

First results of $^{15}\text{N}/^{14}\text{N}$ ratios in nitrate from alpine and polar ice cores

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ABSTRACT

Isotopic analyses of nitrogen were performed in nitrate from alpine and polar snow and ice. Nitrate from recent alpine ice cores showed similar $^{15}\text{N}/^{14}\text{N}$ ratios and seasonal variations as continental rain nitrate. Nitrate from recent Summit (Greenland) precipitation showed also similar isotope composition as European rain but, in ice cores, increasing $^{15}\text{N}/^{14}\text{N}$ ratios with decreasing nitrate concentrations are observed as a function of depth until about the year 1950, which is the time when anthropogenic emissions of nitrogen oxides started to increase rapidly in the Northern Hemisphere. In recent Antarctic ice from the South Pole, nitrate concentrations are nearly the same as in the measured Greenland ice up to the year 1967, where the record for South Pole ice stops. No conclusions on recent nitrate pollution in the Antarctic could be given from this poorly documented core. Measured isotopic ratios for the Greenland ice core for the preanthropogenic period correspond to one Antarctic ice core (D47); both cores show similar snow accumulation rates. Isotopic ratios for other Antarctic ice cores are different from the Greenland ratio and a clear relationship is found between the isotopic composition and the snow accumulation rate with heavier ratios observed with decreasing accumulation rates. It is proposed that physical phenomena occurring in the firn and linked to the low accumulation rates of several Antarctic study sites most likely modify the initial concentration and isotopic composition of the nitrate.

1. Introduction

The atmospheric cycle of nitrogen is most important for the understanding of atmospheric chemistry, in particular because nitrogen oxides control the photochemical production of ozone within the troposphere and are on the other hand involved in the catalytic destruction of ozone within the stratosphere. Moreover nitric acid is a major component of atmospheric acidity and its concentration is increasing rapidly in the atmosphere due to anthropogenic activities such as the burning of petroleum products. In spite of their atmospheric interests, it is still difficult to draw a

global picture concerning nitrogen oxides because of the diversity of processes which significantly contribute to their budget and high input variability in time and space. There is, therefore, the need of a better documentation of the past and present N-cycle. Nitrate, the end product of the oxidation chain of the various atmospheric N-species, is commonly determined in precipitation. In remote areas, measurements are less frequent. In this respect, polar regions are of particular interest, since they are generally most remote from anthropogenic sources and the study of deposited polar snow and ice has been demonstrated to be relevant to document past atmospheric composition (Delmas, 1992; Legrand, 1994).

Large amounts of nitrate data extracted from polar ice cores exist but much of them are still dif-

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difficult to interpret (Wolff, 1995). For instance, it is clear that Greenland ice cores have recorded a recent trend over the last decades (Neftel et al., 1985) in relation with growing emissions of anthropogenic nitrogen oxides in the Northern Hemisphere while no trend is detectable in Antarctica (Legrand and Delmas, 1986). It has been proposed that lightning and the stratospheric reservoir represent major sources of nitrogen oxides for the Antarctic boundary layer (Legrand and Kirchner, 1990). Nitrate may be present in the atmosphere as a gas (HNO_3) or as an aerosol (e.g., ammonium nitrate or fixed on sea salt or mineral dust particles). It has been shown that the acid form dominates (Legrand and Delmas, 1986) in present day polar precipitation while in ice from the last glaciation nitrate is present as neutral salt (Legrand et al., 1988). The relation linking nitric acid concentrations in ice and atmospheric content at the time of the deposition is still poorly understood. Furthermore, several studies have pointed out changing concentrations in snow after deposition both in Antarctic (Neubauer and Heumann, 1988; Mayewski and Legrand, 1990) and in Greenland (De Angelis and Legrand, 1995; Silvente and Legrand, 1995) sites.

The analysis of stable isotope ratios of light elements (i.e., H, C, N, O, S) in atmospheric trace gases for identification of sources and sinks or chemical/physico-chemical reactions has been used. A detailed review on isotope fractionation effects in atmospheric trace compounds has been given by Kaye (1987).

Little information exists concerning the $^{15}\text{N}/^{14}\text{N}$ isotope composition of reactive atmospheric nitrogen oxides. Nitrate in rain, as well as atmospheric particulate nitrate, sampled at different sites in the Northern Hemisphere (Freyer, 1978, 1991) and nitrate in rain sampled at Pretoria in the Southern Hemisphere (Heaton, 1987) show a seasonal variation in the $^{15}\text{N}/^{14}\text{N}$ ratio with lower values during summer than during winter. Very recently, these seasonal variations of $^{15}\text{N}/^{14}\text{N}$ at Jülich, Germany, have been traced back to the interactions of isotopic exchange processes and photochemical reactions between atmospheric NO and NO_2 depending on the concentration ratio of atmospheric oxides of nitrogen (NO_x) to ozone (O_3) (Freyer et al., 1993). The major recent anthropogenic NO_x source at Jülich is from automobile exhaust. Relevant data of the undisturbed,

pre-anthropogenic nitrogen cycle are unknown, however.

This paper reports the first N-isotope measurements of nitrate from snow and ice samples collected in glaciers with various glaciometeorological regimes (Greenland, Antarctica, high Alpine glaciers) and corresponding to different time periods (industrial, pre-industrial and glacial). Some preliminary results have been reported earlier (Bordat et al., 1993).

2. Experimental protocol

2.1. Field sampling

Ice samples selected for this study have various origins. They include the following.

(i) A 7.4 m shallow firn core was hand-drilled on 9 July 1992 at Col du Dôme (elevation 4250 m, mean annual temperature -14°C) located below the Mt. Blanc summit, French Alps. Handling conditions were similar to polar cores (see below). The core, which covers about 2.5 years of precipitation, was dated stratigraphically (in particular by stable isotope analysis of oxygen and hydrogen in water) with a temporal resolution of about 3 months.

(ii) A 70 m firn core was obtained in July 1989 at Dome Summit (Central Greenland, elevation 3250 m, mean annual temperature -32°C , accumulation rate $23.5 \text{ g cm}^{-2} \text{ a}^{-1} \pm 5\%$) during the Eurocore field operation. Only part of this core has been made available for this study, other levels having been used for other measurements. Immediately after recovery, the core was placed into polyethylene bags which were sealed in the field and placed in insulated metal boxes maintained constantly well under 0°C . The core was dated (± 1 year) by comparison with the 300 m Eurocore, accurately by using various methods such as seasonal stratigraphy and identification of volcanic horizons (Clausen et al., 1995). The weight of each sample was a few kilograms.

(iii) 11 shallow snow samples were collected in July 1991, using contamination free techniques, in a snowpit at Summit. The weight of each sample was 1.2 to 2.5 kg. The studied time period spanned from summer 1986 to winter 1989/90. One sample was lost and after combining together some samples, eight N-isotope analyses have been obtained.

(iv) An ice core was recovered in January 1989 at D47, Terre Adélie, East Antarctica (elevation 2050 m, mean annual temperature -26°C , accumulation rates 25 to $18\text{ g cm}^{-2}\text{ a}^{-1} \pm 5\%$ decreasing with depth of the samples). The core was also stored in sealed polyethylene bags. Due to the surface velocity and flow of the ice-sheet at this location, dating of the core is not straightforward. It was achieved with the aid of a flow model, using calculated snow accumulation rates and a few volcanic horizons (Ciais, 1991; Ciais et al., 1994). The accuracy of the dating is variable, depending on the depth of the analyzed sample (200 to 832 m depth). The time period covered by each sample is a few years.

(v) Various remaining sections of the 906 m deep ice core were obtained by LGGE in January–February 1978 at Dome C, East Antarctica (elevation 3240 m, mean annual temperature -53°C , accumulation rate $3.4\text{ g cm}^{-2}\text{ a}^{-1} \pm 10\%$), stored then at about -15°C . This core which covers the last 40 kyrs (Jouzel et al., 1989) has been extensively analyzed for various species including nitrate whose concentrations are larger in glacial ice than in Holocene ice (Legrand and Delmas, 1988b). Each sample analyzed spans at least a 10-year period.

(vi) Samples from 7 levels (from 5 to 20 m depth) selected along from a firn core (PS4, South Pole) obtained in 1983 at the Amundsen-Scott Station (elevation 2835 m, mean annual temperature -51°C , accumulation rate $8\text{ g cm}^{-2}\text{ a}^{-1} \pm 10\%$) were also analyzed. Each piece of firn was 0.2 to 0.7 m long and covered 0.9 to 4.8 years of precipitation. Dating and chemical composition of snow layers at this site have been studied extensively. In particular nitrate concentrations have been determined in detail (Legrand and Kirchner, 1990). The time period discontinuously covered by this sampling is 1876–1967. Due to the too low nitrate amounts in each individual sample, firn pieces have been combined together for analysis. Moreover, due to incidents during the analytical procedure, some samples were lost and only two levels were measured (1897–1903 and 1949–1954 plus 1963–1967). Two other samples from a very close drilling site (PS11) were analyzed as well covering the period 1700–1710 and 1770–1780. The older sample has a depth of about 40 m. The $\delta^{15}\text{N}$ values for both cores are in excellent agreement.

2.2. Sample handling, decontamination and subsampling

All samples were transported in the solid state to Grenoble where they were stored for variable times in commercial freezers well below -15°C until subsampling, decontamination and further N-isotope analysis.

Ice and firn cores are generally heavily contaminated during drilling and handling and it has been demonstrated by previous studies that a serious decontamination of the samples is mandatory before analysis (Legrand and Kirchner, 1990). Various techniques have been used in the past. The most recent and efficient one is the use of a vertical lathe specially designed for that purpose of removing the contaminated outside layers of the ice/firn and operated in cold conditions in a snow trench in the field or in a cold room at LGGE (Legrand et al., 1993). In our case, the first 2 cm were removed from the surface of the cylindrical core. The freshly prepared core samples were stored in cleaned and sealed polyethylene bags, shipped in the frozen state to Jülich and kept in a freezer at -20°C prior to analysis.

2.3. Laboratory work and isotopic measurements in Jülich

For analyses of the ice, the bags were opened inside a clean air bench. Each ice sample was melted under pure nitrogen in a glass container by microwave heating and transferred manually to 2-litre sized HPLC glass bottles, which had been previously rinsed with ultrapure water. Acetonitrile CHROMASOLV (Riedel-deHaen) was added to the sample to prevent microbial activity (10 ml/liter of sample volume). In later analyses, methanol LiChrosolv (Merck) was added, because acetonitrile tends to polymerize and plug up the HPLC columns. Before concentrating the sample, the nitrate concentration was measured by analytical HPLC. Several ice cores of similar age (or seasons) were combined together (2 kg of ice or more, depending on the nitrate concentration) to get a sample of a nitrogen equivalent amount of 30–40 bar μl of N_2 for mass-spectrometric analysis.

The preconcentration step by preparative HPLC and the additional analytical process has been described in detail by Bordat et al. (1992). The nitrate sample, concentrated into a volume of 4 ml of water, was then freeze-dried and com-

Table 1. $\delta^{15}\text{N}$ values of high-volume aerosol nitrate (Neumayer station, Antarctica, 1992) sampled by D. Wagenbach (unpublished results, 1994)

Sampling date	Amt. of $\text{NO}_3^- - \text{N}^*$ (μg)	Total air volume (m^3)	$\delta^{15}\text{N}$ (‰) analyses at Jülich	$\delta^{15}\text{N}$ (‰) analyses by F. Pichlmayer
14 March–6 June 1992	52	18255.0	–7.6	–7.5
6 June–1 August 1992	52	11822.0	+0.1	± 0.0
12 September–3 October 1992	84	4904.8	–36.5**; –36.9**	–38.3
14 November–24 December 1992	72	3442.0	–59.5**; (–61.2**)**	–63.0

Comparison of values analyzed at Jülich and by F. Pichlmayer on liquid aliquots of the samples. Similar seasonal variations have been reported earlier (Pichlmayer and Blochberger, 1991).

* Jülich samples.

** Portioning the sample and separate work-up.

*** Fractionation in the gas inlet of the mass spectrometer due to incomplete balance of the sample and reference gas.

busted in a closed quartz tube to molecular nitrogen with Cu, CuO and CaO as reagents (600°C, 6 h) using the Dumas procedure (modified after Fiedler and Proksch, 1975).

Finally, the molecular nitrogen was analyzed by isotope mass-spectrometry using a Micromass 602C mass-spectrometer. For later analyses of the older Antarctic ice cores, a Fisons Instruments Optima mass-spectrometer equipped with a Hall sonde was used. The overall analytical precision of the method was ± 0.4 ‰ $\delta^{15}\text{N}$ at a sample size of 35 bar μl of N_2 . $\delta^{15}\text{N}$ is defined in the usual way as per mil deviation of the $^{15}\text{N}/^{14}\text{N}$ ratio from atmospheric nitrogen as standard:

$$\delta^{15}\text{N} (\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000$$

$$\text{with } R = [^{15}\text{N}]/[^{14}\text{N}]. \quad (1)$$

Ice from Dome C was occasionally contaminated by kerosene which was utilized during the drilling procedure. Before performing the preconcentration step, kerosene was extracted by petroleum ether (b.p. 40–60°C; 200 ml petroleum ether/2 liter melted ice) which later was removed from the solution using 6.0 grade helium. The purity of the analyzed nitrogen gas corresponding to the unusable high $\delta^{15}\text{N}$ values obtained for the Antarctic ice cores has been checked in detail. After isotopic analyses, the method of mass-spectrometric peak jumping was used to fragmentation masses of nitrogen, H_2O , NO , NO_2 , $\text{CO}_2/\text{N}_2\text{O}$ and hydrocarbon compounds. There were no

anomalies detected, so we have concluded that the measured isotopic ratios are unambiguously that of molecular nitrogen.

An intercalibration of our procedure (without the HPLC preconcentration step) with the different procedure of Pichlmayer (Pichlmayer and Blochberger, 1988) for nitrogen isotope analyses of aerosol nitrate samples from Antarctica is given in Table 1. The unusual negative values in aerosol nitrate from Antarctica will not be discussed in this publication.

3. Results

3.1. Alpine ice cores

Nitrate concentrations and $\delta^{15}\text{N}$ values of nitrate in the samples (Table 2) are compared with relevant data found in Jülich rain (Freyer, 1991). Isotope composition that are similar in high altitude snow and in rain from polluted areas, indicates the overwhelming common anthropogenic origin for present atmospheric nitrate in Europe. Nitrate concentrations at Col du Dôme exhibit minima in winter and maxima in summer. These results agree with observations from snow samples from the Austrian (Puxbaum et al., 1991) and French Alps (Maupetit et al., 1995). In summer, convective vertical mixing occurs between the boundary layer and the free atmosphere. In winter, no such vertical mixing operates near the Alps and deposited nitrate probably originates from air

Table 2. Concentrations and $\delta^{15}\text{N}$ values of nitrate in firn samples from Cole du Dôme; comparison with relevant data found in Jülich rain

	Season*	Nitrate concentration (ng NO_3^- /g ice or ml rain)	$\delta^{15}\text{N}$ (‰)
Col du Dôme	Sp 1991	55.0	
	Sp 1992	294.2	
	Sp 1992	350.4	
	Spring 1991/92	190.8**	-1.90
	Su 1990	449.4	
	Su 1990	431.7	
	Su 1990	374.4	
	Summer 1990	420.2**	-4.46
	Summer 1991	923.0**	-5.07
	Su 1991	382.4	
	Su 1991	305.9	
	Summer 1991	344.7**	-3.68
	Wi 1990/91	170.0	
	Wi 1990/91	132.5	
	Wi 1990/91	409.3	
	Wi 1991/92	315.4	
	Wi 1991/92	231.2	
	Wi 1991/92	502.4	
Winter 1990/92	276.0**	-0.15	
Jülich	Spring 1979/84	3900 ± 3150	-2.6 ± 3.0
	Summer 1979/84	3770 ± 2750	-4.9 ± 2.4
	Fall 1979/84	3460 ± 2790	-0.9 ± 1.9
	Winter 1979/84	2570 ± 1640	0.0 ± 2.4

* The samples are different seasonal fragments of the core.

** Volume weighted mean of the samples considered for isotopic measurements.

Note. Our measured concentrations for Col du Dôme nitrate of 233 ± 157 and 478 ± 224 ng NO_3^- /g ice for spring and summer, respectively, correspond nearly to volume weighted mean concentrations reported by Maupetit et al. (1995). Our measured concentrations of 293 ± 143 ng NO_3^- /g ice for winter are higher by a factor of about 3 than the values of Maupetit et al. and correspond more to fall concentrations. (Volume weighted mean concentrations from Maupetit et al. (1995) for Col du Dôme nitrate for the years summer 1987 to spring 1991 are: 288, 646, 263 and 109 ng NO_3^- /g ice for spring, summer, fall and winter, respectively, from a total of 85 measurements of acid samples. Volume weighted annual concentrations, not separated by seasons, of alkaline samples are higher by a factor of about 2 than acid samples).

masses long-range transported in the apparently less polluted free troposphere. During this transport from industrial central European areas, a significant removal of oxidized nitrogen species occurs by scavenging and precipitation so that the concentration of nitrate in the high elevation Alpine snow is markedly lower in winter than in summer.

The seasonal variation of $\delta^{15}\text{N}$ values observed at Col du Dôme (higher values in winter than in summer) is similar as in Jülich rain nitrate (Table 2). An explanation for the variation in Jülich rain nitrate has been discussed elsewhere (Freyer et al., 1993). Due to this similarity, it seems

that the $\delta^{15}\text{N}$ value of atmospheric nitrate during winter is not affected during the long range transport of oxidized nitrogen species from their source regions. The range of all measured nitrogen isotope data in atmospheric nitrate species is shown in Fig. 1. A similar ^{15}N pattern of nitrate in snow from the Goldbergkees, Sonnblick, Austria (elevation 3106 m) has been reported by Pichlmayer et al. (1993).

3.2. Ice cores from Greenland

A nearly two-fold increase of nitrate concentrations from about 60–80 ng NO_3^- /g ice (pre-1950 values) to about 90–180 ng NO_3^- /g ice (post-1950

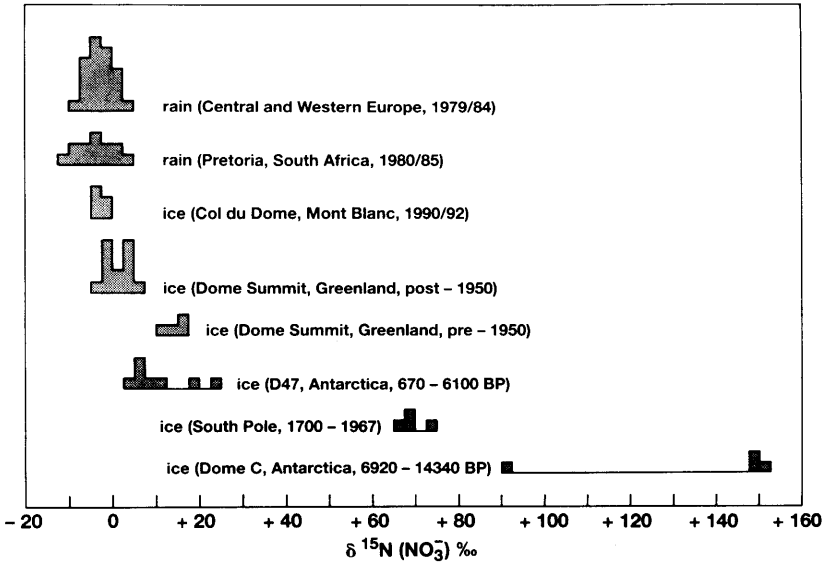


Fig. 1. Histogram of $\delta^{15}\text{N}$ values of nitrate in recent rain samples (Central and Western Europe rain from Freyer (1991); Pretoria (South Africa) rain from Heaton (1987)) and in recent and old ice-cores (this work; exclusion of three Ice Age samples from Dome C, Antarctica). The size of considered and analyzed samples is completely different (e.g., sample size of Central and Western Europe rain: > 250, sample size of pre-1950 Dome Summit ice: 4).

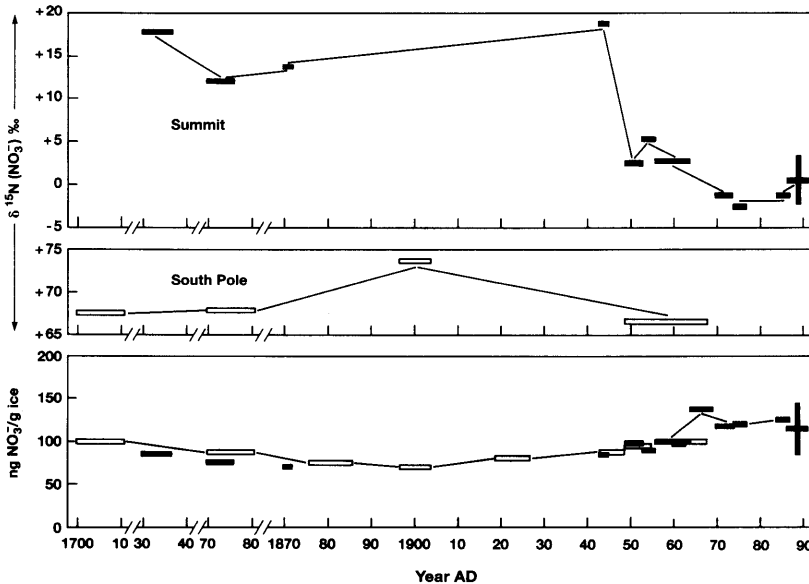


Fig. 2. $\delta^{15}\text{N}$ values and nitrate concentrations in ice-cores from the EUROCORE site at Dome Summit (Central Greenland) (solid blocks). Comparison with relevant data from the South Pole (open blocks). (For individual data from Dome Summit for the years 1986 to 1990, see Table 3.)

values) is seen (Fig. 2) in agreement with a previous study from Mayewski et al. (1993). This increase is similar to that observed by others in ice cores from Dye 3 (Southern Greenland) (Neftel et al., 1985; Mayewski et al., 1986). This phenomenon has been attributed to the deposition of oxidized nitrogen species from air masses carrying increasing amounts of North American and Eurasian anthropogenic nitrogen compounds. Thereafter, the nearly constant nitrate concentrations in Dome Summit ice cores during the last 20 years reflect NO_x emissions which have been maintained constant in Western Europe and North America during this period (OECD, 1991).

The $\delta^{15}\text{N}$ values decrease within the studied period from about $+(12-18)\text{‰}$ (pre-1950 values) to about $+5$ to -5‰ (post-1950 values). The latter values correspond to those found in recent continental rain nitrate (Fig. 1). This suggests that the polluted troposphere exhibit a rather similar N-isotopic composition above NO_x source and remote areas of the Northern Hemisphere. The comparison of Alpine snow and European rain led to the same conclusion (see above). The higher pre-1950 values in Greenland remain unexplained up to now. (The snow accumulation rates for pre- and post-1950 samples showed no systematic difference and amounted to $23.5 \text{ g cm}^{-2} \text{ a}^{-1}$ at the mean; see discussion of ice samples from Antarctica). Assuming mixing of natural (n) and anthropogenic (a) nitrate for the recent ice core

data with doubling of total (t) nitrate concentrations (M) since 1950 and using $\delta^{15}\text{N} = +15\text{‰}$ (n) and $\delta^{15}\text{N} = 0\text{‰}$ (t) as mean for pre- (natural) and post-1950 (total) values, respectively, $\delta^{15}\text{N}$ values of -15‰ for anthropogenic nitrate are calculated from a simple isotope-mass balance given below:

$$\delta^{15}\text{NO}_3^-(t) \cdot M(t) = \delta^{15}\text{NO}_3^-(n) \cdot M(n) + \delta^{15}\text{NO}_3^-(a) \cdot M(a). \quad (2)$$

Such low values can not be explained by an isotopic shift during long-range transport of nitrogen compounds from North American and Eurasian anthropogenic NO_x sources. This is because during transport generally positive fractionations of ^{15}N are expected, since deposited nitrate in rain has lower $\delta^{15}\text{N}$ values than HNO_3 , NO_x and particulate nitrate (Freyer, 1991; Freyer et al., 1993), and recent continental nitrate samples of anthropogenic origin are not lower than -5‰ . A depletion of ^{15}N in anthropogenic nitrate might be explained by a kinetic isotope fractionation during oxidation of atmospheric ammonia from nearby sources. Because of the unknown oxidation mechanism of ammonia in the atmosphere, however, no statements of a possible contribution of ammonia to the cycle of oxidized nitrogen species can be given at this time. The influence of other effects due to changing atmospheric

Table 3. Seasonal concentrations and $\delta^{15}\text{N}$ values of nitrate in snow samples from Dome Summit (Greenland)

No.	Season	Nitrate concentration (ng NO_3^- /g ice)	$\delta^{15}\text{N}$ (‰)
1	Summer 1986	145	+0.92
2	Winter 1986/87	114	+2.65
3	Spring 1987	94	+0.30
4	Summer 1987	133	+3.48
5	Winter 1987/88	98	
6	Spring 1988	69	
5 + 6			-5.01
7	Summer 1988	112	-0.54
8	Winter 1988/89	103	
9	Spring 1989	72	
8 + 9			-0.15
10	Summer 1989	177	
11	Winter 1989/90	136	
10 + 11			+2.62

chemistry by increased atmospheric pollution cannot be predicted. It has been shown that the largest fraction of transported NO_x in the Arctic is PAN (Barrie and Bottenheim, 1991; Jacob et al., 1992; Sandholm et al., 1992; Wofsy et al., 1992). It is presently not known, however, if the conversion of NO_x into PAN and its subsequent destruction into NO_3^- can modify the usual isotopic signature of nitrate.

Data for the shallow Dome Summit snow (11 samples), analyzed for different seasons over the time period 1986–1990, are given in Table 3. Nitrate concentrations of 69–94, 112–177 and 98–136 $\text{ng NO}_3^-/\text{g}$ for spring, summer and winter snow, respectively, were found. These seasonal variations of nitrate concentrations in the Greenland precipitation were discussed elsewhere in detail (Steffensen, 1988; Davidson et al., 1989; Whitlow et al., 1992). The corresponding $\delta^{15}\text{N}$ values ranged from -5 to $+3$ ‰, with slight preference of positive values during summer.

The lowest and highest value of $\delta^{15}\text{N}$ were -5.01 and $+3.48$ ‰ and were found for a combined winter 1987/88 (98 $\text{ng NO}_3^-/\text{g}$)-spring 1988 (69 $\text{ng NO}_3^-/\text{g}$) sample and a summer 1987 (133 $\text{ng NO}_3^-/\text{g}$) sample, respectively. The positive correlation of $\delta^{15}\text{N}$ values with nitrate concentrations is, however, not significant due to the few measurements performed and a disagreement in the seasonal variation of $\delta^{15}\text{N}$ values between Greenland ice and continental rain nitrate cannot be derived.

3.3. Ice cores from Antarctica

Unlike Greenland samples, Antarctica samples have very variable ages. They range from recent centuries to the last millennia. It should be mentioned also that the three deepest Dome C samples correspond to ice-age precipitation.

In contrast to all other $\delta^{15}\text{N}$ data presented here, most of the Antarctic values are significantly more positive (Fig. 1). Highest $\delta^{15}\text{N}$ values (up to

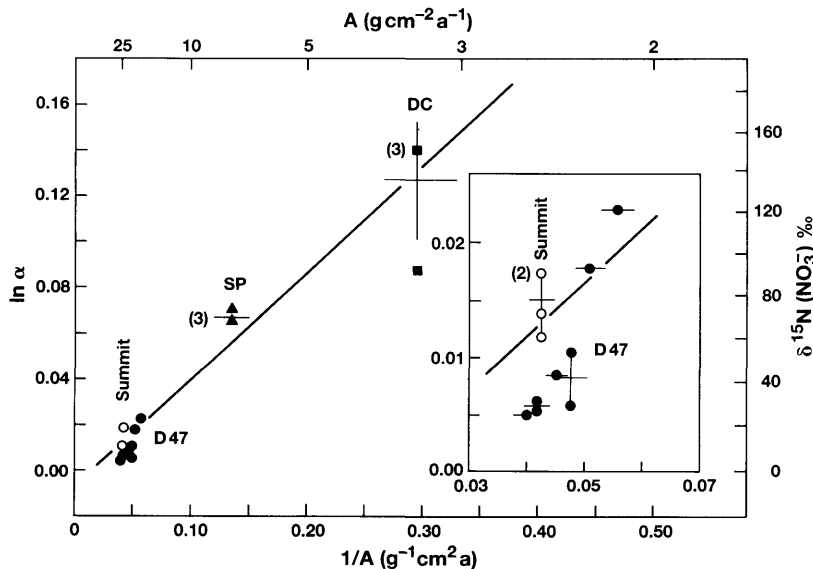


Fig. 3. Logarithm naturalis of the ^{15}N isotope fractionation factor α for nitrate as function of the inverse snow accumulation rate $1/A$ in ice cores from Antarctica: Dome C (DC; solid squares), South Pole (SP; solid triangles) and D47 (solid dots), and corresponding preindustrial values for Dome Summit (Greenland) ice cores (open dots). A regression of the data yields the line: $\ln \alpha = 0.468 \cdot 1/A - 0.007$ ($r = 0.966$). The data for the deepest three ice cores from Dome C (Ice Age data) were not included. Numbers in parenthesis on the data points indicate multiple measurements and of $1/A$ for the range of accumulation rates given in Section 2. Data of Summit and D47 are also given with a 5-fold expansion of scale. (Note: Definition of $\alpha = (R_{\text{sample}}/R_{\text{standard}}) = [(\delta^{15}\text{N} + 1000)/1000]$; see eq. (1). α can also be used for correlation, since $\ln \alpha \approx \alpha - 1$ for $\alpha = 1 + \epsilon$ and $\epsilon \ll 1$).

+150 ‰) are observed at Dome C. Spatial variations in the origin of atmospheric nitric acid could be an explanation for the various $\delta^{15}\text{N}$ values of nitrate obtained in Antarctic snow from different locations. However, the data suggest that $\delta^{15}\text{N}$ values are related to the snow accumulation rate (A) (Fig. 3). This plot shows that $\ln \alpha$ [$\alpha = (\delta^{15}\text{N} + 1000)/1000$] increase with the inverse accumulation rate $1/A$. Nitrate concentrations themselves seem to be lower for low- A sites, but the case of the South Pole is puzzling. In 4 samples from the South Pole Station, covering the 1700–1967 AD period, very high $\delta^{15}\text{N}$ values from +66 to +74 ‰ were observed with no systematic variation in nitrate concentrations from 70 to 100 ng NO_3^-/g ice. In any case, no recent anthropogenic nitrate increase had been detected in Antarctic ice cores (Herron, 1982; Legrand and Delmas, 1986). For recent years since the mid-1980s, increasing spring nitrate concentrations at low accumulation sites (South Pole, Vostok) were found (Mayewski and Legrand, 1990) and interpreted as a result of denitrification of polar stratospheric clouds. According to new data, this increase is an artefact due to post-depositional alteration by HNO_3 losses from the firn and diffusion from deeper firn layers (unpublished; Delmas, pers. comm.).

At D47, the present snow accumulation rate A is about $25 \text{ g cm}^{-2} \text{ a}^{-1}$, i.e., very similar to that one of Summit (Greenland). For the most recent D47 and pre-industrial Summit nitrate samples, isotopic compositions of nitrogen are also not very different. At other Antarctic study sites, the value of A is markedly lower than in Greenland. For aerosol deposition, it has been found that the relative contribution of dry to total deposition fluxes increases considerably as A decreases. For instance, it was shown (Legrand and Delmas, 1988a) that sea salt aerosol is deposited in equal amounts by wet and dry processes at the South Pole where the A value is close to $8 \text{ g cm}^{-2} \text{ a}^{-1}$. It was concluded however (Legrand and Kirchner, 1990) that this interpretation was not valid for HNO_3 , which is deposited primarily as a gas.

The $\delta^{15}\text{N}$ values and nitrate concentrations of the older samples from the coastal station D47 (670 to 6100 BP period) and the central Antarctic station Dome C (6910 to 19,670 BP period) are given in Figs. 4, 5. At D47, there is a clear increase of $\delta^{15}\text{N}$ values as a function of age, but this finding

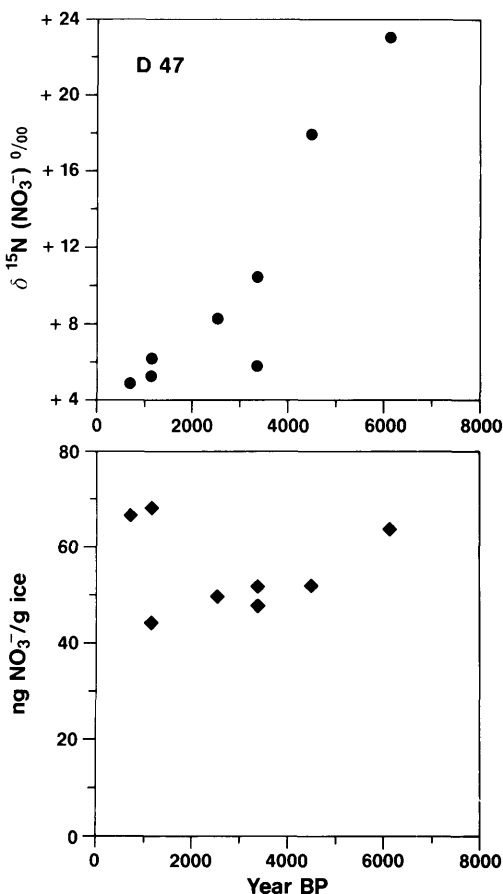


Fig. 4. $\delta^{15}\text{N}$ values and nitrate concentrations in ice-cores from the D47 station (Coastal Antarctica).

is misleading due to a systematic change in the origin of ice as a function of depth. Since D47 is a site where ice flow is relatively rapid, the origin of the ice at depth is upstream, where main glaciological parameters are different from those of the present day D47 site. Calculations (Ciais, 1991; Ciais et al., 1994) for assessing the age have shown that the accumulation rate in this core is a function of depth. An irregular variation with substantial higher $\delta^{15}\text{N}$ values as in D47 was found in the older Dome C samples including samples from the ice age (i.e., >15,000 yr BP).

Field experiments reveal that the deposition process of nitric acid is complex and that post-depositional effects by loss of HNO_3 most likely occur in the shallow firn layers (De Angelis and

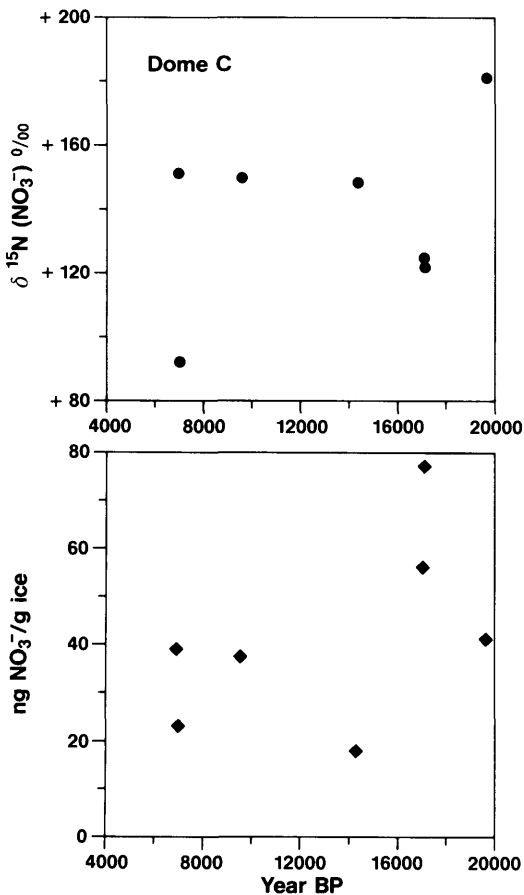


Fig. 5. $\delta^{15}\text{N}$ values and nitrate concentrations in ice-cores from the Dome C station (Central Antarctica).

Legrand, 1995; Silvente and Legrand, 1995; Bales, 1995). This loss should favour the lighter nitrogen isotope and lead to ^{15}N enrichments in the remaining nitrate in the ice. This would lead to larger fractionations at sites with lower snow accumulation rates. However, no relationship between nitrate concentrations and accumulation rates can be derived from our samples.

The snow accumulation rates for the Dome C samples are $2\text{--}3\text{ g cm}^{-2}\text{ a}^{-1}$ (with the lower values during the end of the ice age). They show no relationship with $\delta^{15}\text{N}$ values of nitrate. In present climatic conditions (Holocene period), nitrate is deposited as a gas (HNO_3). In glacial conditions, ion balance measurements (Legrand et al., 1988)

show that nitrate was also deposited as an aerosol (called "terrestrial salts" by Legrand et al., 1988). Consequently, the total concentration of nitrate in the ice was significantly higher at that time than in Holocene ice. This phenomenon has been observed at various central Antarctic sites (Delmas and Legrand, 1989). As the isotope fractionation affects only nitrate in the form of a gas (HNO_3) and not the fraction deposited as an aerosol, it is presently difficult to assess the overall isotopic effect since the respective fractions of gaseous and particulate nitrate are not accurately known (in ice age ice). Moreover there was a change (decrease) of snow accumulation rates during the cold periods. That means that the fractionation effect of gaseous HNO_3 was probably more marked at this time than now. It is suggested to perform additional measurements of deep samples concerning ice containing particulate nitrate.

As earlier mentioned, there is apparently a rapid loss of HNO_3 (evaporation?) at the surface of the snow after deposition. This means that the isotopic composition of nitrate in the atmosphere and in recently deposited snow at the surface could be different. Our measurements are inconclusive regarding this issue. However the plot of Fig. 3 suggests, at least, that this effect, if it exists, is similar in Antarctica and in Greenland. It is suggested to measure the isotopic composition of nitrate in fresh snow (with a high HNO_3 content) and aged snow (snow having lost part of its HNO_3).

Glaciological effects, linked to migration phenomena in the firm, seem to be much larger than non-glaciological (atmospheric) effects on the $\delta^{15}\text{N}$ composition, which probably are limited around zero. Therefore, the data do not allow any conclusions on potential sources of nitrate for Antarctica. Lightning which has been suggested to contribute significantly to the nitrate budget even in polar regions (Legrand et al., 1989) should produce $\delta^{15}\text{N}$ values in nitrate near zero or give slight negative values as found for NO_x from automobile exhausts (Heaton, 1990; Freyer et al., 1993). Ammonia oxidation should produce negative $\delta^{15}\text{N}$ values (Freyer, 1991). Long range transport from the tropical middle troposphere of surface emissions of oxidized nitrogen species such as from biomass burning (Mayewski and Legrand, 1990), however, should produce positive $\delta^{15}\text{N}$ values, since wet removal of nitrogen species

during transport favours the lighter nitrogen isotope.

The isotopic signature of stratospheric HNO_3 may be completely different from tropospheric HNO_3 . Some nitrate deposited in the Antarctic may result from denitrification of polar stratospheric clouds. The corresponding $\delta^{15}\text{N}$ effects for stratospheric NO_x are not known and can not be easily predicted, e.g., the effect for N_2O oxidation or the effect of fixation of nitrogen atoms by oxygen atoms influenced by N_2 photolysis or by galactic and solar particle precipitation. It is noteworthy, in this context, that in laboratory experiments unexplained ^{15}N enrichments up to 210‰ ($\delta^{15}\text{N}$) have been found in the products (NO , N_2O , NO_2) of the nitrogen fixation process by oxygen in a glow discharge at 77 K (Manuccia and Clark, 1976). It is however highly unlikely that similar reactions could occur in the Antarctic stratosphere with temperatures at about 140 K higher.

4. Conclusions

The N isotope analyses of nitrate in ice cores have been accomplished using the method developed by Bordat et al. (1992). In alpine ice cores, a similar seasonal relationship of $\delta^{15}\text{N}$ values of nitrate has been found as in continental rain nitrate. However, the issue of the origin of polar NO_3^- is far from resolved. The fractionation effects occurring in the firn have to be clearly separated from pure atmospheric processes. For reliable confirmation of a decreasing trend of $\delta^{15}\text{NO}_3^-$ with increasing nitrate concentrations in Greenland ice cores, the number of measured samples is still insufficient. Especially, more samples should be analyzed covering the time period of increasing nitrate concentrations from

about 1920 to 1970 AD. For the Antarctic samples, a systematic variation of the $\delta^{15}\text{NO}_3^-$ values with the snow accumulation rates has been found, pointing out that physico-chemical phenomena that could fractionate the isotopes occur in the firn. Other gaseous species, in particular HCl, could undergo similar processes. This should also be investigated in the future.

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