Supplement of Atmos. Chem. Phys. Discuss., 14, 31813–31841, 2014
http://www.atmos-chem-phys-discuss.net/14/31813/2014/
doi:10.5194/acpd-14-31813-2014-supplement

Atmospheric Chemistry and Physics
Discussions

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Chlorine isotope composition in chlorofluorocarbons CFC-11, CFC-12 and CFC-113 in firn, stratospheric and tropospheric air

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1. Determination of non-linearities

A static dilution series was analysed to determine whether the measured isotope ratio of a sample is dependent on its mole fraction (i.e. whether a change in chromatographic peak size alters the measured isotope delta). Table S1 gives details of the samples analysed in the dilution series.

Figure S1 shows that delta values derived from the smallest peak areas exhibit erroneously low $\delta(^{37}Cl)$ values for all three species, which requires a correction. 99 % of the samples analysed have peak areas in the region where the dilution series showed no bias in the isotope delta. However, a total of 1 (CFC-11), 2 (CFC-12) and 2 (CFC-113) $\delta(^{37}Cl)$ measurements were corrected based on the instrument bias quantified by the smallest peaks in the dilution series analysis (Figure S1 insets). A linear regression line was used to track the depletion in the smallest peaks produced during the dilution series analysis. This line was then used to correct the firn measurements, based on their peak areas. An additional error was applied to each corrected measurement based on the uncertainty in the regression line. This uncertainty was factored such that the size of the additional error applied to a measurement is directly related to the size of the correction required.

This dilution series analysis shows an isotope delta bias which is limited to the lowest abundance samples; most samples display no bias. The unaffected samples cover a large range of mole fractions and were analysed using a variety of air volumes. Any systematic effect should be shown in these data. The absence of an effect suggests that the GC, MS and inlet system do not affect isotope deltas. It is likely that the bias shown in small peaks is introduced during data processing steps, rather than during the measurement acquisition.

2. Firn modelling

The diffusivity of firn largely determines its gas transport characteristics. The physical basis of this model is described in Witrant et al. (2012). Recent algorithm development allows the use of several reference gases to adjust the firn diffusivity, improving the quality of firn models (e.g. Buizert et al., 2012). Two gases (CO_2 and CH_4) were used to evaluate the firn diffusivity of the NEEM 2009 borehole

(Zuiderweg et al., 2013). Fletcher Promontory firn was sampled by the British Antarctic Survey in December 2011. An accumulation rate of 38 cm water equivalent per year (nearly twice the NEEM value) results in high downward advection in Fletcher firn and thus younger gas ages than at NEEM (see Tables S3 and S4). The reference gases used to estimate the Fletcher firn diffusivity are: CH_4, SF_6, CFC-11, CFC-12, CFC-113, CH_3CCl_3 and HFC-134a.

Diffusion coefficient ratios were calculated in the same way as Buizert et al. (2012). Diffusion coefficients for “major isotopologues” (including their temperature dependencies) were taken from the Matsunaga data series and relative diffusion coefficients for pairs of isotopologues were calculated from Equation (6) (all in the Supplement of Buizert et al., 2012). The corresponding values are shown in Table S2. Here we assumed that $C^{35}Cl_2F_2$ (the “major isotopologue”) has the same diffusion coefficient as the inclusion of all isotopologues. The diffusion coefficients of the isotopologues of a given CFC differ by less than the uncertainty on the total diffusion coefficient (~2 %).

A correction for within-firn isotope fractionation is calculated using a reconstructed scenario for each gas and assuming a constant atmospheric isotope composition over time. Changes in fractionation with depth therefore reflect firn fractionation processes alone; they are used to correct the measured values. The corrections made to the Fletcher Promontory $\delta(^{37}Cl)$ measurements are shown in Figure S2. At the greatest depths, the corrections were around +2 ‰ for CFC-11 and CFC-12, and around +1 ‰ for CFC-113. For the NEEM data (not shown), the corrections were broadly similar.

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Table S1. Dilution series mole fractions for CFC-11, CFC-12 and CFC-113. 1σ standard deviation errors are given.

	Compound		
Sample ID	**CFC-11 / pmol mol^{-1}**	**CFC-12 / pmol mol^{-1}**	**CFC-113 / pmol mol^{-1}**
SX-0706077	245.1 ± 3.6	540.0 ± 3.4	78.1 ± 0.2
K1579	164.9 ± 2.4	363.4 ± 0.7	52.7 ± 0.1
K1578	75.9 ± 0.7	167.0 ± 0.8	24.1 ± 0.1
K1583	38.5 ± 0.3	84.1 ± 0.4	12.2 ± 0.1
K1569	17.7 ± 0.2	38.8 ± 0.1	5.6 ± 0.02
K1575	2.9 ± 0.02	6.6 ± 0.1	0.9 ± 0.01
K1576	0	0.1	0

Table S2. Molecular weights and relative diffusion coefficients (with respect to the reference gas shown) used in the firn model.

Species	CFC-11	CFC-11	CFC-11	CFC-12	CFC-12	CFC-12	CFC-113	CFC-113	CFC-113
Isotopologue	${}^{12}C^{35}Cl_3F$	${}^{12}C^{35}Cl_2{}^{37}ClF$	${}^{12}C^{35}Cl^{37}Cl_2F$	${}^{12}C^{35}Cl_2F_2$	${}^{12}C^{35}Cl^{37}ClF_2$	${}^{12}C^{37}Cl_2F_2$	${}^{12}C_2{}^{35}Cl_3F_3$	${}^{12}C_2{}^{35}Cl_2{}^{37}ClF_3$	${}^{12}C_2{}^{35}Cl^{37}Cl_2F_3$
Molar mass / gmol^{-1}	136.3998	138.3969	140.3939	119.9452	121.9423	123.9393	186.4073	188.4044	190.4014
Reference	CO_2	${}^{12}C^{35}Cl_3F$	${}^{12}C^{35}Cl_3F$	CO_2	${}^{12}C^{35}Cl_2F_2$	${}^{12}C^{35}Cl_2F_2$	CO_2	${}^{12}C_2{}^{35}Cl_3F_3$	${}^{12}C_2{}^{35}Cl_3F_3$
D/D_{ref} NEEM	0.5251	0.9987	0.9975	0.5965	0.9984	0.9969	0.4527	0.9993	0.9986
D/D_{ref} FLT	0.5250	0.9987	0.9975	0.5961	0.9984	0.9969	0.4526	0.9993	0.9986

Table S3. Median air age width (15 % to 85 % accumulated probability interval i.e. ± 1σ equivalent) for NEEM 2009. Results are given for closest model depths to measurement depths.

Depth	CFC-11	CFC-12	CFC-113
0.00 m	0.0(0.0-0.0)	0.0(0.0-0.0)	0.0(0.0-0.0)
10.60 m	0.2(0.0-1.0)	0.2(0.0-1.0)	0.2(0.0-1.1)
20.40 m	0.7(0.2-3.3)	0.7(0.2-3.1)	0.7(0.2-3.6)
30.20 m	1.8(0.5-6.5)	1.6(0.5-5.9)	1.9(0.6-7.3)
39.20 m	3.1(1.1-9.4)	2.8(1.0-8.4)	3.5(1.3-11.)
50.80 m	5.3(2.2-13.)	4.8(1.9-12.)	6.0(2.5-15.)
60.20 m	8.3(4.0-18.)	7.5(3.6-16.)	9.5(4.7-20.)
62.00 m	9.8(4.9-20.)	8.9(4.4-19.)	11.(5.7-23.)
63.80 m	16.(8.8-30.)	15.(8.0-28.)	18.(9.8-32.)
66.80 m	30.(19.-46.)	28.(18.-45.)	32.(21.-49.)
69.40 m	41.(29.-59.)	39.(28.-57.)	43.(31.-61.)
72.00 m	54.(41.-72.)	52.(40.-70.)	56.(43.-74.)
73.60 m	61.(49.-79.)	59.(47.-77.)	63.(51.-81.)

Table S4. Preliminary median age and age width (15 % to 85 % accumulated probability interval i.e. ± 1σ equivalent) for Fletcher. Results are given for closest model depths to measurement depths.

Depth	CFC-11	CFC-12	CFC-113
0.00 m	0.0(0.0-0.0)	0.0(0.0-0.0)	0.0(0.0-0.0)
3.00 m	0.1(0.0-0.5)	0.1(0.0-0.4)	0.1(0.0-0.6)
7.00 m	0.3(0.0-2.1)	0.3(0.0-1.8)	0.3(0.1-2.3)
11.00 m	0.7(0.2-4.5)	0.6(0.2-4.0)	0.8(0.2-5.2)
18.60 m	1.9(0.5-9.5)	1.7(0.4-8.4)	2.3(0.6-11.)
22.00 m	2.6(0.8-11.)	2.3(0.7-10.)	3.0(0.8-13.)
26.60 m	3.7(1.1-14.)	3.2(0.9-12.)	4.2(1.3-16.)
38.00 m	6.3(2.2-18.)	5.5(1.9-16.)	7.3(2.5-21.)
44.80 m	7.9(3.0-21.)	7.0(2.6-18.)	9.1(3.4-24.)
50.20 m	9.3(3.8-23.)	8.3(3.3-20.)	11.(4.3-26.)
56.20 m	11.(4.8-25.)	9.8(4.3-22.)	13.(5.6-28.)
59.20 m	12.(5.5-26.)	11.(4.8-23.)	14.(6.3-30.)
62.20 m	13.(6.3-27.)	12.(5.5-24.)	15.(7.3-31.)
65.20 m	15.(7.3-29.)	13.(6.4-26.)	17.(8.3-33.)
68.20 m	16.(8.7-31.)	15.(7.7-27.)	19.(9.9-35.)
70.20 m	20.(12.-34.)	18.(10.-31.)	22.(13.-38.)
72.00 m	24.(16.-39.)	23.(14.-36.)	27.(17.-43.)
74.40 m	30.(21.-44.)	28.(19.-41.)	32.(22.-49.)
76.20 m	34.(25.-49.)	32.(24.-46.)	36.(27.-53.)
78.20 m	39.(29.-53.)	37.(28.-50.)	41.(31.-58.)
79.20 m	41.(32.-56.)	39.(30.-52.)	43.(33.-60.)
80.60 m	44.(35.-59.)	42.(33.-56.)	46.(36.-63.)

Figure S1. Dilution series measured for $\delta(^{37}Cl)$, plotted against the integrated peak area of the $C^{35}Cl^{37}ClF^+$ fragment ion (*m/z* 103). 1σ standard deviation error bars are shown. Insets highlight the firn air measurements that fall within the depleted region of the dilution series analysis (red highlighted regions on the left). Linear regression lines are used to adjust the firn samples, based on the observed dilution series depletion. Unaffected samples are not displayed. All delta values are relative to 2006 standard air.

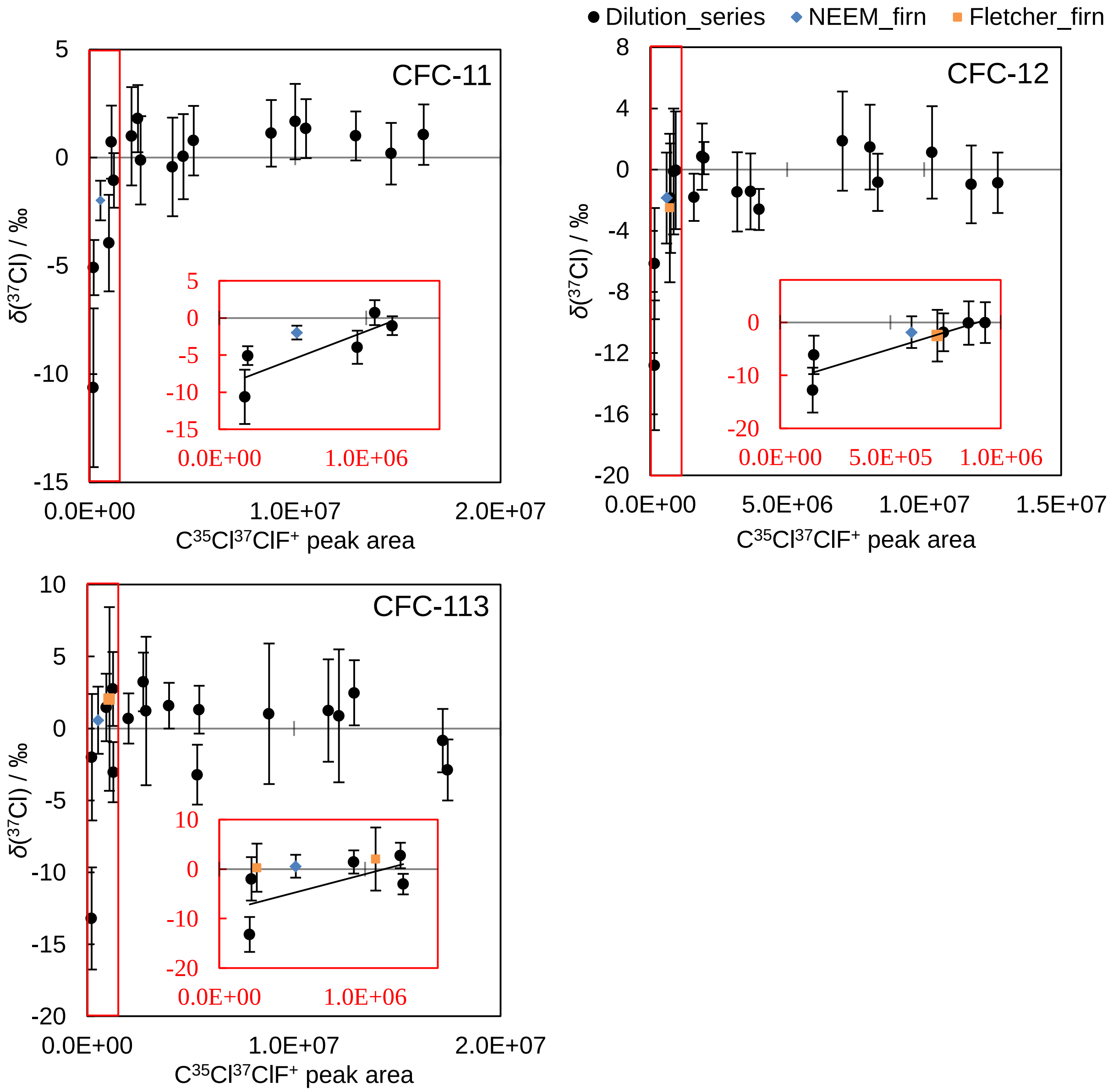

Figure S2. Measured $\delta(^{37}Cl)$ values (blue circles, with 1σ standard deviation error bars), and the same after correcting for gravitational and diffusional fractionations (green diamonds, error bars not included), as a function of firn depth at Fletcher Promontory.