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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 uncertainty was carried forward for each corrected measurement based on the uncertainty in the regression line. This uncertainty was factored such that the size of the additional uncertainty 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 concentration 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). Originally two gases

(CO_2 and CH_4) were used to evaluate the firn diffusivity of the NEEM 2009 borehole (Zuiderweg et al., 2013). In the present study, SF_6, CFC-11, CFC-12, CFC-113, CH_3CCl_3 and HFC-134a have been used to update this diffusivity profile. Fletcher Promontory firn air 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 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) and relative diffusion coefficients for pairs of isotopologues were calculated from Equation (6) (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 and NEEM $\delta(^{37}Cl)$ measurements are shown in Figures S2 and S3, respectively. At the greatest depths, the corrections were around +3 ‰ for CFC-11 and CFC-12, and around +1 ‰ for CFC-113.

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Table S1. An air sample collected at Niwot Ridge in 2009 (SX-0706077) was diluted with nitrogen. Mole fractions for CFC-11, CFC-12 and CFC-113 were measured using the most abundant fragment ion (*m/z* 101). 1σ standard deviations are given. $\delta(^{37}Cl)$ measurements were also made on these samples (Figure S1 and Table S10).

	Compound		
Sample ID	***y*(CFC-11) / pmol mol^{-1}**	***y*(CFC-12) / pmol mol^{-1}**	***y*(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 masses 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 / g mol^{-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 and the width of the age distribution (15 % to 85 % accumulated probability interval i.e. ± 1*σ* 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. Median air age and the width of the age distribution (15 % to 85 % accumulated probability interval i.e. ± 1*σ* 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)

Table S5. The CFC-11 stratospheric data used in Figure 1. The ID code, latitude, longitude and altitude of each sample are also included.

Sample ID	Latitude / ° N	Longitude / ° E	Altitude / km	ln [1+ δ] / ‰	ln [1+ uncertainty] / ‰	ln (y/y_T)
Mid-latitude samples:						
F2-18 (N5)	48.47	10.29	10.00	0.04	1.88	-0.01
F1-18 (B1/9)	48.08	10.44	10.05	2.37	1.65	-0.02
F1-17 (B1/12)	48.43	10.13	12.96	2.00	1.65	-0.01
F1-0 (81)	48.34	10.24	13.97	0.06	2.78	-0.01
F2-8 (R3/16)	53.14	10.28	14.69	0.11	1.61	-0.08
F2-17 (707)(R2/6)	48.93	9.26	15.03	-0.96	1.88	-0.07

F1-16 (R2/3)	48.21	10.79	15.58	0.45	1.65	-0.07
F2-7 (N4)	53.36	8.89	16.76	0.46	1.88	-0.25
F1-1 (B1/3)	48.29	10.58	16.85	0.81	1.65	-0.24
F1-15 (102)	48.44	10.17	17.57	0.53	3.43	-0.30
F2-3 (R3/9)	50.02	8.86	17.86	0.68	2.49	-0.82
F1-5 (S1/14)	51.54	11.46	17.99	1.45	3.43	-0.33
F1-4 (T3/15)	50.69	10.93	18.01	1.22	1.65	-0.40
F1-3 (S3/18)	49.83	10.46	18.02	3.32	3.43	-0.40
F2-6 (N3)	52.89	8.42	18.29	1.12	2.49	-0.73
F2-5 (B1/18)	51.93	8.55	18.30	2.35	1.88	-0.93
F2-16 (R3/3)	49.27	8.28	18.40	2.83	1.88	-0.87
F1-6 (R2/19)	51.76	12.02	18.50	3.55	3.43	-0.55
F2-10 (R3/4)	52.50	11.35	18.58	4.02	1.88	-0.94
F1-7 (B1/2)	50.75	11.63	18.60	2.49	2.78	-0.62
F1-8 (R1/2)	49.77	11.28	18.63	2.86	3.43	-0.49
F1-9 (S2/5)	48.85	10.69	18.65	3.96	1.65	-0.61
F1-11 (B1/13)	49.93	10.57	18.68	1.57	2.49	-0.69
F1-10 (R2/13)	49.03	10.09	18.69	2.15	3.43	-0.42
F1-12 (N1)	50.80	11.16	18.73	0.91	3.43	-0.49
F2-11 (B1/7)	52.26	10.29	18.77	5.18	1.61	-1.13
F2-14 (R3/13)	51.27	7.66	18.78	2.69	1.88	-1.46
F2-13 (R3/18)	52.19	7.67	18.79	3.65	1.88	-1.37
F2-15 (R3/17)	50.33	7.80	19.26	5.49	1.61	-1.24
F1-13(R2/4)	50.38	11.37	19.52	1.53	2.78	-0.79
F1-14 (N2)	49.46	10.81	19.82	1.11	1.65	-0.91
High-latitude samples:						
Kiruna_U133	67.72	20.50	9.27	0.59	0.74	0.00
Kiruna_U174	67.90	20.28	10.95	0.15	2.47	-0.08
Kiruna_F1_U112	68.21	20.81	13.00	-0.78	4.02	-0.13
Kiruna_U160	67.24	18.93	13.55	2.49	0.85	-0.31
Kiruna_U128	68.71	20.42	14.33	0.39	0.74	-0.32
Kiruna_U140	67.04	20.75	14.51	1.92	0.74	-0.33
Kiruna_U134	70.98	23.06	15.45	0.91	2.47	-0.53
Kiruna_U137	71.78	24.44	15.92	2.11	2.47	-0.55
Kiruna_F1_U239	71.17	20.74	16.17	3.32	4.10	-0.76
Kiruna_F1_U113	68.99	21.60	16.28	0.94	4.02	-0.69
Kiruna_F1_U237	69.49	20.68	16.61	1.74	4.02	-0.86
Kiruna_U176	67.67	16.16	17.30	4.81	2.53	-1.56
Kiruna_U130	72.53	25.87	17.33	4.12	0.74	-0.87
Kiruna_U182	68.85	21.83	17.45	2.45	0.74	-0.91
Kiruna_F1_U104	76.24	20.10	17.66	4.84	4.10	-1.36
Kiruna_F1_U101	73.69	20.48	17.67	3.51	4.10	-1.31
Kiruna_F1_U109	75.84	21.62	17.69	1.83	4.06	-1.25
Kiruna_U253	67.15	9.48	17.70	4.57	2.53	-1.57
Kiruna_F1_U103	75.45	20.22	17.71	1.33	4.06	-1.20
Kiruna_U249	66.83	8.09	17.73	3.26	0.85	-1.71
Kiruna_U254	66.85	10.35	17.74	4.93	0.85	-1.55

Kiruna_U132	73.33	27.25	18.09	4.34	0.85	-1.43
Kiruna_U155	66.27	10.88	18.20	4.11	2.53	-1.30
Kiruna_F1_U106	73.30	23.08	18.34	3.08	4.06	-1.47
Kiruna_U170	67.75	16.11	18.35	3.30	2.53	-1.63
Kiruna_F1_U105	72.39	22.77	18.50	3.15	4.06	-1.54
Kiruna_U145	69.50	24.23	18.55	3.99	0.85	-1.63
Kiruna_U135	68.68	23.31	18.64	4.90	0.74	-1.70

Table S6. The CFC-12 stratospheric data used in Figure 1. The ID code, latitude, longitude and altitude of each sample are also included.

Sample ID	Latitude / ° N	Longitude / ° E	Altitude / km	ln [1+ δ] / ‰	ln [1+ uncertainty] / ‰	ln (y/y_T)
Mid-latitude samples:						
F2-18 (N5)	48.47	10.29	10.00	-3.54	3.33	0.00
F1-18 (B1/9)	48.08	10.44	10.05	0.57	1.72	0.00
F1-17 (B1/12)	48.43	10.13	12.96	-0.80	1.72	0.00
F2-0 (R2/16)	48.16	10.15	13.61	-2.30	3.65	0.01
F1-0 (81)	48.34	10.24	13.97	-1.93	1.78	0.00
F2-8 (R3/16)	53.14	10.28	14.69	-1.57	3.20	-0.04
F2-17 (707)(R2/6)	48.93	9.26	15.03	0.19	3.33	-0.03
F1-16 (R2/3)	48.21	10.79	15.58	0.07	1.72	-0.02
F2-7 (N4)	53.36	8.89	16.76	-0.06	3.33	-0.13
F1-1 (B1/3)	48.29	10.58	16.85	-1.13	1.72	-0.12
F2-9 (R3/5)	53.33	11.28	17.03	0.67	3.33	-0.14
F1-15 (102)	48.44	10.17	17.57	0.06	4.58	-0.14
F2-2 (R3/15)	49.08	8.97	17.77	2.75	3.65	-0.38
F2-3 (R3/9)	50.02	8.86	17.86	5.37	3.65	-0.38
F1-5 (S1/14)	51.54	11.46	17.99	1.03	4.58	-0.15
F1-4 (T3/15)	50.69	10.93	18.01	-0.39	1.72	-0.19
F1-3 (S3/18)	49.83	10.46	18.02	1.68	4.58	-0.20
F2-6 (N3)	52.89	8.42	18.29	0.98	3.65	-0.34
F2-5 (B1/18)	51.93	8.55	18.30	6.32	3.33	-0.43
F2-4 (R3/7)	50.97	8.68	18.30	6.81	3.65	-0.57
F1-6 (R2/19)	51.76	12.02	18.50	-1.26	4.58	-0.25
F2-10 (R3/4)	52.50	11.35	18.58	6.29	3.33	-0.43
F1-7 (B1/2)	50.75	11.63	18.60	2.60	1.78	-0.29
F1-8 (R1/2)	49.77	11.28	18.63	4.14	4.58	-0.24
F1-9 (S2/5)	48.85	10.69	18.65	1.19	1.72	-0.29
F1-11 (B1/13)	49.93	10.57	18.68	1.26	3.65	-0.32

F1-10 (R2/13)	49.03	10.09	18.69	1.63	4.58	-0.20
F1-12 (N1)	50.80	11.16	18.73	0.14	4.58	-0.23
F2-11 (B1/7)	52.26	10.29	18.77	5.50	3.20	-0.50
F2-14 (R3/13)	51.27	7.66	18.78	4.48	3.33	-0.61
F2-13 (R3/18)	52.19	7.67	18.79	3.35	3.33	-0.58
F2-15 (R3/17)	50.33	7.80	19.26	3.94	3.20	-0.54
F1-13(R2/4)	50.38	11.37	19.52	5.60	1.78	-0.36
High-latitude samples:						
Kiruna_U133	67.72	20.50	9.27	1.52	2.68	0.00
Kiruna_U174	67.90	20.28	10.95	-0.21	1.78	-0.02
Kiruna_F1_U112	68.21	20.81	13.00	-1.58	1.32	-0.07
Kiruna_U160	67.24	18.93	13.55	0.87	1.12	-0.15
Kiruna_F1_U240	71.99	20.66	14.16	1.59	1.32	-0.09
Kiruna_F1_U236	68.58	20.36	14.21	-1.42	1.32	-0.13
Kiruna_U128	68.71	20.42	14.33	0.35	2.68	-0.17
Kiruna_U140	67.04	20.75	14.51	1.15	2.68	-0.17
Kiruna_U183	67.74	18.05	14.73	-1.25	1.94	-0.29
Kiruna_U180	68.19	20.89	14.98	-1.15	1.94	-0.20
Kiruna_U134	70.98	23.06	15.45	3.27	1.78	-0.24
Kiruna_U137	71.78	24.44	15.92	2.51	1.78	-0.27
Kiruna_F1_U239	71.17	20.74	16.17	3.11	3.60	-0.37
Kiruna_F1_U113	68.99	21.60	16.28	0.54	1.32	-0.34
Kiruna_F1_U241	72.81	20.59	16.50	4.07	1.32	-0.31
Kiruna_F1_U237	69.49	20.68	16.61	2.74	1.32	-0.42
Kiruna_F1_U238	70.34	20.83	16.79	2.57	1.95	-0.39
Kiruna_U131	70.31	22.04	17.10	1.05	2.16	-0.47
Kiruna_U176	67.67	16.16	17.30	4.33	1.50	-0.70
Kiruna_U130	72.53	25.87	17.33	5.26	2.68	-0.41
Kiruna_U149	66.52	21.21	17.43	3.22	1.88	-0.55
Kiruna_U182	68.85	21.83	17.45	3.06	2.68	-0.44
Kiruna_F1_U104	76.24	20.10	17.66	1.21	3.60	-0.62
Kiruna_F1_U101	73.69	20.48	17.67	4.89	3.60	-0.60
Kiruna_U177	66.87	12.61	17.68	2.56	1.94	-0.70
Kiruna_F1_U109	75.84	21.62	17.69	4.53	1.95	-0.59
Kiruna_U253	67.15	9.48	17.70	6.54	1.50	-0.69
Kiruna_U246	67.13	7.08	17.71	6.23	1.94	-0.83
Kiruna_F1_U103	75.45	20.22	17.71	4.66	1.95	-0.55
Kiruna_F1_U108	75.05	23.40	17.72	5.75	1.95	-0.56
Kiruna_U150	67.09	4.68	17.73	1.32	1.12	-0.66
Kiruna_U243	66.81	3.60	17.74	2.11	1.94	-0.68
Kiruna_U254	66.85	10.35	17.74	6.62	1.12	-0.66
Kiruna_F1_U102	74.59	20.43	17.74	4.84	1.32	-0.58
Kiruna_U226	67.00	-0.73	17.77	3.27	1.94	-0.83
Kiruna_F1_U107	74.19	23.39	18.07	6.10	1.95	-0.64
Kiruna_U184	67.13	14.53	18.09	5.06	1.94	-0.80
Kiruna_U132	73.33	27.25	18.09	5.22	1.12	-0.65
Kiruna_U129	74.06	27.88	18.15	2.48	1.88	-0.68

Kiruna_U141	73.65	27.62	18.16	6.35	2.16	-0.67
Kiruna_U178	72.62	27.89	18.20	5.25	2.16	-0.56
Kiruna_U155	66.27	10.88	18.20	4.63	1.50	-0.56
Kiruna_U125	72.26	27.54	18.25	3.52	1.94	-0.51
Kiruna_U143	72.74	28.10	18.28	3.35	2.16	-0.71
Kiruna_U173	71.90	27.69	18.31	4.67	2.16	-0.52
Kiruna_F1_U106	73.30	23.08	18.34	5.28	1.95	-0.66
Kiruna_U170	67.75	16.11	18.35	4.36	1.50	-0.69
Kiruna_U144	71.90	27.34	18.37	4.14	2.16	-0.70
Kiruna_F1_U114	69.75	22.01	18.47	5.08	1.32	-0.71
Kiruna_U153	70.31	25.17	18.52	2.57	2.16	-0.69
Kiruna_U145	69.50	24.23	18.55	3.81	1.12	-0.72
Kiruna_F1_U110	71.51	22.45	18.67	7.50	1.95	-0.66
Kiruna_U142	66.97	22.03	18.81	4.02	1.94	-0.82
Kiruna_F1_U111	70.62	22.20	18.83	6.13	1.95	-0.68

Table S7. The CFC-113 stratospheric data used in Figure 1. The ID code, latitude, longitude and altitude of each sample are also included.

Sample ID	**Latitude / ° N**	**Longitude / ° E**	**Altitude / km**	**ln [1+ δ] / ‰**	**ln [1+ uncertainty] / ‰**	**ln (y/y_T)**
Mid-latitude samples:						
F2-18 (N5)	48.47	10.29	10.00	-0.06	3.27	0.00
F1-18 (B1/9)	48.08	10.44	10.05	-2.31	2.89	-0.01
F1-17 (B1/12)	48.43	10.13	12.96	-2.22	2.89	0.01
F2-0 (R2/16)	48.16	10.15	13.61	0.09	3.70	-0.02
F1-0 (81)	48.34	10.24	13.97	3.17	1.81	0.00
F2-8 (R3/16)	53.14	10.28	14.69	2.66	2.54	-0.04
F2-17 (707)(R2/6)	48.93	9.26	15.03	-0.54	3.27	-0.03
F1-16 (R2/3)	48.21	10.79	15.58	-4.19	2.89	-0.04
F2-1 (R3/19)	48.24	9.31	16.26	-0.29	3.70	-0.18
F2-7 (N4)	53.36	8.89	16.76	-0.58	3.27	-0.18
F1-1 (B1/3)	48.29	10.58	16.85	-0.48	2.89	-0.14
F2-9 (R3/5)	53.33	11.28	17.03	2.02	3.27	-0.17
F1-15 (102)	48.44	10.17	17.57	-0.49	3.56	-0.17
F2-2 (R3/15)	49.08	8.97	17.77	0.97	3.70	-0.48
F2-3 (R3/9)	50.02	8.86	17.86	-1.43	3.70	-0.46
F1-5 (S1/14)	51.54	11.46	17.99	2.21	3.56	-0.18
F1-4 (T3/15)	50.69	10.93	18.01	-1.97	2.89	-0.23
F1-3 (S3/18)	49.83	10.46	18.02	1.94	3.56	-0.23

F2-6 (N3)	52.89	8.42	18.29	-3.70	3.70	-0.40
F2-5 (B1/18)	51.93	8.55	18.30	2.92	3.27	-0.51
F2-4 (R3/7)	50.97	8.68	18.30	0.05	3.70	-0.70
F2-16 (R3/3)	49.27	8.28	18.40	0.44	3.27	-0.49
F1-6 (R2/19)	51.76	12.02	18.50	-1.66	3.56	-0.31
F2-10 (R3/4)	52.50	11.35	18.58	-0.87	3.27	-0.51
F1-7 (B1/2)	50.75	11.63	18.60	-1.74	1.81	-0.32
F1-8 (R1/2)	49.77	11.28	18.63	-1.94	3.56	-0.28
F1-9 (S2/5)	48.85	10.69	18.65	-1.31	2.89	-0.35
F1-11 (B1/13)	49.93	10.57	18.68	-1.32	3.70	-0.38
F1-10 (R2/13)	49.03	10.09	18.69	1.66	3.56	-0.24
F1-12 (N1)	50.80	11.16	18.73	2.66	3.56	-0.28
F2-11 (B1/7)	52.26	10.29	18.77	5.41	2.54	-0.60
F2-14 (R3/13)	51.27	7.66	18.78	2.80	3.27	-0.75
F2-13 (R3/18)	52.19	7.67	18.79	3.62	3.27	-0.71
F2-15 (R3/17)	50.33	7.80	19.26	3.96	2.54	-0.66
F1-13(R2/4)	50.38	11.37	19.52	-1.80	1.81	-0.43
F1-14 (N2)	49.46	10.81	19.82	1.27	2.89	-0.49
High-latitude samples:						
Kiruna_U133	67.72	20.50	9.27	-0.28	3.44	0.00
Kiruna_U174	67.90	20.28	10.95	-0.51	1.33	-0.04
Kiruna_F1_U112	68.21	20.81	13.00	1.66	4.84	-0.08
Kiruna_U160	67.24	18.93	13.55	-2.51	2.87	-0.20
Kiruna_F1_U240	71.99	20.66	14.16	4.71	4.84	-0.10
Kiruna_F1_U236	68.58	20.36	14.21	3.75	4.84	-0.14
Kiruna_U128	68.71	20.42	14.33	2.46	3.44	-0.20
Kiruna_U140	67.04	20.75	14.51	-1.66	3.44	-0.19
Kiruna_U180	68.19	20.89	14.98	-2.66	4.93	-0.23
Kiruna_U134	70.98	23.06	15.45	-3.06	1.33	-0.30
Kiruna_F1_U239	71.17	20.74	16.17	2.33	3.62	-0.45
Kiruna_F1_U113	68.99	21.60	16.28	0.29	4.84	-0.41
Kiruna_F1_U241	72.81	20.59	16.50	6.18	4.84	-0.37
Kiruna_F1_U237	69.49	20.68	16.61	-0.16	4.84	-0.51
Kiruna_F1_U238	70.34	20.83	16.79	6.09	3.89	-0.44
Kiruna_U131	70.31	22.04	17.10	6.57	10.73	-0.59
Kiruna_U176	67.67	16.16	17.30	3.90	3.64	-0.86
Kiruna_U130	72.53	25.87	17.33	-1.71	3.44	-0.50
Kiruna_U149	66.52	21.21	17.43	7.47	2.60	-0.68
Kiruna_U182	68.85	21.83	17.45	7.75	3.44	-0.52
Kiruna_F1_U104	76.24	20.10	17.66	0.06	3.62	-0.76
Kiruna_F1_U101	73.69	20.48	17.67	4.52	3.62	-0.73
Kiruna_U177	66.87	12.61	17.68	0.79	4.93	-0.87
Kiruna_F1_U109	75.84	21.62	17.69	4.20	3.89	-0.70
Kiruna_U253	67.15	9.48	17.70	2.63	3.64	-0.85
Kiruna_F1_U103	75.45	20.22	17.71	0.50	3.89	-0.67
Kiruna_F1_U108	75.05	23.40	17.72	0.97	3.89	-0.67
Kiruna_U249	66.83	8.09	17.73	-1.09	2.87	-0.91

Kiruna_U150	67.09	4.68	17.73	3.31	2.87	-0.84
Kiruna_U243	66.81	3.60	17.74	3.09	4.93	-0.83
Kiruna_U254	66.85	10.35	17.74	2.31	2.87	-0.84
Kiruna_F1_U102	74.59	20.43	17.74	5.72	4.84	-0.71
Kiruna_U226	67.00	-0.73	17.77	5.77	4.93	-1.01
Kiruna_F1_U107	74.19	23.39	18.07	7.26	3.89	-0.79
Kiruna_U132	73.33	27.25	18.09	2.29	2.87	-0.78
Kiruna_U129	74.06	27.88	18.15	1.25	2.60	-0.82
Kiruna_U141	73.65	27.62	18.16	0.96	10.73	-0.83
Kiruna_U178	72.62	27.89	18.20	1.82	10.73	-0.66
Kiruna_U155	66.27	10.88	18.20	5.82	3.64	-0.70
Kiruna_U125	72.26	27.54	18.25	-0.41	4.93	-0.62
Kiruna_U173	71.90	27.69	18.31	4.20	10.73	-0.63
Kiruna_F1_U106	73.30	23.08	18.34	4.44	3.89	-0.80
Kiruna_U170	67.75	16.11	18.35	0.14	3.64	-0.84
Kiruna_F1_U114	69.75	22.01	18.47	4.07	4.84	-0.87
Kiruna_U139	71.11	26.13	18.47	1.78	2.60	-0.85
Kiruna_F1_U105	72.39	22.77	18.50	3.59	3.89	-0.84
Kiruna_U153	70.31	25.17	18.52	4.07	10.73	-0.85
Kiruna_U145	69.50	24.23	18.55	3.06	2.87	-0.89
Kiruna_U135	68.68	23.31	18.64	4.13	3.44	-0.91
Kiruna_F1_U110	71.51	22.45	18.67	8.32	3.89	-0.80
Kiruna_U136	67.82	22.65	18.71	7.67	2.60	-0.95
Kiruna_U142	66.97	22.03	18.81	3.37	4.93	-0.99
Kiruna_U179	69.63	23.11	18.82	-1.66	4.93	-0.70
Kiruna_F1_U111	70.62	22.20	18.83	-1.64	3.89	-0.84

Table S8. The firn air data used in Figure 3.

		CFC-11			CFC-12			CFC-113		
Sample ID	**Depth / m**	**Age / years AD**	**$\delta(^{37}Cl)$ / ‰**	**1σ uncertainty / ‰**	**Age / years AD**	**$\delta(^{37}Cl)$ / ‰**	**1σ uncertainty / ‰**	**Age / years AD**	**$\delta(^{37}Cl)$ / ‰**	**1σ uncertainty / ‰**
NEEM 2009 firn air:										
1, 14 and 15	0	2009.54	-0.997	1.71	2009.54	-0.331	2.515	2009.54	0.05	2.151
2	10.5	2009.46	0.89	1.512	2009.46	-0.591	1.687	2009.46	2.082	1.908
3	20.4	2008.96	3.026	1.847	2008.96	0.557	3.748	2008.87	-2.252	1.453
4	30.2	2007.46	-0.877	2.718	2007.71	-3.253	0.927	2007.21	0.026	4.546
5	39.23	2005.71	-1.045	2.886	2006.12	-0.185	3.192	2005.12	0.934	3.798
6	50.7	2003.37	0.608	1.293	2004.04	-1.297	1.132	2002.46	-2.72	1.512
7	60.3	1999.79	-0.224	2.765	2000.79	1.042	1.866	1998.37	-0.375	1.145
8	62.02	1998.12	-0.705	0.734	1999.29	1.645	2.326	1996.62	0.753	3.378

9	63.8	1991.46	-2.292	1.702	1992.96	0.257	2.793	1989.62	1.472	4.6
10	66.8	1977.54	-0.56	2.247	1979.29	-0.029	1.728	1975.37	2.181	1.637
11	69.4	1965.29	-0.822	1.815	1967.21	0.914	1.915	1962.96	6.647	2.900
12	71.9				1955.62	5.342	3.197			
13	73.6	1946.37	7.814	2.032						
Fletcher Promontory firn air:										
12 and 25	0	2011.96	1.626	4.837	2011.96	-0.009	4.99	2011.96	1.319	5.58
28	3.035	2011.88	-2.093	3.219	2011.88	2.693	2.983	2011.88	1.037	4.459
22	6.905	2011.71	3.681	3.458	2011.71	3.162	2.227	2011.63	-2.588	4.78
18	10.985	2011.29	0.783	2.923	2011.38	1.378	1.472	2011.21	2.393	4.582
30	18.58	2010.04	0.673	4.932	2010.29	-1.7	3.048	2009.71	-1.747	3.602
14	21.925	2009.38	1.153	3.282	2009.63	-0.466	3.555	2008.96	0.05	5.464
20	26.57	2008.29	-0.334	2.923	2008.79	-2.109	1.472	2007.79	-0.592	4.582
8	38.06	2005.71	2.607	3.713	2006.46	1.919	6.138	2004.71	4.116	6.688
16	44.7	2004.04	-0.821	0.365	2004.96	-1.491	2.129	2002.88	2.509	3.008
24	50.19	2002.63	0.172	0.365	2003.71	-0.629	2.129	2001.21	-3.63	3.008
13	56.245	2000.88	1.364	2.267	2002.13	-3.699	4.53	1999.13	-1.153	2.201
E	59.23	1999.88	-1.76	0.365	2001.21	-4.736	2.129	1998.04	-2.636	3.008
G	62.17	1998.79	1.022	4.837	2000.21	-4.444	3.351	1996.79	0.845	3.827
K	65.18	1997.38	-4.301	4.932	1999.04	-4.646	3.048	1995.29	-2.958	3.602
D	68.15	1995.63	3.879	4.415	1997.38	2.674	3.916	1993.38	-0.142	6.721
J	70.15	1992.21	-1.965	3.933	1994.04	0.278	2.816	1989.88	5.064	6.456
C	71.98	1987.63	0.318	2.923	1989.46	-0.827	1.472	1985.21	-0.642	4.582
B	74.33	1982.38	-0.714	4.932	1984.29	-7.528	3.048	1979.88	-5.107	3.602
23	76.13	1978.04	0.599	4.715	1979.96	-3.242	4.085	1975.63	3.089	6.391
27	80.57	1968.13	6.576	1.545	1970.04	2.043	4.910	1965.63	8.317	5.412

Table S9. The Cape Grim data used in Figure 3.

CFC-11				CFC-12				CFC-113			
Sample ID	**Age / years AD**	**δ(^{37}Cl) / ‰**	**1σ uncertainty / ‰**	**Sample ID**	**Age / years AD**	**δ(^{37}Cl) / ‰**	**1σ uncertainty / ‰**	**Sample ID**	**Age / years AD**	**δ(^{37}Cl) / ‰**	**1σ uncertainty / ‰**
SIL-K1514	2010.94	2.744	1.954	K1511	2012.93	0.244	1.749	SIL-K1524	2011.47	3.951	2.950
SIL-K1517	2009.57	2.029	1.770	K1509	2012.66	0.437	1.749	SIL-K1523	2011.40	4.219	3.332
SIL-K1525	2009.18	-1.046	1.823	K1508	2012.32	1.059	1.749	SIL-1522	2011.30	-0.823	3.522
S320-U105	1995.45	1.774	2.793	SIL-K1524	2011.47	0.842	2.552	SIL-K1516	2011.21	6.759	3.332
S320-U32	1993.43	-0.531	2.793	SIL-K1523	2011.40	0.443	2.532	SIL-K1515	2011.11	-0.706	3.571
S320-U19	1991.20	0.818	3.469	SIL-1522	2011.30	0.015	2.228	SIL-K1514	2010.94	3.825	3.869
S320-U06	1989.32	-0.890	2.793	SIL-K1516	2011.21	-1.261	2.310	SIL-K1517	2009.57	-0.273	2.930
S320-U05	1987.41	-2.161	2.793	SIL-K1515	2011.11	-2.708	3.069	SIL-K1525	2009.18	0.204	3.386
S320-U13	1985.60	-1.316	2.793	SIL-K1514	2010.94	-1.280	2.370	S320-U105	1995.45	1.905	3.671
S320-U09	1983.58	1.016	2.783	SIL-K1517	2009.57	-1.883	1.074	S320-U32	1993.43	1.437	3.671

S320-U12	1980.65	3.084	2.793
S320-U29	1978.52	1.670	2.234

SIL-K1525	2009.18	-1.209	4.592
SIL-1146B	2008.45	2.675	3.467
SIL-1141	2007.51	2.390	2.684
SIL-1175	2006.64	0.382	3.467
1148	2005.76	1.233	2.480
SIL-1127	2005.26	1.259	3.784
SIL-1155	2005.11	1.253	1.749
1128	2004.96	-0.641	2.480
SIL-1138	2004.67	-1.641	3.383
1135	2004.50	-0.144	2.480
1146	2003.39	-1.068	2.882
SIL-1144	2002.47	-0.302	3.467
1295	2001.95	-2.240	2.480
1276	2001.32	0.077	2.720
SIL-1129	2000.75	-0.953	3.467
S320-U203	2000.15	0.081	2.480
S320-U216	1999.47	1.113	3.081
#213	1998.29	-1.720	1.969
UEA97	1997.02	-2.622	4.709
S320-U105	1995.45	5.955	1.719
S320-111	1994.12	3.541	3.553
S320-U33	1993.49	-2.149	1.969
S320-U32	1993.43	1.434	1.719
S320-U19	1991.20	0.472	1.564
S320-U06	1989.32	3.962	1.719
S320-U05	1987.41	-1.453	3.341
S320-U13	1985.60	6.704	1.719
S320-U09	1983.58	1.211	2.235
S320-U12	1980.65	2.103	1.719
S320-U17	1979.10	-2.604	1.969
S320-U29	1978.52	3.103	1.863
S320-U23	1978.32	-2.208	1.969

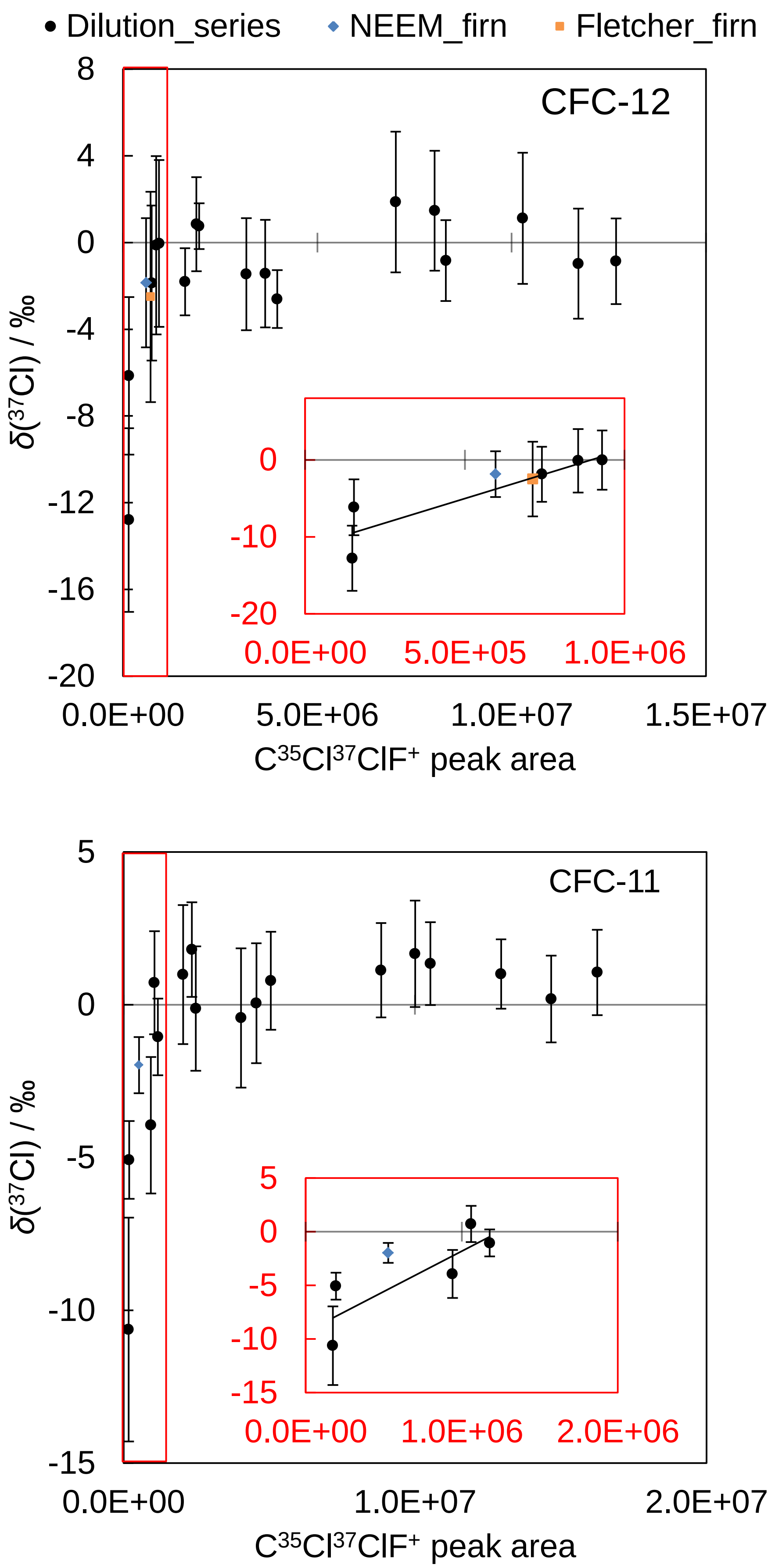
S320-U19	1991.20	0.905	4.809
S320-U06	1989.32	0.304	3.671
S320-U05	1987.41	6.030	3.671
S320-U13	1985.60	3.088	3.671
S320-U09	1983.58	0.909	2.222
S320-U12	1980.65	1.578	3.671
S320-U29	1978.52	2.455	4.356

Table S10. The data used in Figure S1. The sample IDs refer to the diluted air samples detailed in Table S1.

Sample ID	CFC-11			CFC-12			CFC-113		
	$C^{35}Cl^{37}ClF^{+}$ peak area	$\delta(^{37}Cl)$ / ‰	1σ uncertainty / ‰	$C^{35}Cl^{37}ClF^{+}$ peak area	$\delta(^{37}Cl)$ / ‰	1σ uncertainty / ‰	$C^{35}Cl^{37}ClF^{+}$ peak area	$\delta(^{37}Cl)$ / ‰	1σ uncertainty / ‰
SX-0706077	16253338.5	1.05782	1.39632	12686959.5	-0.8629	1.97051	17441913	-2.8783	2.11851
	14672027	0.1872	1.42331	11717824	-0.9739	2.53866	17202522	-0.8435	2.19575
	12951190	1.00753	1.13404	10285792	1.1173	3.02452	12920942.5	2.47961	2.25934

K1579	10527296	1.34422	1.35948	8308076	-0.834	1.86769	12179131.67	0.88014	4.60998
	10001930	1.6686	1.74426	8019910	1.46511	2.76813	11666651	1.24218	3.55465
	8836375.5	1.12902	1.5406	7017476	1.86524	3.24583	8797107	1.01759	4.88259
K1578	5056587.5	0.78529	1.60417	3969374.5	-2.6067	1.33767	5413831	1.3018	1.66084
	4556389	0.04723	1.96261	3661516	-1.4332	2.48087	5326372	-3.2186	2.08051
	4032314.5	-0.4322	2.2791	3174294	-1.4598	2.58697	3958446	1.58713	1.59149
K1583	2478613	-0.1251	2.03851	1959719	0.75495	1.05459	2847635	1.21639	5.15792
	2345094.5	1.80598	1.54955	1889938.5	0.8507	2.16988	2716815.5	3.23799	2.0351
	2041025	0.98848	2.2754	1596358	-1.8126	1.54831	2000064.5	0.69131	1.74905
K1569	1178474.5	-1.0532	1.25676	929655	-0.0425	3.85089	1262753	-3.0363	2.09579
	1059251	0.71974	1.68739	854573	-0.1272	4.11566	1243590	2.7468	2.56427
	940497	-3.9446	2.23401	740710.5	-1.8695	3.5773	923461	1.46313	2.34042
K1575	193281.5	-5.0797	1.26942	152500.5	-6.1505	3.63347	220193	-1.9928	4.39585
	173429	-10.633	3.6622	147147	-12.798	4.23373	207857.5	-13.201	3.54046

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.


Dilution_series
NEEM_firn
Fletcher_firn
CFC-12
δ(37Cl) / ‰
8
4
0
-4
-8
-12
-16
-20
0
-10
-20
0.0E+00
5.0E+05
1.0E+06
0.0E+00
5.0E+06
1.0E+07
1.5E+07
C35Cl37ClF+ peak area
CFC-11
δ(37Cl) / ‰
5
0
-5
-10
-15
5
0
-5
-10
-15
0.0E+00
1.0E+06
2.0E+06
0.0E+00
1.0E+07
2.0E+07
C35Cl37ClF+ peak area

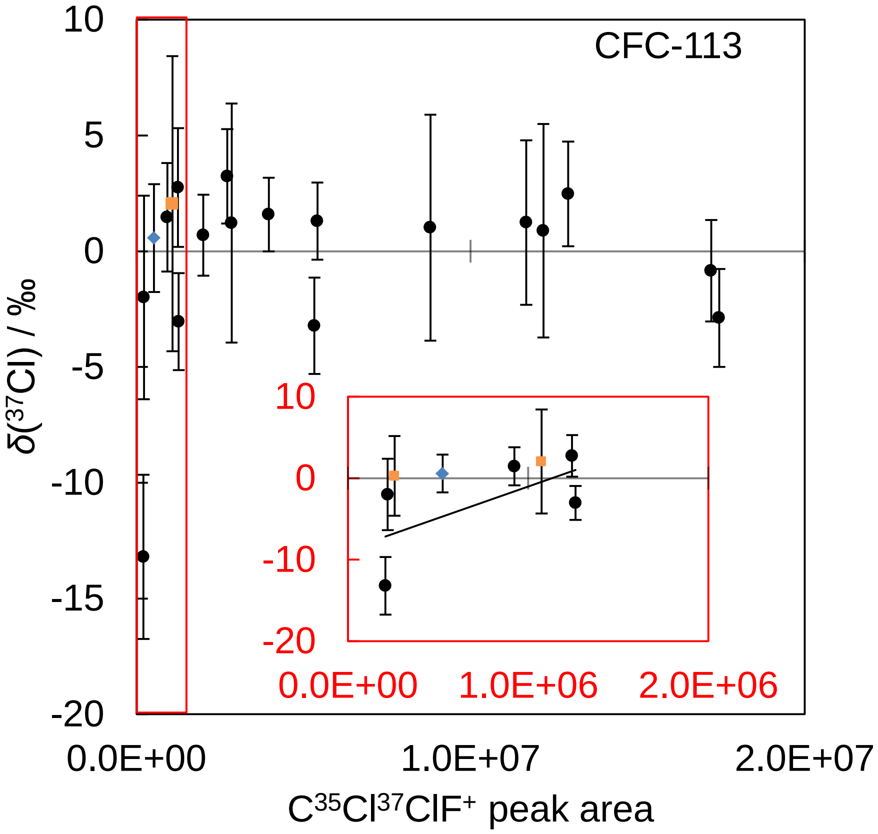
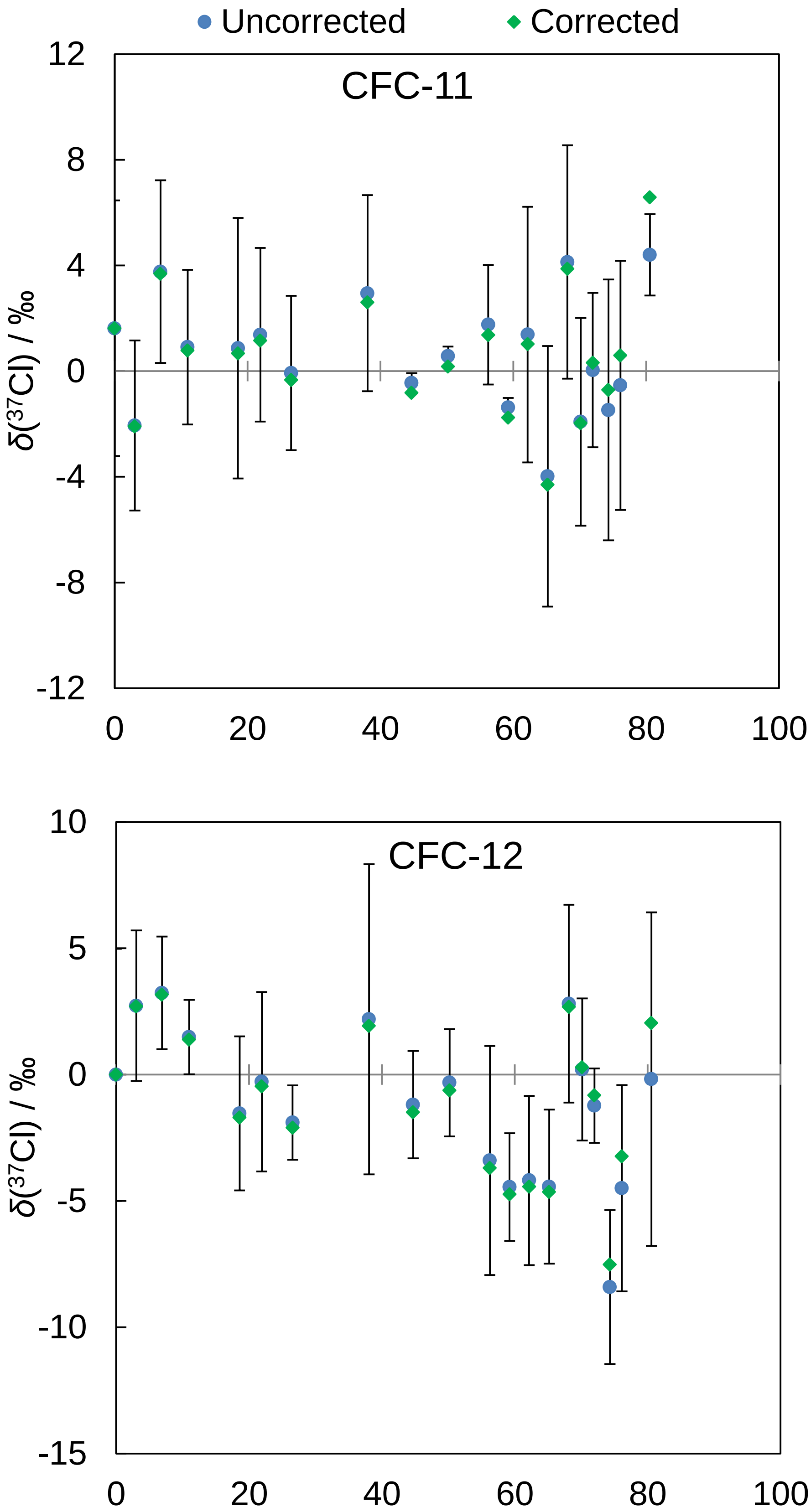


Figure S2. Measured $\delta(^{37}Cl)$ values (blue circles, with 1σ standard deviation error bars), and the same after correcting for gravitational and diffusional fractionations (green diamonds, error bars not included), as a function of firn depth at Fletcher Promontory.



Uncorrected
Corrected
CFC-11
CFC-12
δ(37Cl) / ‰
12
8
4
0
-4
-8
-12
10
5
-5
-10
-15
0
20
40
60
80
100

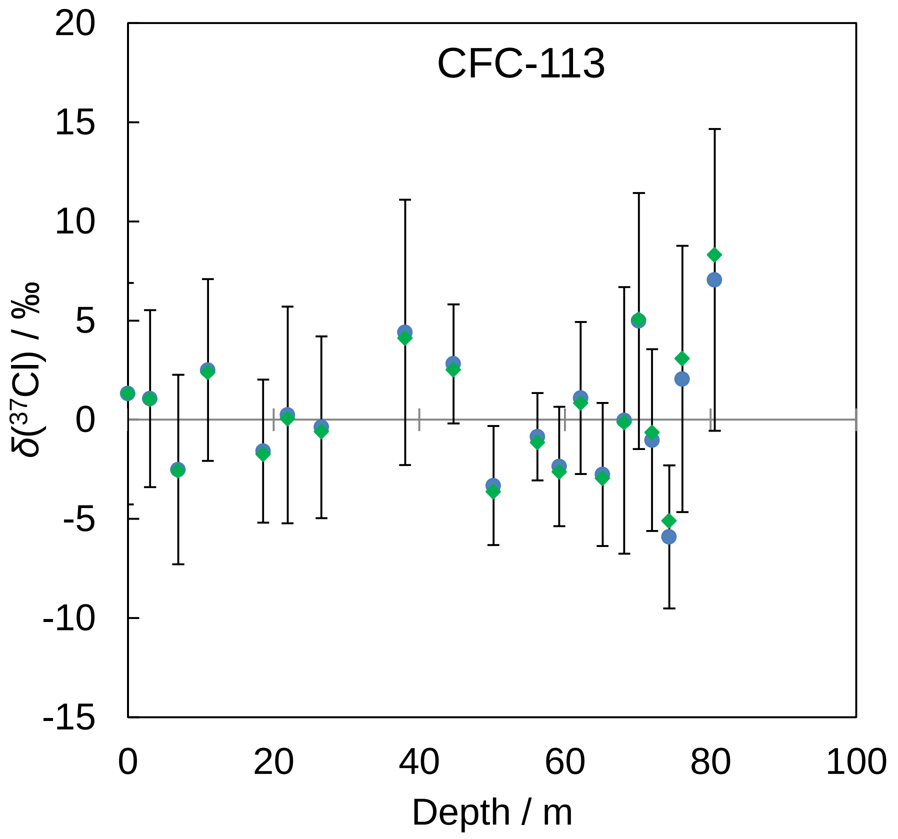
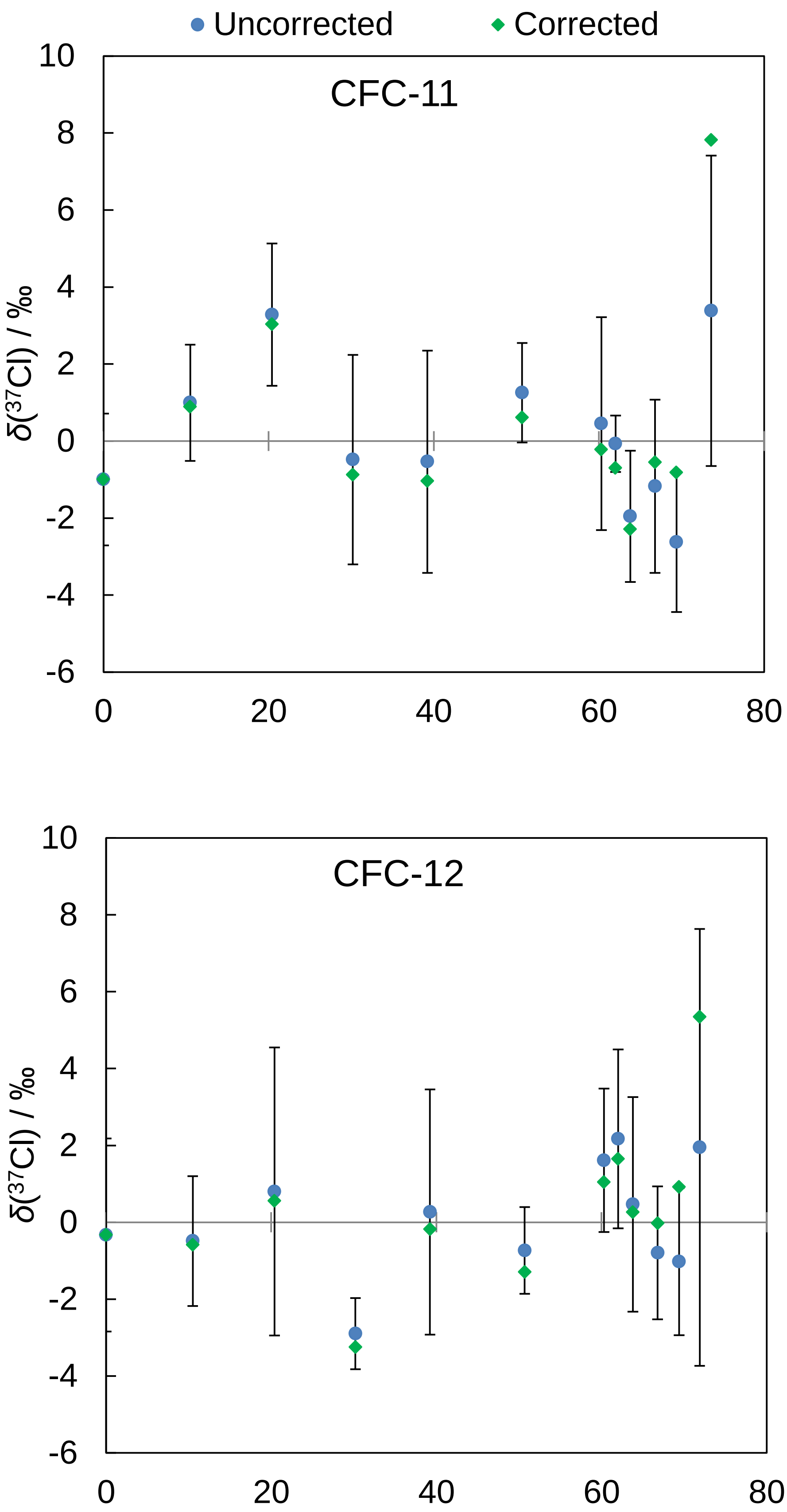
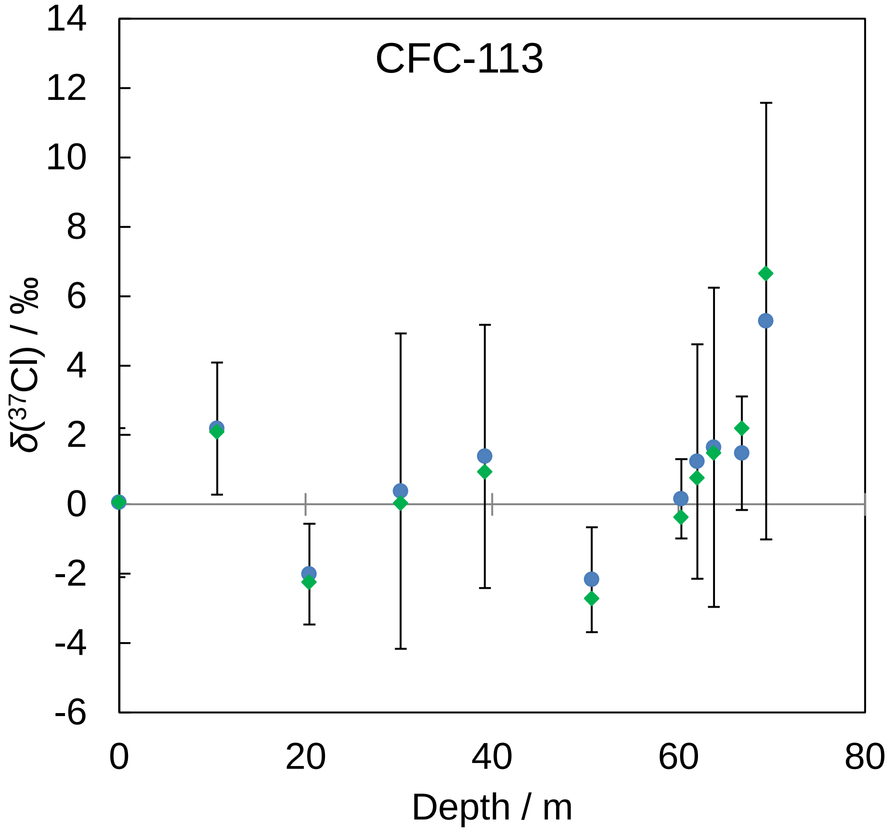


Figure S3. Measured $\delta(^{37}\mathrm{Cl})$ values (blue circles, with 1σ standard deviation error bars), and the same after correcting for gravitational and diffusional fractionations (green diamonds, error bars not included), as a function of firn depth at NEEM.


Uncorrected
Corrected
CFC-11
δ(37Cl) / ‰
10
8
6
4
2
0
-2
-4
-6
0
20
40
60
80
CFC-12
δ(37Cl) / ‰
10
8
6
4
2
0
-2
-4
-6
0
20
40
60
80


CFC-113
14
12
10
8
6
4
2
0
-2
-4
-6
δ(³⁷Cl) / ‰
0
20
40
60
80
Depth / m