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Atmospheric Chemistry and Physics Discussions

ACPD

12, C9825–C9834, 2012

Interactive Comment

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

A. Zuiderweg et al.

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We would like to thank the referees for their input. As a result there has been improvement to the manuscript and we are grateful for their efforts in this regard.

Response to Referee #5

Comment 1. page 18501, line 15-17 - I would recommend deleting the last sentence of the abstract, about propagating into the future. Certainly it could be mentioned in the paper, but I don't believe that it is an important result that deserves mention in the abstract. Isotopes are used here to understand the processes in the CFC-12 budget, their future behavior only matters in this context, and not in its own right. Deleting the sentence would avoid the possibility that a reader could think that there is anything

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significant about the future levels of 13C in CFC-12.

Author Response: The sentence has been deleted from the abstract.

Comment 2. page 18503, line 20 - Why "unusually". What is usual? Perhaps "unexpectedly" would be a better word, or nothing.

Author Response: The word “unusual” has been removed.

Comment 3. Page 18504, line 22 - You could specify here whether the FASD was expanded with air from the firn hole or the atmosphere.

Author Response: The FASD was inflated by compressed surface air. This detail has been added.

Comment 4. Page 18508, Section 3.2 - what values of the diffusion coefficients were used for CFC- 12 and 13C in CFC12?

Author Response: The diffusion coefficients used were D(CFC-12)/D(CO2) = 0.596 and D(13CFC-12)/D(12CFC-12) = 0.9992, derived from equations in Buizert et al. (2012). This detail has been added as well.

Comment 5. page 18511, line 5 - You could mention that although Buizert et al 2012 showed a significant range between models in the calculated diffusive fractionation for d13CO2 at depth, that because the magnitude of the diffusive fractionation in 13C in CFC-12 is so small compared to the variation measured in the firn, the uncertainty in parameterisation of lock-in zone diffusion is not important here.

Author Response: Thank you for the hint; this has been added.

Comment 6. Page 18512, line 17 - rather than "epsilon is estimated at -35 permil", you should put "epsilon is assumed to be -35 permil", to be clear that it is deltaP that you are estimating with this calculation, not epsilon.

Author Response: Has been added.

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Comment 7. Page 18513, line 4 - add "to estimate deltaP" at the end of the sentence, after 2000. This will help make it very clear for the reader what you are estimating.

Author Response: Has been added.

Comment 8. Sapart et al 2012 is mentioned in the text but is not listed in the references.

Author Response: The reference has been added.

Comment 9. You could give the equation for the best-case 3rd order polynomial, in case someone in the future would like to compare it to new reconstructions of 13C in CFC-12 from archived air or firn.

Author Response: This has been added in the model discussion in section 3.2.

Comment 10. Can you rule out fractionation during collection of firn air as a possible cause of the depletion?

Author Response: The isotope ratio could in theory be influenced by the collection process: For example, CFC-12 can diffuse through the rubber bladder used in the firn-air sampling device. The FASD is filled with atmospheric air, and atmospheric CFC-12 could diffuse through the bladder and introduce diffusion-depleted CFC-12 into the samples at depths where CFC-12 mixing ratio is low. The diffusive properties of the butyl rubber used have, as far as we know, not been quantified with regards to CFC δ13C fractionation. However, our results are inconsistent with this idea. If we assume an ambient background of -41‰ the sample from 66.8 m is depleted by -12‰ with respect to the ambient background. In a worst case scenario we could assume that the depletion is not real and entirely caused by the diffusion artifact. At the 69.4 m level (VMR of 168 ppt) this artifact would cause a depletion of $\sim$-22‰ which is by far insufficient to explain the measured depletion of -37‰ (with respect to an ambient background of -41‰. Likewise, the pumps, compressors, lines, etc. (or similar firn-sampling equipment), have been shown in many other campaigns (including that mentioned in Buizert et al., 2012, which used the exact same sampling equipment) to produce reliable samples, so we can be confident that the NEEM CFC samples should be free from artifacts.

Comment 11. Fig 3 - I recommend adding the profile of CFC-12 from the firn model calculated with the atmospheric scenario from Buizert et al, instead of the lines between symbols, noting the instrument and calibration error described on page 18507. Although the match might not be perfect, this would demonstrate general consistency with the atmospheric scenario (and therefore the NEEM 2008 campaign).

Author Response: This trace has been added as suggested here.

Comment 12. Fig 4 - As in Fig 3, rather than the line between points, you could show the firn model profile of d13C for the best case, either the 3rd or 4th degree polynomial. Just one case, not the envelope as in Fig 5.

Author Response: This has been added as suggested.

Comment 13. Fig 6 - Add "atmospheric" after "Reconstructed".

Author Response: Has been added.

Comment 14. Fig 7 - Make the symbols clearer, it is hard to see them. Perhaps filled symbols would be better.

Author Response: This has been changed as appropriate.

Comment 15. Fig 8 - Could you split the contributions of fractionation into diffusion and gravitation? This would be useful for comparison with other estimates of these quantities, particularly as they partly cancel each other.

Author Response: This has been done.

Comment 16. Fig 9 - In the legend, specify which of these refer to the atmosphere and which to the emissions.

Author Response: This has been added.

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

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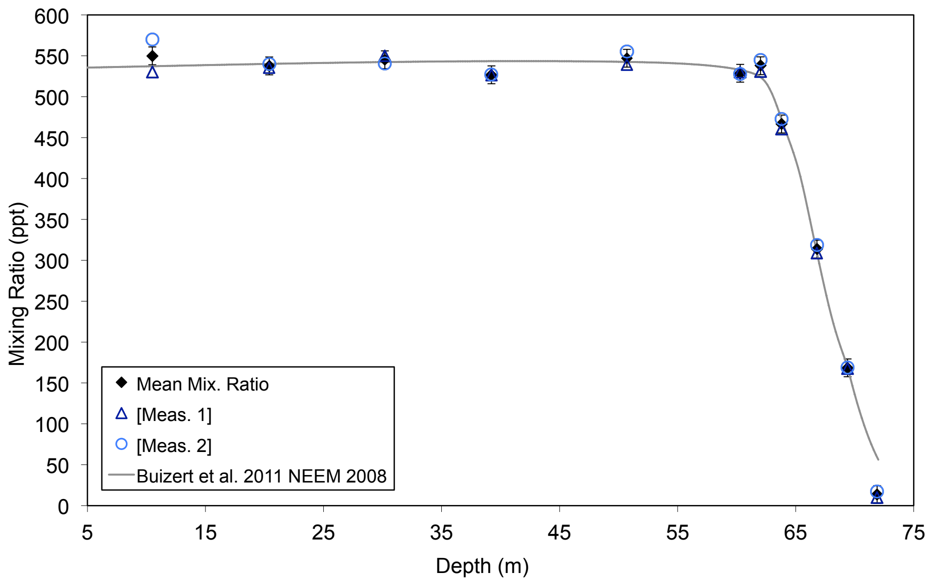

Fig. 1. Fig 3. Update

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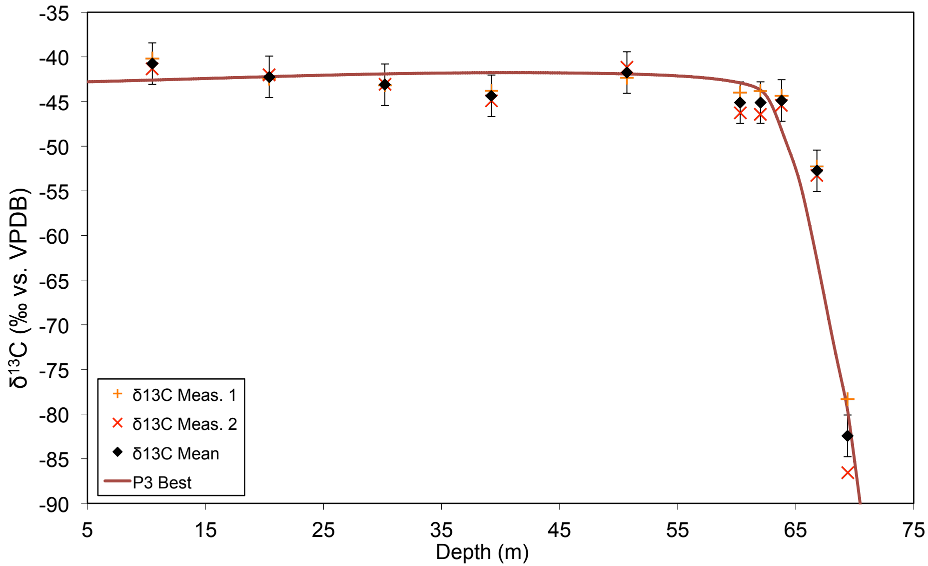

Fig. 2. Fig 4. Update

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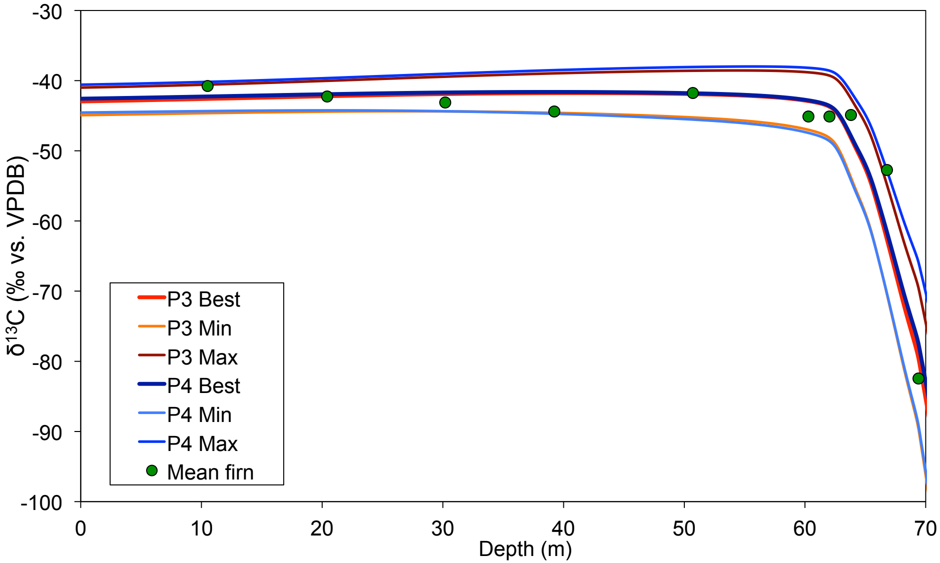

Fig. 3. Fig. 7 Update

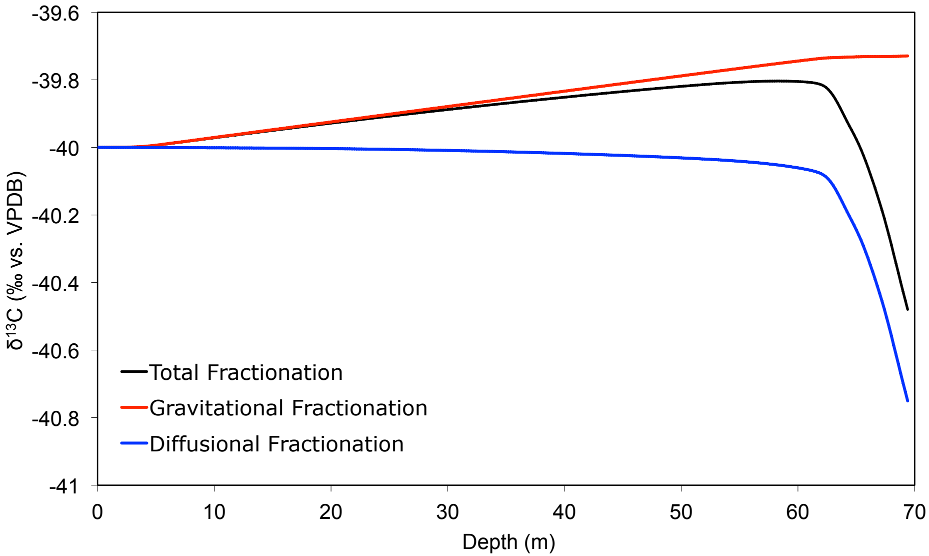

Fig. 4. Fig 8. Update

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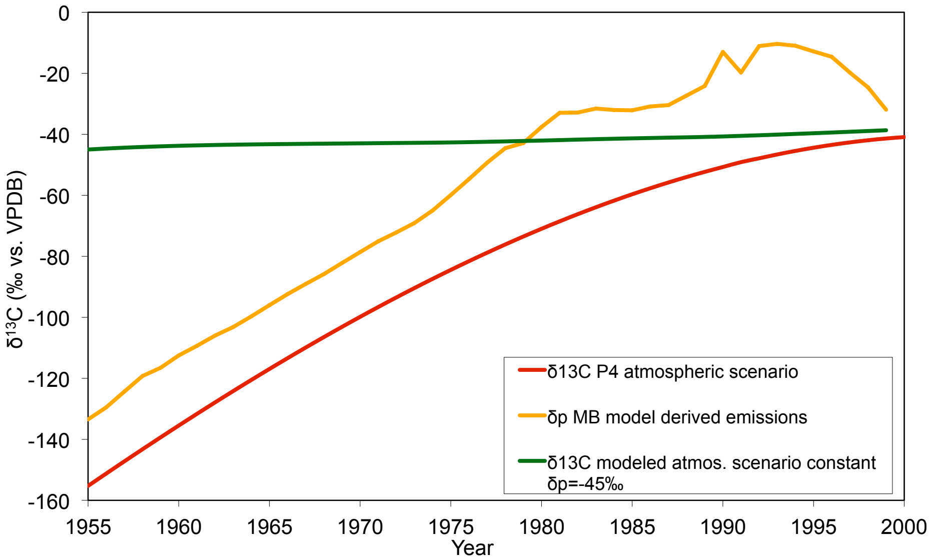

Fig. 5. Fig 9. Update