Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow

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ABSTRACT

The nitrate contents of nearly 500 firn samples collected at various sites on the Antarctic ice sheet are reported. Additional chemical measurements of all major ions, in particular protons, have also been performed so that new conclusions regarding the most probable form and origin of nitrate in the Antarctic can now be drawn.

It is shown that nitrate is deposited as gaseous HNO_3 and that tropospheric sources dominate in this remote region. Continental and anthropogenic nitrates are not significant contributors. It is suggested that lightning at tropical and/or mid latitudes is the most likely source of Antarctic nitrate. The formation of HNO_3 (or its precursors) in the stratosphere is discussed and the possible evidence for this contribution in several profiles is carefully investigated. The absence of a convincing correlation between solar factors and nitrate concentrations in snow confirms that past solar activity fluctuations cannot be reconstructed from polar ice cores. The spatial and temporal variations observed in this study are, however, not fully explained. Finally, emphasis is placed on the necessity of undertaking HNO_3 measurements in the Antarctic atmosphere in order to elucidate the deposition mechanism of this major component of atmospheric chemistry.

1. Introduction

In recent years, much attention has been focused on the atmospheric nitrogen cycle, the second major biogenic cycle. In comparison to the sulfur cycle, the nitrogen cycle is more complicated, since it comprises multiple compounds which are capable of participating in numerous reactions in stratospheric and tropospheric chemistry. In particular the oxides of nitrogen NO_x (nitric oxide NO and nitrogen dioxide NO_2) play a key role in various atmospheric processes involving OH radicals and ozone. An ultimate derivative of the atmospheric reactions of NO_x is nitric acid (HNO_3), the second most important mineral acid implicated in the acid rain phenomenon. The tropospheric cycle of NO_x has been reviewed recently by several authors (Crutzen, 1979; Ehhalt and Drummond, 1982; Logan, 1983; Stedman and Shetter, 1983). However, the sources, sinks and distribution of NO_x and HNO_3 in the atmosphere are not very well defined. The tropical and midlatitude tropospheres are very complicated systems where many compounds and parameters have to be taken into account to model the atmospheric concentrations of NO_x and HNO_3. On the other hand, the atmospheric system becomes simpler as we move into polar latitudes.

The study of the remote polar atmospheres may therefore provide new and valuable data for the study of global atmospheric chemistry. Moreover the chemical analysis of polar snow and ice has proved to be a very powerful tool in investigating polar atmospheric chemistry, provided that one pays attention to certain limitations regarding the comparison of air and snow concentrations.

We are aware of the difficulties which may arise when interpreting glaciochemical profiles in terms of atmospheric changes. However we are nevertheless confident that the temporal

variations of concentrations recorded in snow can be a major aid in unraveling certain aspects of the atmospheric chemistry. For instance, on the basis of glaciochemical results, it has been proposed that background atmospheric nitrate was directly linked to solar activity. This assertion was subsequently refuted by others again using measurements of nitrate in polar snow. Recently the production of large amounts of NO_x and HNO_3 by meteor falls has been also strongly debated.

In recent publications, we have already discussed concentrations of nitrogen compounds in Antarctic snow, but until now, the origins of nitrate have not been clearly determined. In this paper, our intention is to use an extended set of data to make a choice among all the potential sources of remote tropospheric HNO_3 background, and to examine the various causes of its natural and anthropogenic disturbances.

2. Experimental procedures

2.1. Sampling and decontamination

The samples analysed for this work were collected at several sites (Fig. 1) and processed under different conditions (Table 1). Generally, the sampling equipment was cleaned several times with ultrapure water in a clean room before being shipped to the site in sealed plastic bags. Samples were collected by operators wearing clean room clothing, plastic gloves and masks. Blanks were always included in each sampling series.

Recoring and/or sub-sampling were always

performed in a cold room under stringent contamination free conditions. A detailed account of the various steps of the sampling, decontamination and test procedures has been given elsewhere (Legrand et al., 1984).

2.2. Chemical analysis

In this study, not only nitrate has been measured, but also other major ions involved in the calculation of the ionic balance of Antarctic precipitation (i.e. Na^+ NH_4^+ K^+ H^+ Cl^- NO_3^- SO_4^{--} and H^+—Legrand and Delmas, 1984; Legrand and Delmas, 1985). Moreover Mg^{++} has been estimated from Na^+ assuming that both ions are present in the bulk sea-salt ratio (0.25). All ions were determined by ion chromatography (Legrand et al., 1984) except H^+ which was titrated (Legrand et al., 1982). Analytical preci-

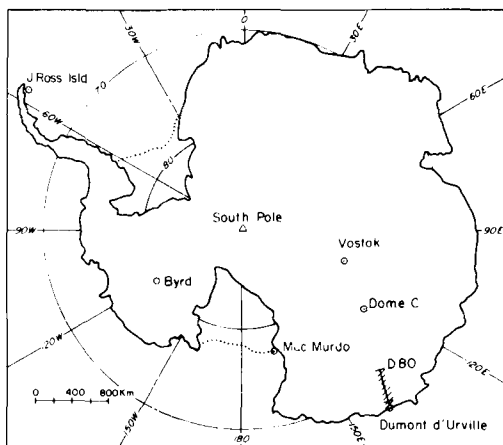*Fig. 1.* Map of Antarctica showing the location of the sites studied in this work—Hatched area: Adelie Land.
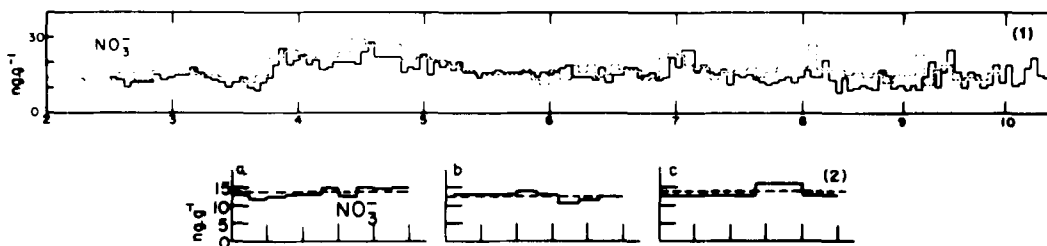
Fig. 2. (2.1) Comparison of two nitrate profiles in Dome C snow between 2.5 and 10.5 m depth: core cutting with handsaw (solid line), subcoring with mini drill (dashed line). (2.2) Comparison of three profiles in Dome C snow between 2.3 and 2.8 m depth: (a) in a pit, (b) core cutting with handsaw, (c) subcoring with drill.

Table 1. *Sampling and decontamination procedures*

Location of sampling	Number of samples	Sampling and decontamination procedure	Year of sampling (summer)
Surface samples			
Along the Dumont d'Urville to Vostok axis from Cap Prud'homme to D80 (Terre Adélie)	18	A	1982–83
Time period 1959–69			
D 55	68	B	1980–81
D 80	37	C	1982–83
Dome C	80	D	1979–80
South Pole	90	D	1977–78
Dome C (The last 220 years)	190	C	1979–80

A. Shallow samples collected in PTFE Tubes (40 cm long) by pushing the tubes into the snow. This sampling covers variable time periods (1–3 years) depending on the local snow accumulation rate.
B. Snow layers collected in pits each cm with the aid of a stainless steel plate. Snow was transferred to polyethylene bags which were then sealed.
C. Collection of a firncore and subsequent re-coring in a cold clean room with the aid of small drill.
D. Sampling in pits by pushing precleaned 30 ml plastic vials (Accuvettes) into the snow.

sion is typically 5–10% (at the 95% confidence level). However, the lowest concentrations of NH_4^+ and K^+ at the ppb (ng g^{-1}) level are known only to within ±100%. The most complete analytical procedure is described in Legrand (1985).

First of all we assessed the reproducibility of our nitrate data by comparing the results obtained from two adjacent firn cores between 2.5 and 10.8 m depth (Fig. 2). These cores were cleaned by two different techniques: cutting off the external part with the aid of a PTFE coated saw or subcoring with the aid of a small subcorer. An even more complete check was achieved using an additional sampling set from a snow pit according to the procedure given in caption of Table 1. The results of these comparisons, reported graphically in Fig. 2, are very encouraging. Although random variations do exist, probably linked with the superficial irregularities of the snow surface, long-term variations (on a decadal scale) are maintained when two different firn cores are compared. It may be concluded that the observed fluctuations are most probably linked to actual changes in the atmospheric nitrate content.

3. Results and discussion

3.1. Ion balance

Determination of the ion balance of Antarctic precipitation is an important step in the study of precipitation chemistry and consequently of aerosols in the Antarctic (Legrand et al., 1984, Legrand and Delmas, 1985). The ion balance may be written (eq. 1):

$$[Na^+] + [K^+] + [Mg^{++}] + [NH_4^+] + [H^+] = [SO_4^=] + [NO_3^-] + [Cl^-] \tag{1}$$

(symbols in brackets represent concentrations in μEq. l^{-1}).

Eq. (2) describes the acid components:

$$[H^+] = [SO_4^=]^* + [NO_3^-] + [Cl]^*. \tag{2}$$

SO_4^* and Cl^* are excess-sulfate and excess-chloride, respectively (non sea-salt fractions). They may be calculated by eq. (3) and (4):

$$[SO_4^=]^* = [SO_4^=] - 0.12\,[Na^+], \tag{3}$$

$$[Cl]^* = [Cl] - 1.18\,[Na^+]. \tag{4}$$

0.12 and 1.18 are the respective values of the SO_4/Na and Cl/Na ratios in bulk sea-water.

Any imbalance in eq. (1) and (2) would indicate that the chemical composition we have assumed for the Antarctic precipitation is incorrect (for instance due to an important compound not taken into account). In the particular case of nitrate, no significant imbalance is observed in the calculation of eq (2), providing a strong indication that NO_3^- is present in meltwater samples entirely as an acid (HNO_3). Fig. 3 is an example of a graphical check of eqs. 1 (Fig. 3a) and 2 (Fig. 3b) for D80 over the 1959–69 time period. The highest imbalance of eq. (1) is equal to 13% of the ionic budget. Taking into account the sum of all measurement errors, it is reasonable to consider that the two sides of the equation are balanced and we can therefore assume that no important ion has been missed in the calculations.

The excellent agreement between measured and calculated H^+ values (Fig. 3b) confirms that NO_3^- has no neutral contribution. At the South Pole, a similar confirmation was already obtained (Legrand and Delmas, 1984). This conclusion allows us to discard the possible formation of $NaNO_3$ and NH_4NO_3 (by the reaction of gaseous NO_2 on sea salt particles for the former and of NH_3 with HNO_3 for the latter). The interest of measuring all major ions for the identification of HNO_3 in Antarctic snow is therefore amply demonstrated.

3.2. Possible sources of nitric acid in Antarctic snow

In the troposphere nitric acid is formed by the reaction of OH˙ radicals with NO_2 according to eq. (5) (where M is a catalyst):

$$NO_2 + OH˙ \xrightarrow{M} HNO_3 \qquad (5)$$
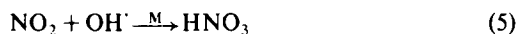
Similarly the reaction of NO with OH˙ leads to the formation of nitrous acid:

$$NO + OH˙ \xrightarrow{M} HNO_2 \qquad (6)$$

There is a rapid interchange between NO and NO_2 through reactions involving ozone and sunlight. HNO_3 can be considered as the final stage of the relatively rapid reaction of NO_x with OH˙ radicals (the life time of NO_x in the troposphere is in the order of 1 day, Logan et al., 1981). On the other hand, HNO_3 has a fairly long tropospheric residence time, probably between a few days and one week. It is removed from the atmosphere mainly by heterogeneous processes such as rainout and dry deposition (Ehhalt and Drummond, 1982). The chemical composition of the aerosol deposited in Antarctic snow reflects the geographical position of this continent. The crustal component is extremely low and the main contributions are essentially secondary aerosol and sea salt particles (Delmas et al., 1982). Therefore it seems reasonable to assume that the nitric acid level found in these areas is similar to that found in the remote marine troposphere (median:
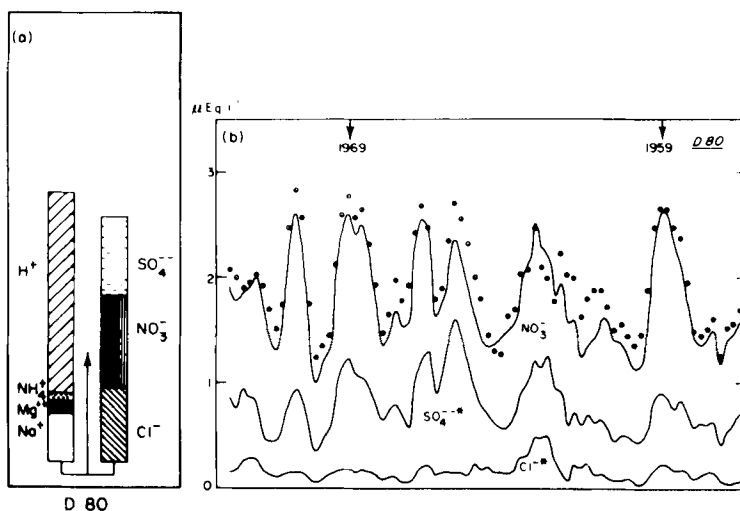

Fig. 3. Comprehensive study of soluble ionic impurities in snow deposited at D 80 (Adelie Land) between 1959 and 1969. (a) Mean ion balance. (b) Acid reconstruction curve: the upper curve refers to the sum: $[Cl^-]^* + [SO_4^=]^* + [NO_3^-]$, dots are measured acidity $[H^+]$.

0.11 ppbv of HNO_3 in the air, Huebert and Lazrus, 1980). It is generally accepted that sea-salt does not contribute significantly to the particulate nitrate content in the marine troposphere, because of the low nitrate content of sea water.

Gravenhorst et al. (1979) noted however that nitrate exists on large aerosol particles (> 1 micron) over the Atlantic, suggesting that nitrate is attached to sea salt particles. This conclusion was supported more recently by Savoie and Prospero (1982) on the basis of aerosol measurements at Atlantic coastal sites. These observations indicate that a reaction probably occurs over the ocean between N-gaseous species (NO_2 and HNO_3) and sea-salt particles, leading to the fixation of NO_3^- on these particles of primary aerosol which are clearly different from the submicron secondary aerosol particles.

In order to investigate the possible correlation between the sea-salt and nitrate ion deposits in Antarctic snow we collected surface samples over a limited geographical area of Adelie Land (see Table 1). Our results clearly indicate that sodium and nitrate concentrations do not vary in the same manner (Fig. 4). The detailed variations of nitrate and sodium are also entirely dissimilar at individual sites. For instance on James Ross Island, in the vicinity of the Antarctic Peninsula (elevation 1600 m) Aristarain et al. (1982) have clearly shown that the histograms of nitrate and sodium concentrations have very different shapes. At D10 where the Na concentrations are relatively high (mean value 9.8 μEq. l^{-1}) due to the heavy sea-salt deposition at this very coastal site of Adelie Land, 6 samples taken at 6 different depths between 23 and 85 m have given the following NO_3/Na weight ratios: 0.19, 0.17, 0.26, 0.06, 0.07 and 0.22. On James Ross Island as well as at D10 the variability of this ratio is essentially linked to the high variability of sodium concentrations, nitrate varying over a relatively narrow concentration range.

It may therefore be concluded that in the coastal Antarctic areas we have studied, no evidence of nitrate fixation to sea salt particles has been found. As the contribution of sea salt to snow chemistry decreases strongly on the Antarctic Plateau, we rule out entirely this phenomenon as a factor in Antarctic atmospheric chemistry.

It is necessary to examine the question of a possible continental contribution to the nitrate content of the marine troposphere, and here especially of the Antarctic troposphere and snow chemistry. Antarctica is very remote from other continents and, as already noted, the transport of
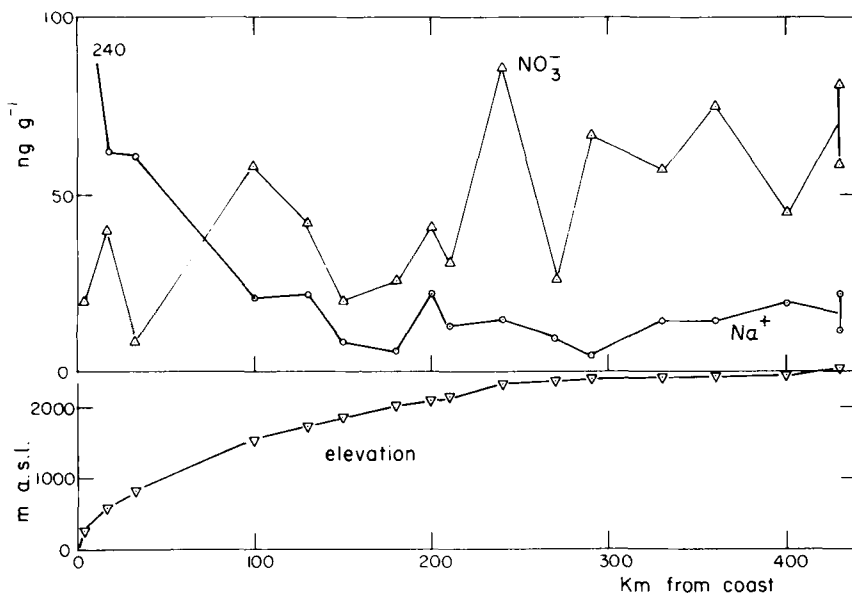

Fig. 4. Na$^+$ and NO$_3^-$ content in shallow snow samples from Adelie Land as a function of the distance from the sea and the elevation.

continental aerosol to high Southern latitudes is severely hampered by the general atmospheric circulation in these regions. Nitrogen found in Antarctic snow may have traveled not only as HNO_3 but also in the form of its gaseous precursors (NO_x) or even as derivates such as PAN (peroxyacetylnitrate), HCN or other organic nitrates. Several arguments support the low continental contribution to Antarctic nitrate deposition. First of all, the concentrations of NO_3^- in preindustrial Greenland ice (Herron, 1982a) are not significantly higher than in the Antarctic, although continental surface areas, particularly at high latitudes, are much greater in the Northern than in the Southern Hemisphere. Secondly, continental sources are located at ground level and only a small fraction of the N-compounds emitted are able to reach the free troposphere and are therefore available for long-range transport (Chatfield et al., 1985). Ehhalt and Drummond (1982) emphasized that most of the NO_x produced at the surface of the earth (10–20·10^{12} g N a^{-1}) "is relatively quickly converted to NO_3^- within the boundary layer and does not travel very far. Therefore, it is the atmospheric sources, especially those above the planetary boundary layer that determine the NO_x concentrations in the free troposphere and remote areas".

Two significant sources of N-compounds exist at high altitudes: lightning and stratospheric intrusions. In the Southern Hemisphere, particularly because of the low level of anthropogenic and nitrogen sources, these two natural sources may be dominant. To estimate nitrogen production by lightning we have taken the most recent paper by Borucki and Chameides (1984): 1.3 (0.4–4) Tg of N (1 Tg = 10^{12} g) and the detailed model by Hameed et al. (1981): 1.07 Tg for the Southern Hemisphere. The stratospheric source may contribute only 0.2 Tg a^{-1} in the Southern Hemisphere (Levy et al., 1980). However for polar regions the model leads to a 1:1 ratio for the contributions of both sources because of the increased stratospheric-tropospheric exchange over the poles, a point which conflicts with the finding of greater ^{90}Sr fallout at midlatitudes after nuclear tests (Davidson et al., 1965).

How compatible are these estimates with our results? A mean accumulation rate of 170 kg H_2O m^{-2} a^{-1} (Kotlyakov et al., 1974) gives a mean nitrate deposition rate of ~ 11 kg km^{-2} a^{-1}, i.e., about 2.5 Kg N km^{-2} a^{-1} was found for the Antarctic. This deposition (a total of 140,000 Tonnes of NO_3 for the continent) has been obtained from nitrate measurements at four Antarctic locations (South Pole, Dome C, D 55 and D 80) and for the same time period 1959–69 (see Subsection 3.4 below). If we extrapolate this deposition to the Southern Hemisphere (2.5 10^8 km^2), we find a total deposition equal to ~ 0.6 Tg, a value which is located at the lower limit of the range for the sum (0.6–4.2 Tg) of the two natural sources given above.

South Pole deposition amounts to 1.7 Kg N km^{-2} a^{-1} with about 0.85 Kg N km^{-2} a^{-1} (50% of total deposition if Hameed's model is valid, but this is an upper limit) being of stratospheric origin. For the same time period, we have already measured another stratospheric product in snow: the sulfuric acid introduced into the stratosphere by the explosive volcanic eruption of Agung in Indonesia (1963). This eruption gave rise to an important H_2SO_4 signal in Antarctic snow (Legrand and Delmas, 1985) and particularly at the South Pole (Legrand and Delmas, 1984). The amount of Agung sulfate deposited at this site has been found to be 11 Kg km^{-2} (Legrand, 1985) and the source function of this eruption has been estimated by Cadle et al. (1976) and more recently by Devine et al. (1984). The estimates differ significantly. Moreover the eruption affected the Southern more seriously than the Northern Hemisphere (Castleman et al., 1974) so that the amount of sulfate from this eruption present in the Southern stratosphere in 1964–65 may be estimated to be in the range 2–12 Tg. Therefore 1 Tg of sulfate in the stratosphere would correspond to 0.9–5.4 Kg km^{-2} in South Pole snow. Using the same type of calculation, we calculate that 0.2 Tg of stratospheric nitrogen (Hameed's estimate) corresponds to 0.18–1.1 Kg km^{-2} in the snow, a range which compares well with the value of 0.85 Kg N km^{-2} a^{-1} given above. Here again the good result of this comparison suggests that the estimated values chosen by Borucki and Chameides (1984) and by Hameed et al. (1981) are, although not accurately known, in the correct magnitude range to be in agreement with our data. Therefore both the stratospheric and the lightning sources of NO_x probably contribute to the nitrate deposited in the Antarctic. Their

relative importance is however still uncertain at this stage, although lightning seems to be dominant on a hemispheric scale.

We shall now discuss whether the temporal variations observed in Antarctic snow are able to shed additional light on this question. Moreover, various recent publications have proposed that background nitrate atmospheric concentrations could be strongly influenced by solar activity as well as by sporadic events such as large meteorite falls or atmospheric nuclear tests. These assumptions will also be discussed.

3.3. Interpreting the temporal variations of nitrate in Antarctic snow

The analysis of the firn samples collected at Dome C in summer 1979–80 (see Table 1) has given the nitrate profile reported in Fig. 2 (dotted line). The solid line corresponds to samples found to be contaminated by K^+ and NH_4^+. We have chosen to base our discussion only on the cleanest profile. Moreover additional sampling above 2 m and below 10.8 m depth has given the nitrate profile reported in Fig. 5 and spanning nearly continuously the last 220 years.

It is clear that this profile exhibits significant natural fluctuations (in the range 8–30 ng g^{-1}) which probably reflect changes in the nitrate source intensities and/or atmospheric transport. The scatter around the mean value (15 ng g^{-1}) is similar to that found in the work of Herron (1982b) for the 1923–37 time-period at the South Pole.

We shall first examine the possible imprint of various secondary and transient sources of atmospheric nitrate.

3.3.1. Anthropogenic emissions. On the basis of

NO_3 measurements along an ice-core collected in Greenland covering the last 100 years, Neftel et al. (1985) have demonstrated that the atmospheric NO_3 budget of the Northern Hemisphere has been heavily modified by human activity. The long-range transport of pollutants towards high Southern latitudes is a much less probable phenomenon. Our results at Dome C (Fig. 5) confirm that the long term trend of NO_3 deposition in the Antarctic is apparently unaffected by the increase of atmospheric pollutant emissions. However the natural fluctuations appearing on our profile are such that only well marked effects and definite trends could be detected. The case of nitrate is indeed very similar to that of sulfate for which recent studies (MARC, 1985) led to the conclusion that anthropogenic pollution is insignificant in Antarctica.

3.3.2. Nuclear tests and volcanic eruptions. The amount of HNO_3 produced by atmospheric nuclear tests is a controversial subject. Around 1–2 Tg may have been produced in the northern stratosphere in 1961–62 (Bauer and Gilmore, 1975) and therefore be susceptible to global spreading. Based on what occurred for beta radioactivity (Pourchet et al., 1983), we suggest that this nitrate fallout was deposited in the Antarctic mainly in the years 1964–65 i.e. between 1.63 and 1.33 m depth in the most detailed study listed in Table 1.

The dating of the snow layers at this time is particularly well delineated by the sudden sulfate increase caused by the explosive volcanic eruption of Agung. This eruption injected huge amounts of gaseous sulfur compounds into the stratosphere which were thereafter converted into
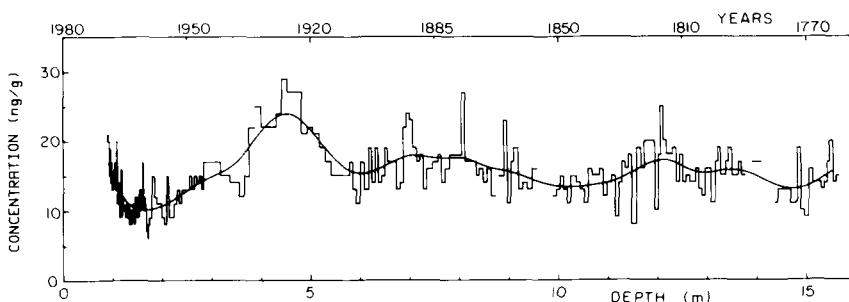

Fig. 5. NO_3^- content in snow deposited at Dome C since ~1760: the general trend is shown with a spline-smoothed curve ($\rho = 0.01$).
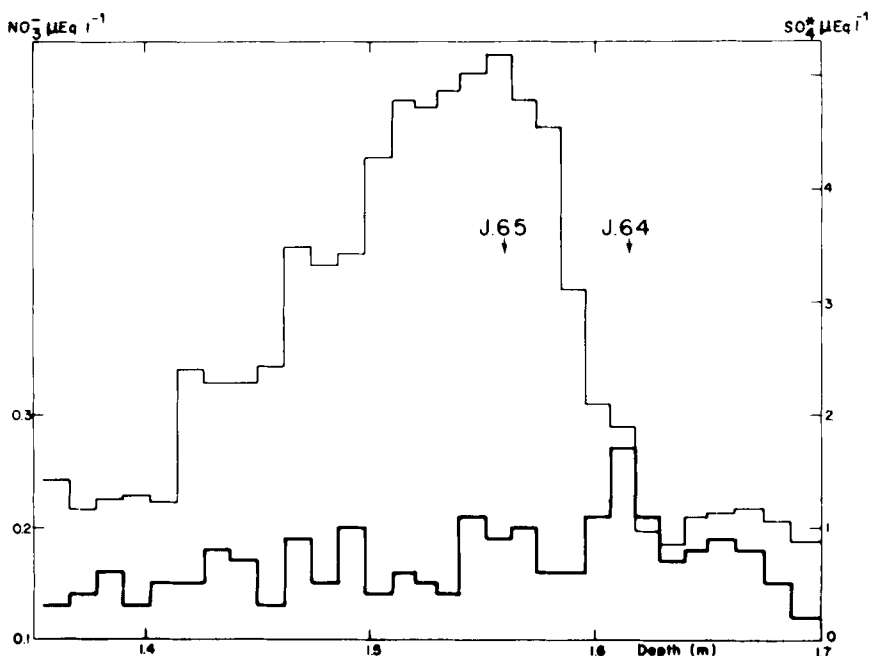
Fig. 6. NO_3^- and $SO_4^=$* content in Dome C snow during the years following the large nuclear test series in 1961–62 and the volcanic eruption of Agung (1963). The two arrows refer to January 1964 and 65. ——$SO_4^=$* ——NO_3^-.

H_2SO_4. This sulfuric acid was included in Antarctic snow during the years 1964–65 as already mentioned above. In the profile studied here, it may be expected that both stratospheric products ("nuclear" HNO_3 and volcanic H_2SO_4) were deposited simultaneously. It is clear from our excess-sulfate ($SO_4^=$*) and NO_3^- measurements (Fig. 6) that nitrate levels at Dome C did not rise exceptionally (within the experimental uncertainties) above normal levels during the years 1964–65. It can even be said that nitrate remained very constant from 1963 to 1968, lowest and highest values being 0.12 and 0.27 $\mu Eq \cdot l^{-1}$ respectively for a total of 30 samples.

This observation leads to the conclusion that either "nuclear" nitrate has had no impact on the stratospheric budget of N-compounds or that the stratospheric contribution is negligible in the deposition of nitrate in the Antarctic. At the South Pole, our nitrate measurements for the same time period (Legrand and Delmas, 1984) clearly show that the snow layers corresponding to the years 1964–65 have a relatively low nitrate content. Besides the conclusion regarding "nuclear" nitrate, these results suggest therefore also that large volcanic eruptions do not

contribute significantly to the global budget of nitric acid. The Tambora eruption was detected at 12 m and the Krakatoa eruption at 7.7 m depth (Legrand, 1985). None of these depths exhibit particularly high nitrate levels, which confirms the absence of a link between volcanic activity and the atmospheric nitrate content, in agreement with findings in Greenland (Risbo et al., 1981).

As a concluding remark, it may be pointed out that no nitrate spike was observed by Neftel et al. (1985) in the Greenland snow layers corresponding to the most intense nuclear tests at high Northern latitudes (1961–62).

3.3.3. Tunguska event. In June 1908, a huge meteor ("the Tunguska meteor") exploded in the Siberian atmosphere. This event has recently been the subject of multiple speculations regarding its possible effects on global atmospheric chemistry and climate (Turco et al., 1982). In this paper our discussion will be focused on the possible effect of the atmospheric burst on the global nitrate budget. Park (1978) calculated that $6 \cdot 10^{35}$ molecules of NO may have been produced between altitudes of 10 and 60 km by the thermal decomposition of N_2 and O_2 and the subsequent

recombination of N and O atoms into NO.

In comparison to the stratospheric-tropospheric exchange (2.2 Tg of HNO_3, Levy et al., 1980), the Tunguska event with a 16 Tg average production of HNO_3 for 3 years (Turco et al., 1982) may have had a marked impact on the global nitrate budget, and more particularly on nitrate deposition in polar regions. Rasmussen et al. (1984) have already examined this question for Greenland snow and concluded that the estimates of Turco et al. (1982) are too high by 1 to 2 orders of magnitude. Three profiles obtained from Greenland firn cores show that the nitrate levels in the post-Tunguska period are definitely burried in the natural scatter of experimental results.

We have examined our nitrate profile obtained at Dome C (Fig. 5) in order to detect the Tunguska impact, arriving in Antarctica possibly in 1909–11. The corresponding levels, relatively well dated, are located between 5.6 and 6.0 m depth. It is clear that no exceptional NO_3 value is recorded at this time, which leads to a similar conclusion as for "nuclear" and volcanic nitrate: either no significant amount of nitrate was formed during this meteor fall, or the stratospheric nitrate plays a negligible role in the Antarctic NO_3 budget (see section 3.3.2). In any case, Turco et al. themselves had predicted that the Tunguska event would hardly be detected in polar ice cores.

3.3.4. Solar activity. The possible link between nitrate deposition in the Antarctic and solar activity is a matter of a serious controversy which deserves theoretical and experimental investigations.

The explanation put forward by Parker, Zeller and coworkers (Parker et al., 1977, 1978; Zeller and Parker, 1981; Laird et al., 1982; Parker et al., 1982) is that various stratospheric sources of odd nitrogen species are indirectly modulated by solar activity so that the deposition rate of nitrate in Antarctic snow, via the stratosphere-troposphere exchange, depends strongly on the 11-year solar cycle.

The oxidation of N_2O by O atoms is the major source of NO in the stratosphere ($4.5 \cdot 10^{34}$ molecules a^{-1} Johnston et al., 1979), particularly at low latitudes ($1.4 \cdot 10^{33}$ molecules of NO a^{-1} for latitudes higher than 50°). As the amount of O atoms available for this reaction depends on stratospheric ozone, this source of NO could

depend on solar variations, but this assumption remains uncertain.

Galactic cosmic rays (G.C.R's) deposit their energy in the low stratosphere and produce NO at ratios depending on the phase of the solar cycle and the latitude. For instance, above 50° latitude, Jackman et al., 1980 calculated that between 1.1 and $1.6 \cdot 10^{33}$ molecules of NO can be produced annually by this mechanism.

Solar proton events (S.P.E.) occur sporadically, essentially at high latitudes and in phase with the solar cycle. They interact with stratospheric air mainly between 15 and 50 km in altitude. Crutzen et al. (1975) calculated that about $2.5 \cdot 10^{33}$ molecules of NO were produced in 1972 by a single exceptionally large S.P.E.

Beside these three mechanisms (oxidation of N_2O, G.C.R. and S.P.E.) which occur in the stratosphere, 90–180 10^{35} molecules a^{-1} of NO are produced in the ionosphere by the ionizing action of U.V. radiations and 9 10^{35} by auroral activity at solar maximum (Crutzen, 1979). But in this region of the atmosphere the residence time of NO is shorter in the low stratosphere due to an important destruction of NO:

$$NO + h\nu \rightarrow N + O$$

$$NO + N \rightarrow N_2 + O.$$
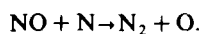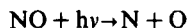
Jackmann et al. (1980) estimated the downward flux of NO from the thermosphere (up to 90 km altitude) to the mesosphere at $3.7 \cdot 10^{33}$–$1.5 \cdot 10^{34}$ molecules a^{-1} and the flux from the mesophere to the stratosphere as insignificant.

On the base of these theoretical considerations, we attempted to model the temporal variations of the nitrate content of the Antarctic atmosphere. We considered three major sources of stratospheric NO: N_2O oxidation, G.C.R., and S.P.E. (Fig. 7). The upper high stratospheric contribution was considered to be taken negligible. N_2O oxidation was assumed to be constant at a level of $1.4 \cdot 10^{33}$ molecules of NO per year. The production by G.C.R. was assumed to vary in a sinusoidal manner according to Jackman et al. (1980).

For the production by S.P.E., we used the values given by Jackman et al. (1980) for each of the years encompassed in this study (1954 to 1975). These values must be considered as an upper limit since S.P.E.'s are short lived and there is most probably a spreading of the NO

produced by this process from the polar regions towards mid latitudes.

The temporal trend of the sum of these three contribution is given in Fig. 7 for the 1954–75 time period. Total NO production (upper curve) exhibits no systematic variation in phase with the solar cycle. If we lower the influence of S.P.E., G.C.R. production dominates and in this case an anticorrelation with solar cycles would be expected. The variation range is evaluated between $2.5 \cdot 10^{33}$ (in 1970) up to $5.2 \cdot 10^{33}$ (in 1972) mole-

cules of NO per year, i.e. a relative variation of $1:2$ between these two extreme years. How does this figure compare with the HNO_3 content in Antarctic snow?

The South Pole is the most adequate site for this comparison since recent snow layers are particularly well dated. The work of Zeller and Parker (1981) and Laird et al. (1982) also involved this location. Our own results are based on the analysis of 90 snow-pit samples collected in summer 1977–78 (Table 1). All results are reported in Fig. 7 where they can be compared to the values calculated by the above NO production model. Our data is first given in concentrations (curve 4) since the concentration in snow is the parameter which is expected to covary directly with the concentrations in the air. But we have also calculated fluxes (concentrations × snow deposition) which can be obtained very accurately here since the thickness of each annual layer was determined individually in the pit (Jouzel et al., 1983) for this sampling (Fig. 7.3). On the other hand Zeller and Parker (1981) and Laird et al. (1982) gave their results only in terms of nitrate deposition fluxes (Figs 7.1 and 7.2). The concentrations (Fig. 7.4) vary in the range 80 and 100 ng g^{-1}. This variability is higher than the experimental uncertainties but no clear correlation appears between this profile and the stratospheric production (Fig. 7, bottom profile). Therefore there is no evidence of a possible modulation of the nitrate concentrations in snow with the intensity of the stratospheric source nor with the solar cycle as proposed by Zeller and by Parker et al. The results of Zeller and Parker (1981) and Laird et al. (1982) (curves 1 and 2 in Fig. 7) exhibit a very high variability (one order of magnitude) incompatible with the results of our model. In any case, our flux variations, when corrected for changes in snow accumulation rates, are lower than those reported in profiles 1 and 2 (Fig. 7). Finally the Dome C nitrate profile (Fig. 5), which covers several solar cycles, does not indicate any relation between nitrate concentration and solar activity. The natural scatter of nitrate values must depend on other factors which will be examined below.

3.3.5. Other possible causes of variability. The seasonal variations of nitrate are particularly well marked in Greenland snow, where they can be used for dating snow layers. At the South Pole we
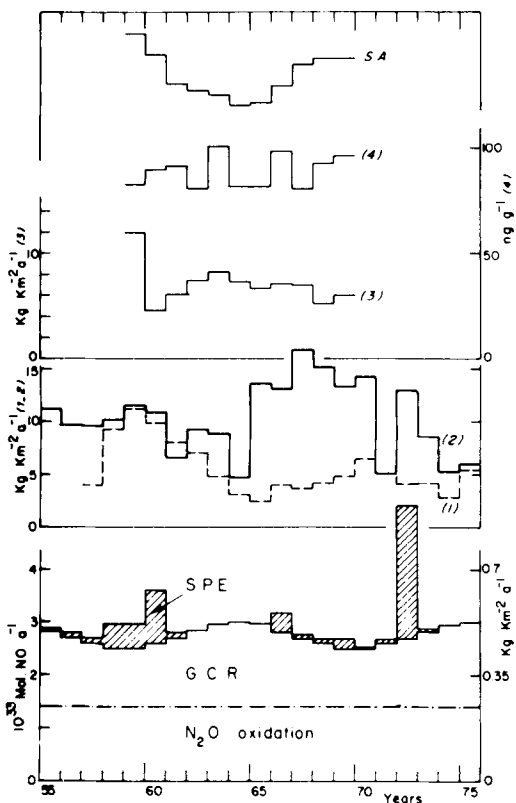

Fig. 7. The lower part of the diagram refers to the estimated amount of NO produced in the stratosphere by the 3 possible mechanisms N_2O oxidation, galactic cosmic rays (G.C.R.) and solar proton events (S.P.E.) from 1955 to 1975 (see text). Curves 1, 2 and 3 are the fluxes of nitrate (in kg·km^{-2}·a^{-1} of NO_3) deposited in snow at the South Pole according to Zeller and Parker (1981), Laird et al. (1982) and Legrand and Delmas, 1985 (this work), respectively. Nitrate concentrations (curve #4) found at the South Pole are compared to the index of solar activity (S.A.) between 1959 and 1970.

have also found a seasonal pattern for the deposition of nitrate, with a maximum during summer (Legrand and Delmas, 1984), but this seasonal effect may be difficult to detect if the sampling frequency is not high enough (Herron, 1982b). In coastal areas seasonal variations are sometimes observed, for instance on the Ross Ice Shelf (Herron, 1982a), and sometimes not, for instance on the Antarctic Peninsula (Aristarain et al. (1982).

We have suggested (Legrand and Delmas, 1984) that the seasonal effect could be linked to the chemical process leading to the formation of HNO_3. The present paper does not introduce strong arguments either in favor of or against this proposition. However, if lightning at midlatitudes is the primary source of HNO_3, the seasonal photochemical effect might be less important than the meteorological effects which influence the long range transport.

These transport phenomena could be the major cause of the natural long term variance of nitrate in the Dome C profile (Fig. 5). This profile exhibits a few "bumps". One of them is particularly well marked: between 3.8 and 5.4 m i.e. from 1915 to 1935. Its duration ($\sim$20 years) suggests that it could be linked to a change in the atmospheric circulation of the Southern atmosphere at this time. It is worth noting that the H_2SO_4 profile obtained on the same samples also presents relatively high levels during this period and that Boutron (1980) found a similar effect for the crustal derived elements. Unfortunately we have no indication of a significant change in the meteorological conditions prevailing at high Southern latitudes in the first half of the century.

3.4. Spatial variations of nitrate deposition

The concentrations of nitrate in Antarctic snow may be very different from one location to another (see for instance the spatial variations found in Adelie Land, reported Fig. 4 and also Herron (1982a)). We have listed in Table 2 the mean concentrations we have obtained at four central Antarctic locations (South Pole, Dome C, D 80 and D 55) for the same time period (1959–69).

Concentrations are in the range 3.4–23.7 ng g^{-1} whereas deposition fluxes vary from 0.36 to 13.1 kg km^{-2} a^{-1}. We have plotted these fluxes as a function of snow accumulation rates (Fig. 8). On the same figure we have also drawn the same relationship obtained for sodium (Legrand, 1985). This diagram indicates that there is no clear linear relationship between ϕ and A whereas such a relationship exists for Na$^+$. On the other hand, at a given location (South Pole), a satisfactory linear correlation is obtained for nitrate if the data pairs of each individual year between 1959 and 1970 are plotted:

$$\phi = 0.8A + 0.9 \qquad \text{with } r = 0.96.$$

The low value of the y-intercept (0.9) suggests little dry deposition of this compound.

The absence of a linear relationship for nitrate deposition at the four locations studied may be due to uneven atmospheric concentrations of this gas in the Antarctic. These four sites are located at various elevations (from 2028 m for D55 to 3240 m for Dome C). Model calculations lead to large vertical variations in the distribution of HNO_3 with altitude (Böttger et al., 1978) which could explain the observed variations of snow concentrations. An explanation may also be proposed based on the (unknown) inclusion mechanisms of HNO_3 in the snow flakes. The presence or absence of supercooled water droplets could markedly influence the deposition of this extremely soluble gaseous compound. Extremely cold central areas like Dome C could have less supercooled water in the atmosphere and conse-

Table 2. *Mean nitrate concentrations and deposition fluxes at four central Antarctic sites for the 1959–69 period*

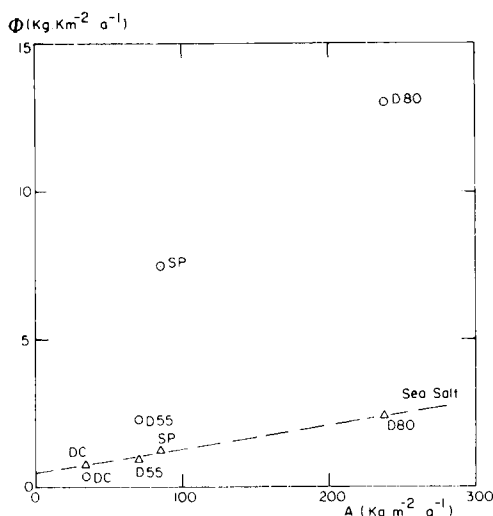| Site	Mean NO$_3^-$ concentrations (ng g^{-1})	Snow accumulation rate (A) (kg m^{-2} a^{-1})	Deposition flux ϕ (kg km^{-2} a^{-1})
D 55	33	70	2.3
D 80	55	237	13.1
Dome C	10	34	0.36
South Pole	88	85	7.5

Fig. 8. Circles: mean deposition fluxes of NO_3^- (Φ) at Dome C (DC), D 55, D 80 and South Pole (SP) as a function of the snow accumulation rate (A) between 1959 and 1969. The straight line refers to the mean deposition of sea-salt sodium obtained on the same samples (triangles).

quently the dissolution of HNO_3 would be hampered. This phenomenon should not however explain the low nitrate contents (25 ng g^{-1}) found on James Ross Island (elevation 1600 m).

Herron (1982a) found experimentally that the nitrate concentration C dependence on accumulation rate A may be expressed as:

$$C = C_0\, A^{-0.5} \quad \text{(where } C_0 \text{ is a constant).}$$

However, the combination of his data with our present results leads to the conclusion that this relationship is not applicable to all Antarctic areas and should be abandoned, particularly due to the very low concentrations of nitrate found at East Central Antarctic sites (Vostok, Dome C, D 55...). The concentrations measured at the South Pole (Laird et al., 1982; Herron, 1982a; Legrand and Delmas, 1984 and this work) seem to represent extreme values for the Antarctic continent.

The calculation of the deposition velocity of HNO_3 in snow is not possible in our case because of the lack of atmospheric concentration data. However, assuming a mean annual deposition of 11 kg km^{-2} a^{-1} in the Antarctic and a mean deposition velocity V_d equal to 1.4 cm s^{-1} (Cadle

et al., 1985), a tentative atmospheric concentration C_A can be assessed:

$$C_A = \frac{3.5 \cdot 10^{-14}\,(\text{g}\cdot\text{cm}^{-2}\,\text{s}^{-1})}{1.4\,(\text{cm s}^{-1})},$$

$$C_A = 0.025\ \mu\text{g m}^{-3}.$$

Huebert and Lazrus (1980) reported HNO_3 concentrations in the free troposphere ranging from <0.03 to 0.54 ppbv (<0.08–1.5 μg m^{-3}). Antarctic atmospheric concentrations of HNO_3 therefore appear to be slightly lower than the variation range found by Huebert and Lazrus (1980). However the value of V_d given by Cadle et al. (1985) seems to be an upper limit, particularly for the very cold temperature conditions prevailing in Antarctica.

4. Conclusions

The interpretations developed in this paper are based on the analysis of 480 firn samples collected at various sites on the Antarctic continent. The time period covered spans the last two centuries.

From our measurements in snow, we demonstrate that Antarctic nitrate is present as nitric acid, most probably in gaseous form in the atmosphere. The highest concentrations (~ 1.5 μEq·l^{-1}) were found at the South Pole, and the lowest in central areas of East Antarctica (~ 0.2 μEq·l^{-1}).

We may conclude that no effect due to atmospheric pollution by anthropogenic gaseous N-compounds is superimposed on the natural scattering of the 220 year nitrate profile.

As already pointed out by Herron (1982a) and by ourselves (Legrand and Delmas, 1984), the proposition made by certain concerning a record of solar activity in Antarctic nitrate profiles is not supported by the present results.

Among all known sources of nitrate in remote atmospheres, we have retained two contributions to explain the presence of this compound in Antarctica: lightning at midlatitudes and nitrogen fixation in the stratosphere. However we have found no evidence that the stratospheric contribution is important. We conclude therefore that Antarctic nitrate is mainly contributed by lightning with a modulation of the concentrations in snow possibly by transport or deposition.

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