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Serge Bernard, T. Röckmann, J. Kaiser, J.-M. Barnola, H. Fischer, et al.. Constraints on N₂O budget changes since pre-industrial time from new firn air and ice core isotope measurements. *Atmospheric Chemistry and Physics*, 2006, 6 (2), pp.503. hal-00328418

HAL Id: hal-00328418

<https://hal.science/hal-00328418>

Submitted on 18 Jun 2008

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Constraints on N₂O budget changes since pre-industrial time from new firn air and ice core isotope measurements

S. Bernard¹, T. Röckmann^{2,3}, J. Kaiser^{2,4}, J.-M. Barnola¹, H. Fischer⁵, T. Blunier⁶, and J. Chappellaz¹

¹Laboratoire de Glaciologie et Géophysique de l'Environnement (CNRS-UJF), St Martin d'Hères, France

²Max-Planck Institute for Nuclear Physics, Heidelberg, Germany

³Institute for Marine and Atmospheric Research Utrecht, Utrecht University, Utrecht, The Netherlands

⁴Department of Geosciences, Princeton University, Princeton, New Jersey, USA

⁵Alfred-Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

⁶Climate and Environmental Physics Institute, University of Bern, Bern, Switzerland

Received: 20 April 2005 – Published in Atmos. Chem. Phys. Discuss.: 29 August 2005

Revised: 15 December 2005 – Accepted: 5 January 2006 – Published: 16 February 2006

Abstract. A historical record of changes in the N₂O isotope composition is important for a better understanding of the global N₂O atmospheric budget. Here we have combined measurements of trapped gases in the firn and in ice cores of one Arctic site (North GRenland Ice core Project – NGRIP) and one Antarctic site (Berkner Island). We have performed measurements of the ¹⁸O and position dependent ¹⁵N isotopic composition of N₂O. By comparing these data to simulations carried out with a firn air diffusion model, we have reconstructed the temporal evolution of the N₂O isotope signatures since pre-industrial times. The decrease observed for all signatures is consistent from one pole to the other. Results obtained from the air occluded in the ice suggest a decrease of about –2.8‰, –2.4‰, –3.2‰ and –1.6‰ for δ¹⁵N, ¹δ¹⁵N, ²δ¹⁵N and δ¹⁸O, respectively, since 1700 AD. Firn air data imply a decrease of about –1.1‰, –1.2‰, –1.0‰ and –0.6‰ for δ¹⁵N, ¹δ¹⁵N, ²δ¹⁵N and δ¹⁸O, respectively, since 1970 AD. These results imply consistent trends from firn and ice measurements for δ¹⁵N and δ¹⁸O. The trends for the intramolecular distribution of ¹⁵N are less well constrained than the bulk ¹⁵N trends because of the larger experimental error for the position dependent ¹⁵N measurements. The decrease in the heavy isotope content of atmospheric N₂O can be explained by the increasing importance of agriculture for the present atmospheric N₂O budget.

1 Introduction

Over the past 200 years the mixing ratio of atmospheric N₂O has increased from ~270 nmol mol⁻¹ (Flückiger et al., 1999) to the value of 319 nmol mol⁻¹ in 2004. It is currently rising at a rate of (0.25±0.05)% per year (IPCC, 2001). Increasing N₂O levels are of concern for two reasons. Firstly, N₂O is a potent greenhouse gas and contributes a significant portion to anthropogenic climate change, even though it is more than 1100 times less abundant than carbon dioxide. This is due to the fact that the Global Warming Potential per molecule N₂O over a 100-yr time horizon is about 300 times greater than for CO₂ (IPCC, 2001). Secondly, N₂O plays an important role in ozone chemistry, because it is the main source of NO_x in the stratosphere (Crutzen, 1970; Minschwaner et al., 1993). N₂O is mainly produced by microbial nitrification and denitrification processes in soils and water. Minor contributions come from biomass burning, industry, combustion in vehicles and power plants. The main sink of N₂O is UV photolysis in the stratosphere (90%) with additional contributions from the reaction with electronically excited oxygen atoms (10%). Although precise estimates of the global N₂O source can be deduced from the global rate of increase and the sink terms (Minschwaner et al., 1993), the contribution of individual source terms remains poorly constrained.

A way to constrain the N₂O budget is to monitor its isotopic composition in the atmosphere (Dore et al., 1998; Kaiser et al., 2003a; Kim and Craig, 1993; Naqvi et al., 1998; Pérez et al., 2000, 2001; Röckmann et al., 2003a, 2001a, b; Sowers et al., 2003, 2002; Yoshida and Toyoda, 2000). Because the different sources and sinks of N₂O have

Correspondence to: T. Röckmann
(t.roeckmann@phys.uu.nl)

Table 1. Comparison between the resulting N₂O isotopic ratios after extraction and the standard gas.

	$\delta^{15}\text{N}/\text{‰}$ (vs. atm. N ₂)	$^1\delta^{15}\text{N}/\text{‰}$ (vs. atm. N ₂)	$^2\delta^{15}\text{N}/\text{‰}$ (vs. atm. N ₂)	$\delta^{18}\text{O}/\text{‰}$ (vs. VSMOW)
Stand SM25 + bubble free ice	6.6±0.1	-16.9±0.8	30.1±1.0	44.5±0.5
Stand SM25	6.72±0.01	-16.4±1.4	29.8±1.4	44.0±0.2

characteristic isotope signatures, the cause of the increase of atmospheric N₂O since pre-industrial times can be determined from the simultaneous evolution of its isotopic composition. Using a simple one box model accounting for the natural and anthropogenic sources and sinks of N₂O, Rahn and Wahlen (2000) predicted an isotopic difference between the pre-industrial and modern troposphere in the range -1.6 to -1.9‰ for $\delta^{15}\text{N}$ and -1.8 to -2.4‰ for $\delta^{18}\text{O}$. Similarly, Pérez et al. (2001) proposed that the tropospheric $\delta^{15}\text{N}$ of N₂O should have dropped by -2.2 to -3‰ over the last two centuries, assuming that one half of the increase of N₂O emissions is due to the use of synthetic N fertilizers.

Air trapped in Arctic and Antarctic firn and ice provides a way to quantify the magnitude of the atmospheric N₂O isotope changes. From analyses of Antarctic firn air, Röckmann et al. (2003a) extrapolated a decrease since the pre-industrial era, of -2‰ and -1.2‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively, whereas Sowers et al. (2002), using both firn air and ice core samples, suggested a decrease of -1.9‰ and -2.9‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively.

Here, we reconstruct the isotopic composition of atmospheric N₂O since pre-industrial times, using air from ice cores and firn, from an Arctic (North GRIP) and an Antarctic (Berkner Island) site. A firn-air diffusion model (Romme-laere et al., 1997) is used to take into account physical processes occurring in the firn column and to test atmospheric scenarios of N₂O isotope signatures against the measurements.

2 Experimental procedure

In the framework of the European Project CRYOSTAT (CRYospheric STudies of Atmospheric Trends of stratospherically and radiatively important gases), 15 samples of firn air were obtained from North GRIP in June 2001 (Greenland, 75° N 42° W) and from Berkner Island in January 2003 (Antarctica, 79° S 45° W). NGRIP (Berkner Island) has a mean annual temperature of -31°C (-26°C) and a surface accumulation rate of 20 cm (13 cm) water equivalent per year; its firn-ice transition is located at ~78 m (~64 m) and the mean N₂O age at this depth is 60 years (90 years).

The air sampling procedure is described in Bräunlich et al. (2001). Briefly, air samples were obtained by incrementally drilling into the firn with a standard electromechanical

drill. Drilling was interrupted at each prescribed depth and a “bladder” made of natural rubber was lowered to the bottom of the hole and inflated, thereby sealing the hole. Firn air was then pumped, dried using magnesium perchlorate (MgClO₄) and Drierite (calcium sulfate) and ultimately stored in Restek Silcocans (3 liter, 3 bar) and Scott Marin cylinders (5 liter, 120 bar).

In addition to the firn air, two ice samples from NGRIP and six ice samples from Berkner Island were analyzed. A new technique to extract the air enclosed in the ice bubbles was used. A sample of ~1 kg is inserted into a glass container sealed with an indium wire. After evacuation, the sample is melted under vacuum with continuous transfer of the released gases into an electropolished stainless steel cryotrap of 14 cm³ held at liquid helium temperature. Two coiled glass traps and one stainless steel trap between the container and the cryotrap are maintained at ~-50°C and -80°C, respectively, in order to trap water vapor. The efficiency of the system was tested as following. To assure the absence of leaks in the extraction and transfer system, three artificial bubble-free ice samples of ~1 kg each were melted and “transferred” into the cryotrap. No detectable N₂O or permanent gas could be detected. Next, to investigate possible isotopic fractionation, three ~1 kg bubble-free ice samples were processed together with ~100 cm³ of an atmospheric standard having known N₂O isotopic composition. Table 1 shows that overall no significant isotopic fractionation was observed between N₂O after extraction and the standard gas measured on the same day straight from its cylinder, although $\delta^{18}\text{O}$ may be slightly enriched. Based on these tests, we chose to apply no extraction correction to the ice-core results.

A potential source of error is the dissolution of N₂O in water due to its high solubility of 0.0005855 mol m⁻³ Pa⁻¹ at 0°C in fresh water (Weiss and Price, 1980), which implies that in equilibrium about 30% of the N₂O is dissolved in the water. The equilibrium isotope effect between N₂O dissolved in water and N₂O in the gas phase is known, -0.75‰ for $^{15}\text{N}/^{14}\text{N}$ and -1.06‰ for $^{18}\text{O}/^{16}\text{O}$ (Inoue and Mook, 1994), respectively. This would cause under equilibrium conditions a change of the N₂O isotopic composition in the gas phase of less than 0.3‰ and 0.5‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. However, during the entire extraction the gas phase above the water is constantly pumped off, so that N₂O is continuously removed, and we do not expect a significant isotope fractionation due to remaining dissolved N₂O for our measurements.

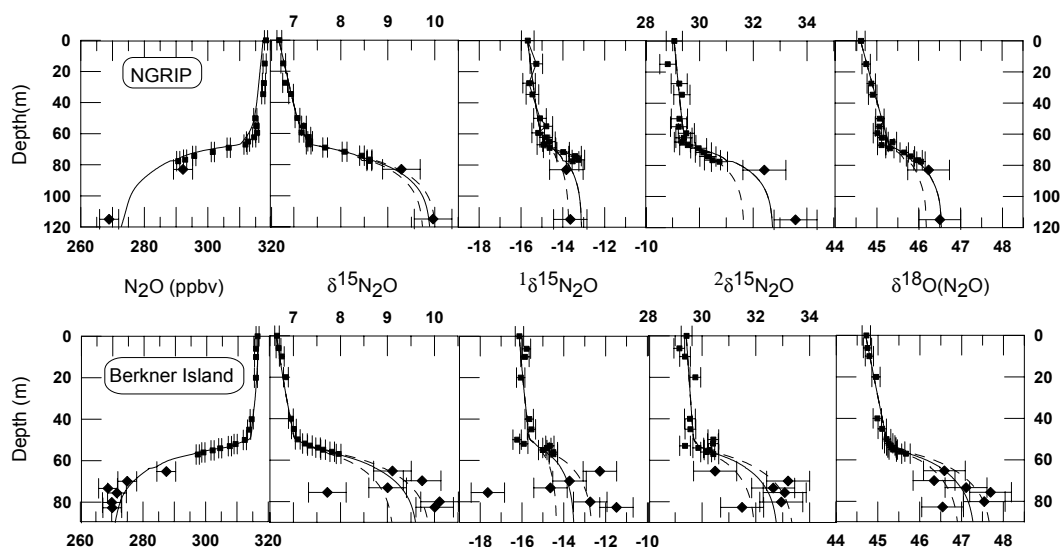


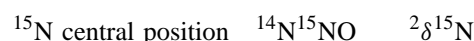
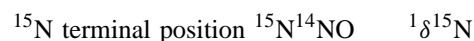
Fig. 1. Mixing and isotopic ratios of N₂O in NGRIP and Berkner Island. Square: firn samples; diamonds: ice samples; solid line: best scenario, i.e., profile calculated from the N₂O isotope scenario that best fits our data set; dashed lines: envelope of accepted scenarios, i.e., profiles calculated from N₂O isotope scenario that still fit the data set within the specified errors. In some cases the upper or lower envelope coincides with the best scenario.

Also the kinetic fractionation, which would affect the results on incomplete extraction of N₂O, is small, $-0.7\pm\text{‰}$ for $\delta^{15}\text{N}$ and -1.9‰ for $\delta^{18}\text{O}$ (Inoue and Mook, 1994), and should thus have no significant effect on our results.

The N₂O isotopic composition (^{18}O , average ^{15}N and position dependent ^{15}N) was measured using continuous-flow isotope ratio mass spectrometric techniques. The principle is described in Röckmann et al. (2003a, b). We only give a brief summary here. About 300 cm³ of firn air are injected into a He carrier gas stream of a modified ThermoFinnigan PreCon system. After removal of most of CO₂ over Ascarite (NaOH coated silica), N₂O is cryogenically preconcentrated. Final separation from the remaining CO₂ occurs on a capillary GC column (Poraplot Q, 0.32 mm i.d., 25 m) after cryo-focusing the sample. The column is separated into a pre-column and an analytical column. The pre-column is backflushed after each measurement which eliminates interferences from other atmospheric compounds, in particular on *m/z* 31 for quantifying the NO⁺ fragment. The sample is then transferred to the IRMS via an open split interface.

For the measurements presented here, two different mass spectrometers were used. The firn air samples were analyzed on a ThermoFinnigan Delta plus XL and the ice air samples on a ThermoFinnigan Delta plus XP. On the Delta plus XL, three collectors can be monitored simultaneously, therefore requiring two separate sample injections: one for the N₂O⁺ ions at *m/z* 44, 45 and 46, and one for the NO⁺ fragment at *m/z* 30 and 31 (Brenninkmeijer and Röckmann, 1999; Röckmann et al., 2003b). On the Delta plus XP, all five mass-to-charge ratios can be monitored simultaneously. Thus, only a single injection is needed (Röckmann and Levin, 2005).

As laboratory reference gas, we use a carefully calibrated atmospheric air sample (Kaiser et al., 2003a) with a N₂O mixing ratio of 319.0 ppbv and isotope ratios of $\delta^{15}\text{N}=6.6\text{‰}$ vs. atmospheric N₂ and $\delta^{18}\text{O}=44.6\text{‰}$ vs. VSMOW. The mass spectrometer reference gas (N₂O, purity 99.9999%) has an isotopic composition of $\delta^{15}\text{N}=0.53\text{‰}$ vs. atmospheric N₂ and $\delta^{18}\text{O}=39.60\text{‰}$ vs. VSMOW. The calibration of the intramolecular distribution in N₂O is not straightforward; a mass spectrometric calibration method using mixtures of isotopically labeled N₂O isotopologues has recently been developed (Kaiser et al., 2004). This calibration will be used in this work, but we note that there exists a large difference to the only other calibration available (Toyoda and Yoshida, 1999). Using that calibration shifts $^1\delta^{15}\text{N}$ values up by about 21‰ and $^2\delta^{15}\text{N}$ values down by about 21‰, so it is very important to compare the reference scale when comparing absolute $^1\delta^{15}\text{N}$ and $^2\delta^{15}\text{N}$ values from different publications. To distinguish between the N₂O isotopomers, we adopt the following notation:



The samples were measured three times and the standard deviations on the measured values in the firn are 0.05‰, 0.3‰, 0.3‰ and 0.1‰ for $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. Due to the limited sample amount the ice core samples were only measured once, and the sample size was at most 100 cm³. The standard deviations are deduced from the tests with reference gas and bubble-free ice and amount to 0.4‰, 0.8‰, 0.8‰ and 0.5‰ for $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively.

3 Results

N₂O concentration and isotope profiles in firn and ice air are shown in Fig. 1. As expected from its atmospheric evolution, the N₂O mixing ratio at each sampling site decreases with depth. The overall shape of the N₂O isotopic signals is similar for both sites and we identify three zones with similar characteristics: (1) a small increase of the heavy isotopes from the surface to the depth where closed porosity (see description of the firn column in the next section) appears (50 to 65 m depending on the site); (2) a large increase from this particular depth down to the bottom part of the firn; (3) a stabilization or slower increase (but with large scatter of the measurements) within the ice. In Berkner Island, the gas extracted at 75 m exhibits depleted isotopic values for $\delta^{15}\text{N}$ and $^{1}\delta^{15}\text{N}$. This is due to an unusually depleted measurement for $\delta^{15}\text{N}$, which affects strongly the ^{15}N value calculated for the terminal position, whereas the central position, which is measured independently, is much less affected. Since no repeated measurements are possible on the ice air samples, this discrepancy cannot be explained. However, it is highly unlikely that this is indeed an atmospheric signal. Therefore, we present this point in Fig. 1, but have excluded it from the further analysis. In addition, at this site, analyses conducted on other gases, like CH₄ and CFCs, showed that the firn air sampled between 58 m and the close-off depth (64 m) may be contaminated by ambient air. However, the CO₂ mixing ratio was monitored using an infra-red analyzer (LICOR), during firn air sampling. Below 58 m, the CO₂ mixing ratio was stable and below the ambient air level, thus contradicting the hypothesis of a contamination. As the validity of the last points is questionable, we decided to remove them and we consider the firn profile from the surface to 57 m. This observation does not concern the ice samples.

4 Modelling

4.1 Firn air model

Physical processes, like diffusion or gravitation, affect the trace-gas isotopic composition within the firn column; therefore, firn air measurements cannot be directly used to derive the atmospheric history of trace-gas isotopes. Firn air diffusion models take these effects into account and allow the selection of atmospheric scenarios compatible with the firn profile. In addition, N₂O extracted from our ice samples dates from 1740 AD to 1910 AD, a time period when the atmospheric N₂O mixing ratio increased. This increase could affect the air isotopic profile through diffusion along the concentration gradient. To take this potential effect into account, the composition of bubbly ice is also computed using the diffusion model.

We employed a 1-D gas diffusion model in Eulerian coordinates developed by Rommelaere et al. (1997). The pro-

cesses taken into account include (1) air mixing by pressure and temperature gradient down to a few meters from the surface (i.e. the so-called convection zone), (2) molecular diffusion in the open pore space and gravitational fractionation (entrainment toward the deeper firn depends on concentration gradients, diffusivities and molar mass), (3) a downward air flux in the open porosity zone due to bubble closure removing air from open pores; this removed air has to be replaced by air coming from the upper parts of the firn, thus creating this downward flux. These phenomena also affect the isotopologues of trace gases. The model computes them as independent species and calculates the resulting isotopic ratios in the firn afterwards. Temperature, accumulation rate and firn structural parameters (density, open and closed porosity, tortuosity) are set to their present-day measured values. The diffusivity profile for any trace gas and the firn-ice transition depth thus remain constant with time. Assuming a constant temperature in our model, we are not resolving variations over the top 10 m, where seasonal temperature effects are imprinted.

One big “unknown” of the firn air model is the diffusivity profile at a specific location. Diffusivities have not been measured at the locations discussed here. We calculate the diffusivity profile from the well-known CO₂ evolution in the atmosphere and our measured CO₂ mixing ratio profile. As CO₂ and N₂O both exhibit an approximately exponential increase since pre-industrial time, N₂O diffusivities are then calculated according to $D(\text{N}_2\text{O})/D(\text{CO}_2)=1.004$ (Trudinger et al., 1997). According to their mass difference, the diffusivities for the heavy N₂O isotopologues relative to CO₂ are then 0.999656 for $^{15}\text{N}^{14}\text{NO}$ and $^{14}\text{N}^{15}\text{NO}$ and 0.995441 for $^{14}\text{N}^{14}\text{N}^{18}\text{O}$. In order to validate the diffusivity profile, we apply the firn model using a historical record of N₂O mixing ratio. This scenario is derived from an interpolation of ice core data (Flückiger et al., 1999), the scenario deduced from firn air measurements at South Pole (Battle et al., 1996), and direct atmospheric observations at Cape Grim, Tasmania, from the ALE/GAGE/AGAGE measurements (http://cdiac.esd.ornl.gov/ftp/ale_gage_agage/AGAGE/gc-md/complete/tasmania). The agreement between the N₂O data and the model reconstruction is good, as seen in Fig. 1, thus validating the density and diffusivity profiles used in the model.

4.2 Monte-Carlo modelling of N₂O evolution

Although routinely used for trace gas mixing ratios, the implementation of the inversion technique to isotope ratios in the firn air model is complicated, owing to the nonlinearity of the forward model in the case of isotopes. We use a Monte Carlo approach instead where a wide range of hypothetical scenarios for the atmospheric evolutions of isotopologue concentrations are tested using the firn air model in the forward mode. As the evolution of N₂O mixing ratio since the pre-industrial era is close to an exponential increase, we

parameterize the input scenarios for the atmospheric δ value as an exponential function. This is a good mathematical approximation for the assumption that one source with constant isotopic composition has been responsible for the change in isotopic composition since pre-industrial times. We note that this is a strong constraint from the model, which does not allow that various sources with distinct isotopic composition have contributed differently at different times. Furthermore, we note already here that the fact that the atmospheric δ value decreases does not necessarily mean that the isotopic composition of the sources also decreases. In a disequilibrium situation between sources and sinks, which is driven by strong source changes, the atmospheric δ value will always change in the direction of the isotopic composition of the global average source. Since the global average N₂O source is isotopically depleted versus atmospheric N₂O, the atmospheric δ value would also decrease if the source signature had stayed constant and even if it slightly increased.

The validity of each scenario is assessed based on agreement between the modelled and experimental firn profiles using a χ^2 test. A scenario is classified acceptable if the corresponding calculated isotope profile in the firn falls within a given range of the experimental data (Table 2) (Aballain, 2002; Bräunlich et al., 2001). The accepted scenarios form the envelope that is presented in Fig. 2 for the scenarios and in Fig. 1 for the corresponding firn profiles. A measured atmospheric isotopic evolution was used as input data, from 1990 AD to present. This profile comes from direct atmospheric measurements on air samples collected in Neumayer, Antarctica (70° S, 8° W) from 1990 AD to 2002 AD (Röckmann and Levin, 2005). A trend on each isotopologue was deduced from this profile at this specific site. Then, starting from the measured surface value, this trend was set as a “known” isotopic evolution for the last 12 years at each studied site (i.e. NGRIP and Berkner Island), i.e. the isotopic evolution since 1990 was fixed. Note that the surface firn air values differ slightly between NGRIP and Berkner, but this difference is within the analytical uncertainty and does not alter the general trends derived from the firn air diffusion model.

4.3 Comparison of model and data

For NGRIP, the average difference between the model and the data is less than 0.15‰ for $\delta^{15}\text{N}$ and less than 0.20‰ for $\delta^{18}\text{O}$. The input scenario, constrained by direct isotope measurements between 1990 AD and the present, allows reproducing the top part of the firn within uncertainties. The $^1\delta^{15}\text{N}$ and $^2\delta^{15}\text{N}$ profiles are more scattered due to the difficulty of measuring the (^{15}N)N₂O isotopomers. In addition to the generally larger scatter, the ice core results do not seem to extend the firn air data smoothly; for the $^1\delta^{15}\text{N}$ the ice core data appear rather depleted, whereas they are rather enriched for $^2\delta^{15}\text{N}$ compared to the firn data. Although the model is able to reproduce on average the trends of the data, the resulting scenarios should be regarded with caution, due

Table 2. Parameters that are used in Monte Carlo runs of the firn air diffusion model to qualify calculated scenarios as acceptable or rejected.

	$\delta^{15}\text{N}$	$^1\delta^{15}\text{N}$	$^2\delta^{15}\text{N}$	$\delta^{18}\text{O}$
Monte Carlo parameters (‰)				
NGRIP	± 0.3	± 0.5	± 2	± 0.3
Berkner Island	± 1	± 2	± 1.4	± 0.9

to the larger uncertainty of the measurements on ice samples. Given the large experimental uncertainty of the ice core measurements and the fact that we only have two data points from ice air, we believe that the constraints from the ice data are probably over-represented in our model. If we use the ice core data at their respective 1σ error limits, the ice and firn data are much more consistent. This indicates that the trends estimated from our combined data are likely underestimated for $^1\delta^{15}\text{N}$ and overestimated for $^2\delta^{15}\text{N}$.

Also in the case of Berkner Island, the model reproduces the measured firn profile well. The ice data are more scattered but taking into account the error bars, the data lie within the envelope of accepted scenarios defined by the χ^2 test, except for the point at 75 m which is very low for $\delta^{15}\text{N}$ and $^1\delta^{15}\text{N}$ (previously mentioned). As for NGRIP, the larger scatter of intramolecular ^{15}N measurements implies more caution for the interpretation of the deduced atmospheric scenario.

The reconstructed atmospheric trends for both sites and for each isotopologue are represented in Fig. 2, together with the experimental values of the ice samples corrected for gravitation. The N₂O in an air sample at a certain depth has a wide age spectrum due to mixing processes in the firn column. This age spectrum widens with depth and the constraints from the firn air measurements on the atmospheric scenarios become successively weaker with depth. Thus the probability that the derived atmospheric scenario is constrained by the firn data can be computed from the green functions deduced from the inverse model (Rommelaere et al., 1997). This probability is only calculated for gases in the open porosity region. Thus, it has no significance for the air extracted from the ice. We evaluate our results for two age ranges: one from 1970 AD to present, which is the well-constrained period (constrained by the firn data only), and one using all data. The latter is then primarily constrained by the ice air. The values are summarized in Table 3.

For NGRIP, the colour scale shows that the firn data can constrain the atmospheric scenario at, at least 50% from 1970 AD on. From 1970 AD to 2001 AD, the evolution of the isotopic composition of atmospheric N₂O is about -1.1‰ , -1.1‰ , -1.1‰ and -0.5‰ for $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. The long term evolution, given by the ice data, leads to an overall decrease of the signal since 1700

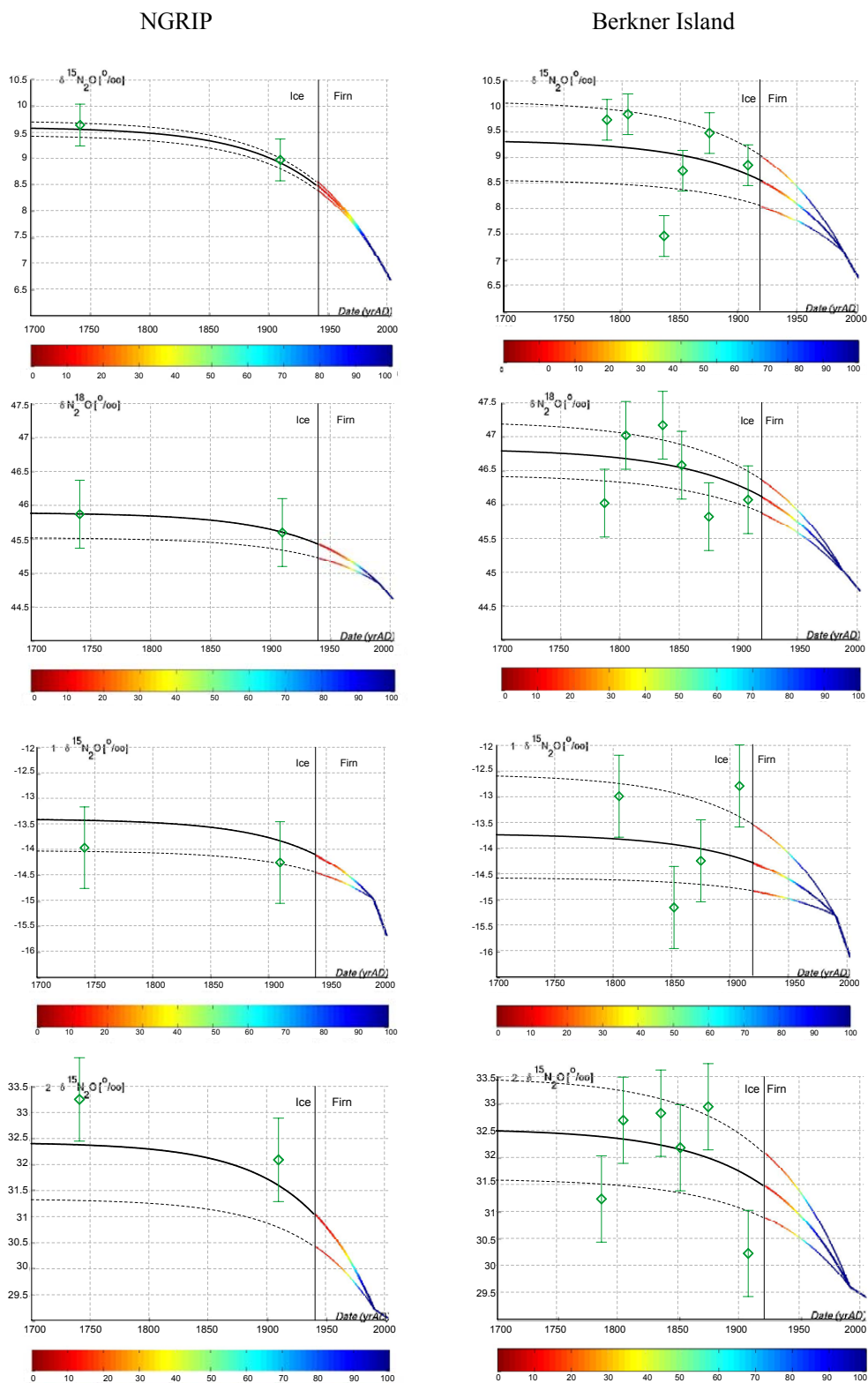


Fig. 2. Evolution of the atmospheric isotopic composition of N₂O since 1700 AD in NGRIP and Berkner Island. Dashed lines: envelope of accepted scenarios; solid line: best scenario; green diamonds: ice samples corrected for gravitational fractionation. The colour scale represents the probability that a given atmospheric scenario is constrained by the firm data. For Berkner Island two $\delta^{15}\text{N}$ data points are missing because they are off scale. The kinks in the scenarios for the individual ^{15}N isotopomers in 1990 (see continuation of figure on next page) indicate a discrepancy between the scenarios presented here and the direct measurements on Antarctic air samples since 1990 (Röckmann and Levin, 2005); see text for further discussion.

Table 3. Atmospheric change of $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ since pre-industrial times in NGRIP, Berkner Island and average value.

	NGRIP (‰)	Range (‰)	Berkner Island (‰)	Range (‰)	Average value (‰)	Range (‰)
1700 AD						
$\delta^{15}\text{N}$	-2.9	-3.0 to -2.7	-2.7	-3.4 to -1.8	-2.8	-3.4 to -1.8
$^1\delta^{15}\text{N}$	-2.3	-2.3 to -1.6	-2.5	-3.5 to -1.5	-2.4	-3.5 to -1.5
$^2\delta^{15}\text{N}$	-3.3	-3.3 to -2.2	-3.1	-4.0 to -2.2	-3.2	-4.0 to -2.2
$\delta^{18}\text{O}$	-1.3	-1.3 to -0.9	-2.1	-2.5 to -1.7	-1.6	-2.5 to -1.3
1970 AD						
$\delta^{15}\text{N}$	-1.1	-1.1 to -1.0	-1.0	-1.2 to -0.8	-1.1	-1.2 to -0.8
$^1\delta^{15}\text{N}$	-1.1	-1.2 to -1.0	-1.3	-1.5 to -1.2	-1.2	-1.5 to -1.0
$^2\delta^{15}\text{N}$	-1.1	-1.1 to -0.7	-0.9	-1.2 to -0.7	-1.0	-1.2 to -0.7
$\delta^{18}\text{O}$	-0.5	-0.5 to -0.4	-0.7	-0.8 to -0.6	-0.6	-0.8 to -0.5

AD of -2.9‰ , -2.3‰ , -3.3‰ and -1.3‰ for $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively.

For Berkner Island, the color scale indicates that the atmospheric scenario is constrained by the firn data at, at least 80% from 1970 AD on. From 1970 to 2003 AD, the evolution on the isotopic composition of atmospheric N₂O is about -1.0‰ , -1.3‰ , -0.9‰ and -0.7‰ for $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively. Since 1700 AD, the depletion of the isotopic signal is about -2.7‰ , -2.5‰ , -3.1‰ and -2.1‰ or $\delta^{15}\text{N}$, $^1\delta^{15}\text{N}$, $^2\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively.

The depletion observed for the oxygen isotopes since pre-industrial times is smaller than that observed for the nitrogen isotopes. Consistent atmospheric scenarios are deduced at both sites within the error limits for the nitrogen isotopes. For the $\delta^{18}\text{O}$ scenarios, slightly different results are derived for the two sites. Since the NGRIP scenarios are only constrained by two data points, the data from Berkner Island are likely more reliable, and we extend the range of possible scenarios from the best scenario for NGRIP to the upper limit for Berkner Island. In addition, Fig. 2 shows that for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ the trends measured recently on the archived Antarctic air samples (Neumayer) are in very good agreement with our results from firn and ice air. On the other hand, this is obviously not the case for individual ^{15}N signatures, where the trends from the direct measurements are too high for $^1\delta^{15}\text{N}$ and far too low for $^2\delta^{15}\text{N}$, which produces the kink in the isotope scenarios in Fig. 2 at the year 1990.

A similar discrepancy between the Neumayer observations and the earlier firn data from Dome C and Dronning Maud Land (Röckmann et al., 2003a) was noted in Röckmann and Levin (2005). On the other hand the data from the different firn air studies show similar trends (see below). The combined evidence from the old (Dome C and DML) and new (this study) firn and ice air data now indicates that indeed the trends at the terminal and central nitrogen positions are not so different. Trends in $^2\delta^{15}\text{N}$ are slightly larger than those

for $^1\delta^{15}\text{N}$ when the whole period is considered, but smaller in the recent period since 1970 AD. However, due the large uncertainties on the intramolecular measurements, this is not significant.

5 Discussion

Only one previous study of N₂O isotopologues in pre-industrial ice has been performed so far, using ice from GISPII (Greenland) (Sowers et al., 2002). Sowers et al. (2002) found that the ^{18}O trends were not consistent between firn air and ice air measurements. In particular, the isotope trends deduced from the ice core samples are much stronger. Note, however, that the analytical errors for ice core measurements (also in our measurements) are large. To explain this observation, the authors suggested a decoupling of the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ trends over the last 200 years: the majority of $\delta^{18}\text{O}$ change would have occurred in the 19th century whereas most of the $\delta^{15}\text{N}$ change took place during the 20th century. This would be isotopic evidence showing that the increase of N₂O since pre-industrial times was not due to one common source with constant isotopic composition. However, in our study we deduce from both NGRIP and Berkner Island firn and ice air samples consistent trends between the ice core and firn air results for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, which show a larger depletion of $\delta^{15}\text{N}$ compared to $\delta^{18}\text{O}$, since 1700 AD. This does not confirm the proposed decoupling of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ but rather suggests that they have changed in parallel over the entire time period. We cannot completely rule out that our extraction method may introduce a $\delta^{18}\text{O}$ enrichment of $\sim +0.5\text{‰}$ (see Table 1). As mentioned above, we did not correct for this enrichment, which is at the limit of significance. However, accounting for this effect would only increase the difference between our $\delta^{18}\text{O}$ results and the results of Sowers et al. (2002).

Table 4. Evolution of N₂O isotopic signatures since 1970 AD in different polar sites.

	NGRIP / Berkner Island ^(a) (‰)	Range (‰)	Dome C / DML ^{(b),(c)} (‰)
$\delta^{15}\text{N}$	-1.1	-1.2 to -0.8	-0.9
$^1\delta^{15}\text{N}$	-1.2	-1.5 to -1.0	-0.8
$^2\delta^{15}\text{N}$	-1.0	-1.2 to -0.7	-1.0
$\delta^{18}\text{O}$	-0.6	-0.8 to -0.5	-0.5

^(a) this study^(b) Röckmann et al. (2003a)^(c) range not modelled

Another possible explanation for the difference between both studies could lie in the fractionation related to the N₂O mixing ratio gradient between the atmosphere and the pore close-off during the early part of the atmospheric N₂O increase. It amounted to ~ 0.02 ppbv yr⁻¹ between 1700 AD and 1900 AD. Sowers et al. (2002) only corrected their results for gravitational fractionation. On the other hand our model corrects for gravitation as well as for diffusion due to mixing ratio changes that have occurred since 1700 AD. To check this hypothesis, we used the diffusion model to simulate $\delta^{15}\text{N}$ at NGRIP in the forward mode. The input scenario included the historical [N₂O] record and the atmospheric $\delta^{15}\text{N}(\text{N}_2\text{O})$ was kept constant over time. In this case the resulting signal in the ice has an amplitude of 0.32‰. The gravitational fractionation in NGRIP has been measured (A. Landais, personal communication, 2005) and is close to 0.32‰ for $\delta^{15}\text{N}$. We deduce that the increase of N₂O mixing ratio between 1700 AD and 1900 AD is not sharp enough to introduce a measurable fractionation; thus, the different model corrections applied by Sowers et al. (2002) and our analysis cannot explain the difference between the two sets of results.

Finally, it appears that our measurements have smaller errors, and that the larger errors in the Sowers et al. (2002) study provide only rather weak constraints that such a decoupling has actually taken place. We can thus conclude that the observed $\delta^{18}\text{O}$ trend is smaller than the $\delta^{15}\text{N}$ trend since pre-industrial times.

The $\delta^{18}\text{O}$ of N₂O reflects the oxygen isotopic signatures of its different sources such as molecular oxygen, soil water (nitrification) and substrate NO₃⁻ (denitrification). It also reflects the oxygen isotope enrichment factors associated with each reaction step. So far, it has not been possible yet to determine the relative contribution of these different oxygen sources in today's N₂O budget, because no consistent picture has yet emerged (Gros et al., 2004). Recent studies have also emphasized the importance of the population of microorganisms involved in the ¹⁸O-enrichment (Schmidt et al., 2004; Sutka et al., 2003).

In addition, since N₂O sources and sinks are presently not in equilibrium, the isotopic composition of tropospheric N₂O is shifting from its pre-industrial value towards the isotopic composition of the global average sources. The total offset between the global average source and the troposphere is determined by the fractionations in the stratosphere, and these are smaller for ¹⁸O than for ¹⁵N due to the smaller stratospheric fractionation constants (Kaiser et al., 2002b, 2003b; Röckmann et al., 2001a). When the atmosphere is moving towards the source isotopic composition, the absolute shifts are smaller for ¹⁸O than for ¹⁵N, simply because the isotopic difference to the global average sources is smaller for $\delta^{18}\text{O}$.

Our results show that $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ have both obviously decreased since 1700 AD. Making the assumptions that the N₂O lifetime, the stratospheric fractionation constants and the average troposphere/stratosphere exchange rate have remained constant since 1700 AD, Röckmann et al. (2003a) suggested that the depletion of the tropospheric signal is due to an increase of sources depleted in heavy isotopes, whereas the flux of isotopically enriched N₂O from the stratosphere to the troposphere has not had time to increase proportionally yet. Assuming further that natural sources have remained constant, the source responsible for the depletion must thus be a depleted anthropogenic source. Agriculture represents a major depleted anthropogenic source and its contribution to the N₂O global budget has increased since 1900 AD (Kroeze et al., 1999). The intensification of agriculture, at first order proportional to the population increase, involved an intense use of natural fertilizers until the middle of the 20th century, followed by the enhanced use of synthetic fertilizers after 1930 AD. Perez et al. (2000, 2001) suggested that synthetic fertilizers may be more depleted in heavy isotopes than natural ones, implying that recent agricultural-derived N₂O emissions are even more depleted than about one century ago. Assuming that half of the increased N₂O emission from agriculture during the past century has been from application of synthetic fertilizers, whereas the other half has come from natural fertilizers and indirect emissions (nitrate leaching and runoff), Pérez et al. (2001) predicts a decrease in $\delta^{15}\text{N}$ of tropospheric N₂O since pre-industrial times by 2

to 3‰. This deduction is in good agreement with our results. Therefore, the decrease of the isotope ratios, observed for all isotopologues, could be explained by the increase of anthropogenic sources, agriculture in particular.

Röckmann et al. (2003a) performed measurements of the ¹⁸O and position-dependent ¹⁵N isotopic composition of N₂O from Antarctic firn air sampled at Dome C (75° S, 123° W) and Dronning Maud Land (77° S, 10° W). By comparing these firn data to simulations carried out with the same firn air diffusion model as ours (without using the Monte-Carlo model), they reconstructed the temporal evolution of the N₂O isotope signatures, since pre-industrial times. However, the long-term trend that they reported is not constrained by ice air values since no ice samples were analyzed. Nevertheless, the trends deduced in the two studies from the firn data, with different approaches are quite consistent. By using the Green function, the age of N₂O at the firn-ice transition, as well as its distribution has been calculated for all sites. The mean age of N₂O is about 35, 40, 60 and 90 years old at Dome C, Dronning Maud Land, NGRIP and Berkner Island, respectively. Note, however, that in particular near the firn-ice transition, the age spectrum has a very wide distribution. So, for all sites, the evolution of the atmospheric isotopic signal can be constrained by the data measured in the firn over the last 30 years, i.e. until 1970 AD. Those trends are summarized in Table 4. The atmospheric histories of the isotope ratios derived in both studies are similar for all isotopologues. There is a slight difference in the position-dependent ¹⁵N values, but this is within the combined error range. In general, consistent results are found for all locations. They show that ¹⁵N depletion is distributed quite evenly within the N₂O molecule.

At this time, it is still difficult to draw conclusions from our intramolecular nitrogen results due to the high experimental errors as discussed above. Nevertheless, several tracks could be followed. Previous studies have shown that the stratospheric ¹⁵N enrichments are position-dependent (Griffith et al., 2000; Park et al., 2004; Röckmann et al., 2001a; Toyoda et al., 2004). Whereas ¹⁵N¹⁴NO is photolyzed faster than ¹⁴N¹⁵NO, ¹⁴N¹⁵NO is removed faster in the reaction with O(¹D) (Hessberg et al., 2004; Kaiser et al., 2002a, 2003b; Röckmann et al., 2001a). This difference provides the possibility to distinguish between the two processes in the atmosphere based on the isotope fractionation pattern they leave in N₂O. In principle this may allow us to investigate the relative strength of the stratospheric N₂O sinks since the pre-industrial era, but this sink signature then has to be distinguished from variations in the two main production processes. It seems that nitrification, favored in dry and aerobic systems, preferentially enriches the central N position, compared to denitrification, favored in wet and anaerobic systems (Pérez et al., 2001). The enzymatic reaction pathways involved in N₂O production may also suggest that the site preference could be characteristic from the involved microorganisms. The intramolecular distribution of ¹⁵N in

N₂O could thus provide a basis for distinguishing biological processes (Schmidt et al., 2004; Sutka et al., 2003). Further work needs to be performed to improve the precision of N position dependent measurements, so that they could add another constraint on the N₂O evolution.

6 Conclusions

Isotope measurements on N₂O from both Antarctic and Arctic firn and ice air samples show that the observed increase in the atmosphere since pre-industrial times is accompanied by a significant isotopic depletion in ¹⁵N at both positions in the molecule and in ¹⁸O. Using the data in combination with a firn air diffusion model, the evolution of the isotope signatures has been precisely quantified, which is important for global isotope budget calculations.

Consistent trends are found for ¹⁵N and ¹⁸O changes derived from firn air since 1970, from ice air since pre-industrial times, and from recent direct measurements on Antarctic air samples dating back to 1990 (Röckmann and Levin, 2005). The trends for those different time periods are less consistent for the ¹⁵N-isotopomers. In particular, the trends derived from the recent air samples are much stronger for ¹δ¹⁵N than for ²δ¹⁵N, whereas the firn and ice core data imply that they are more similar. This is unlikely to reflect an atmospheric signal and may be due to presently not resolved systematic errors in the analytical procedure.

The depletion of the signal for all the isotopologues can be partly related to the increase of agriculture, in particular to the use of fertilizers and is in good agreement with predictions made using bottom-up calculations. The different isotope signatures may potentially be used to discriminate between source and sink effects as origin of variations in the N₂O mixing ratio on long time scales. Further work needs to be performed to improve the precision on the intramolecular ¹⁵N measurements, in order to reduce the uncertainty and to better quantify weak isotopic variations.

Acknowledgements. This work is a contribution to the European Commission project CRYOSTAT (EVK2-CT2001-00116) funded under the Energy, Environment and Sustainable Development Programme; 1998–2002. Laboratory work was also funded by the German AFO2000 program within the project ISOSTRAT and by the French-German “Programme d’Actions Intégrées” PROCOPE. The NorthGRIP project is directed and organized by the Department of Geophysics at the Niels Bohr Institute for Astronomy, Physics and Geophysics, University of Copenhagen. It is being supported by Funding Agencies in Denmark (SNF), Belgium (FNRS-CFB), France (IPEV and INSU/CNRS), Germany (AWI), Iceland (RannIs), Japan (MEXT), Sweden (SPRS), Switzerland (SNF) and the United States of America (NSF). The Berkner Island field project is a collaborative programme supported by the British Antarctic Survey, the french IPEV and INSU/CNRS. We thank all participants to the field work at both sites for drilling and firn air sampling operations. We also thank B. Knappe for help with the isotope measurements in the laboratory.

Edited by: D. Lowe

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