

Different post-depositional processes of NO_3^- in snow layers in East Antarctica and on the northern Qinghai–Tibetan Plateau

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ABSTRACT. Through comparison of snow-pit NO_3^- profiles from central East Antarctica and the northern Qinghai–Tibetan Plateau (QTP), we conclude that NO_3^- peaks in the uppermost surface snow layers in central East Antarctica are not related to an atmospheric signal and that they need to be accounted for by post-depositional effects. Such effects, however, are not found in the snow-pit NO_3^- profiles from the northern QTP. NO_3^- can be deposited as a gas (HNO_3^-) or as a neutral salt, particularly by reaction with ammonia to form NH_4NO_3 , or fixed by sea salt or terrestrial dust (Mulvaney and others, 1998). Thus, a difference in speciation between NO_3^- in snow layers in East Antarctica and at the northern QTP is suggested as the reason for the different post-depositional processes of NO_3^- in the two areas.

INTRODUCTION

NO_3^- in polar snow and firn layers is “reversibly” deposited, and undergoes significant post-depositional exchange between snow/firn and the atmosphere, provided decreasing atmospheric concentrations result in supersaturated concentrations in the snow (De Angelis and Legrand, 1995). This loss by re-equilibration is moderated by the rate of snow accumulation, with greater losses possible where low accumulation keeps a given layer of snow in “contact” with the atmosphere for longer periods (De Angelis and Legrand, 1995). However, it is still unclear how such processes would differ in alkaline snow layers from the Qinghai–Tibetan Plateau (QTP). Ice cores drilled from the polar regions and the QTP for paleo-reconstruction necessitate a better understanding of the relationship between the chemical concentrations in the atmosphere and in the ice.

In this paper, we compare the NO_3^- profiles of the snow pits in central East Antarctica (Fig. 1) with those in the northern QTP (Fig. 2), and try to account for the post-depositional differences between these two very different areas with very different chemical and physical conditions in the local atmosphere.

POST-DEPOSITIONAL MODIFICATION OF NO_3^- IN EAST ANTARCTICA

Figure 3 shows NO_3^- profiles from snow and ice cores from South Pole (accumulation rate $80 \text{ kg m}^{-2} \text{ a}^{-1}$), Vostok ($23 \text{ kg m}^{-2} \text{ a}^{-1}$) and Dome C ($34 \text{ kg m}^{-2} \text{ a}^{-1}$), Antarctica. Compared to the mean, and fairly constant, NO_3^- concentration of 100 ng g^{-1} observed at South Pole during the last several decades, cores from Vostok and Dome C exhibit lower NO_3^- concentrations before 1975 and a sharp increase since then.

Since all the sites are located on the high Antarctic plateau, it is unlikely that the difference by a factor of 5 between NO_3^- levels at these sites before 1975 really reflects different

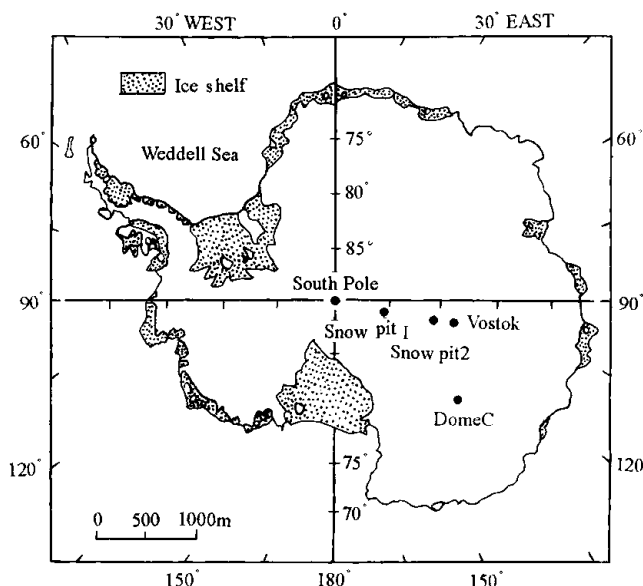


Fig. 1. Map of Antarctica showing locations of snow pits.

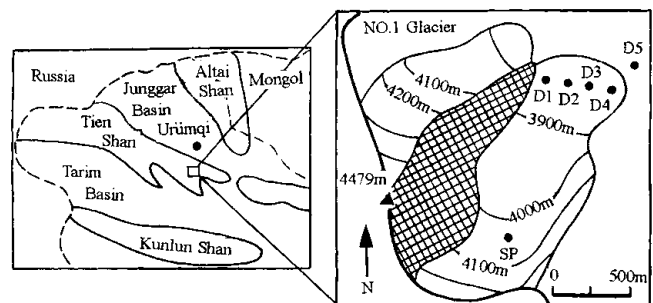


Fig. 2. Map of the head of Ürümqi River, Tien Shan, China, showing sampling locations.

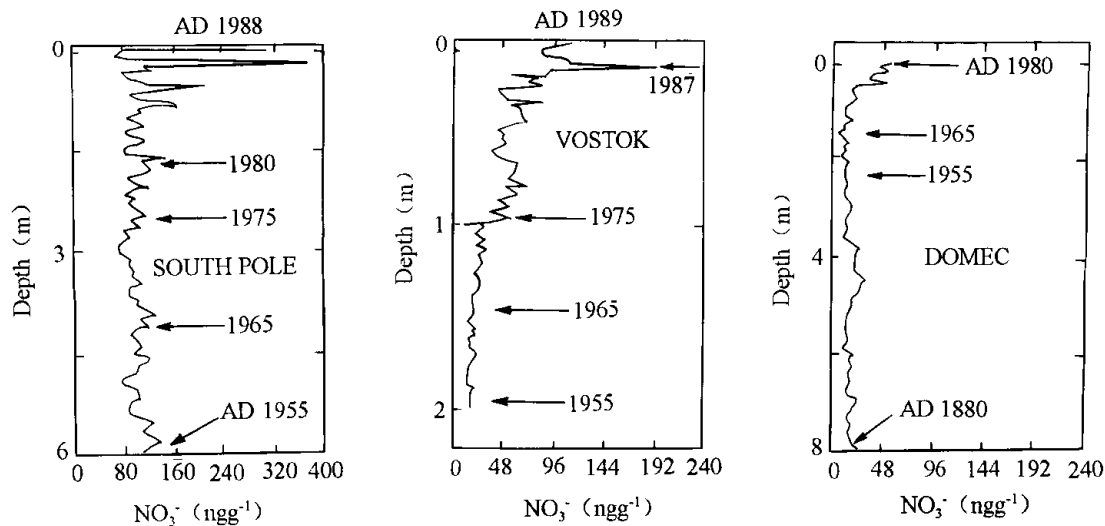


Fig. 3. NO_3^- profiles from ice cores drilled at South Pole, Vostok and Dome C, Antarctica (adapted from Mayewski and Legrand, 1990).

atmospheric NO_3^- levels (Legrand and others, 1996). Instead, it has been proposed that low NO_3^- concentrations in deep snow layers at sites like Dome C and Vostok reflect a re-emission of NO_3^- from the snow after deposition (Mayewski and Legrand 1990; De Angelis and Legrand, 1995). Legrand and others (1996) further suggested that a snow-accumulation rate in the order of $80 \text{ kg m}^{-2} \text{ a}^{-1}$ (the accumulation rate at South Pole) is large enough to strongly limit post-depositional effects.

Another three 2 m snow pits dug at South Pole in 1994 provide detailed (2 cm resolution) NO_3^- profiles for the period 1987–94 (Dibb and Whitlow, 1996). The annual spring NO_3^- peaks increase progressively toward the surface, although Mayewski and Legrand (1990) noted that the highest NO_3^- peak in the South Pole snow corresponded to spring 1987, which was the year of the deepest ozone hole measured up to that point. These three new NO_3^- profiles, however, show no correspondence to the severity of ozone depletion, and the very high NO_3^- concentrations in the 1987 snow layer at 20 cm depth in the 1988 snow pits are not apparent in the 1987 layer in any of the 1994 snow pits. This implies that even at a relatively high-accumulation area such as South Pole, interpretation of NO_3^- profiles must still account for post-deposition losses. In addition, it is noticed that the mean NO_3^- concentration of these snow pits is around 100 ng g^{-1} , similar to the previous results (Mayewski and Legrand, 1990).

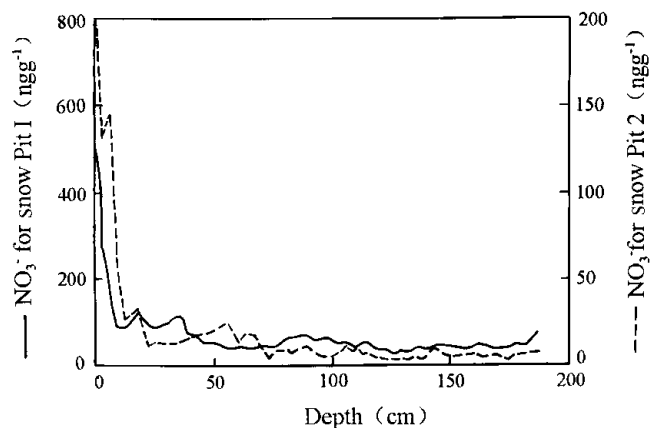


Fig. 4. NO_3^- profiles from two snow pits on the ITAE route in central East Antarctica.

Two 2 m snow pits were sampled in central East Antarctica along the route of the 1990 International Trans-Antarctic Expedition (ITAE). Snow pit 1 ($85^\circ 53' \text{ S}$, $105^\circ 29' \text{ E}$; 3150 m a.s.l.) was sampled on 27 December 1989. The annual mean temperature is -51.6° C and the annual accumulation is $44 \text{ kg m}^{-2} \text{ a}^{-1}$. Snow pit 2 ($81^\circ 50' \text{ S}$, $106^\circ 28' \text{ E}$; 3310 m a.s.l.) was sampled on 8 January 1990. The annual mean temperature is -53.9° C and the annual accumulation is $33 \text{ kg m}^{-2} \text{ a}^{-1}$. The detailed sampling and analysis processes are described elsewhere (Qin and others, 1992). Figure 4 shows NO_3^- profiles of the two snow pits with significant NO_3^- spring peaks in the surface snow layers. The maximum NO_3^- concentrations in pits 1 and 2 are 575 and 198 ng g^{-1} , respectively, and the mean NO_3^- concentrations are 67 and 17 ng g^{-1} , respectively.

The three independent experiments mentioned above at least validate the facts that (1) the annual spring NO_3^- peaks in the uppermost surface snow layers are distributed widely in central East Antarctica, and (2) high NO_3^- levels are present in the South Pole region (snow pit 1), while low NO_3^- levels are evident in the Vostok–Dome C region (snow pit 2). Similar NO_3^- snow-pit profiles from a wide spatial and temporal scale clearly demonstrate the post-depositional modification of NO_3^- in snow layers of East Antarctica.

Candidate processes of NO_3^- loss include photochemical destruction of NO_3^- , wind-scouring of the surface snow layer, loss of HNO_3 in the vapour phase, and scavenging of NO_3^- by other wind-blown particulates or gases, probably aided by windpumping of the snowpack (Pomeroy and Jones, 1996). However, the difference by a factor of about 4 between NO_3^- levels in these two regions of East Antarctica might be accounted for by atmospheric ionization products (Qin and others, 1992). Thus the annual mean NO_3^- concentration in snow might be proportional to its annual mean concentration in the atmosphere despite the post-depositional process, as long as the depositional environment does not vary significantly (Yang and others, 1995).

POST-DEPOSITIONAL PROCESSES AT THE NORTHERN QTP

Four snow pits were sampled at the east branch of Ürümqi Glacier No. 1 at the head of Ürümqi River, Tien Shan, China (shown as SP in Fig. 2), on 25 December 1995 and 8, 19 and

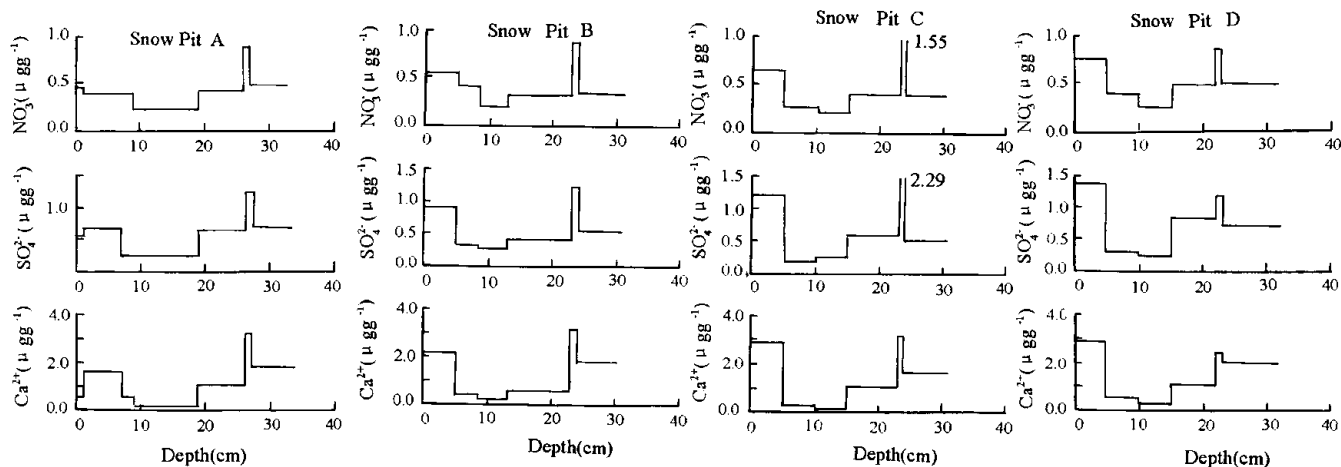


Fig. 5. NO_3^- , SO_4^{2-} and Ca^{2+} snow-pit profiles from samples collected at Ürümqi Glacier No. 1 at the head of Ürümqi River.

29 January 1996. They are designated snow pits A, B, C and D, respectively. In addition, surface snow sampling was conducted during the period 12–29 January 1996 (shown as D1–D5 in Fig. 2). During sampling, personnel wore disposable polyethylene gloves to minimize contamination. After sampling, the snow pit was partially refilled, and sampling on successive days involved digging out the pit and refacing the sampling surface by at least 1 m. The same strata were resampled on each occasion after allowing for accumulation or ablation. Snow samples were transferred into pre-cleaned polyethylene bags with plastic scoops, then transferred into a pre-cleaned polyethylene container after melting. For surface snow sampling, the uppermost stratigraphic layer was cut and scraped into a cubic block with a clean stainless-steel knife for further processing as discussed above. Because of the surface irregularities mainly caused by snowdrifting,

the depth of the uppermost stratigraphic layer varied from 5 to 10 cm. Each sample was taken from a fresh surface slightly upwind of the previously disturbed area.

Bottled samples were returned frozen to the laboratory and kept in a cold room at $-20^{\circ}C$ until chemical analysis was performed in a class 100 clean room. The cations were determined by a PE-2380 atomic absorption spectrometer, and the anions by Dionex DX-100 ion chromatography using the IonPac AS4A-SC column system and an isocratic carbonate/bicarbonate eluent. Precision is estimated to be within $<5\%$, with a detection limit of 5 ng g^{-1} for all the ions discussed (Huang and others, 1998).

The NO_3^- , SO_4^{2-} and Ca^{2+} profiles of the snow pits are shown in Figure 5. Similar trends are observed among these profiles. The peak ion concentrations below 20 cm depth correspond to the dirty layer formed the previous autumn. Extremely high NO_3^- and SO_4^{2-} concentrations in snow pit C might reflect the spatial variance, but ion elution processes may also contribute since snowmelt percolation is involved in the firnification and densification processes during autumn. However, all the ions considered remain rather stable in the low parts of the snow pits, while they increased approximately 1.6-, 2.5- and 6.1-fold for NO_3^- , SO_4^{2-} and Ca^{2+} , respectively, in the uppermost snow layers between 25 December 1995 and 29 January 1996.

The NO_3^- and SO_4^{2-} (no data available for Ca^{2+}) profiles of the surface snowpack from the D1–D5 sites are shown in Figure 6. Though spatial variation of the NO_3^- concentrations can be identified at the five sampling sites, it is also apparent that the NO_3^- and SO_4^{2-} concentrations increase during the sampling period, and they display similar trends. No apparent precipitation event occurred over the period considered, but this does not rule out possible changes in the surface snow layer that may be taking place due to slight scouring by the wind, or accumulation of light snowfall.

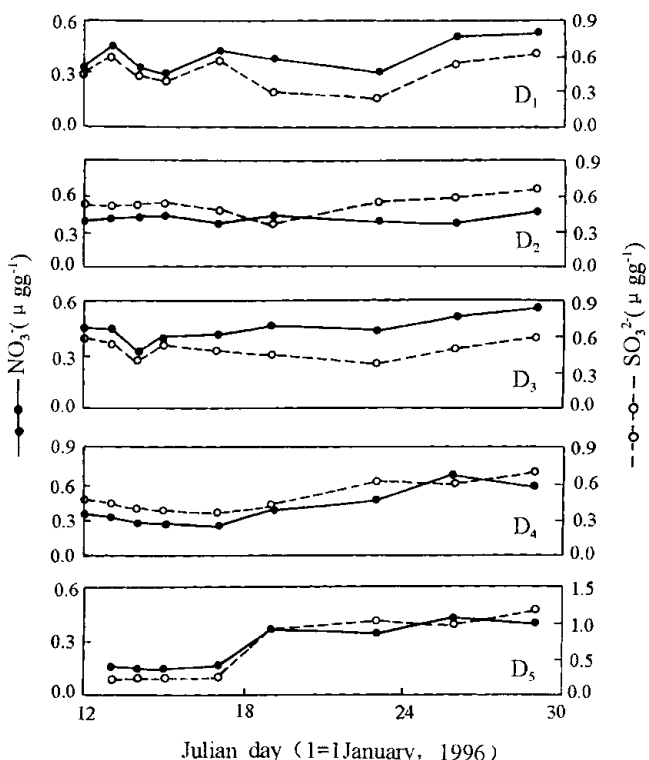


Fig. 6. NO_3^- and SO_4^{2-} profiles of the surface snowpack at the head of Ürümqi River.

DISCUSSION AND CONCLUSIONS

From rocket measurements it has been reported that the principal ions at very high altitudes (80–90 km) appear to be hydrated NO_3^- , possibly in the form of small agglomerates (Narcisi and others, 1971). It has also been found that polar stratospheric clouds contain substantial quantities of nitric acid (McElroy and others, 1988). Wofsy and others

(1988) show that nitric acid can be removed from the gas phase during very low stratospheric temperatures in the polar night and early spring. Thus, NO_3^- in polar snow is present mainly in the form of HNO_3 (in the gas phase) rather than as aerosol-associated NO_3^- ($p\text{-NO}_3^-$) (Legrand and Kirchner, 1990).

By contrast, Lyons and others (1990) report that crustally derived NO_3^- from soils appears to be the main source of NO_3^- in snow samples from central Asia. Williams and others (1992) performed comprehensive research on the sources and spatial variation of the chemical content of winter snowpack at the head of Ürümqi River, and confirmed that terrestrial dust may be the primary source of NO_3^- in the snowpack. Their analysis of variance tests indicated that NO_3^- was grouped with Ca^{2+} (mainly in the form of CaCO_3 in the atmosphere of China (Galloway and others (1987)) and ANC (acid-neutralizing capacity, representing primarily carbonate/bicarbonate). Since the primary source of Ca^{2+} and ANC in the snowpack may be aeolian dust, the grouping of NO_3^- with Ca^{2+} and ANC suggests that NO_3^- should have a similar source at the head of Ürümqi River.

In addition, crustal dust in the form of CaSO_4 is a potential source of SO_4^{2-} , which is consistent with the high correlation between Ca^{2+} and SO_4^{2-} (Williams and others, 1992). Therefore similar trends for the NO_3^- , SO_4^{2-} and Ca^{2+} snow-pit profiles (Fig. 5) and for the NO_3^- and SO_4^{2-} variances in the surface snowpack (Fig. 6) confirm the co-deposition of NO_3^- with neutral associated species.

Sun and others (1998) suggest that anthropogenic emissions are a more important source of NO_3^- than dust, based on simultaneous sampling of aerosol and snow at Ürümqi Glacier No. 1 between 19 May and 29 June 1996. However, they also propose the presence of NH_4NO_3 in snow samples because the equivalence ratio of ammonium to sulfate exceeds 1 in some cases. Neutralization of nitric acid by ammonia was observed to have the effect of fixing NO_3^- and preventing re-emission at several coastal Antarctic sites, though the efficiency of this process has yet to be determined (Mulvaney and others, 1998). Unfortunately, NH_4^+ measurements were not performed on either our snow-pit or surface-snow samples; but under an alkaline atmospheric environment, gaseous HNO_3 can be absorbed on the surface of alkaline particles and react to form salts (Mamane and Gottlieb, 1992), which could cause NO_3^- to conform to the seasonality of the fixing agent (Mulvaney and others, 1998).

Legrand and others (1988) reported enhanced NO_3^- concentrations in ice deposited during the last glacial period. Though based on a good correlation between calcium and NO_3^- concentrations along the Vostok ice core, it is suggested that the NO_3^- increase corresponds to an additional input of neutral associated species. However, it is still uncertain whether or not the observed NO_3^- increase during cold stages reflects higher atmospheric levels of NO_3^- related to the scavenging of HNO_3 by dust particles (e.g. CaCO_3) or less efficient losses due to the enhanced presence of dust particles in the snow grains (Legrand and others, 1996). Evaluation of this problem might be facilitated by a better understanding of the NO_3^- depositional mechanism in the northern QTP.

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