervals and any corrections made to our measurements. The discrepancy is larger when $\delta_T(^{13}$C, CFC-12)

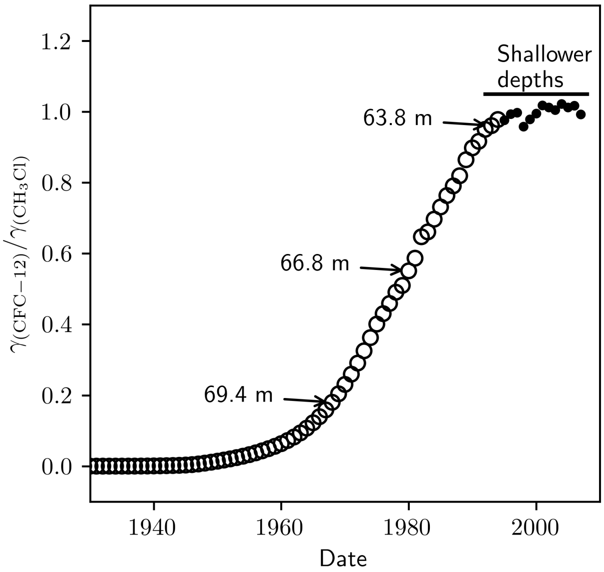

Figure C1. The ratio of the tropospheric mole fraction of CFC-12 to CH_3Cl. Circles were taken from Butler et al. (1999). The dots were calculated using data from NOAA-HATS. The annotations indicate the points on the curve that correspond to different depth samples in the NEEM 2009 firn profile.

is considered, with the tropospheric scenario presented by Zuiderweg et al. (2013) predicting $\delta_\mathrm{T}(^{13}\mathrm{C}) = -123$ ‰ in 1965, whereas our measured $\delta_\mathrm{T}(^{13}\mathrm{C}, \mathrm{CFC\text{-}12}) = (-46.8 \pm 2.4)$ ‰ (2 standard errors). Assuming sample integrity was preserved between studies, at most one data set can be accurate.

The cause of this discrepancy was likely a measurement artefact in Zuiderweg et al. (2013). In the method of Zuiderweg et al. (2013), methyl-chloride elutes before CFC-12~~, such that the tail of the~~. Zuiderweg et al. (2013) model the methyl-chloride ~~peak must be modelled and accounted for in the~~ tail using an exponentially decaying function, and subtract this signal from their CFC-12 peak before integration. Zuiderweg et al. (2013) performed a dilution series to evaluate their method, including their treatment of the methyl-chloride peak. However, in their dilution series the proportion of methyl-chloride to CFC-12 was constant because methyl-chloride and CFC-12 were diluted concurrently. In the NEEM 2009 firn air samples, the proportion of methyl-chloride to CFC-12 increased in the deeper samples (see Figure 2 in Zuiderweg et al. (2013)). This increase reflects the changing ratio of the ~~abundance of~~ CFC-12 mole fraction, $\gamma(\mathrm{CFC\text{-}12})$, to the CH_3Cl mole fraction, $\gamma(\mathrm{CH_3Cl})$, since the early 1900s (Figure C1). The methyl-chloride baseline correction was therefore performed, on the sample at 69.4 m – and, to a lesser extent, on the sample at 66.8 m – on a methyl chloride peak that was larger than that evaluated in the dilution series for a given CFC-12 peak area. Indeed, the trend in $\delta(^{13}\mathrm{C})$ depletion in the NEEM 2009 profile was qualitatively similar to the trend in tropospheric $\gamma(\mathrm{CFC\text{-}12})/\gamma(\mathrm{CH_3Cl})$ over that time period, with lower $\gamma(\mathrm{CFC\text{-}12})/\gamma(\mathrm{CH_3Cl})$ for the depleted $\delta(^{13}\mathrm{C})$ measurements, and relatively constant $\gamma(\mathrm{CFC\text{-}12})/\gamma(\mathrm{CH_3Cl})$ in the period of little change in $\delta(^{13}\mathrm{C})$. The dilution series performed by Zuiderweg et al. (2013) therefore did not adequately assess variations in $\gamma(\mathrm{CFC\text{-}12})/\gamma(\mathrm{CH_3Cl})$.

Appendix D: Stratospheric CFC-11

We presented ϵ_{app}(CFC-11) based on scaling of our measured ϵ_{app}(CFC-12) (Table 2, Equation 4). These best estimate values were used in our analysis and modelling. We took this approach because the ϵ_{app}(CFC-11) derived from our stratospheric measurements were inadequate. Figure 3 shows stratospheric Rayleigh plots for our CFC-11 data, from which we derived ϵ_{app}(CFC-11, high-lat) $= (-3.8 \pm 4.9)$ ‰ and ϵ_{app}(CFC-11, mid-lat) $= (-26.5 \pm 4.0)$ ‰ (one standard error). ϵ_{app}(CFC-11, high-lat) is not significantly different from 0 ‰ and therefore, when used to force our model, gives confidence intervals that, while consistent with our observations, span 0 ‰. ϵ_{app}(CFC-11, high-lat) derived from our stratospheric CFC-11 measurements is consistent with our presented best estimate, ϵ_{app}(CFC-11, high-lat) $= (-7.8 \pm 1.7)$ ‰. We do not reject our ϵ_{app}(CFC-11, high-lat) derived directly from our CFC-11 observations as it is reasonable and derived from relatively many data. We used a different estimate in our analysis simply to achieve the best possible model precision. In contrast, we do not believe our derived ϵ_{app}(CFC-11, mid-lat) $= (-26.5 \pm 4.0)$ ‰ is correct based on consideration of previously reported ϵ_{p} (Zuiderweg et al., 2012, Table 2). Our ϵ_{app}(CFC-11, mid-lat) derived from our stratospheric CFC-11 measurements is greater than previously reported ϵ_{p}(CFC-11), which is inconsistent with our best understanding of atmospheric mixing (Kaiser et al., 2006). Also, our derived $\frac{\epsilon_{\mathrm{app}}(\text{CFC-11, mid-lat})}{\epsilon_{\mathrm{app}}(\text{CFC-12, mid-lat})} = 0.87 \pm 0.33$, which is inconsistent with $\frac{\epsilon_{\mathrm{p}}(\text{CFC-11})}{\epsilon_{\mathrm{p}}(\text{CFC-12})} = 0.39 \pm 0.02$. Our mid-latitude stratospheric CFC-11 regressions were derived from few data ($n = 5$) and are heavily influenced by one data point with ln(1-f) $= -1.49$. We believe, with additional measurements, ϵ_{app}(CFC-11) would likely decrease in magnitude.

Author contributions. MT prepared the manuscript with JCL and JK, with contributions from all authors. SA measured the firn air samples and AR measured the stratospheric samples, under the supervision of JCL, JK, and WTS. PM and EW provided the firn air modelling and JK provided the tropospheric modelling. TR was responsible for the Geophysika aircraft sampling while RM, TR, JK and WTS led the firn sampling activities.

Competing interests. The authors declare no competing interests.

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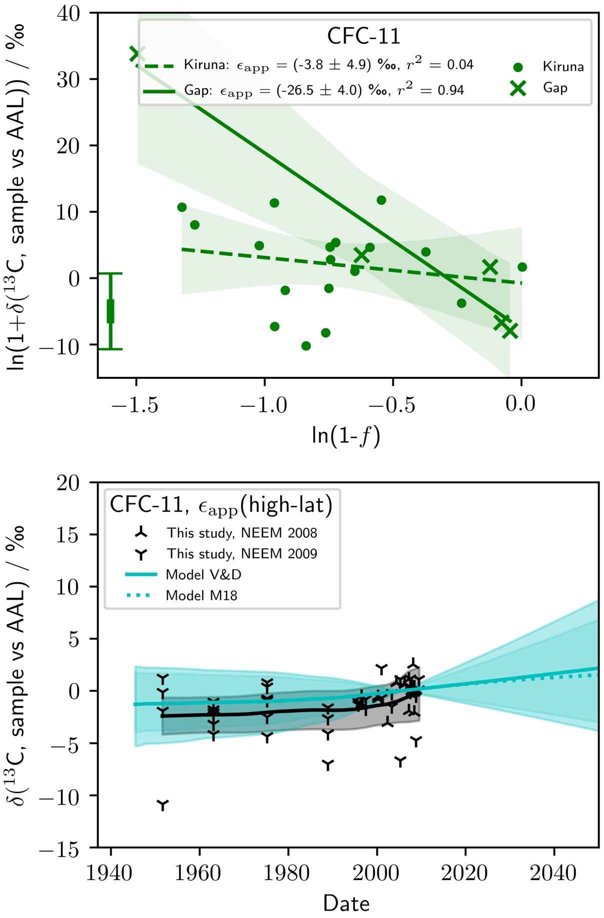

Figure D1. Rayleigh plot showing observations of δ^{13}(C, CFC-11), and derived ϵ_{app}(CFC-11, high-lat) and ϵ_{app}(CFC-11, mid-lat) (top). Also shown is measured and modelled δ_{T}(CFC-11) (see Figure 4 and Section 2.5 for a description of the model). The model was forced with ϵ_{app}(CFC-11, high-lat). The errorbar in the bottom left corner of each graph shows the median repeatability of the reference gas measurements over the measurement days and the median error deriving from the fractional release factor.

and others involved in the NOAA-HATS program and NOAA/ESRL Global Monitoring Division for CFC-12 and CH_3Cl mole fraction data (ftp://aftp.cmdl.noaa.gov/data/hats/cfcs/cfc12/combined/ and ftp://aftp.cmdl.noaa.gov/data/hats/methylhalides/ch3cl/flasks/).

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