Auxiliary Material: The response of atmospheric nitrous oxide to climate variations during the last glacial period

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1. Consistency of the NGRIP N_2O record

The North Greenland Ice Core Project (NGRIP) nitrous oxide (N_2O) record presented in this study includes earlier published measurements from analyses of more than a decade. In order to ensure consistency throughout the whole NGRIP N_2O record, remeasurements in earlier analyzed intervals are performed. These remeasurements over Termination 1, as well as the Dansgaard/Oeschger (DO) events 9 to 12 and 15 to 17 are shown in Figure A1. Outside these intervals, the NGRIP record consists of new measurements only (analyzed in the years 2010, 2011, and 2012).

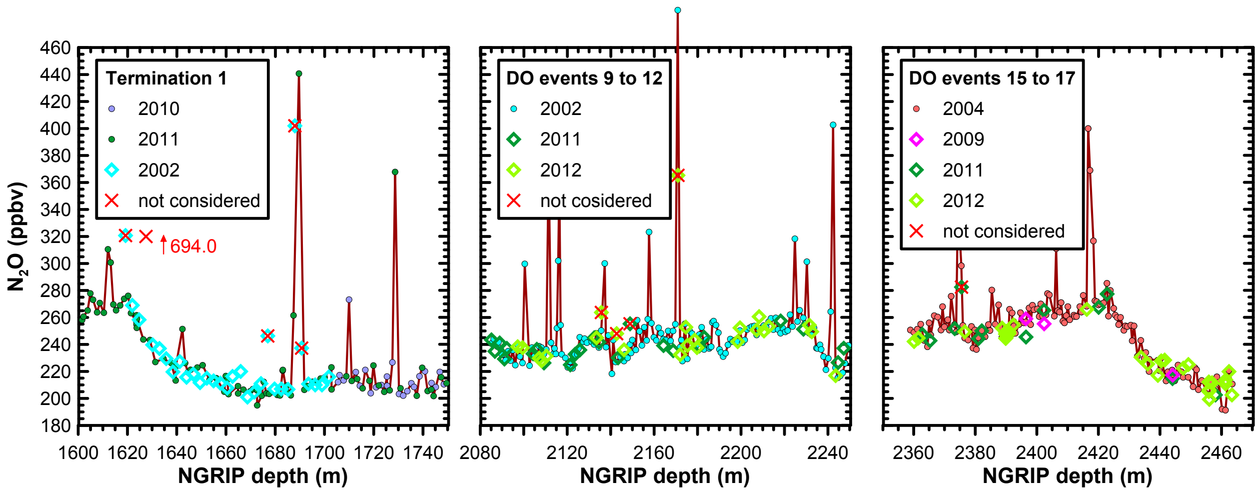

Figure A1: Remeasurements along the NGRIP ice core. Previous measurements from the years 2002 and 2004 over Termination 1 and the DO events 15 to 17 are from Schilt et al. [2010b], previous measurements from the year 2002 over the DO events 9 to 12 are from Flückiger et al. [2004]. Large diamonds indicate the measurements from the lower resolved record, which are then compared with the interpolated values of the higher resolved record (at the depths of the lower resolved record) in order to calculate differences. See Table A1 for a statistics of the results.

Table A1 summarizes the medians including 95 % confidence intervals of the differences between new and previous measurements (note that the median is less sensitive to potential outliers than the average). Overall, 10 values are excluded from the analysis, as they are clearly affected by

Table A1: Statistics of the remeasurements along the NGRIP ice core. The medians of the differences between new and previous measurements are statistically indistinguishable from zero for all intervals, indicating a completely consistent NGRIP N_2O record.

Interval	Median of differences (ppbv)	95 % confidence interval (ppbv)	n	First analysis	Second analysis
Termination 1	1.5	[-4.1; 4.1]	26	2002	2011
DO events 9 to 12	0.4	[-2.3; 3.9]	43	2002	2011/2012
DO events 15 to 17	-1.8	[-4.4; 0.1]	44	2004	2011/2012[a]

[a] Including three measurements from the year 2009.

artifacts (see Figure A1). For all intervals, the medians of the differences between new and previous measurements are statistically indistinguishable from zero, i.e. the whole NGRIP record is consistent. However, in order to be consistent with N_2O records obtained along other ice cores, an offset correction of +10 ppbv is applied to the complete NGRIP record, in line with previous studies from the same lab. More details about the offset correction, which has also been applied to the complete Talos Dome and EPICA Dronning Maud Land (EDML) records, as well as to the EPICA Dome C (EDC) record older than 40 kyr BP, are presented in Spahni et al. [2005], Schilt et al. [2010b], and Schilt et al. [2010a]. As an important consequence, we also need to increase by +10 ppbv the NGRIP measurements performed in the year 2002 over Termination 1 [Schilt et al., 2010b] and over the DO events 9 to 12 [Flückiger et al., 2004], which have previously been published without the offset correction. This stresses the importance of our extensive reanalysis campaign along the NGRIP ice core.

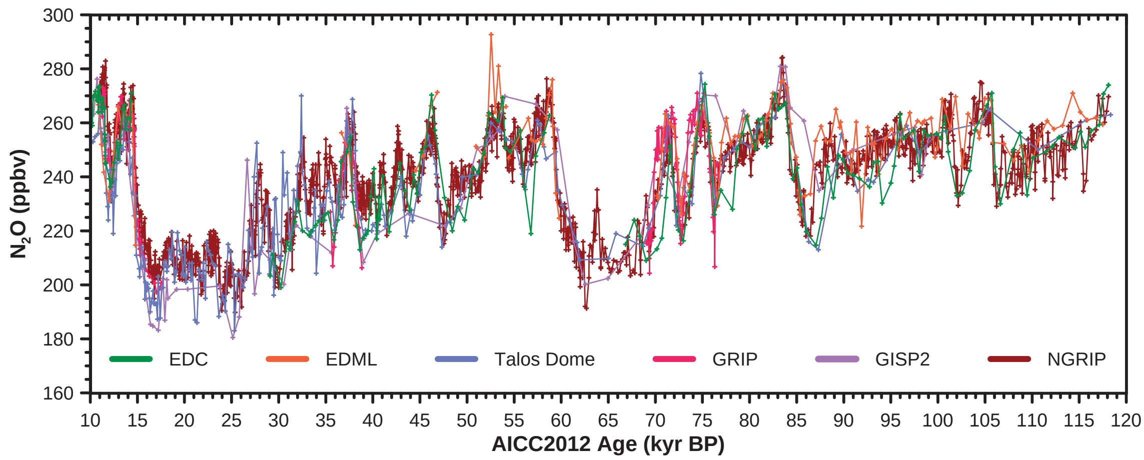

Figure A2: Available N_2O records from different ice cores (offset corrections applied). Beside the NGRIP record [Flückiger et al., 2004; Schilt et al., 2010b, and new data], results from the following ice cores drilling sites are shown: EDC [Flückiger et al., 2002; Stauffer et al., 2002; Spahni et al., 2005], EDML [Schilt et al., 2010a], Talos Dome [Schilt et al., 2010b], Greenland Ice Core Project (GRIP) [Flückiger et al., 1999], and Greenland Ice Sheet Project 2 (GISP2) [Sowers et al., 2003]. The records are synchronized using the AICC2012 time scale [Bazin et al., 2012; Veres et al., 2012] and methane (CH_4) synchronization according to Schilt et al. [2010b].

In Figure A2, the NGRIP record is compared to available records from other ice cores covering the same time interval. The histogram in Figure A3, where the differences NGRIP values (interpolated to the corresponding age) minus values from other ice cores are summarized, shows that the mean value of the Gaussian distribution fitted through all differences is 2.2 ppbv (SD=12.9 ppbv). This highlights that the NGRIP records is in general agreement with records from other ice cores after applying the +10 ppbv offset correction (to most of the cores as mentioned above). However, some major differences between the new NGRIP and N_2O records from other ice cores exist. They mostly correspond to single measurements and may thus point to either measurements affected by in situ production (and not properly excluded from the atmospheric records) or problems during the measurement process. In particular, the variations observed in the Talos Dome N_2O record around 30 kyr BP are not confirmed by the new measurements along the NGRIP ice core. These variations seen in the Talos Dome record have already been questioned by Schilt et al. [2010b], as they do not have a counterpart in the CH_4 record.

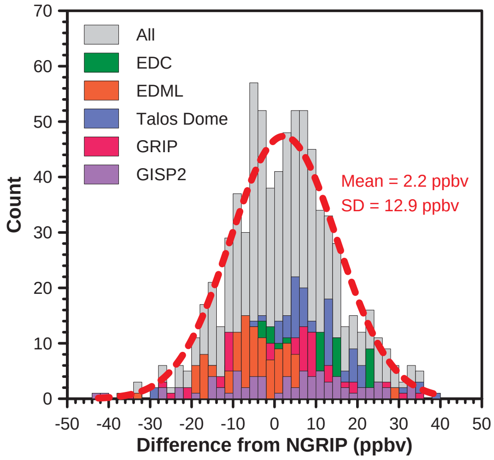

Figure A3: Histogram of the differences between the N_2O records from the NGRIP and other ice cores as shown in Figure A2. The red dashed line shows the Gaussian distribution fitted through the differences of all records together, with a mean of 2.2 ppbv. Note that uncertainties in the synchronization of the records may substantially increase the scatter of the results.

2. Effect of firn on the N_2O record measured along the NGRIP ice core

At the NGRIP site, atmospheric air can circulate in about the upper 70 m of the Greenland ice sheet. As a consequence, the air which finally gets trapped in the ice does not stem from a single point in time, but has an age distribution. This age distribution mainly depends on temperature and accumulation rate. As shown in Figure A4, the full widths at half amplitude of the age distributions at the NGRIP site are about 36 and 83 yr under interstadial and LGM conditions, respectively.

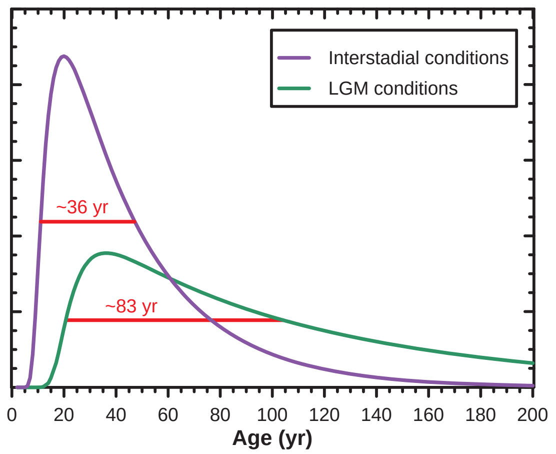

Figure A4: Age distributions of air trapped in the Greenland ice sheet at the NGRIP site. The full widths at half amplitude are about 36 and 83 yr under interstadial and LGM conditions, respectively [Herron & Langway, 1980; Schwander et al., 1993; Spahni et al., 2003].

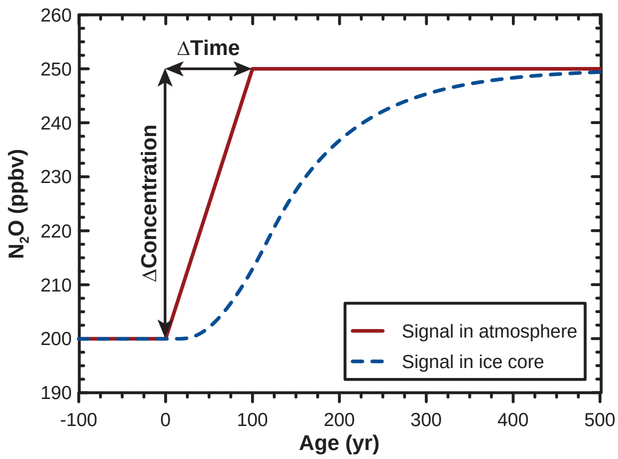

Figure A5: Hypothetical N_2O increase in the atmosphere and after getting trapped in the Greenland ice sheet at the NGRIP site under LGM conditions (see Figure A4). Different values of ΔConcentration and ΔTime are used for the calculations shown in Figure A6.

The smoothing caused by the age distributions may alter the increase rate of an atmospheric trend when the air gets trapped in the ice. Figure A5 shows a hypothetical atmospheric N_2O increase in form of a ramp, as well as the same signal after passing the firn and getting trapped in the ice under the most extreme LGM conditions.

Figure A6 shows the differences between the maximum increase rates of ramps with different values for ΔConcentration and ΔTime (see Figure A5) and the corresponding trend as it would be trapped in the NGRIP ice core. For events lasting about 250 to 500 yr or longer (depending on the climatic conditions), the maximum increase rate of a hypothetical atmospheric increase in form of a ramp can be completely reconstructed from the ice core. Accordingly, we point out that the calculations of increase rates presented in Figure 3 and Table 1 of the main manuscript are virtually unaffected by the smoothing of the firn at the NGRIP site, as the increases last longer than 500 yr (with the exception of the late increase into DO event 8).

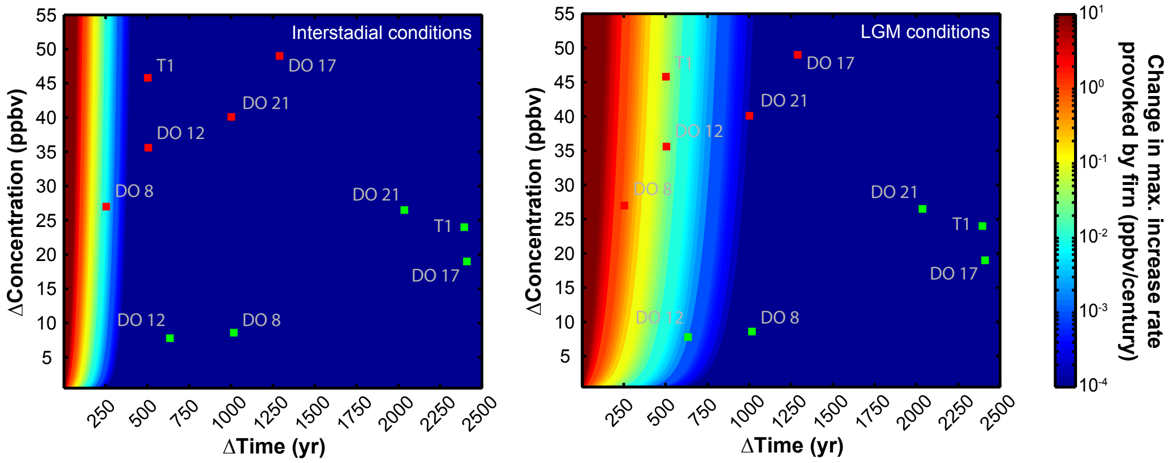

Figure A6: Change in the maximum increase rates of ramps in the atmosphere with different values for ΔConcentration and ΔTime (see Figure A5) when passing the firn and getting trapped in the ice at the NGRIP site under interstadial and LGM conditions. The green dots indicate the early increases and the red dots indicate the late increases at the start of Termination 1, as well as the DO events 8, 12, 17 and 21 (as presented in Figure 3 and Table 1 of the main manuscript). With the exception of the late increase of DO event 8 under LGM conditions, the smoothing of the firn does not significantly affect the maximum increase rates of the early and late increases of the events considered in this publication.

3. Synchronization of marine sediment cores

The different records shown in Figure 2 of the main manuscript are synchronized to the AICC2012 time scale [Bazin et al., 2012; Veres et al., 2012]. The defined tie points between the different records are shown in Figure A7 to A10.

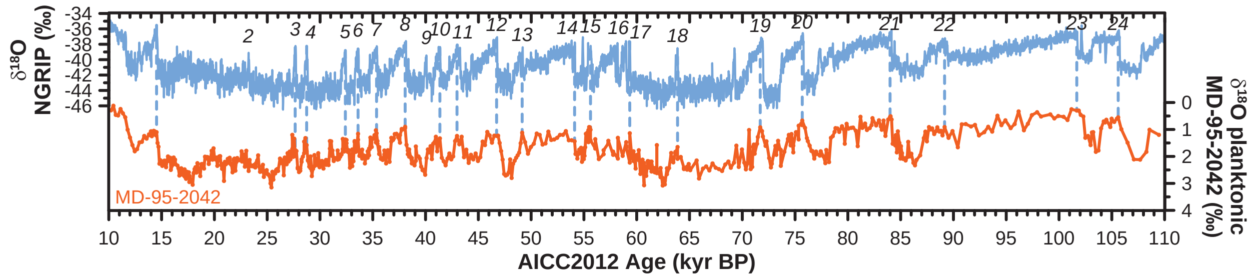

Figure A7: Synchronization of the marine sediment core MD-95-2042 to AICC2012. MD-95-2042 δ^{18}O of (planktonic) *Globigerina bulloides* [Shackleton et al., 2000], co-varying with Greenland temperature, is synchronized to NGRIP δ^{18}O [NGRIP Community Members, 2004]. Italic numbers denote DO events.

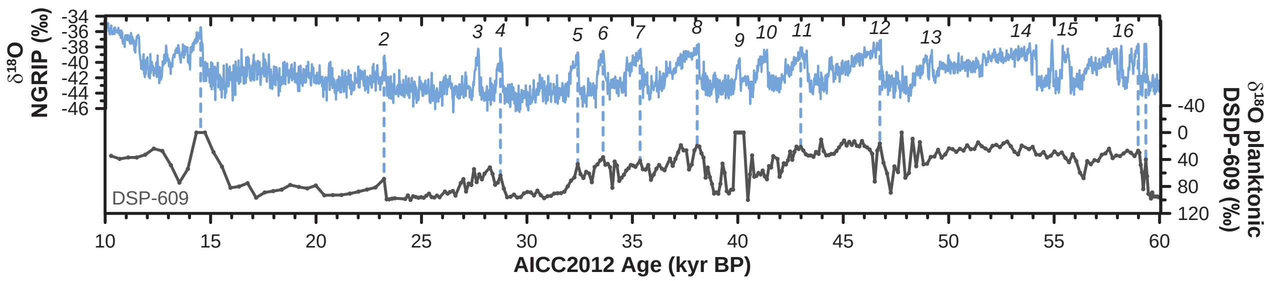

Figure A8: Synchronization of the marine sediment core DSDP-609 to AICC2012. DSDP-609 δ^{18}O of (planktonic) *Neogloboquadrina pachyderma* [Bond et al., 1992], a proxy for local North Atlantic sea surface temperature, is synchronized to NGRIP δ^{18}O [NGRIP Community Members, 2004]. Italic numbers denote DO events.

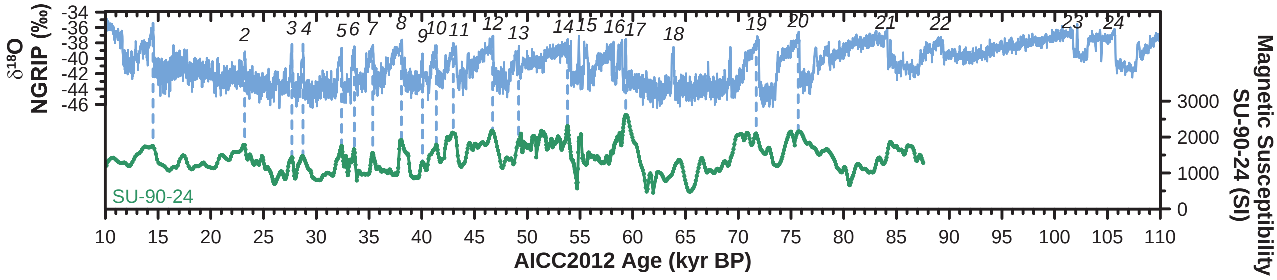

Figure A9: Synchronization of the marine sediment core SU-90-24 to AICC2012. SU-90-24 magnetic susceptibility [Elliot et al., 2002], co-varying with Greenland temperature, is synchronized to NGRIP δ^{18}O [NGRIP Community Members, 2004]. Italic numbers denote DO events.

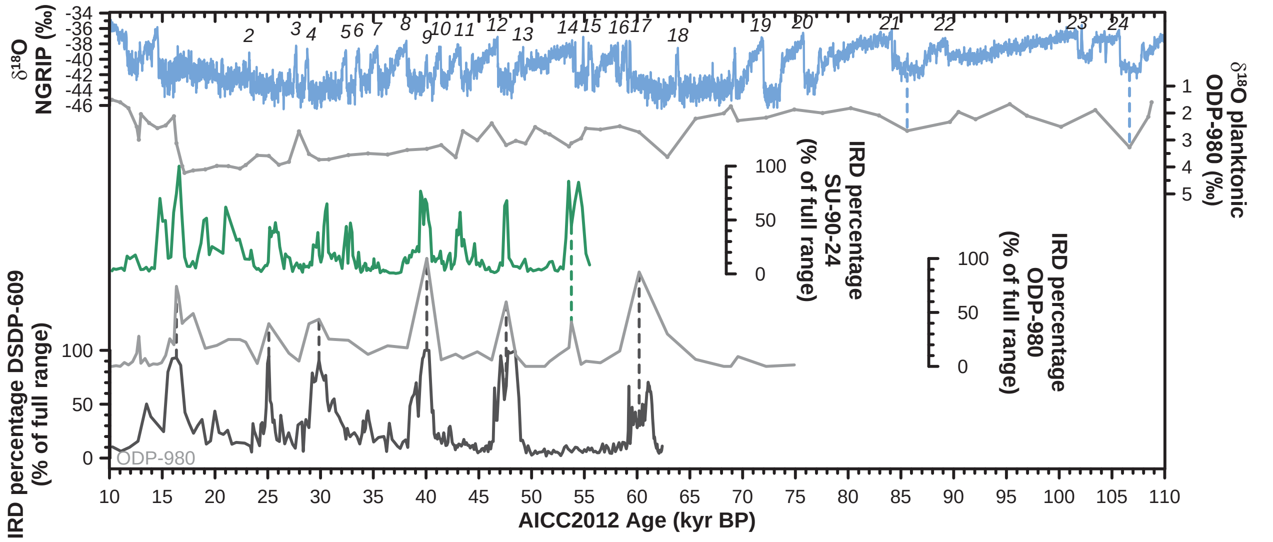

Figure A10: Synchronization of the marine sediment core ODP-980 to AICC2012. ODP-980 δ^{18}O of (planktonic) *Neogloboquadrina pachyderma* [McManus et al., 1999], co-varying with Greenland temperature, is synchronized to NGRIP δ^{18}O [NGRIP Community Members, 2004]. Due to the low time resolution, ODP-980 ice-rafted debris (IRD) is further synchronized to SU-90-24 IRD [Elliot et al., 2002] and DSDP-609 IRD [Bond et al., 1992]. Italic numbers denote DO events.

Figure A11 compares the time scales produced by the synchronization to the time scales as presented in the original publications of the records.

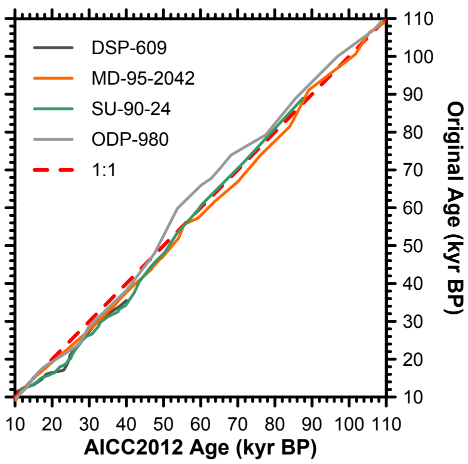

Figure A11: Comparison of the time scales as in the original publications of the records and after the synchronization to AICC2012 performed in Figure A7 to A10.

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