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

Adrian Schilt,[1,3] Matthias Baumgartner,[1] Olivier Eicher,[1] Jérôme Chappellaz,[2] Jakob Schwander,[1] Hubertus Fischer,[1] and Thomas F. Stocker[1]

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[1] Detailed insight into natural variations of the greenhouse gas nitrous oxide (N_2O) in response to changes in the Earth's climate system is provided by new measurements along the ice core of the North Greenland Ice Core Project (NGRIP). The presented record reaches from the early Holocene back into the previous interglacial with a mean time resolution of about 75 years. Between 11 and 120 kyr BP, atmospheric N_2O concentrations react substantially to the last glacial-interglacial transition (Termination 1) and millennial time scale climate variations of the last glacial period. For long-lasting Dansgaard/Oeschger (DO) events, the N_2O increase precedes Greenland temperature change by several hundred years with an increase rate of about 0.8–1.3 ppbv/century, which accelerates to about 3.8–10.7 ppbv/century at the time of the rapid warming in Greenland. Within each bundle of DO events, the new record further reveals particularly low N_2O concentrations at the approximate time of Heinrich events. This suggests that the response of marine and/or terrestrial N_2O emissions on a global scale are different for stadials with and without Heinrich events. **Citation:** Schilt, A., M. Baumgartner, O. Eicher, J. Chappellaz, J. Schwander, H. Fischer, and T. F. Stocker (2013), The response of atmospheric nitrous oxide to climate variations during the last glacial period, *Geophys. Res. Lett.*, *40*, 1888–1893, doi:10.1002/grl.50380.

1. Introduction

[2] N_2O is a trace gas in the atmosphere, involved in the destruction of stratospheric ozone and acting as a strong greenhouse gas [*IPCC*, 2007; *Ravishankara et al.*, 2009]. Due to anthropogenic emissions from fertilized agricultural lands, burning of fossil fuels and biomass, as well as industrial processes, the atmospheric N_2O concentration recently increased from a preindustrial level of ∼270 ppbv to a present-day (2011) concentration of 324.2 ppbv, accounting for ∼6 % of the global radiative forcing of all long-lived greenhouse gases [*Machida et al.*, 1995; *Battle et al.*, 1996; *Flückiger et al.*, 1999, 2002; *Meure et al.*, 2006; *IPCC*, 2007; *WMO*, 2012].

[3] Natural N_2O sources are soils and the ocean, where the emission rates today are about 3.3–9.0 and 1.2–4.0 TgN yr^{-1}, respectively [*Denman et al.*, 2007; *Rhee et al.*, 2009]. This gives both sources the potential to significantly influence the globally well-mixed atmospheric concentration. The major sinks are photodissociation and chemical reactions with excited oxygen in the stratosphere. N_2O has a relatively long atmospheric life time of ∼120 years [*Volk et al.*, 1997; *Minschwaner et al.*, 1998].

[4] Ice cores provide valuable information about former states of the Earth's climate system, as well as insight into the past composition of the atmosphere, thanks to ancient air enclosed in the ice. Over the last 800 kyr, N_2O shows substantial variations in line with climate, with high concentrations of up to ∼300 ppbv during interglacial and low concentrations of down to ∼200 ppbv during glacial periods [*Flückiger et al.*, 1999; *Spahni et al.*, 2005; *Schilt et al.*, 2010a]. The atmospheric N_2O concentration further shows variations on millennial time scales during the last glacial period, with low concentrations during stadials and high concentrations of up to typical interglacial values during interstadials [*Flückiger et al.*, 1999, 2004; *Schilt et al.*, 2010b].

[5] Here we considerably augment previous N_2O concentration records, measuring samples along the North Greenland Ice Core Project ice core (75°06′N, 42°20′W). The high-resolution NGRIP N_2O record now completely covers the time interval from ∼11 to ∼120 kyr BP, providing a detailed reconstruction of the N_2O response to Termination 1 and all millennial time scale climate variations of the last glacial period back to Dansgaard/Oeschger event 25 (Figure 1).

2. Methods

[6] As previously described [e.g., *Flückiger et al.*, 2002; *Schilt et al.*, 2010b], ancient air is extracted from polar ice samples of ∼40 g using a melt-refreezing technique and then analyzed for N_2O concentrations by a gas chromatography system. The calibration of the thermal conductivity detector (TCD) and the electron capture detector (ECD) used to determine the amount of air and N_2O, respectively, is renewed approximately every hour by analysis of two standard gases with N_2O concentrations of 201 and 304 ppbv. Measurements of a third standard gas serve to check each calibration. The latter measurements show a standard deviation of

Additional supporting information may be found in the online version of this article.

[1]Climate and Environmental Physics, Physics Institute, and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland.

[2]Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France.

[3]Now at College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.

Corresponding author: A. Schilt, College of Earth, Ocean, and Atmospheric Sciences, 104 CEOAS Admin Bldg, Oregon State University, Corvallis, OR 97331-5503, USA. (schilta@science.oregonstate.edu)

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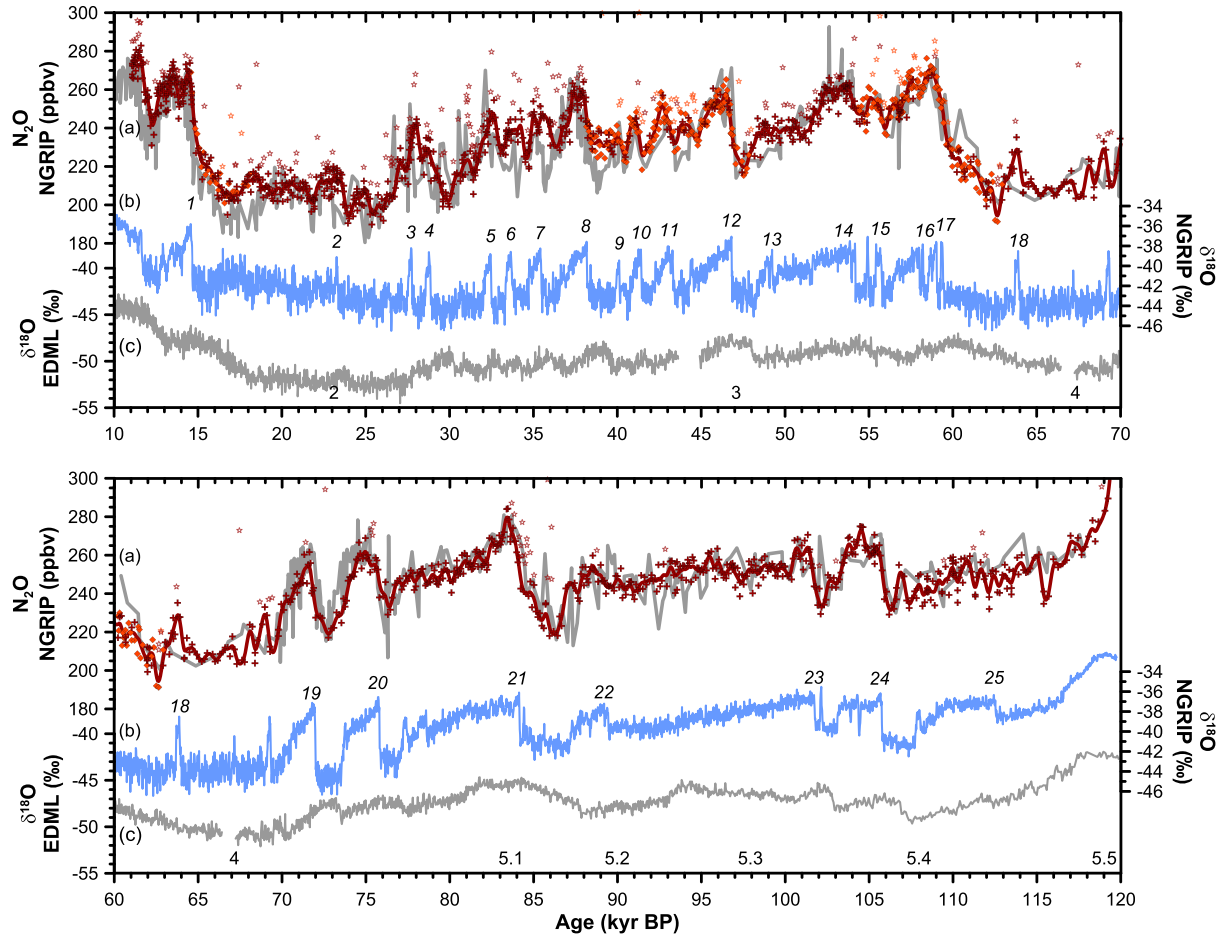

Figure 1. Termination 1 and the last glacial period (10 to 70 kyr BP in the upper panel, 60 to 120 kyr BP in the lower panel). (a) NGRIP N_2O, diamonds [*Flückiger et al.*, 2004; *Schilt et al.*, 2010b] and crosses (new data). Stars indicate published and new measurements affected by artifacts. The red line shows a spline with a cutoff period of 600 years calculated through the atmospheric N_2O record [*Enting*, 1987]. Note that the remeasurements in previously published time intervals (i.e., over Termination 1 as well as the DO events 9 to 12 and 15 to 17) are in good agreement with new measurements (details in the supporting information). The gray line in the background shows the N_2O composite record derived from various ice cores [*Schilt et al.*, 2010b], excluding NGRIP. The composite and the new NGRIP records generally agree, with some larger differences (mostly single data points) as discussed in the supporting information. (b) NGRIP $\delta^{18}O$, a proxy for Greenland temperature [*NGRIP Community Members*, 2004]. Italic numbers denote DO events. (c) EPICA Dronning Maud Land (EDML) $\delta^{18}O$, a proxy for temperature in Antarctica [*EPICA Community Members*, 2006]. Numbers denote Marine Isotope Stages. All records are shown on the AICC2012 age scale [*Bazin et al.*, 2012; *Veres et al.*, 2012].

3.2 ppbv for the calibrations (n = 630) used to produce the new data of this study in the years 2010, 2011, and 2012. Due to the relatively high solubility of N_2O in water, the melt-refreezing technique leads to a net decrease of the true N_2O concentration by 4.5 ± 3.0 ppbv on average as determined by measurements of standard gas injected over samples of bubble-free ice. All measurements are corrected for this effect; however, gravitational fractionation in the firn, which leads to an enrichment of 2.2 ± 0.3 ppbv at the NGRIP site [*Flückiger et al.*, 2004], is not taken into account, in line with previous studies.

[7] The reproducibility of the new N_2O measurements is determined by analyzing 22 series of five adjacent ice samples with different N_2O concentrations similar to the procedure described by *Schilt et al.* [2010b]. The overall standard deviation of the reproducibility measurements, which are randomly performed throughout the measurement series, excluding four clearly identified outliers, is 4.9 ppbv (n = 106). This standard deviation is given as the uncertainty of the N_2O concentration measurements along the NGRIP ice core, although it may slightly underestimate the uncertainty on an absolute scale due to additional sources of error (e.g., standard gas scale, gravitational fractionation, representation of bubble-free ice blanks).

[8] Remeasurements of samples in previously published intervals allow us to verify that the whole NGRIP N_2O record measured in different measurement series and over several years is on a consistent reference scale. As visible in Figure 1 and detailed in the supporting information, we do not observe any statistically significant difference between new and previous measurements, indicating the consistency of the whole NGRIP N_2O record. However, in order to be on the same reference scale as the N_2O records from other studies on different ice cores, we need to take into account an offset correction of +10 ppbv for all N_2O measurements performed along the NGRIP ice core. Note that the offset

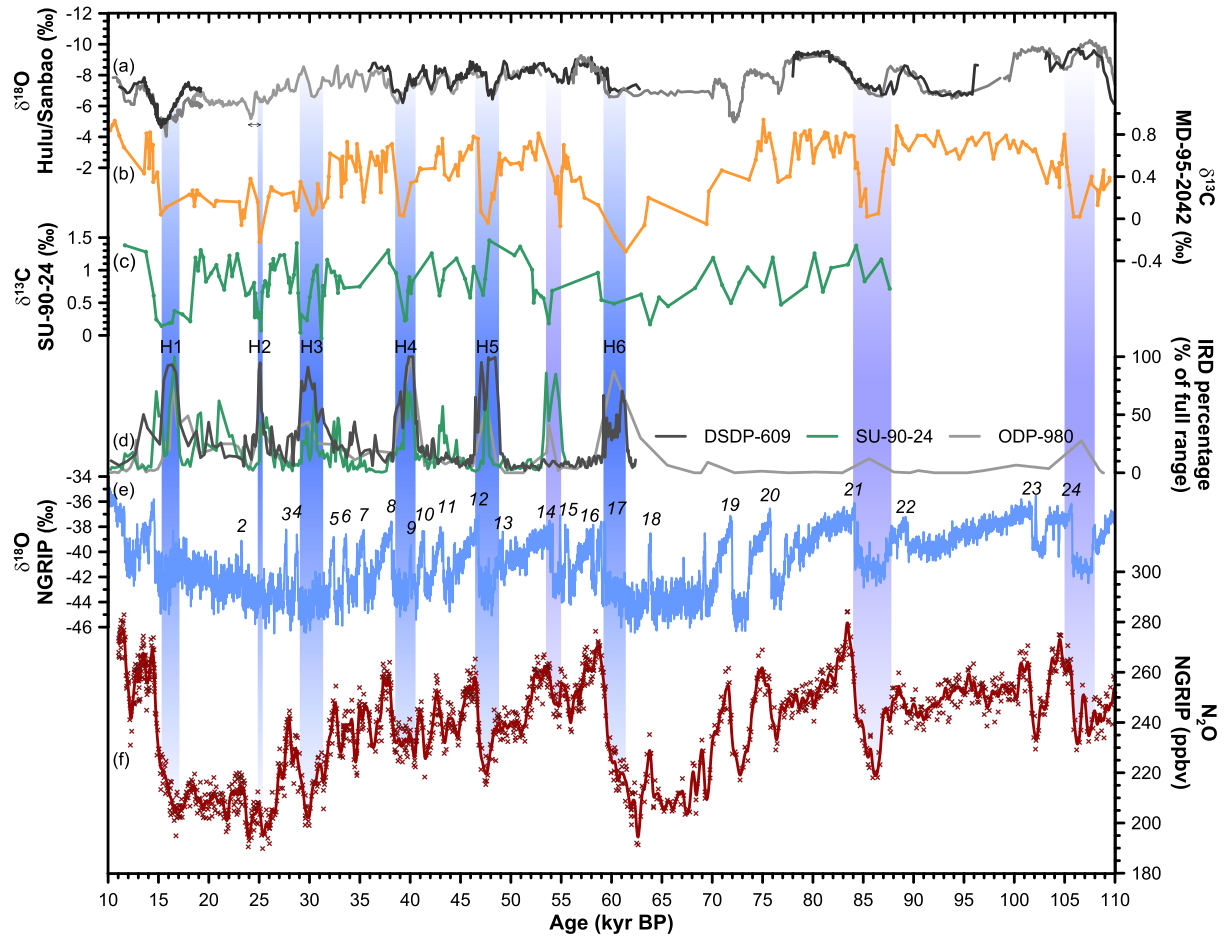

Figure 2. The response of N_2O to Heinrich events and comparison to high-resolution proxy records. (a) Sanbao/Hulu Cave $\delta^{18}O$ (combined record of several stalagmites), a proxy for the East Asian Monsoon intensity [*Wang et al.*, 2001, 2008]. (b and c) $\delta^{13}C$ isotopic signatures of *Cibicidoides wuellerstorfi* from the marine sediment cores MD-95-2042 (37°48′N, 10°10′W) [*Shackleton et al.*, 2000] and SU-90-24 (62°04′N, 37°02′W) [*Elliot et al.*, 2002], indirect proxies for the strength of the AMOC. (d) IRD percentages from the marine sediment cores DSDP-609 (49°53′N, 24°14′W) [*Bond et al.*, 1992], SU-90-24 [*Elliot et al.*, 2002], and ODP-980 (55°29′N, 14°42′W) [*McManus et al.*, 1999], revealing Heinrich events (H1 to H6, highlighted by blue shadings). (e) NGRIP $\delta^{18}O$ (as in Figure 1). (f) NGRIP N_2O (as in Figure 1), without showing artifacts. The NGRIP records are shown on the same time scale as in Figure 1. The marine sediment core records are synchronized to the ice core time scale as detailed in the supporting information. The Sanbao/Hulu Cave record is shown on its original time scale.

correction has already been applied to N_2O records from various ice cores measured in the same lab in the course of the last decade (*Spahni et al.* [2005]; *Schilt et al.* [2010a], and supporting information). However, the previously published NGRIP N_2O measurements over Termination 1 [*Schilt et al.*, 2010b] and the DO events 9 to 12 [*Flückiger et al.*, 2004], which were not corrected for this offset, are now increased by +10 ppbv.

[9] N_2O records along polar ice cores may to some extent be affected by in situ production of N_2O in the ice, resulting in elevated values above the atmospheric concentration at the time of air inclusion [e.g., *Sowers*, 2001; *Flückiger et al.*, 2004; *Schilt et al.*, 2010a, 2010b] (Figure 1). In order to exclude such measurements affected by artifacts from the atmospheric record, we apply the artifact detection algorithm introduced by *Flückiger et al.* [2004]. This algorithm, which is suitable for high-resolution N_2O records only, iteratively excludes values which exceed by more than 8 ppbv a spline with a cutoff period of 600 years calculated through the data [*Enting*, 1987]. We recognize that this artifact detection algorithm is an empirical approach; however, the resulting atmospheric NGRIP N_2O record agrees with N_2O records obtained along other ice cores (Figure 1).

3. Results

[10] We provide 1398 new NGRIP N_2O measurements covering Termination 1, as well as the DO events 2 to 8, 13, 14, and 18 to 25 (depth intervals: 1481 to 2084 m, 2250 to 2358 m, and 2463 to 3082 m). In combination with previously published NGRIP measurements covering the DO events 9 to 12 [*Flückiger et al.*, 2004] as well as the DO events 15 to 17 and parts of Termination 1 [*Schilt et al.*, 2010b], the NGRIP N_2O record now covers the entire period from the early Holocene to the previous interglacial (~11 to ~120 kyr BP), with a mean time resolution of ~75 years. In comparison, the full widths at half amplitude of the age distributions of the air trapped in the ice at the NGRIP site

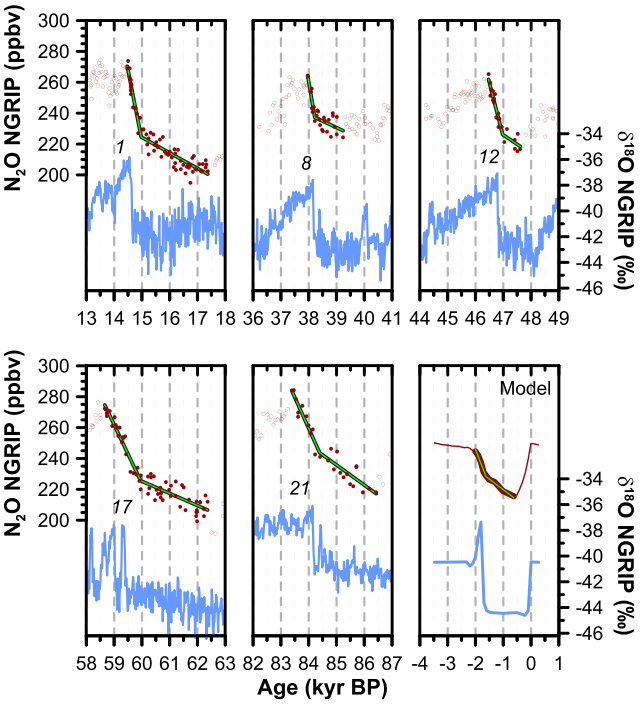

Figure 3. N_2O evolution at the ending of long stadials (NGRIP $\delta^{18}O$ serves as a proxy for Greenland temperature). The filled circles mark the data points used to calculate the best fit of the increase with two linear trends allowing for one kink. The corresponding increase rates and their uncertainties are summarized in Table 1. As shown in the supporting information, the increase rates are virtually unaffected by the smoothing of the atmospheric signal by the firn column. The last panel shows the modeled evolution from *Schmittner and Galbraith* [2008], where the AMOC is switched back on after 1700 years (the shut-off takes place at year 0). Note that the modeled Greenland temperature is shown on an arbitrary *y*-axis.

are about 36 and 83 years under interstadial and Last Glacial Maximum (LGM) conditions, respectively (see supporting information). This effectively limits the temporal resolution in the ice core record that can be achieved.

[11] The general trend of the NGRIP N_2O record confirms and extends results from previous studies along different ice cores [*Flückiger et al.*, 1999, 2004; *Stauffer et al.*, 2002; *Sowers et al.*, 2003; *Spahni et al.*, 2005; *Schilt et al.*, 2010a, 2010b], as shown in Figure 1. In response to Termination 1, N_2O increases from a low glacial value of ~205 ppbv (mean between 16.5 and 17.5 kyr BP) to a typical interglacial value of ~261 ppbv during the Bølling/Allerød (mean between 13 and 14 kyr BP). After a decrease of 20 to 30 ppbv in response to the Younger Dryas, N_2O reaches a value of ~274 ppbv during the Pre-boreal, which corresponds to the upper end of measured preindustrial Holocene concentrations [*Flückiger et al.*, 2002]. In the course of the last glacial period, N_2O varies within the concentration range covered during Termination 1. Indeed, N_2O shows a clear increase at the warming of every DO event, occasionally reaching typical interglacial concentrations [*Flückiger et al.*, 1999, 2004; *Schilt et al.*, 2010b]. This strong N_2O response to DO events is now unambiguously confirmed also for DO events where previous records were less detailed.

4. Discussion

[12] During the last 60 kyr, the long stadials are accompanied by the well-studied Heinrich events H1 to H6, which are characterized by large amounts of ice-rafted debris (IRD) originating from the Laurentide ice sheet (Hudson Strait) and visible in marine sediment cores drilled in the North Atlantic (Figure 2) [*Heinrich*, 1988; *Bond et al.*, 1992; *McManus et al.*, 1999; *Elliot et al.*, 2002; *Hemming*, 2004]. These Heinrich stadials are followed by bundles of DO events (with similar stadial but varying interstadial temperatures), which finally terminate in another Heinrich stadial. As during each bundle of DO events N_2O concentrations reach remarkably low values during the Heinrich stadials, the Heinrich event cycles are clearly visible in the atmospheric N_2O record (Figures 1 and 2). This behavior suggests a different response of the global N_2O budget to stadials with and without Heinrich events.

[13] The $\delta^{13}C$ isotopic signatures of benthic foraminifera in North Atlantic marine sediment cores indicate water mass distributions and can thus be interpreted as an indirect proxy of Atlantic meridional overturning circulation (AMOC). $\delta^{13}C$ records from SU-90-24 [*Elliot et al.*, 2002] and MD-90-2042 [*Shackleton et al.*, 2000] show a particularly strong reduction of the AMOC during Heinrich stadials, while stadials without a Heinrich event are less pronounced (Figure 2). Since the available modeling studies simulating the N_2O response to freshwater perturbations to the North Atlantic suggest a reduction of marine N_2O emissions in response to a complete shut-off of the AMOC [*Goldstein et al.*, 2003; *Schmittner and Galbraith*, 2008], it appears straightforward to assume that a partial reduction of the AMOC leads to a less pronounced decrease in marine N_2O emissions. Stadials without a Heinrich event may indeed rather correspond to a dislocation of the deep water formation site, while during Heinrich events, the AMOC is completely shut off (*Stocker and Marchal* [2000]; *Rahmstorf* [2002], in agreement with the $\delta^{13}C$ records of marine sediment cores shown in Figure 2). In addition, *Schmittner and Galbraith* [2008] also simulate stronger reductions when the durations of the stadials increase, which agrees with the data, as stadials with Heinrich events are predominantly longer. Therefore, the low N_2O concentrations during Heinrich stadials could consistently be explained by marine N_2O emissions responding to changes in the AMOC [*Goldstein et al.*, 2003; *Schmittner and Galbraith*, 2008].

[14] It has previously been proposed that for long-lasting DO events following long stadials, N_2O starts to increase several hundred years before Greenland temperature [*Flückiger et al.*, 2004]. This early increase of N_2O is documented in Figure 3 for the rapid warmings at the start of Termination 1 and the DO events 8, 12, 17, and 21. An early N_2O increase has additionally been suggested for the rapid warmings at the start of the DO events 19 and 20 (based on data from the GRIP ice core, *Flückiger et al.* [2004]), and it may also be present at the warming of DO event 4, but the available data are less clear for these events.

[15] The modeling study of *Schmittner and Galbraith* [2008] reproduces the early increase (Figure 3), with consistent increase rates between data and model (Table 1). In the

Table 1. N_2O Increase Rates Extracted From Figure 3[a]

Event	Early Increase Rate (ppbv/century)	Late Increase Rate (ppbv/century)
Termination 1	1.0 ± 0.1	9.1 ± 2.2
DO event 8	0.8 ± 1.0	10.7 ± 4.7
DO event 12	1.2 ± 1.7	7.1 ± 11.2
DO event 17	0.8 ± 0.1	3.8 ± 0.3
DO event 21	1.3 ± 0.3	4.0 ± 0.9
Model[b]	$\sim$1.4	$\sim$4.6

[a]The given uncertainties correspond to the standard deviation of 2500 Monte Carlo simulations, where the best fit is calculated through data points normally distributed around the measured values with a standard deviation of 4.9 ppbv (corresponding to the standard deviation from reproducibility measurements; see section 2). Note that the uncertainties exceed the actual values for the early increases into the DO events 8 and 12, as well as for the late increase into DO event 12.

[b] *Schmittner and Galbraith* [2008].

model, it takes about one millennium before the upper-ocean nitrate and oxygen inventories, and consequently marine N_2O emissions, recover from the AMOC shut-off. This is in agreement with the data, where such an early increase of N_2O cannot be clearly identified at the ending of shorter stadials.

[16] We point out that at the approximate time of the rapid warming in Greenland, the increase rates of N_2O accelerate (Figure 3 and Table 1). This is also modeled by *Schmittner and Galbraith* [2008], but the increase rate is occasionally faster in the data than suggested by the model (in particular for Termination 1 and DO event 8). One has to bear in mind that the mentioned modeling studies do not include terrestrial N_2O emissions. Given the last glacial period's large variations of atmospheric methane (CH_4), which has predominantly terrestrial sources, the scenario of constant terrestrial N_2O emissions throughout time seems unlikely. Indeed, in response to a shut-off of the AMOC under preindustrial conditions, models indicate a substantial reduction of temperature and precipitation over large parts of the Northern Hemisphere, with the corresponding effects on net primary production only partly compensated by the Southern Hemisphere [*Vellinga and Wood*, 2002; *Bozbiyik et al.*, 2011]. As suggested by *Xu et al.* [2012], such climatic changes are expected to influence terrestrial N_2O emissions substantially. Accordingly, we argue that the elevated N_2O increase rates at the onset of DO events may partly also be caused by increased terrestrial N_2O emissions.

[17] That millennial time scale climate variations during the last glacial period indeed have a substantial influence on processes taking place on land is pointed out in Figure 2. The Sanbao/Hulu Cave $\delta^{18}O$ stalagmite record, a proxy for the East Asian Monsoon intensity [*Wang et al.*, 2001, 2008], clearly reveals millennial time scale variations. By analysis of the $\delta^{18}O$ record of atmospheric oxygen from the Siple Dome ice core, *Severinghaus et al.* [2009] infer that a large fraction of the photosynthetic capacity of the terrestrial biosphere is affected by DO and Heinrich events. Both records may reach the strongest extremes at the time of Heinrich events, pointing to a different response of terrestrial systems to DO and Heinrich events cycles, as seen in the global N_2O concentrations.

[18] Overall, the underlying mechanisms responsible for the natural N_2O variations, here reconstructed in detail for Termination 1 and all DO events of the last glacial period, cannot be quantitatively constrained yet. Detailed analysis of the isotopic composition of N_2O, as well as further modeling efforts including both marine and terrestrial processes, may help to better understand the different features found in the new NGRIP N_2O record, in particular the remarkably low concentrations during Heinrich stadials (within a bundle of DO events). Notably, Figure 2 indicates that these low N_2O values are not only found in response to the Heinrich events H1 to H6 during Marine Isotope Stage 3, but a similar response is also observed at around 55 (Heinrich event H5a), 86, and 107 kyr BP, with marine sediment cores indicating corresponding AMOC reductions and IRD events (Figure 2). In view of the observed N_2O response to past variations in climatic and in particular in ocean circulation patterns, future changes of the global natural N_2O sources may be expected caused by the anthropogenic impact on the Earth's climate system.

Appendix A

[19] The N_2O record can be downloaded from the website of the World Data Center for Paleoclimatology at www.ncdc.noaa.gov/paleo.

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