We would like to provide an initial response to several concerns raised by reviewer #1, which in our view mispresent the findings of our manuscript. These concerns focus on methodological details, specifically the lack of standardisation against VPDB, lack of scale normalisation and the use of single-detector mass spectrometry. We conclude in the following that these concerns have no significant bearing on the results and none on the conclusions.

1) Isotope delta standardisation

We measure and report our $\delta(^{13}C)$ 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 $\delta(^{13}C)$ over time (firn) and space (stratosphere) with respect to modern tropospheric air (chosen to be represented by the AAL-071170 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 $\delta(^{13}C)$ 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 GC-combustion-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 AAL-071170 and at that time a retrospective correction be applied.

2) Isotope scale normalisation

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 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 CFC-11 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.

3) Use of single-detector mass spectrometry

Finally, the reviewer commented that single-detector mass spectrometry had not been used previously for carbon isotopes, but also acknowledged that it had found applications for chlorine (Laube et al., 2010; Aeppli et al., 2010; Allin et al., 2015) and bromine (Zakon et al., 2016; Horst et al., 2013) isotope systems. We would like to add sulfur (Angert et al., 2019), nitrogen and oxygen isotopes (Neubauer et al., 2020) to this list, as well as indeed carbon isotopes (Eiler et al., 2017; Hauri et al., 2002; Schutten et al., 1957; Nier, 1940). As the age of some of these references show, single-detector isotope ratio measurements are as old as the field of isotope geochemistry. Their main drawback is the reduced repeatability, but this may be more than offset by a reduced sample size requirement as in our case.

To further validate our single-detector method, we compared δ values of CFC-12 samples from laboratory photolysis experiments (Zuiderweg et al., 2012) against measurements of the same samples on a GC-combustion IRMS system (Fig. 1). This required up to 1000-fold dilution of the photolysis samples to adjust their CFC-12 mole fractions of up to 530 nmol mol^{-1} to match the CFC-12 mole fraction of 534 pmol mol^{-1} in the AAL-071170 reference tank.

The regression coefficient of 1.00±0.09 shows good agreement between both methods, with a high correlation of $R^2 = 0.92$. This suggests that any scale contraction is likely to be small (or fortuitously similar for both methods). Either way, neither the choice of δ scale nor any scale contraction would change our conclusions regarding 1) changes in the tropospheric isotope delta, 2) the stratospheric isotope fractionation or, resulting from that, 3) the isotope deltas of the CFC emissions.

The *y*-axis offset of (46.3±2.7) ‰ can be converted to a δ value of (–44.2±2.5) ‰ for CFC-12 in AAL-071170 on the VDPB scale, which agrees within error with the value of (–43.0±2.3) ‰ obtained independently from the firn sample comparison (Eq. 3 of the manuscript).

In summary, we trust to have allayed the most pressing concerns of reviewer #1. We will provide a more detailed response after the end of the discussion phase.

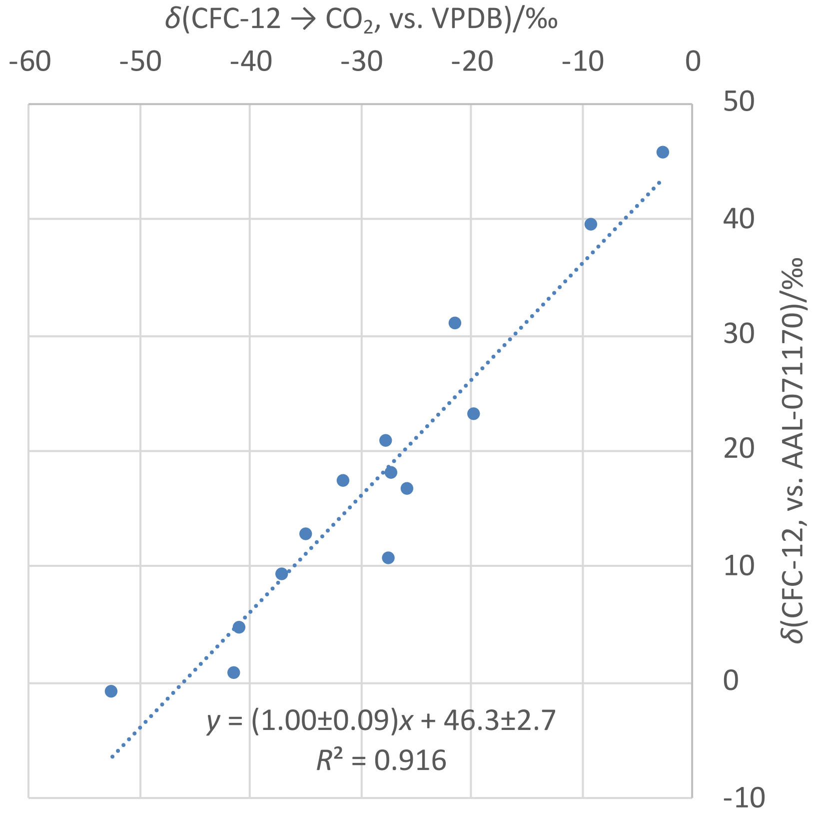

Fig. 1: Comparison between δ values of CFC-12 samples from laboratory photolysis experiments measured using our single-detector method and measurements of the same samples on a GC-combustion IRMS system (Zuiderweg et al., 2012). The fit line was obtained by linear regression.

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