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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Extreme ^{13}C depletion of CCl_2F_2 in firn air samples from NEEM, Greenland" *by* A. Zuiderweg et al.

Anonymous Referee #3

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The authors present new measurements of a quantity not previously measured, the 13C content of CFC-12 in firn air. They have made a reasonably good start, but much could be done to improve the paper. I anticipate that the potential interest from the ACP readership might be on the low side, given that the implications of the work seem limited. The stated goal of the study is to see if a signal associated with a large isotope effect associated with stratospheric loss can be detected in the atmosphere. The authors conclude instead that the uncertainty and time-variation in the source term dominate the derived changes in the isotope signal in the firn-derived atmospheric record. The follow up on understanding the potential future magnitude of this influence is very cursory (29/mill/yr if emissions were zero... is this detectable? Useable for supplying constraints on lifetime? Likely to still be influenced by the source term at all points in

the future?) Some additional discussion in this regard might be worthwhile.

A number of issues need addressing before the paper would be publishable. 1) What are the potential magnitude of sampling artifacts that might affect 13C of CFC-12 with the compressor that was used? One would expect that the magnitude of these influences would increase in the lock-in zone where flow restrictions are larger. Section 2.1 isn't that clear, were samples pressurized with the compressor on site in a single step? Could there be fractionation of CFC-12 through the emission process from compressors, foams, etc.?

2) How was the CFC-12 peak purity assessed throughout the firn? Although the authors have the data, they do not assess the CFC-12 history explicitly in the paper in a way that allows the reader to be sure that the time-inferred history is accurate (something more than what is given in section 3.1 seems worthwhile - how was the consistency with Buizert assessed? Although no independent CFC-12 history can be derived (p. 18509), the firn data could be used with the forward model to derive a history whose consistency could be check with the Walker et al history, for example). This seems important to eliminate the possibility that some unknown contaminant is causing the anomalous isotopic signal. How is it known that the CFC-12 peaks "are free of artifacts"? Even if "all firn samples were treated differently", time - dependent errors could arise from a constant interference.

3) on assessing the influence of induced fractionation within the firn. Does the model used in the present study adequately simulate these effects for those gases for which the effect is larger (p. 18511)? In other words, please demonstrate the skill of the model for accurately simulating isotopic effects for 13CH4, for example.

4) The authors indicate that CFC-12 production methods have changed in the past, but there is no discussion as to whether or not these changes would/could/should/did have an impact on the 13C of CFC-12 produced. Without this evidence or discussion, the text needs some revision - e.g., though production changes have occurred over

time, we do not have independent evidence that these changes actually influenced the isotopic abundance of CFC-12, though the results suggest they do...

Other points: Citations need improving... Assessment reports should be cited with chapter authors, not as WMO (2011) for example. The IPCC chapter (Forster et al.) has older info on halocarbon abundances that could be updated with the latest ozone assessment report.

The ozone assessment also provides updated information about CFC-12 emissions (they remain 10% of peak levels; a improvement over "largely ceased" given on line 1 of p. 18504) and recent mixing ratios.

Stolarski and Cicerone (Canad. J. of Chem., 1974) were actually the first to describe the catalytic decomposition of ozone from Cl. Molina and Rowland proposed CFCs as being a potential source of that Cl.

Chi-squared is likely a better indicator of goodness of fit than RMSD for the different scenarios because it accounts for the magnitude of a residual relative to the magnitude of uncertainty on a measurement, see work by Battle et al. (p. 18510).

What sample volume was injected in making these measurements?

Lines 15-25 of p. 18514. What point is being made here that is relevant for this paper? Needs to be clearer.

Might mention CFC-12 in Table 1, Figure 7, and Figure 8. Might indicate "of CH3Cl and CFC-12 detected as CO2 at ions m/z=44..." in Figure 2 caption.

What is the "ice-core trapped age"? No dates are given for the sampling dates associated with previous atmospheric measurements of 13C in (presumably, but not stated) CFC-12 (p. 18507). I presume the coefficients to the polynomials in the many scenarios were randomly generated (line 26, p. 18509)?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18499, 2012.