

Interactive comment on “Stratospheric carbon isotope fractionation and tropospheric histories of CFC-11, CFC-12 and CFC-113 isotopologues” by Max Thomas et al.

Anonymous Referee #1

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General comments:

In the submitted manuscript “Stratospheric carbon isotope fractionation and tropospheric histories of CFC-11, CFC-12 and CFC-113 isotopologues” Thomas et al. report on the first measurements of the stable carbon isotope composition of CFCs sampled in the stratosphere from which they derived isotopic enrichment factors (ϵ). In addition, firn air samples collected in 2008 and 2009 were re-measured in order to obtain the stable carbon isotope composition of CFCs in the troposphere. These data were used to model the change of $\delta^{13}\text{C}$ in CFCs over time in the troposphere. Initially, this topic appears very interesting and I believe that the interpretation based

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on the presented data is plausible. The major issue of this study is, however, the data itself. First of all, 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 acceptable 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 $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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. 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 $\delta^{13}\text{C}$ and ϵ s 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. Overall this paper presents an interesting research idea but all interpretation is based on very uncertain, not evaluable, data which cannot be compared to any other study. Therefore I cannot recommend this paper for publication. Further comments are given below:

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Specific comments:

- Page 3 line 3-5: Strictly speaking, the Rayleigh model requires a first-order or pseudo-

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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?

- 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.

- 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

- 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

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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

- 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.

- 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% ³⁵Cl) 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.

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- 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).

- 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?

- 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.

- 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.

- 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).

- Page 12 Line 31-32: How can values of about -60‰ (Zuiderweg) be consistent with

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about -20‰. This is a comparison of apples and oranges. With an assumed scale factor eventually all data will be "consistent"

- 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.

- 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.

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

- 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

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

- 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.

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Technical corrections:

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- Page 1 Line 10: delta is expressed in an unusual way: $\delta(13C)$. What is the rationale 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)
- Page 3 line 15: please define epsilon p
- 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).
- Page 5 line 16-17: Only every fourth measurement was a reference. So samples are therefore not "bracketed" by reference measurements because this would require every second measurement to be a reference.
- Page 5 line 19: was AAL used as "bracketing standard"?
- 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.
- Page 5 line 26-30: It is not clear for what the correction is applied
- 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)
- 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
- Page 11 line 9: "while epsilon_{app}(CFC-12) was most negative at high-latitudes" this is not consistent with table 2
- 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 ($\pm 6\%$). Please also give the uncertainty for (1-f) and the calculated ages.

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

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