

Supporting Online Material

Methods Summary

We analyzed 390 ice samples from 175 depths, including data from 36 depths from a previous study (*S1*). For most depths we measured replicate samples within a depth range of 10 cm and we report the mean depths of the replicates (Table S1). Replicate measurements were usually done on different days and averages were used for the data plots. Single measurements were done for two depths due to limited sample size. The standard deviation of the mean for 2~5 replicate ice samples from the same depth averaged 1.5 ppm except for 4 depths (See Table S1). Data for these depths were rejected because the standard deviations of the means were greater than 12 ppm, we believe because of poor quality of the samples. The data are archived at National Snow and Ice Data Center (<http://nsidc.org/>) and also in Table S1. Each ice sample weighed about 13 g after trimming >1 cm from all surfaces. The detailed methods used will be reported elsewhere (*S2*). Briefly, samples were placed in a double-walled stainless steel vacuum chamber at -35°C, cooled using cold ethanol circulation between the walls, and then crushed with steel pins, affixed to a pneumatically actuated linear motion feedthrough. Air liberated from the ice was dried in a cold stainless steel coil at -85°C and then trapped in ~6 cm³ stainless steel sample tubes at -262°C. After warming the trapped air to room temperature, and expanding to a 5 cm³ stainless steel sample loop, the CO₂ mixing ratio was measured with an Agilent 6890N Gas Chromatograph (GC) with flame ionization detector, with nickel catalyst conversion of CO₂ to CH₄ prior to measurement. The pressure in the loop was measured with an MKS Baratron capacitance manometer (accuracy better than 0.15%). CO₂ peak area was divided by the sample pressure and the results quantified with similar measurements of standard air. Daily calibration curves used several measurements of standard air with 197.54 ppm CO₂ (WMO scale). Each air sample was measured two times. Daily corrections for the dry extraction and GC analysis were done using several standard airs (197.54 ppm) that were introduced over the ice samples and transported to sample tubes mimicking the procedure of the air samples from ice. To test the linearity between CO₂ peak area and CO₂ mixing ratio, we analyzed a different standard air with 291.15 ppm CO₂. The difference between assigned concentration and measurements was 0.2-1 ppm on average over the course of two years.

CH₄ concentration was measured for 36 ice samples to better constrain the time age of the abrupt warming in Greenland and CO₂. We used high precision wet-extraction methods (*S3*). One of the CH₄ results from the depth of 2099.31-2099.42 m was rejected due to poor quality of the ice, based on CO₂ results from two ice pieces from the same depth that differed by 53.7 ppm.

We used the Byrd ice core ages of ref. *S4* after slight adjustment, which was needed for consistency with the synchronous rapid rise of CH₄ relative to abrupt warming at Dangaard-Oeschger (DO) events 4, 8, 12, 14, 17, 19, 20 and 21 (*S3*, *S5*, *S6*), consistent with our previous approach (*S1*). This permits precise timing of Byrd CO₂ relative to abrupt warming in Greenland via Byrd CH₄ as shown in Fig. 2. We determined Byrd gas-age tie points on a Greenland (GISP2) ice core time scale (*S4*) by matching of rapid rise of Byrd CH₄ to the abrupt Greenland warming events. The Byrd gas age difference

between the new and previous (*S4*) ages was linearly interpolated for the ages between the DO events. Byrd CO_2 ages older than 88 ka are determined by extrapolation of the depth-age scale for 82~88 ka. The Byrd $\delta^{18}\text{O}_{\text{ice}}$ ages are also adjusted to keep the same gas-ice age difference used in ref. *S4*.

We found slight age discrepancy between the Greenland $\delta^{18}\text{O}_{\text{ice}}$ ages and GISP2 CH_4 in ref. *S4* at the abrupt warming in the DO events. This is due to inaccuracy in gas-ice age difference model used for GISP2 ice core (*S4*). To correct for this we synchronized the GISP2 CH_4 ages to the abrupt warming at DO events 4, 8, 12, 14, 17, 19, 20 and 21.

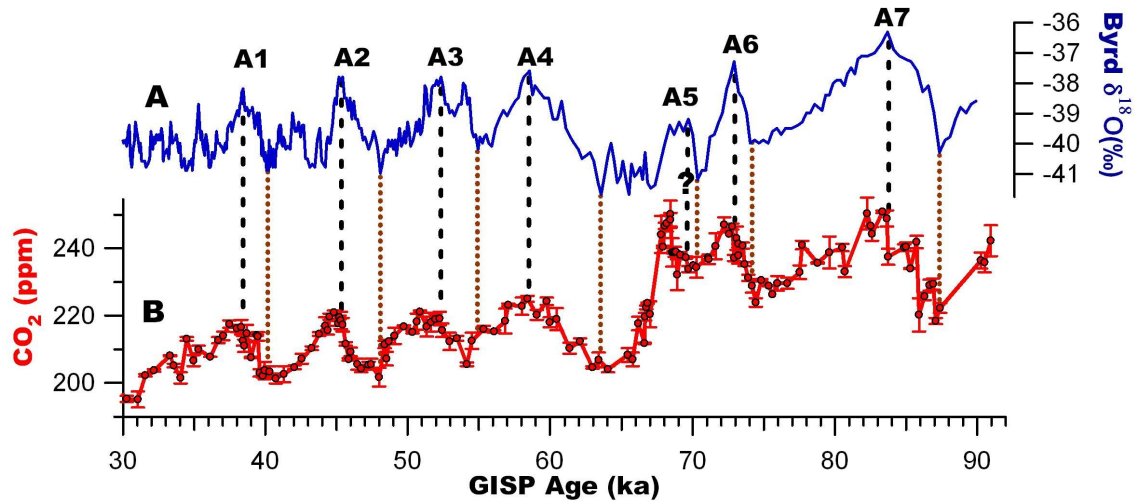


Figure S1. Timing of atmospheric CO_2 and Antarctic temperature. (A) Byrd Station, Antarctica temperature proxy, $\delta^{18}\text{O}_{\text{ice}}$ (*S4*); A1~A6 are Antarctic warming events (*S4*). (B) Atmospheric CO_2 from Byrd ice core (*this study*, *S1*). Black and brown dotted lines indicate the timing of Byrd temperature maxima and minima, respectively. The uncertainty in gas age – ice age difference is conservatively ~125 years (*S4*). The Byrd temperature maximum at A5 seems to occur exceptionally earlier than the abrupt warming in Greenland at Dansgaard-Oeschger (D-O) event 19 (or CO_2 local maximum; see Fig. 1).

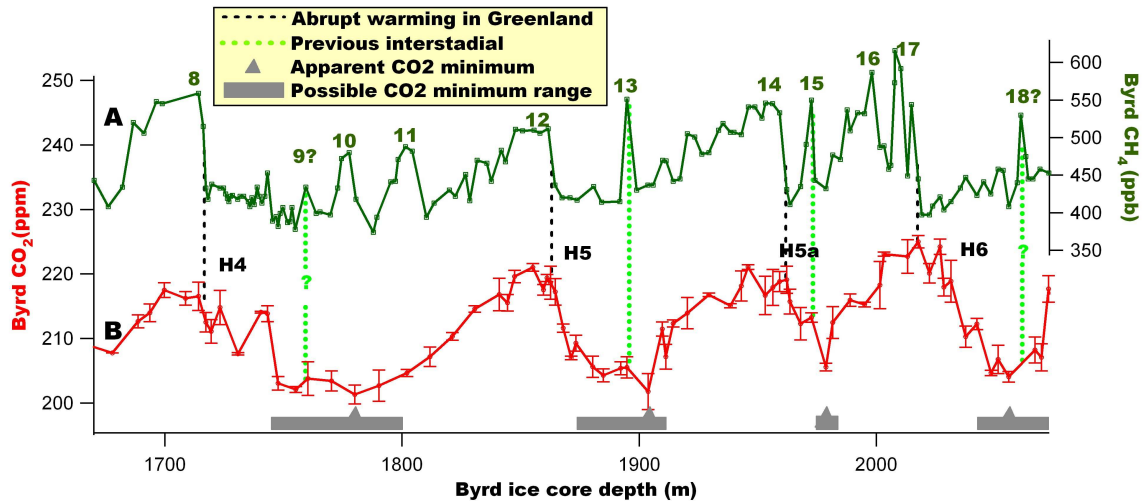


Figure S2. Timing of the CO₂ rise and abrupt warming in Greenland. (A) and (B) are CH₄ and CO₂ from Byrd ice core, respectively on the Byrd ice core depth domain. The green numbers are Dansgaard-Oeschger (DO) events. Black and green dotted lines indicate abrupt warming in Greenland associated with CO₂ maxima and the next previous interstadials, respectively. The timing of the abrupt warming in Greenland is defined by rapid increase of CH₄ because the CH₄ rise and abrupt warming are essentially synchronous (S3, S5, S6). Gray triangles are CO₂ minima with age uncertainties given by horizontal gray bars. Relative ages of Heinrich events (H4~H6) are constrained between two D-O warming events (black and green dotted lines).

Table S1. The last glacial atmospheric CO₂ from the Byrd, Antarctic ice core.

mean depth (m)	Blunier-01 age [†] (ka BP)	Ahn-08age [‡] (ka BP)	mean CO ₂ * (ppm)	#of replicates	uncertainty** (ppm)
1315.91	19.460	19.286	194.36	2	0.97
1332.34	20.061	19.887	191.14	2	0.19
1334.20	20.152	19.978	192.54	2	0.09
1346.28	20.578	20.404	204.27	2	0.48
1353.02	20.759	20.585	195.37	2	0.02
1363.17	21.065	20.891	197.12	2	1.04
1381.14	21.731	21.557	195.81	2	1.66
1401.95	22.399	22.225	199.75	3	4.49
1410.30	22.729	22.555	194.62	2	0.31
1420.27	23.530	23.356	195.97	2	1.88
1430.78	24.824	24.650	194.74	2	1.94
1441.45	26.002	25.828	189.76	2	1.30
1460.20	26.711	26.537	192.21	2	1.28
1470.77	27.148	26.974	184.40	2	1.42
1480.48	27.619	27.445	188.07	2	1.48
1490.87	27.989	27.815	201.96	2	0.46
1496.52	28.135	27.961	204.98	2	1.71
1503.54	28.395	28.221	205.91	3	2.43
1512.46	28.660	28.486	207.48	2	1.73
1523.46	29.147	28.973	205.54	2	0.40
1533.76	29.568	29.396	201.49	2	1.84
1543.63	30.013	29.843	197.51	2	3.18
1552.76	30.412	30.245	195.36	2	0.89
1573.34	31.216	31.053	195.09	3	2.37
1581.93	31.738	31.577	202.29	2	0.38
1594.06	32.328	32.170	203.67	2	0.40
1615.15	33.450	33.297	208.11	2	0.11
1620.38	33.692	33.541	205.25	2	0.53
1631.11	34.183	34.033	201.53	2	1.67
1640.90	34.630	34.484	213.08	2	0.47
1650.56	35.097	34.953	206.62	2	1.72
1658.96	35.428	35.286	209.93	2	1.10
1677.79	36.249	36.111	207.76	2	0.00
1688.63	36.840	36.704	212.63	2	0.99
1693.68	37.167	37.033	213.98	2	1.37
1699.73	37.621	37.488	217.48	2	1.16
1708.70	38.122	37.992	216.21	2	1.03
1714.20	38.428	38.298	216.52	2	2.21
1717.20	38.545	38.415	212.50	2	1.51
1719.47	38.655	38.520	211.09	2	1.83
1723.22	38.850	38.708	214.78	2	2.64
1730.78	39.163	39.006	207.63	2	0.18
1740.51	39.539	39.364	214.06	2	0.14
1743.27	39.651	39.470	213.84	2	1.23
1747.69	39.811	39.621	203.03	2	1.03

1755.15	40.038	39.834	202.11	2	0.45
1760.29	40.172	39.958	203.78	2	2.59
1770.24	40.544	40.311	203.40	2	1.56
1779.99	40.966	40.714	201.30	2	1.46
1790.29	41.585	41.313	202.69	2	2.43
1802.03	42.320	42.025	204.64	2	0.56
1811.74	42.851	42.537	207.18	2	1.53
1821.19	43.591	43.259	210.31	2	0.60
1830.63	44.137	43.786	214.57	2	0.51
1840.93	44.598	44.228	216.83	3	2.50
1844.41	44.760	44.383	215.54	2	1.26
1847.46	44.899	44.516	219.62	2	0.94
1855.09	45.229	44.831	221.00	2	0.60
1859.57	45.526	45.120	217.56	2	0.82
1861.17	45.633	45.223	219.39	2	0.53
1862.59	45.725	45.313	218.62	2	2.56
1864.56	45.852	45.436	217.23	2	2.04
1867.90	46.075	45.654	211.58	2	0.64
1871.26	46.298	45.872	206.99	2	0.29
1873.26	46.431	46.002	209.25	2	1.24
1880.36	46.889	46.448	205.61	2	1.63
1884.88	47.187	46.740	204.28	2	1.02
1892.21	47.687	47.228	205.36	2	1.00
1894.80	47.865	47.402	205.51	2	1.63
1903.72	48.450	47.973	201.79	2	2.79
1909.75	48.874	48.388	211.47	4	1.09
1911.29	48.984	48.495	207.15	4	1.93
1914.31	49.191	48.697	212.35	2	0.57
1920.25	49.596	49.092	213.91	4	2.43
1929.40	50.230	49.712	216.76	2	0.28
1938.50	50.857	50.325	215.07	2	0.30
1943.09	51.175	50.636	218.12	5	2.35
1945.98	51.394	50.850	221.08	3	0.35
1953.17	51.894	51.339	216.69	4	2.96
1956.34	52.193	51.633	217.93	2	2.81
1959.23	52.505	51.941	218.83	2	1.55
1962.18	52.812	52.259	219.08	4	2.10
1963.62	52.963	52.423	215.70	2	1.94
1968.07	53.422	52.923	212.28	2	2.52
1972.66	53.926	53.470	213.25	2	0.74
1978.74	54.577	54.177	205.57	2	0.58
1981.61	54.859	54.486	212.48	4	2.46
1988.98	55.644	55.339	215.94	2	0.96
1995.01	56.317	56.068	215.25	2	0.38
2001.46	57.022	56.833	218.27	2	3.65
2003.23	57.222	57.049	223.09	2	0.30
2013.21	58.096	58.016	222.69	3	2.59
2017.71	58.467	58.421	224.99	2	0.97
2022.42	59.125	59.072	220.11	2	1.49

2026.90	59.806	59.746	224.21	3	1.18
2028.47	60.039	59.976	217.96	2	1.39
2031.50	60.526	60.459	218.85	2	3.26
2037.68	61.451	61.374	210.28	2	1.65
2042.43	62.186	62.102	212.26	2	0.85
2048.32	63.079	62.986	204.65	2	0.39
2051.40	63.526	63.429	206.76	2	2.20
2055.90	64.152	64.048	204.06	2	0.84
2066.85	65.565	65.444	208.22	2	2.01
2069.64	65.938	65.813	207.08	2	2.09
2072.65	66.333	66.204	217.67	2	2.07
2075.59	66.779	66.644	211.79	2	0.25
2075.75	66.818	66.683	219.64	3	1.17
2076.02	66.890	66.755	222.40	2	0.47
2076.43	66.997	66.861	223.63	2	0.27
2077.02	67.151	67.014	220.43	2	3.79
2080.12	67.959	67.818	244.03	2	5.52
2080.61	68.086	67.944	240.28	2	0.28
2081.10	68.213	68.071	246.47	2	0.93
2081.59	68.340	68.197	247.22	2	2.42
2082.54	68.582	68.435	249.96	3	3.97
2082.64	68.608	68.460	248.32	2	2.08
2083.09	68.721	68.571	238.70	4	4.19
2083.54	68.837	68.685	238.61	2	0.33
2083.82	68.908	68.755	238.78	2	1.42
2084.14	68.989	68.834	238.84	2	0.02
2084.52	69.086	68.929	231.99	3	4.59
2085.44	69.314	69.149	237.98	2	0.97
2087.02	69.706	69.527	237.26	3	0.40
2087.75	69.886	69.700	233.74	2	0.93
2089.24	70.246	70.048	234.85	2	0.19
2090.16	70.469	70.262	234.35	2	3.03
2093.50	71.337	71.101	237.17	2	0.49
2093.71	71.395	71.158	236.62	3	1.43
2095.46	71.875	71.622	240.58	2	3.79
2097.91	72.515	72.240	246.81	3	2.23
2099.29	72.885	72.598	244.19	1	N/A
2100.05	73.073	72.783	246.30	2	0.85
2100.69	73.230	72.937	236.93	2	0.88
2101.27	73.369	73.079	242.80	2	3.41
2101.80	73.492	73.209	241.26	2	0.14
2101.97	73.531	73.251	237.79	4	2.31
2103.15	73.805	73.542	240.63	3	0.85
2103.60	73.909	73.653	235.11	2	0.58
2104.68	74.184	73.944	231.11	2	0.89
2105.52	74.410	74.182	228.82	2	2.08
2106.32	74.656	74.440	223.79	2	1.22
2107.63	75.055	74.858	230.49	2	0.28
2109.17	75.518	75.343	228.85	2	0.25

2110.06	75.783	75.621	226.25	1	N/A
2111.20	76.120	75.975	229.45	2	2.14
2113.37	76.765	76.651	229.56	2	1.56
2116.08	77.586	77.513	232.82	3	1.97
2116.73	77.785	77.721	240.83	3	1.24
2120.16	78.809	78.795	235.51	2	0.11
2122.78	79.604	79.628	238.65	2	4.76
2125.62	80.449	80.515	240.08	3	1.03
2126.13	80.635	80.708	233.00	3	1.69
2130.20	82.116	82.248	250.22	2	4.72
2130.67	82.399	82.539	246.47	2	0.04
2130.78	82.466	82.607	244.08	2	2.06
2131.99	83.195	83.354	250.70	2	0.33
2132.50	83.503	83.669	248.75	2	2.37
2132.66	83.600	83.766	237.44	2	2.38
2134.46	84.687	84.855	240.19	2	1.00
2134.70	84.828	84.996	240.36	2	1.19
2135.22	85.133	85.301	233.84	2	0.20
2135.97	85.572	85.740	241.73	2	1.76
2136.25	85.734	85.902	220.23	2	5.01
2136.93	86.127	86.295	225.72	2	1.15
2137.57	86.498	86.666	228.99	3	1.73
2138.02	86.764	86.932	229.26	2	1.58
2138.32	86.942	87.110	218.37	2	0.94
2138.79	87.221	87.389	222.25	2	1.43
2143.57	90.075	90.266	236.19	5	2.31
2144.02	90.342	90.534	235.65	2	2.86
2144.72	90.759	90.953	242.07	3	4.54

[†]Depth-age scale from ref. S4. BP = Before 1950

[‡]Depth-age scale for this study

*CO₂ data of the depths of 1894.8 ~ 2055.9 m are from ref. S1.

**The uncertainty is estimated from the standard deviation of the mean for 2~5 ice samples

References

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