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Atmospheric nitrous oxide during the last 140,000 years

Adrian Schilt^{a,b,*}, Matthias Baumgartner^{a,b}, Jakob Schwander^{a,b}, Daphné Buiron^c, Emilie Capron^d, Jérôme Chappellaz^c, Laetitia Loulergue^c, Simon Schüpbach^{a,b}, Renato Spahni^{a,b}, Hubertus Fischer^{a,b}, Thomas F. Stocker^{a,b}

^a Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland

^b Oeschger Centre for Climate Change Research, University of Bern, CH-3012 Bern, Switzerland

^c Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS-UJF, 38400 St Martin d'Hères, France

^d Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, 91191 Gif-sur-Yvette, France

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ABSTRACT

Reconstructions of past atmospheric concentrations of greenhouse gases provide unique insight into the biogeochemical cycles and the past radiative forcing in the Earth's climate system. We present new measurements of atmospheric nitrous oxide along the ice cores of the North Greenland Ice Core Project and Talos Dome sites. Using records of several other ice cores, we are now able to establish the first complete composite nitrous oxide record reaching back to the beginning of the previous interglacial about 140,000 yr ago. On the basis of such composite ice core records, we further calculate the radiative forcing of the three most important greenhouse gases carbon dioxide, methane and nitrous oxide during more than a full glacial–interglacial cycle. Nitrous oxide varies in line with climate, reaching very low concentrations of about 200 parts per billion by volume during Marine Isotope Stages 4 and 2, and showing substantial responses to millennial time scale climate variations during the last glacial. A large part of these millennial time scale variations can be explained by parallel changes in the sources of methane and nitrous oxide. However, as revealed by high-resolution measurements covering the Dansgaard/Oeschger events 17 to 15, the evolution of these two greenhouse gases may be decoupled on the centennial time scale. Carbon dioxide and methane concentrations do not reach interglacial levels in the course of millennial time scale climate variations during the last glacial. In contrast, nitrous oxide often reaches interglacial concentrations in response to both, glacial terminations and Dansgaard/Oeschger events. This indicates, from a biogeochemical point of view, similar drivers in both temporal cases. While carbon dioxide and methane concentrations are more strongly controlled by climate changes in high latitudes, nitrous oxide emissions changes may mainly stem from the ocean and/or from soils located at low latitudes. Accordingly, we speculate that high latitudes could play the leading role to trigger glacial terminations.

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1. Introduction

Anthropogenic emissions of nitrous oxide (N₂O) led to an ongoing increase of this important greenhouse gas from a preindustrial value of about 270 parts per billion by volume (ppbv) to a present-day (2008) concentration of 322 ppbv (Flückiger et al., 1999; Machida et al., 1995; WMO, 2009). N₂O is naturally produced by nitrification and denitrification in terrestrial soils (about two thirds of total N₂O emissions) and in the ocean (about one third of total N₂O emissions) (Bouwman et al., 1993; Kroeze et al., 1999; Nevison et al., 1995). The main sink of N₂O is photodissociation in the stratosphere, followed by chemical reactions with excited oxygen (Minschwaner et al., 1998).

Compared to the mixing time of the atmosphere, N₂O has a relatively long atmospheric lifetime of about 120 yr (Minschwaner et al., 1998; Volk et al., 1997), and accordingly shows no significant interhemispheric concentration gradient.

Thanks to the analysis of air enclosed in ice cores from polar ice sheets, paleo-atmospheric concentration records of the greenhouse gases carbon dioxide (CO₂) and methane (CH₄) are available for the entire last 800,000 yr (800 kyr) (Loulergue et al., 2008 and references therein; Lüthi et al., 2008 and references therein). For this time interval, past natural variations of N₂O have been reconstructed for all interglacials and parts of glacials (Flückiger et al., 2002; Schilt et al., 2010; Sowers et al., 2003; Spahni et al., 2005). In addition, there exist N₂O records covering selected Dansgaard/Oeschger (DO) events (Flückiger et al., 1999, 2004). DO events are millennial time scale climate variations during the last glacial as recorded in Greenland ice cores (e.g. Dansgaard et al., 1984; NGRIP Members, 2004) with counterparts visible over a wide spread of latitudes (e.g. Bond et al.,

* Corresponding author. Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. Tel.: +41 31 631 44 76; fax: +41 31 631 87 42.

E-mail address: schilt@climate.unibe.ch (A. Schilt).

1993; Voelker, 2002). However, N₂O records have remained fragmentary due to the occurrence of in situ artefacts (Section 3), which has so far precluded to reconstruct the evolution of the N₂O concentration in the course of a full glacial–interglacial cycle. New measurements along

the ice cores of the Talos Dome (TD, Antarctica, 72°47' S, 159°04' E) and North Greenland Ice Core Project (NGRIP, Greenland, 75°06' N, 42°20' W) sites now fill existing gaps in the N₂O records of the last 140 kyr.

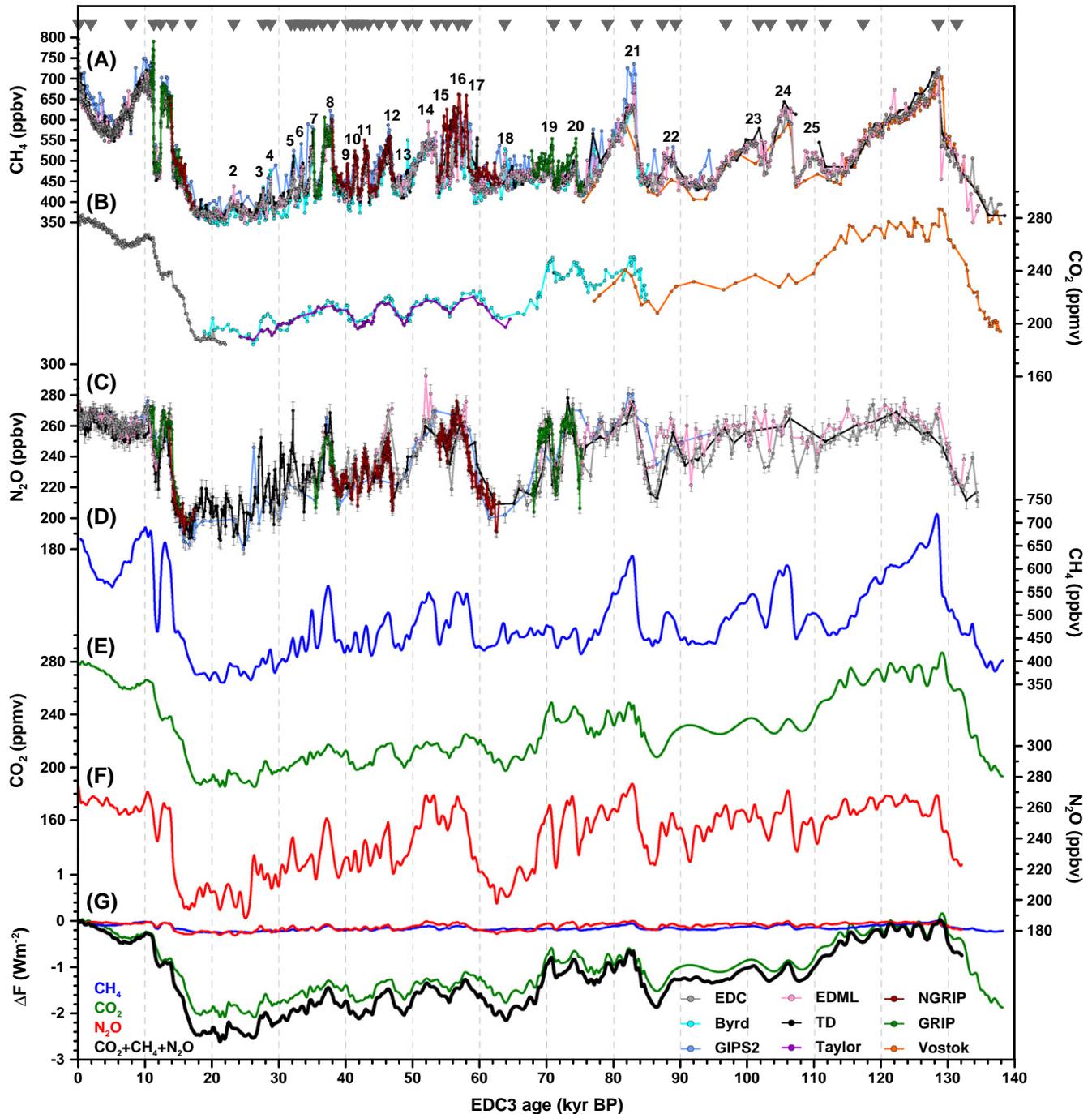


Fig. 1. Greenhouse gas records covering the last 140 kyr on the EDC3 time scale (Loulergue et al., 2007). (A) Synchronised CH₄ records of EDC (Flückiger et al., 2002; Monnin et al., 2001; Spahni et al., 2005), EDML (Capron et al., 2010; EPICA Community Members, 2006; and new data), NGRIP (Flückiger et al., 2004; Huber et al., 2006; and new data), Byrd (Blunier et al., 1998), TD (Buiron et al., 2010; Stenni et al., submitted for publication), GRIP (Blunier et al., 1998; Chappellaz et al., 1993, 1997; Dällenbach et al., 2000; Flückiger et al., 2004), GISP2 (Brook et al., 1996, 2000) and Vostok (Petit et al., 1999). The grey triangles on top of the CH₄ records indicate the locations of the tie points used for the CH₄ synchronisation (see Appendix A.4). Numbers denote DO events. (B) CO₂ records from EDC (Monnin et al., 2001, 2004), Byrd (Ahn and Brook, 2007, 2008), Taylor Dome (Indermühle et al., 2000) and Vostok (Pepin et al., 2001; Petit et al., 1999). (C) N₂O records from EDC (Flückiger et al., 2002; Spahni et al., 2005; Stauffer et al., 2002), EDML (Schilt et al., 2010), NGRIP (Flückiger et al., 2004; and new data), TD (new data), GRIP (Flückiger et al., 1999) and GISP2 (Sowers et al., 2003). (D) CH₄ smoothing spline, cutoff period of 1000 yr (Enting, 1987), only EDC CH₄ data used. (E) CO₂ smoothing spline, cutoff period of 1000 yr (Enting, 1987), all data used. (F) N₂O smoothing spline, cutoff period of 1000 yr (Enting, 1987), all data used. (G) Radiative forcing (relative to the year 1750) of CH₄ (blue), CO₂ (green), N₂O (red) and all three greenhouse gases together (black) calculated according to Ramaswamy et al. (2001). The legend at the lower right corner indicates the colour code for the ice core measurements.

2. Data records

We present 287 N₂O measurements performed along the TD ice core reaching back to about 140 kyr before present (140 kyr BP) covering Termination 2, Marine Isotope Stage (MIS) 5.5, the last glacial, Termination 1 and the Holocene (Fig. 1). On the TALDICE1 time scale (Buiron et al., 2010), the mean time resolution is about 1150 yr between 140 and 40 kyr BP, and better than 200 yr for the last 40 kyr. In addition, we present 164 N₂O measurements performed along the NGRIP ice core covering the DO events 17 to 15 from 63 to 55 kyr BP and parts of Termination 1 (Figs. 1 and 2). These new NGRIP measurements provide a mean time resolution of 72 yr on the GRIP2001/SS09sea age scale (Huber et al., 2006; Johnsen et al., 2001; NGRIP Members, 2004).

For synchronisation purposes we also use new CH₄ data (Fig. 1). First, 31 new CH₄ measurements cover for the first time parts of Termination 1 along the NGRIP ice core (same samples as for N₂O measurements). Second, we use 197 new CH₄ measurements performed along the ice core of the European Project for Ice Coring in Antarctica (EPICA) Dronning Maud Land (EDML, Antarctica, 75°00' S, 00°04' E) site. These measurements complete the EDML CH₄ record (Capron et al., 2010; EPICA Community Members, 2006) back to 140 kyr BP with a mean time resolution of better than 200 yr on the EDML1 time scale (Loulergue et al., 2007; Ruth et al., 2007).

We further use a new TD dust record reaching back to 140 kyr BP, with some gaps during the Holocene and the last glacial (Figs. 3 and 4).

For the TD N₂O measurements the standard deviation (1σ) is 5.6 ppbv as discussed in Appendix A.1. The standard deviation of our CH₄ measurements is 10 ppbv (Chappellaz et al., 1997). See Appendices A.1 and A.3 for details about the measurement techniques for N₂O, CH₄ and dust. Appendix A.2 describes the offset corrections applied to parts of the N₂O and CH₄ measurements.

3. N₂O artefacts

N₂O records reconstructed from polar ice cores occasionally show elevated values exceeding atmospheric concentrations (e.g. Flückiger et al., 2004; Schilt et al., 2010; Sowers, 2001; Spahni et al., 2005). These N₂O artefacts originate from in situ production of N₂O in the ice, likely due to microbial activity (Miteva et al., 2007; Rohde et al., 2008).

In order to detect measurements affected by artefacts in the NGRIP N₂O record we use the artefact detection algorithm already applied to earlier NGRIP N₂O records (Flückiger et al., 2004). This algorithm is only suitable for high-resolution records, and it iteratively excludes values which deviate more than 8 ppbv from a smoothing spline with a cutoff period of 600 yr (Enting, 1987) calculated through the data. This algorithm is designed to empirically identify values outside the analytical precision that cannot be explained by atmospheric N₂O variability taking into account the long lifetime of N₂O.

Along the EDML and EPICA Dome C (EDC, Antarctica, 75°06' S, 123°21' E) ice cores, N₂O measurements performed on ice samples with dust concentrations above an empirical threshold of 300 parts per billion by weight (ppbw) have been defined as affected by artefacts, because nearby measurements on such samples showed unusually high N₂O concentrations and large scatter (Schilt et al., 2010; Spahni et al., 2005). Note that this does not imply that in situ production of N₂O in the ice is directly related to the dust concentration itself. Rather, the responsible impurities and/or bacterial cells may reach the EDML and EDC sites by the same pathway as the dust particles.

Along the TD ice core, dust concentrations are almost always below this empirical threshold as applied to the EDML and EDC ice cores. The only exception to that are short intervals found in ice of MIS 2, where dust concentrations are above 300 ppbw (Fig. 3). Nevertheless, during these intervals, the TD N₂O record generally shows substantially lower values and lower scatter than the EDML and EDC N₂O records corresponding to the same age (Fig. 4). Looking at ice cores from Greenland, artefacts do not show a correlation with impurities such as e.g. dust and calcium. Instead, they preferentially occur in depth intervals with fast changing concentrations of impurities mainly located at the boundaries of DO events (Flückiger et al., 2004). Given the fact that concentrations of impurities along the TD ice core are

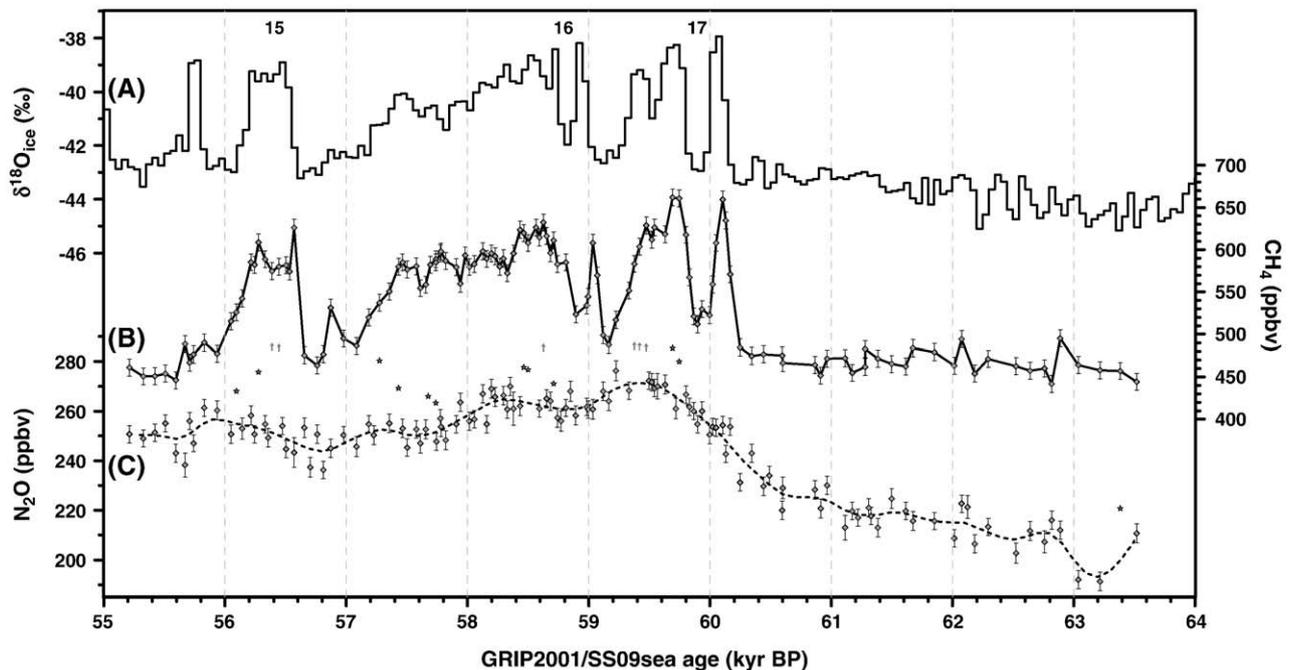


Fig. 2. $\delta^{18}\text{O}_{\text{ice}}$, CH₄ and N₂O during the DO events 17 to 15. (A) NGRIP $\delta^{18}\text{O}_{\text{ice}}$, a qualitative proxy for Greenland temperature variations (NGRIP Members, 2004). As investigated on the basis of $\delta^{15}\text{N}$ measurements on atmospheric nitrogen, Greenland temperature shows very fast increases of 12, 9 and 10 °C at the beginning of the DO events 17, 16 and 15, respectively (Huber et al., 2006). (B) NGRIP CH₄ characterized by nearly in phase increases with $\delta^{18}\text{O}_{\text{ice}}$ (Huber et al., 2006). (C) NGRIP N₂O (new data). Measurements affected by artefacts (stars, values exceeding the y-axis are indicated by arrows) are excluded by the use of the artefact detection algorithm described in Flückiger et al. (2004). The dashed line shows a smoothing spline with a cutoff period of 600 yr (Enting, 1987). All data are plotted on the GRIP2001/SS09sea time scale (Huber et al., 2006; Johnsen et al., 2001; NGRIP Members, 2004).

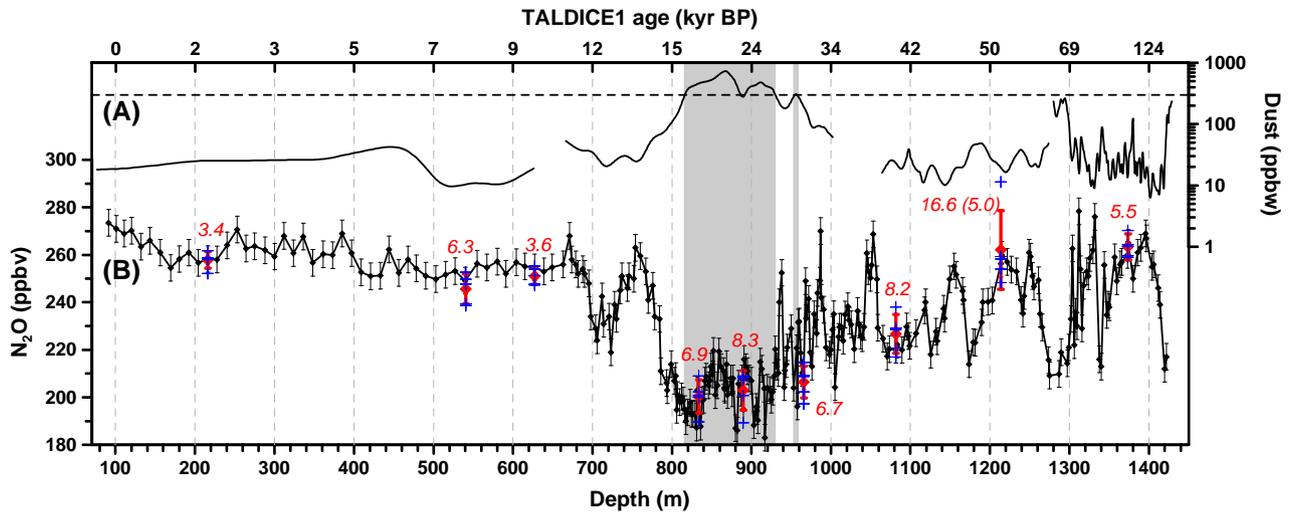


Fig. 3. TD dust and N₂O on their respective depth scale. (A) Solid line: TD dust concentration (smoothing spline with cutoff period of 2000 yr according to Enting (1987), new data). Dashed line: concentration threshold of 300 ppbw as applied to the EDML and EDC ice cores. Grey shaded areas: depth intervals with a dust concentration exceeding the threshold of 300 ppbw. (B) Black: TD N₂O (new data). Red: mean and standard deviation of five adjacent samples for each depth level (see Appendix A.1). Blue crosses show the single measurements and red italic numbers indicate the standard deviations in ppbv. The number in brackets is the standard deviation calculated without taking into account the highest measurement out of the five adjacent samples for this depth. The top x-axis indicates the TALDICE1 gas age (Buiron et al., 2010).

orders of magnitude lower and do not show large and rapid changes at the boundaries of DO events, it appears to be rather unlikely that a similar relationship between impurities and N₂O artefacts as observed along ice cores from Greenland holds also true for this Antarctic ice core. In view of these results, we suggest that the TD ice core reveals a N₂O record of atmospheric origin over its full length (including the late last glacial), regardless of the fact that dust concentrations sometimes

exceed the empirical threshold of 300 ppbw as applied to the EDML and EDC ice cores. However, we cannot strictly exclude a partial contamination of the TD N₂O record during any time interval. In particular, the TD N₂O record during MIS 2 may serve only as an upper concentration limit until verified by N₂O records from other ice cores (note that no indications exist for artefacts leading to values below the atmospheric concentration). Further, the TD N₂O record may be

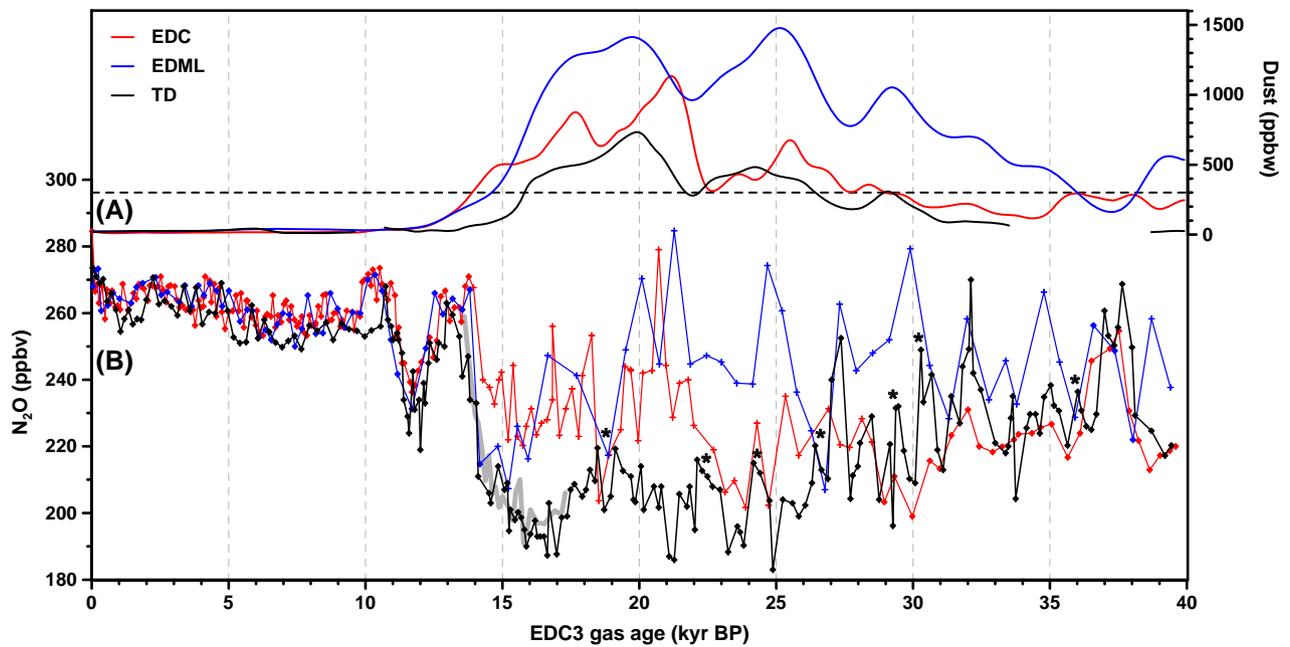


Fig. 4. Comparison of dust and N₂O from the EDC, EDML and TD ice cores. (A) Dust records of EDC (Lambert et al., 2008), EDML (EPICA Community Members, 2006) and TD (new data). Shown are smoothing splines with a cutoff period of 2000 yr (Enting, 1987). The dashed line shows the concentration threshold of 300 ppbw as applied to the EDML and EDC ice cores. (B) N₂O records of EDML (Schilt et al., 2010), EDC (Flückiger et al., 2002; Spahni et al., 2005; Stauffer et al., 2002) and TD (new data). Crosses mark EDC and EDML measurements defined as affected by artefacts, measurements marked with diamonds are thought to represent atmospheric concentrations. Asterisks mark events in the TD N₂O record which do not have a counterpart in CH₄. Note that between 26 and 16 kyr BP, CH₄ only shows very small variations in response to DO event 2 (Fig. 1). Dust and N₂O records are shown on the (CH₄ synchronised) EDC3 gas age scale (Louergue et al., 2007), wherefore dust and gas measurements from each ice core plotted at the same age stem from the same depth. During time intervals with TD dust concentrations above the threshold of 300 ppbw, the mean N₂O concentrations of EDC, EDML and TD are 229.1, 246.3 and 203.3 ppbv, respectively. The standard deviations during these time intervals are 16.5, 18.0 and 10.0 ppbv, respectively. Note that the TD N₂O measurements at the end of MIS 2 and during Termination 1 are in good agreement with the measurements performed along the NGRIP ice core (grey line in the background).

questionable for some of the fast variations found during MIS 3 and 2, since some of these variations do not have a counterpart in CH₄ and, thus, do not correspond to a DO event (see asterisks in Fig. 4). Higher time resolution and verification with N₂O records from other ice cores will help to draw final conclusions regarding these fast N₂O variations during MIS 3 and 2.

Overall, we observe a satisfactory agreement between TD and other atmospheric N₂O records during overlapping time intervals during the last 140 kyr (Figs. 1, 4, and 7 and Appendix A.2), increasing our confidence in the atmospheric origin of the TD N₂O record.

4. Results

4.1. Glacial N₂O variations

The new NGRIP and TD measurements reproduce the evolution of atmospheric N₂O during Termination 1 and the Holocene as revealed by earlier studies (Flückiger et al., 1999, 2002; Schilt et al., 2010; Sowers et al., 2003), and fill gaps in the existing N₂O records of the last glacial (Fig. 1). In particular, the TD measurements allow for a reconstruction of the atmospheric N₂O concentration during MIS 2 including the Last Glacial Maximum (LGM), where we observe a concentration of 202 ± 8 ppbv (mean and standard deviation from 25 to 15 kyr BP). The records confirm the glacial–interglacial concentration increase from about 200 ppbv during the LGM to about 270 ppbv during the early Holocene (Flückiger et al., 1999). Further, the TD N₂O record reveals large variations in response to the DO events of the last glacial. The amplitudes of CH₄ variations decrease approximately linearly from the DO events 8 to 2. This trend is probably caused by (i) reduced summer insolation in the tropical and mid-northern latitudes (Brook et al., 1996; Flückiger et al., 2004), (ii) spreading ice sheets increasingly covering boreal source regions, and (iii) decreasing temperature amplitudes in the high northern latitudes for the DO events 8 to 2. The last hypothesis is not supported by measurements of the oxygen isotopic composition of precipitation ($\delta^{18}\text{O}_{\text{ice}}$, a qualitative proxy for temperature variations) along Greenland ice cores, since such measurements do not show decreasing amplitudes for the DO events 8 to 2 (NGRIP Members, 2004). However, the real temperature changes could differ from the $\delta^{18}\text{O}_{\text{ice}}$ temperature proxy, e.g. due to changing origin or seasonality of precipitation (Masson-Delmotte et al., 2005). Further, the temperature changes over Greenland may not completely be representative for the temperature changes in most of the northern hemisphere, and Greenland ice cores may primarily record winter-time temperature changes (Denton et al., 2005), which are less important for the emissions of greenhouse gases. All three hypothesis suppose that CH₄ emissions (from wetlands) located at high northern latitudes are of primary importance for CH₄ variations in response to DO events, which is supported by studies of the inter-polar gradient and hydrogen isotopic composition of CH₄ (Bock et al., 2010; Dällenbach et al., 2000). Since the N₂O response to the DO events 8 to 2 does not show a decrease in amplitudes like CH₄, we suggest that the observed N₂O variations are driven by marine and/or terrestrial emissions from low latitudes (Schilt et al., 2010; Schmittner and Galbraith, 2008). Indeed, reconstructions of the isotopic composition of atmospheric oxygen point to large changes in the hydrological cycle and, thus, in the photosynthetic capacity of the terrestrial surface in concert with the DO events during the last glacial (Landais et al., 2007; Severinghaus et al., 2009). These changes are mainly located at low latitudes and they may affect the N₂O emissions from soils. On the other hand, reconstructions of denitrification rates in the Arabian Sea and in the Eastern Tropical North Pacific also show strong reactions to DO events (Emmer and Thunell, 2000; Suthhof et al., 2001). These two important lower latitude regions for marine N₂O emissions alone could be responsible for substantial changes in the atmospheric N₂O concentration.

4.2. N₂O during the DO events 17 to 15

Figure 2 presents the high-resolution NGRIP N₂O record covering the DO events 17 to 15, along with the NGRIP CH₄ record (Huber et al., 2006) and the NGRIP $\delta^{18}\text{O}_{\text{ice}}$ record (NGRIP Members, 2004). As noted for other DO events (Flückiger et al., 2004), the new NGRIP N₂O record generally follows Greenland temperature and CH₄, reaching concentrations of about 260 to 275 ppbv during interstadials. However, N₂O differs from Greenland temperature and CH₄ in its temporal evolution. In the long-lasting stadial preceding DO event 17, the slow N₂O increase (which occurs in concert with increasing $\delta^{18}\text{O}_{\text{ice}}$ but constant CH₄) starts from around 200 ppbv. In the course of the last glacial–interglacial cycle, such low N₂O concentrations have otherwise only been reconstructed for MIS 2 (Fig. 1). Several hundred years before the rapid increase of $\delta^{18}\text{O}_{\text{ice}}$ and CH₄ corresponding to the onset of DO event 17, the increase rate of N₂O changes from ~0.8 ppbv/century to ~4.1 ppbv/century. This increase rate of ~4.1 ppbv/century is still about 10 times slower than the anthropogenic increase rate of the last 50 yr (Khalil et al., 2002). The early increase of N₂O compared to $\delta^{18}\text{O}_{\text{ice}}$ and CH₄ points to changes in the biogeochemical cycles related to N₂O occurring hundreds of years before the rapid temperature increase in Greenland. Note, however, that Bock et al. (2010) also observe a change in the hydrogen isotopic composition of CH₄ (without considerably affecting the CH₄ concentration) about 500 yr before DO event 8, pointing to changes of boreal wetlands before the rapid temperature increase in Greenland. An early increase of N₂O has also been reproduced for other long-lasting DO events (e.g. 20, 19, 12 and 8), while shorter DO events (e.g. 11 and 10) show a rather synchronous increase of CH₄ and N₂O (Flückiger et al., 2004). It has been shown that a substantial Antarctic warming precedes each DO event observed in Greenland (EPICA Community Members, 2006). However, a causal relationship between this early warming in the south and the early increase of N₂O can be excluded because of the different timing (Flückiger et al., 2004). Recent model simulations of Schmittner and Galbraith (2008) rather suggest that long-term adjustment of the nitrate and oxygen content in the thermocline after the collapse of the Atlantic Meridional Overturning Circulation (AMOC) could be responsible for the early increase of N₂O.

The maximum N₂O concentration during DO event 17 is on the order of the preindustrial Holocene value (Flückiger et al., 1999). As for other DO events, N₂O reaches the maximum several hundred years later than $\delta^{18}\text{O}_{\text{ice}}$ and CH₄. This lag is likely caused by the relatively long lifetime of N₂O, and does not necessarily mean that N₂O emissions continued to increase while CH₄ emissions already reached a stable level (Flückiger et al., 2004).

In the course of the DO events 17 and 16, the Greenland $\delta^{18}\text{O}_{\text{ice}}$ record is characterized by fast centennial time scale temperature variations between stadials and interstadials. While CH₄ clearly responds to every single variation in the $\delta^{18}\text{O}_{\text{ice}}$ record within a few decades (Huber et al., 2006), N₂O remains on a typical interstadial level even when $\delta^{18}\text{O}_{\text{ice}}$ and CH₄ drop to stadial levels (Fig. 2). The question is whether the longer atmospheric lifetime of N₂O compared to the atmospheric lifetime of CH₄ can lead to the observed differences between the two greenhouse gas records. To address this question, we calculate the CH₄ emissions required to explain the reconstructed CH₄ concentration under the assumption of a constant lifetime which is set to 10 yr (Chappellaz et al., 1997; Martinerie et al., 1995). Due to this relatively short lifetime, CH₄ emissions and CH₄ concentration change nearly in parallel. Assuming that N₂O emissions are proportional to the CH₄ emissions, the corresponding hypothetical N₂O emissions and the deduced hypothetical N₂O concentration can be calculated, whereby the lifetime of N₂O is set to 120 yr (Minschwaner et al., 1998; Volk et al., 1997). The hypothetical N₂O concentration follows, although in a smoothed way, the rapid changes in $\delta^{18}\text{O}_{\text{ice}}$ and CH₄, and thus contradicts the NGRIP N₂O record which does not respond to the changes in $\delta^{18}\text{O}_{\text{ice}}$ and CH₄ (Fig. 5). Hence, the relatively long lifetime

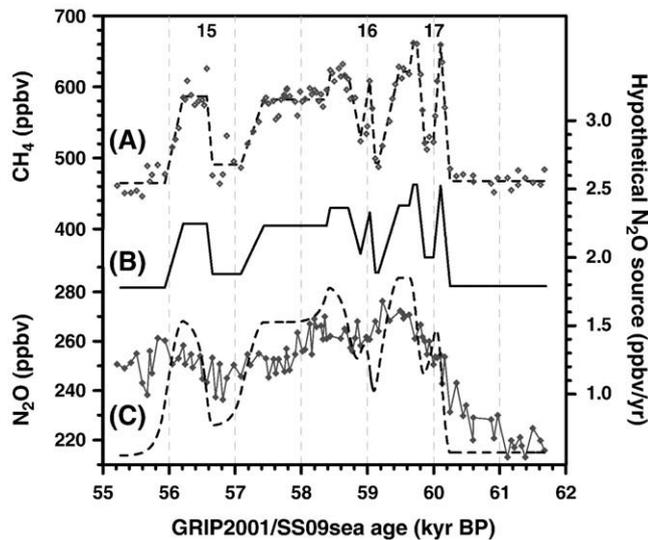


Fig. 5. Influence of the atmospheric lifetime on the N_2O concentration during the DO events 17 to 15. (A) NGRIP CH_4 (diamonds, Huber et al., 2006) with approximated variations (dashed line). (B) Hypothetical N_2O source calculated by scaling the CH_4 source (not shown, calculated from the approximated CH_4 variations) in such a way, that the hypothetical N_2O concentration agrees with the reconstructed values in the stadial before DO event 17. (C) NGRIP N_2O (diamonds, new data) with hypothetical N_2O concentration (dashed line) calculated from the hypothetical N_2O source. The atmospheric lifetimes of CH_4 and N_2O are set to 10 and 120 yr, respectively, and held constant.

of N_2O can only partly explain the slowly varying and high N_2O concentration. The assumption of parallel variations in the emissions of CH_4 and N_2O in response to the centennial time scale climate variations during the DO events 17 and 16 has thus to be rejected.

In the stadial between the DO events 16 and 15, N_2O reaches values of about 240 ppbv. During the subsequent increase into DO event 15, N_2O again does not show any direct response to the fast increase in $\delta^{18}\text{O}_{\text{ice}}$ and CH_4 , and reaches its maximum of about 260 ppbv several hundred years later than CH_4 (Fig. 2).

As discussed in Section 4.1, the high northern latitudes may play an important role for CH_4 emissions in response to DO events. Assuming that these high northern latitude sources are also responsible for the centennial time scale CH_4 variations observed during the DO events 17 and 16, we suggest that terrestrial N_2O emissions from these regions contribute, if at all, weakly to the observed variations in the N_2O concentration. Accordingly, the insensitivity of N_2O concentrations to centennial time scale temperature and CH_4 variations as observed along the NGRIP ice core during the DO events 17 and 16 could add weight to the hypothesis that atmospheric N_2O concentrations observed in response to DO events are mainly driven by marine and/or terrestrial N_2O emissions from low latitudes (Schilt et al., 2010; Schmittner and Galbraith, 2008).

5. Discussion

5.1. Radiative forcing during the last 140 kyr

Detailed knowledge of the past atmospheric greenhouse gas concentrations and thus the radiative forcing of the atmosphere is indispensable for modelling studies of the Earth's climate system. In order to provide records of the three most important greenhouse gases on a common time scale, we assemble and synchronise records of CO_2 , CH_4 and N_2O from numerous ice cores (including new and published data), and calculate the radiative forcing (Fig. 1).

First, we present a composite CO_2 record (smoothing spline with a cut off period of 1000 yr calculated according to Enting (1987)) covering the last 140 kyr and consisting of earlier published records

from the EDC, Taylor Dome (Antarctica, 77°48' S, 158°43' E), Byrd (Antarctica, 80°01' S, 119°31' W) and Vostok (Antarctica, 78°28' S, 106°50' E) ice cores. Second, we calculate a smoothing spline with a cutoff period of 1000 yr (Enting, 1987) through the EDC CH_4 record. We do not use a composite record for CH_4 since doing so would add uncertainties rather than new information. Note that the CH_4 smoothing spline represents a southern hemisphere signal, while the inter-polar gradient of CH_4 has been found to reach values of up to about 50 ppbv (Chappellaz et al., 1997; Dällenbach et al., 2000). Third, we establish a composite N_2O record consisting of measurements obtained from the EDC, EDML, TD and NGRIP ice cores, as well as from the ice cores of the Greenland Ice Core Project (GRIP, Greenland, 72°34' N, 37°38' W) and the Greenland Ice Sheet Project 2 (GISP2, Greenland, 72°36' N, 38°30' W) sites. The composite N_2O record (smoothing spline with a cut off period of 1000 yr calculated according to Enting (1987)) now covers the last 140 kyr without gaps, owing to the new measurements along the TD ice core. In order to put CO_2 , CH_4 and N_2O records from different ice cores on the EDC3 time scale (Loulergue et al., 2007), we perform a CH_4 synchronisation (Appendix A.4).

The records enable a comprehensive insight into the radiative forcing of CO_2 , CH_4 and N_2O during the last 140 kyr. The radiative forcing as shown in Figure 1 is calculated according to Ramaswamy et al. (2001) relative to the year 1750 (preindustrial forcing). As already noted in previous work (e.g. Chappellaz et al., 1990; Leuenberger and Siegenthaler, 1992), CH_4 and N_2O contribute approximately equally to the (natural) global radiative forcing during the last 140 kyr, but their contribution is of secondary importance compared to the radiative forcing of CO_2 (CH_4 and N_2O together contribute about 20% to the total change in the radiative forcing of all greenhouse gases over Termination 1). The provided smoothing splines through the CO_2 , CH_4 and N_2O composite records allow for an insight into long-term evolutions of the paleo-atmospheric greenhouse gas concentrations, however, there are limitations to study detailed responses on centennial to millennial time scales. For this we would rather suggest to rely on high-resolution greenhouse gas measurements from one single ice core.

5.2. Comparison of millennial time scale climate variations and glacial terminations

Investigation of natural mechanisms causing the Earth's climate system to shift between cooler and warmer climate states could provide crucial information to improve projections of the climate in the future. For past natural climate variations on glacial–interglacial time scales, the strong imprint of insolation, which becomes apparent when looking at frequency spectra of climate records and insolation (Hays et al., 1976), shows that external forcing plays an important role or may act as a trigger. While it is clear that external forcing can, however, not quantitatively explain the global changes in the radiative forcing necessary for glacial–interglacial transitions, the interaction of insolation with climate drivers on Earth (such as atmosphere, cryosphere, land, and ocean) leading to a sufficient internal amplification is still not completely understood. As demonstrated by the calculation of the radiative forcing (Section 5.1), CO_2 strongly feeds back on global climate, while CH_4 and N_2O contribute less to the total radiative forcing of greenhouse gases on glacial–interglacial and millennial time scales. Therefore, rather than considering CH_4 and N_2O as first-order climate drivers, we here understand their atmospheric concentrations as globally integrated indicators of changes in the biogeochemical cycles. Thereby, variations in CH_4 are thought to mainly indicate changes in boreal and tropical wetland emissions, and thus changes in precipitation patterns, temperature, sea level and ice sheet extent (e.g. Berrittella and van Huissteden, 2009; Brook et al., 2000; Bubier and Moore, 1994). Variations in N_2O are thought to be caused by changes in

marine and/or terrestrial emissions from low latitudes (e.g. Schilt et al., 2010; Schmittner and Galbraith, 2008). While some studies suggest quite stable atmospheric sinks for CH₄ and N₂O over time (Crutzen and Bruhl, 1993; Martinerie et al., 1995), other investigations indicate that variations in the sinks of the two greenhouse gases could still have the potential to strongly influence the atmospheric budgets (e.g. Fischer et al., 2008; Kaplan et al., 2006).

During the last glacial, records from Antarctic ice cores reveal numerous temperature variations on a millennial time scale. Such Antarctic Isotope Maxima (AIM) events (EPICA Community Members, 2006) correspond to a slow and steady warming around Antarctica followed by a similar cooling, the latter being initiated by a fast increase in the temperature recorded in Greenland ice cores, i.e. a DO event (EPICA Community Members, 2006). This interplay of southern and northern temperatures may be driven by changes in the AMOC and is known as the bipolar seesaw (Broecker, 1998; Stocker, 1998; Stocker and Johnsen, 2003). Wolff et al. (2009) have looked at a proxy for Antarctic temperature variations and have found that initial phases of AIM events and glacial terminations are indistinguishable regarding their temperature evolution. According to Wolff et al. (2009), both, AIM events and glacial terminations, are led by a warming in the southern hemisphere. In case of glacial terminations no northern control sets in, allowing southern warming (and associated atmospheric CO₂) to increase beyond a point of no return that pushes climate into an interglacial state. In turn, during AIM events, the AMOC strengthens which leads to a cooling in the southern hemisphere and an accompanying decline in atmospheric CO₂, finally resulting in a stadial climate.

Here, we look at greenhouse gas concentrations and add a biogeochemical point of view to this discussion. Comparing the greenhouse gas concentrations during the last 140 kyr as recorded in response to DO/AIM events and glacial terminations, we observe that maximum CH₄ and CO₂ concentrations during DO/AIM events never reach values as high as at the end of Termination 1 and Termination 2 (Fig. 1). In contrast, high interglacial N₂O concentrations are very common also during DO events. In order to highlight one particular case of similarities in N₂O responses to DO events and glacial terminations, we compare the evolution of N₂O during the DO events 17 to 15 and Termination 1 (Fig. 6). The former time interval corresponds to the transition from MIS 4 to 3 (Section 4.2), and thus to one of the strongest climate changes during the last glacial not leading to an interglacial. A detailed comparison of the transition from MIS 4 to 3 and Termination 1 can also be found in Liu et al. (2010). Remarkably, the N₂O records of the two selected time intervals evolve virtually identically until 3000 yr after the beginning of the N₂O rise, when N₂O concentrations decrease at the end of DO event 16 on the one hand or increase into the Preboreal on the other hand.

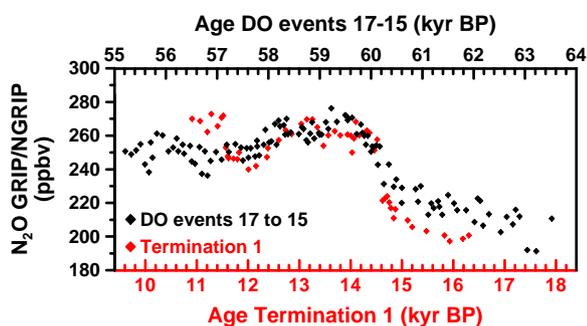


Fig. 6. Comparison of N₂O during Termination 1 and the transition from MIS 4 to 3 corresponding to the DO events 17 to 15. Red: GRIP N₂O (Flückiger et al., 1999) shown on the SS09 time scale (Dansgaard et al., 1993; Johnsen et al., 2001) with gas ages according to Schwander et al. (1997). Black: NGRIP N₂O (new data) shown on the GRIP2001/SS09sea time scale (Huber et al., 2006; Johnsen et al., 2001; NGRIP Members, 2004). Both x-axes span 9 kyr.

Such similarities as for the evolution of N₂O in response to the transition from MIS 4 to 3 and Termination 1 are not apparent for CH₄ and CO₂. The baseline values prior to the two transitions differ by about 50 ppbv for CH₄ and by about 20 ppmv for CO₂. Further, as for DO/AIM events in general, CH₄ and CO₂ concentrations do not reach interglacial levels during the transition from MIS 4 to 3, in contrast to N₂O concentrations. From the point of view of N₂O the DO events 17 to 15 could be classified as “interglacial”. Our observations suggest that the mechanisms leading to DO/AIM events and glacial terminations could have the same influence on the sources (and sinks) of N₂O, while the responses of CH₄ and CO₂ clearly differ for the two types of transitions. Since we think that N₂O is strongly influenced by the ocean and soils located at low latitudes, while CH₄ and CO₂ may also be driven by changes occurring at high latitudes of both hemispheres (in addition to important contributions from the tropics), we finally speculate that processes located at high latitudes are a determining factor on whether an ongoing transition leads to an interglacial or not.

6. Conclusions

New measurements along the TD ice core provide for the first time an entire atmospheric N₂O record during MIS 2, including the LGM which is characterized by a mean N₂O concentration of 202 ± 8 ppbv. The TD N₂O record shows large variations in response to the DO events 8 to 2, while CH₄ amplitudes during these DO events decrease towards the LGM. We therefore suggest that N₂O emissions are not regulated by the very same parameters responsible for the amplitude modulation of CH₄ changes in response to DO events. This could point to a predominance of marine and/or terrestrial N₂O emissions from low latitudes (Schilt et al., 2010; Schmittner and Galbraith, 2008). In view of the large N₂O variations in response to the DO events around the end of the last glacial, N₂O could become a tool for synchronising ice cores during this crucial time interval where only minor changes in CH₄ occur. However, N₂O measurements affected by artefacts could complicate the picture.

High-resolution N₂O measurements along the NGRIP ice core covering the DO events 17 to 15 confirm that N₂O starts to increase hundreds of years before the rapid increase in Greenland temperature and CH₄ at the beginning of long-lasting DO events (Flückiger et al., 2004). While a large part of the CH₄ and N₂O responses to millennial time scale variations during the last glacial can be explained by parallel changes in the sources of the two greenhouse gases, our data show that CH₄ and N₂O emissions evolved independently in the course of centennial time scale variations during the DO events 17 and 16.

A composite N₂O record gives for the first time a complete overview of the evolution of atmospheric N₂O back to the beginning of the previous interglacial. By the additional use of numerous CH₄ and CO₂ ice core records put on a common time scale, we calculate the radiative forcing of these three most important long-living greenhouse gases for the last 140 kyr. Although the provided smoothing splines do not resolve very detailed variations on centennial to millennial time scales, they may be useful for future modelling studies focussing on glacial–interglacial time scales.

The comparison of large climate transitions has revealed that Antarctic temperature evolves similarly during initial phases of DO/AIM events and glacial terminations (Wolff et al., 2009). Because we find that (during the last 140 kyr) N₂O concentrations during DO events often reach levels similar to those at the end of glacial terminations, while CH₄ and CO₂ respond differently to the two types of transitions, we suggest that DO/AIM events and glacial terminations may have a similar influence on N₂O sources (and sinks). Since N₂O concentrations may mainly reflect changes in marine and/or terrestrial emissions from low latitudes, in contrast to CH₄ and CO₂ emission changes which are also influenced by processes located at high latitudes, we speculate that high latitudes could account for the distinction of DO/AIM events and glacial terminations. Nevertheless,

the tropics may strongly support large climate variations by large emissions of greenhouse gases. Explaining why climate does not enter an interglacial after DO/AIM events, in particular after the transition from MIS 4 to 3, could reveal crucial information about the mechanisms at play during glacial terminations.

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Appendix A

A.1. Measurement technique for N₂O and CH₄

Following the extraction of ancient air from polar ice samples of about 40 g (University of Bern) or 50 g (Laboratoire de Glaciologie et Géophysique de l'Environnement, LGGE) by a melt–refreezing method, the air is injected into a sampling loop and analyzed for N₂ + O₂ + Ar, CH₄ (University of Bern and LGGE) and N₂O (University of Bern) by gas chromatography. The gas chromatographs are equipped with a thermal conductivity detector (TCD, for N₂ + O₂ + Ar), a flame ionization detector (FID, for CH₄) and an electron capture detector (ECD, for N₂O). See e.g. Flückiger et al. (2004) and Chappellaz et al. (1997) for detailed descriptions of the melt–refreezing method and the measurement systems. Parts of the N₂O and CH₄ records were measured with a slightly modified measurement system at the University of Bern. This modified system allows for up to 16 measurements per day (instead of up to 8 measurements per day with the unmodified system). The melt–refreezing air extraction method is unchanged. However, with the modified system we perform one single injection per sample instead of three injections with the unmodified system. The amount of analyzed air remains the same, since we now inject the air into a three times larger sampling loop. While with the unmodified system CH₄ and N₂O are cryofocused on one trap (at −196 °C) each, the two gases are now split by Y-splitters after a first chromatographic separation and then cryofocused on three traps each. Since the traps are heated up with some time lag, there are still three peaks in both, the FID and ECD. Both systems produce similar results, as indicated by remeasurements of previously measured samples along the TD ice core (adjacent depth levels, concentrations spanning the whole natural range). 86 reanalysed samples for CH₄ reveal a median of the differences (remeasurements with modified system minus previous measurements with unmodified system) of −1.3 ppbv with a 95% confidence interval of [−3.0, 0.7]

ppbv. 59 reanalysed samples for N₂O reveal a median of the differences of −1.7 ppbv with a 95% confidence interval of [−3.3, 0.3] ppbv. In respect of the median of the differences, the unmodified and the modified system are, thus, statistically undistinguishable for both, CH₄ and N₂O concentrations.

In previous studies, the uncertainty of N₂O measurements has been determined by the square root of the sum of the squared standard deviation of measurements of bubble-free ice with standard gas and the squared standard deviation of the three measurements of each sample, multiplied by the corresponding t-value of the t-distribution due to the small statistics (Flückiger et al., 2004). The uncertainties calculated according to Flückiger et al. (2004) average to 3.8 ppbv and 3.9 ppbv for our new NGRIP record covering the DO events 17 to 15 and our new TD record, respectively. Along the TD ice core, however, we checked the reproducibility of N₂O measurements by series of five adjacent samples at nine different depth levels (Fig. 3). Overall, these measurements reveal a standard deviation of 5.6 ppbv with a 95% confidence interval of [4.6, 7.1] ppbv. Measuring adjacent samples may be the most reliable way to determine the reproducibility of our measurement system, since this method is based on measurements of air extracted from natural ice samples. The new measurements of adjacent samples indicate that the uncertainty could be slightly larger than estimated according to Flückiger et al. (2004). While we still use the latter uncertainty for the NGRIP record (due to missing measurements of adjacent samples along this ice core), we use the uncertainty based on measurements of adjacent samples for the TD N₂O record.

Along the TD ice core, the scatter of five adjacent samples during intervals with dust concentrations above and below the threshold of 300 ppbw is statistically indistinguishable. This observation further increases our confidence in MIS 2 N₂O concentrations measured along the TD ice core. However, we admit that series of adjacent samples may not be unambiguous to detect potential artefacts, since a similar series of adjacent samples along the EDML ice core revealed high concentrations apparently subject to in situ production of N₂O, but the measurements also did not show a large scatter.

A.2. Offset corrections for N₂O and CH₄ measurements

According to Spahni et al. (2005) we correct N₂O records measured at the University of Bern since the year 2003 by +10 ppbv in order to reach consistency with earlier records. This systematic offset of still unknown origin was determined by resampling EDC Holocene ice and by a comparison of the EDC and EDML Holocene N₂O records (Spahni et al., 2005). From the records used for the composite N₂O record (Fig. 1) the whole EDML and TD records, as well as the EDC record older than 40 kyr BP and the NGRIP record covering the DO events 17 to 15 are corrected by +10 ppbv. All other N₂O records have been measured before the shift occurred and are thus uncorrected. The offset correction was recently verified by remeasurements along the EDC and NGRIP ice cores. Along the EDC ice core, 74 remeasurements covering MIS 15, 5 and 3, as well as the Holocene were performed (Schilt et al., 2010). Although some inconsistencies between earlier measurements and remeasurements were observed during MIS 3, the remeasurements overall clearly indicated that the N₂O measurements performed at the University of Bern over many years are on a consistent reference scale, once the shift of 10 ppbv is taken into account (see Schilt et al., 2010 for more details). In order to cross-check the N₂O measurements performed at the University of Bern with measurements from a different lab, we compare all Bern measurements with the GISP2 N₂O record of Sowers et al. (2003). Figure 7 shows the GISP2 N₂O record together with all Bern data from different ice cores (see also Fig. 1) put on the EDC3 time scale by CH₄ synchronisation (Appendix A.4). We calculate the differences between the GISP2 N₂O data and the corresponding values of a smoothing spline through the Bern N₂O data with a cutoff period of 1000 yr according to Enting (1987). The mean of the differences is

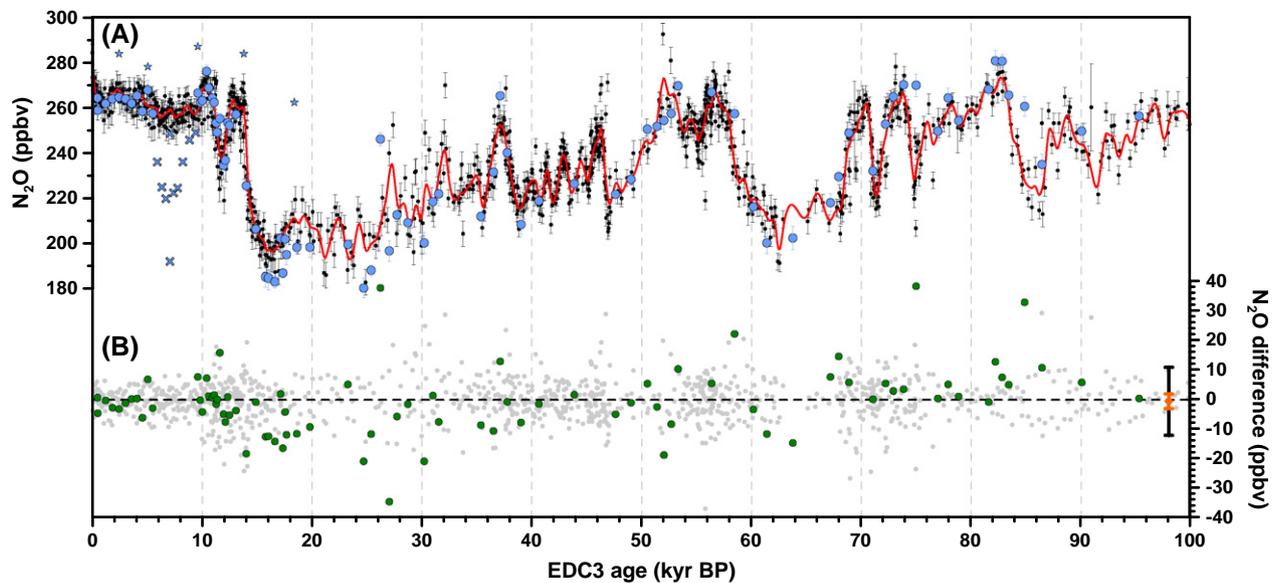


Fig. 7. Comparison of Bern N_2O data with GISP2 N_2O data of Sowers et al. (2003). (A) Black: N_2O data measured at the University of Bern along different ice cores (see Fig. 1). Red: smoothing spline with a cutoff period of 1000 yr calculated according to Enting (1987) through the Bern N_2O data. In contrast to the smoothing spline in Figure 1, this smoothing spline does not include the GISP2 N_2O data. Blue: GISP2 N_2O data (Sowers et al., 2003). Crosses indicate values which are biased by the extraction process. Stars indicate values which we assume to be affected by artefacts. All data are shown on the (CH_4 synchronised) EDC3 time scale (Appendix A.4) (B). Green: differences between GISP2 N_2O data and the smoothing spline calculated through the Bern N_2O data. Grey: differences between Bern N_2O data and the smoothing spline calculated through the Bern N_2O data. The orange diamond on the right shows the mean of the differences between GISP2 N_2O data and the smoothing spline calculated through the Bern N_2O data, with the orange error bar indicating the 95% confidence interval of the mean and the black error bar indicating the standard deviation of the differences. Note that this standard deviation does not correspond to the reproducibility of the measurement system (see Appendix A.2).

–0.5 ppbv with a 95% confidence interval of [–2.9, 1.9] ppbv. The differences between GISP2 and Bern data have a standard deviation of 11.5 ppbv. We note that the scattering of Bern data around the smoothing spline calculated through the Bern data is of the same order (Fig. 7). Accordingly, the scattering, which is larger than the reproducibility of the measurement system at the University of Bern (see Appendix A.1), may at least partly be caused by the applied method using a smoothing spline. In addition, uncertainties in the CH_4 synchronisation may add to the differences between GISP2 and Bern data. The CH_4 synchronisation does for instance not exclude that the high GISP2 N_2O value at around 26 kyr BP corresponds to the high TD values observed slightly earlier. Overall, the GISP2 N_2O record is in very good agreement with the Bern data, and the comparison does not indicate a remaining systematic offset in the presented N_2O composite record.

CH_4 records measured at LGGE are systematically lower than those measured at the University of Bern and are, therefore, corrected by +6 ppbv (Spahni et al., 2005).

A.3. Measurement technique for dust

The dust concentration was measured with a laser based particle detector which has been described in detail in Ruth et al. (2002). The particle detector has been implemented in an established continuous flow analysis (CFA) system (e.g. Kaufmann et al., 2008; Röthlisberger et al., 2000), where ice core pieces of a cross section of 34 mm \times 34 mm and 1 m length are melted continuously along the direction of the ice core. For decontamination reasons only the melt water of the inner of two concentric sections is pumped to the detectors. The dust concentration was recorded at an effective depth resolution of 1 cm (Ruth et al., 2002), however, we here use a smoothing spline with a cutoff period of 2000 yr (Enting, 1987). Gaps in the dust concentration record are due to wrongly calibrated or missing measurements. Note that for the depth interval of the brittle ice (667 to 1002 m) a partial contamination and, thus, too high dust concentrations cannot com-

pletely be ruled out. However, this does not affect the conclusions of this study.

A.4. Time scale synchronisation

In order to establish composite records consisting of CO_2 and N_2O measurements from different ice cores a common time scale is needed. We use the EDC3 gas age scale (Louergue et al., 2007) as a reference and match the gas records of all other ice cores to this time scale. CH_4 is most suited for such synchronisation, since it is globally well mixed and shows rapid and large natural variations synchronous in all ice cores (Blunier et al., 1998, 2007). Along the EDC CH_4 record back to 140 kyr BP, we define 47 tie points which represent characteristic events (Fig. 1). Identification of the tie points in the CH_4 records of all other ice cores and subsequent synchronisation to the EDC ice core leads to the desired common time scale. In order to determine the depth of the tie points we sometimes interpolate (on the depth scale) to the corresponding CH_4 concentration. The age is linearly interpolated in-between the tie points and linearly extrapolated at the beginnings and ends of fragmentary CH_4 records. For TD between 50 and 140 kyr BP we use the TALDICE1 time scale (Buiron et al., 2010), since TALDICE1 has been built based on CH_4 synchronisation to the EDC3 time scale for this time interval. Since the time resolution of the Taylor Dome CH_4 record is not adequate for some time intervals, we directly synchronise the Taylor Dome CO_2 record to the Byrd CO_2 record.

Appendix B. Supplementary data

Files containing new N_2O and CH_4 data from the TD, NGRIP and EDML ice cores, as well as the smoothing splines of the composite greenhouse gas records are linked to the online version of this paper at doi:10.1016/j.epsl.2010.09.027. The ice core records can also be downloaded from the website of the World Data Center for Paleoclimatology at www.ncdc.noaa.gov/paleo.

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