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Post-depositional modification of NO_3^- in snow layers at East Antarctica and at the headwater of Urumqi River

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Abstract Acidic species, such as Nitrate, in polar snow and firn layers are "reversibly" deposited, and are sufficiently volatile to undergo significant post-depositional exchange between snow/firn and the atmosphere. Through comparison of the snowpit and snowpack nitrate concentrations from central East Antarctica and the headwater of Urumqi River, we conclude that the nitrate peaks in the uppermost surface snow layers in central Antarctica are not related to an atmospheric signal and must account for post-depositional effects. Such effects, however, are not found in the surface snowpack nitrate profiles from the headwater of Urumqi River. Two reasons may account for the post-depositional difference. At first, nitrate in the polar snow and firn layers appears to be hydrated ion, which can be taken up by the atmosphere, while at the headwater of Urumqi River it seems mainly as mineral ion, which assembles the behavior of aerosol-derived species that are "irreversibly" deposited and do not undergo significant post-depositional exchange with the atmosphere. Secondly, the chemical features of the snow and ice on the Antarctica are mainly determined by wet deposition, to the contrary, dry deposition is more significant at the headwater of Urumqi River than that on the East Antarctic Plateau.

Key words NO_3^-, surface snowpack, depositional processes, East Antarctica, the headwater of Urumqi River.

1 Introduction

Nitrate in polar snow and ice is previously interpreted as the direct reflection of its source strength (Wolff *et al*. 1995). However, new evidence indicates that nitrate might be "reversibly" deposited, and undergo significant post-depositional exchange between snow/firn and the atmosphere. This loss 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 (Legrand *et al*. 1996; Bales and Wolff 1995). However, it is still unclear how such processes would differ in alkaline snow and ice from the Qinghai-Tibetan Plateau. Ice cores drilled from the polar regions and the Qinghai-Tibetan Plateau for paleoclimatic and paleoenvironmental reconstruction necessitate a better understanding of the relationship between the concentrations in the atmosphere and in the ice.

2 Post-depositional modification of NO_3^- at East Antarctica

Two 2 m snow pits were sampled in the inaccessible region along the route of the 1990 International Trans-Antarctic Expedition (ITAE). Snow pit 1 (85°53′S, 105°29′E) was sampled on December 27, 1989, where the annual average temperature is − 51.6℃ and the annual accumulation is 44 kg m^{-2} a^{-1}. Snow pit 2 (81°50′S, 106°28′E) was sampled on January 8, 1990, where the annual average temperature is − 53.9℃ and the annual accumulation is 33 kg m^{-2} a^{-1}. The detailed sampling and analysis processes are available elsewhere (Qin *et al*. 1992). Fig. 1 shows the nitrate profiles of the two snowpits with the significant spring peaks of nitrate in the surface snow layers. The extremely nitrate concentrations maxima in snow pit 1 and 2 are 575 ng/g and 198 ng/g, respectively, and the mathematic mean values for the two snow pits are 67 ng/g and 17 ng/g, respectively. In fact, such kind of snowpit nitrate profiles also exist at the other sites at East Antarctica (e.g., South Pole, Vostok, Dome C) (Fig. 2). Compared to the mean value of 100 ng/g that remains fairly constant during the last several decades, cores from Vostok and Dome C exhibit lower nitrate 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 4 ~ 5 between nitrate levels at these sites before 1975 really reflects different atmospheric NO_3^- levels. Insteadly, it was proposed that low nitrate concentrations in deep layers of sites characterized by low accumulation rates of snow reflect a re-emission of nitrate from snow after deposition (Legrand *et al*. 1996; Bales and Wolff 1995; Mayewski and Legrand 1990).

Another three 2 m snowpits drilled at South Pole in 1994 provide detailed (2 cm resolution) NO_3^- profiles for the period 1987 ~ 1994 (Dibb and Whitlow 1996). Though the NO_3^- concentrations in the annual spring peaks also increase progressively toward the

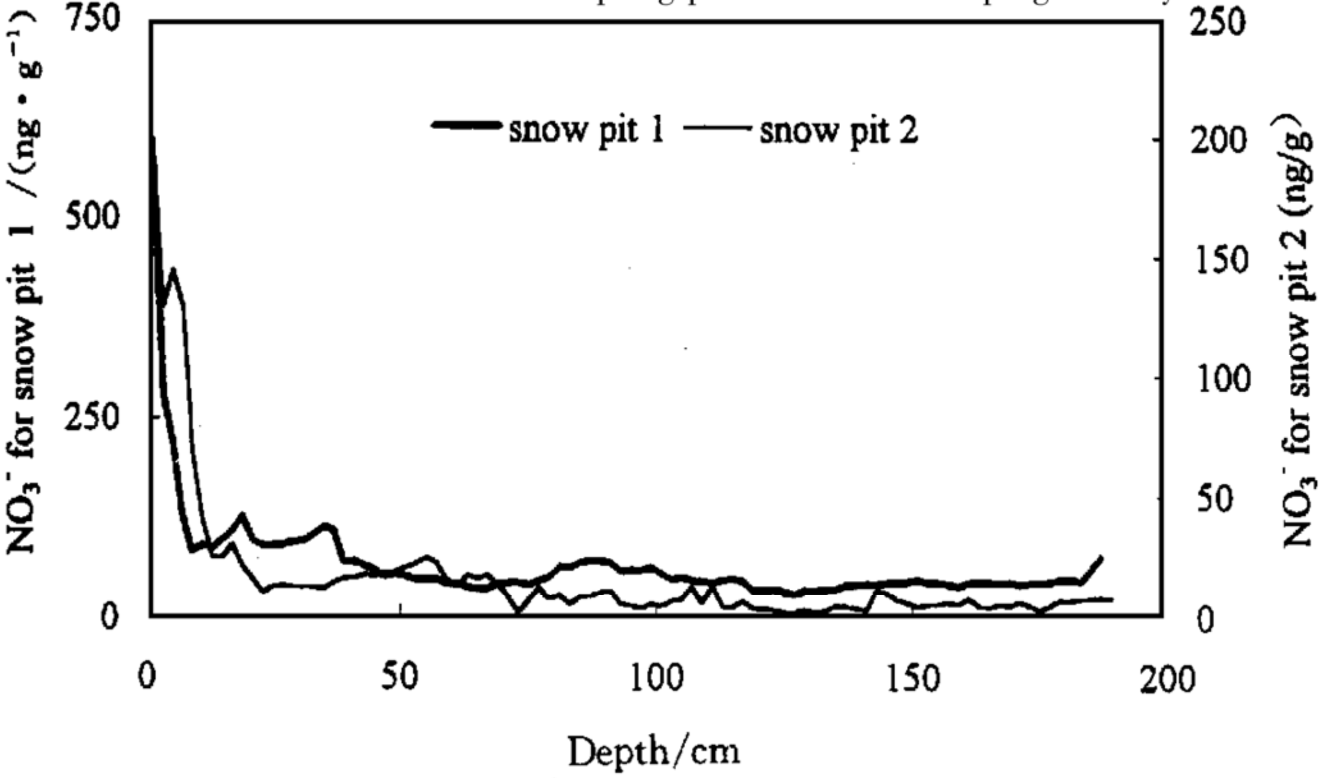

Fig. 1. Nitrate profiles of two snow pits collected in the inaccessible region along the ITAE route.

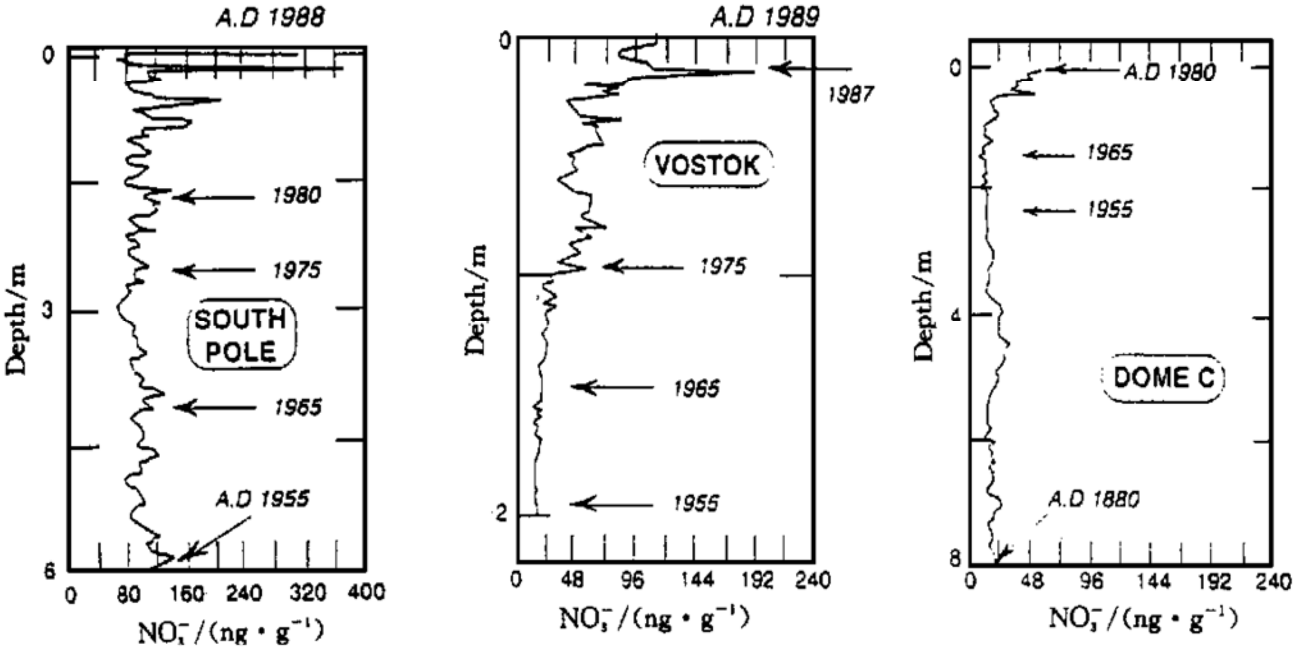

Fig. 2. Nitrate profiles of ice cores from South Pole, Vostok and Dome C (after Mayewski and Legrand 1990).

surface, these three new NO_3^- profiles, however, show that the very high nitrate concentrations in 1987 snow layer at the depth of 20 cm in the 1988 snow pits (Mayewski and Legrand 1990, see Fig. 2) are not apparent in the 1987 layer in any of the 1994 pits. Though Legrand *et al.* (1996) suggested that snow accumulation rate in the order of 80 kg m^{-2} a^{-1}(the accumulation rate at South Pole) is large enough to strongly limit post depositional artefacts, this new fact implies that even in the relative high accumulation area, such as South Pole, interpretation of NO_3^- profiles must still account for post-deposition losses.

Among the several factors that may cause the re-emission of nitrate from surface snowpack at East Antarctica, photochemical reaction over the wavelength range of 300 nm to 320 nm might play a fatal role as follows (Neubauer and Heumann 1988):

$$NO_3^- + h\nu \longrightarrow NO_3^{-*} \quad (1)$$

$$NO_3^{-*} \longrightarrow NO_2 + O^{-*} \quad (2)$$

$$O^{-*} + H^+ \longrightarrow {}^* OH \quad (3)$$

3 Post-depositional modification of NO_3^- at the head of Urumqi River

During the period of January 12 − 29, 1996, surface snow sampling was conducted at the head of Urumqi River, Tien Shan, China (D1 − D5 in Fig. 3). The sites of D1 − D4 are located at the terminus of the No. 1 Glacier (1.84 km^2 in area), and D5 is located on the moraine nearby the No. 1 Glacier. Sampling was made by personnel wearing disposable polythene gloves to minimize contamination. The uppermost stratigraphic layer of the surface snow was cut and scraped into a cubic block with a clean stainless knife, which was then taken directly into pre-cleaned polypropylene bags, then filled into pre-cleaned polythene container after melting. It is worthy to point out that no apparent precipitation event happened over the period considered. Bottled samples were transported frozen to the Laboratory of Ice Core and Cold Regions Environment at Lanzhou, China, and kept in a cold room at − 20℃ until anion analysis was performed in a class 100 clean room by a Dionex DX-100 ion chromatography, using Lonpae AS4A-SC column system and an isocratic carbonate/bicarbonate eluent. Precision is estimated less than 5% with a detection limit of ng/g (Huang *et al*. 1998).

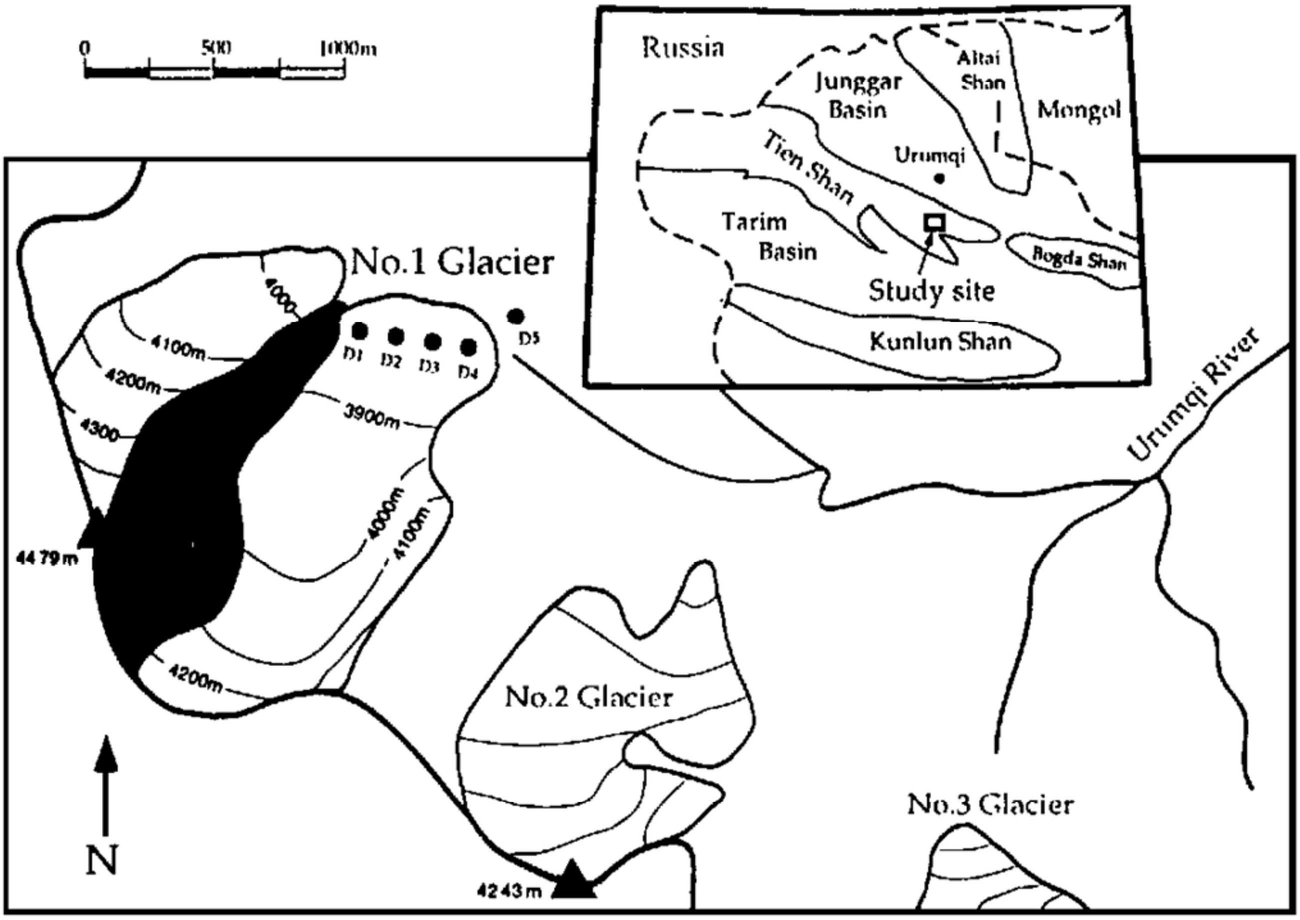

Fig. 3. A map of the head of Ur•mqi River, showing the sampling spots.

We plot the nitrate, together with sulphate, profiles of the surface winter snowpacks from D1 ~ D5 sites in Fig. 4. Though spatial variation of the nitrate concentrations can be identified at the five sampling sites, it is apparent the nitrate concentrations show a virtually stable increasing trend during the sampling period. According to Legrand *et al*. (1996) and Bales and Wolff (1995), sulphate in surface snow and ice is “irreversibly” deposited. However, similar changing feature was observed among the nitrate and sulfate profiles. This fact implies that nitrate in the surface snow at the head of Urumqi River assembles the behavior of aerosol-derived species and does not undergo significant post-depositional exchange with the atmosphere.

The reasons for the increase of the nitrate and sulphate concentrations lie in the redistribution of snow at relative high elevation to the sampling sites by wind snow-blowing, which intensifies the evaporation and sublimation, and consequently increases relatively the soluble concentrations. At the same time, snow particles may react with the surrounding atmospheric acidic gases. This causes the absolute increase of the soluble species in the re-distributed snowpack. For instance, strong wind happened during the night of January 18, 1996, this might account for the sharp nitrate increase from Jan-

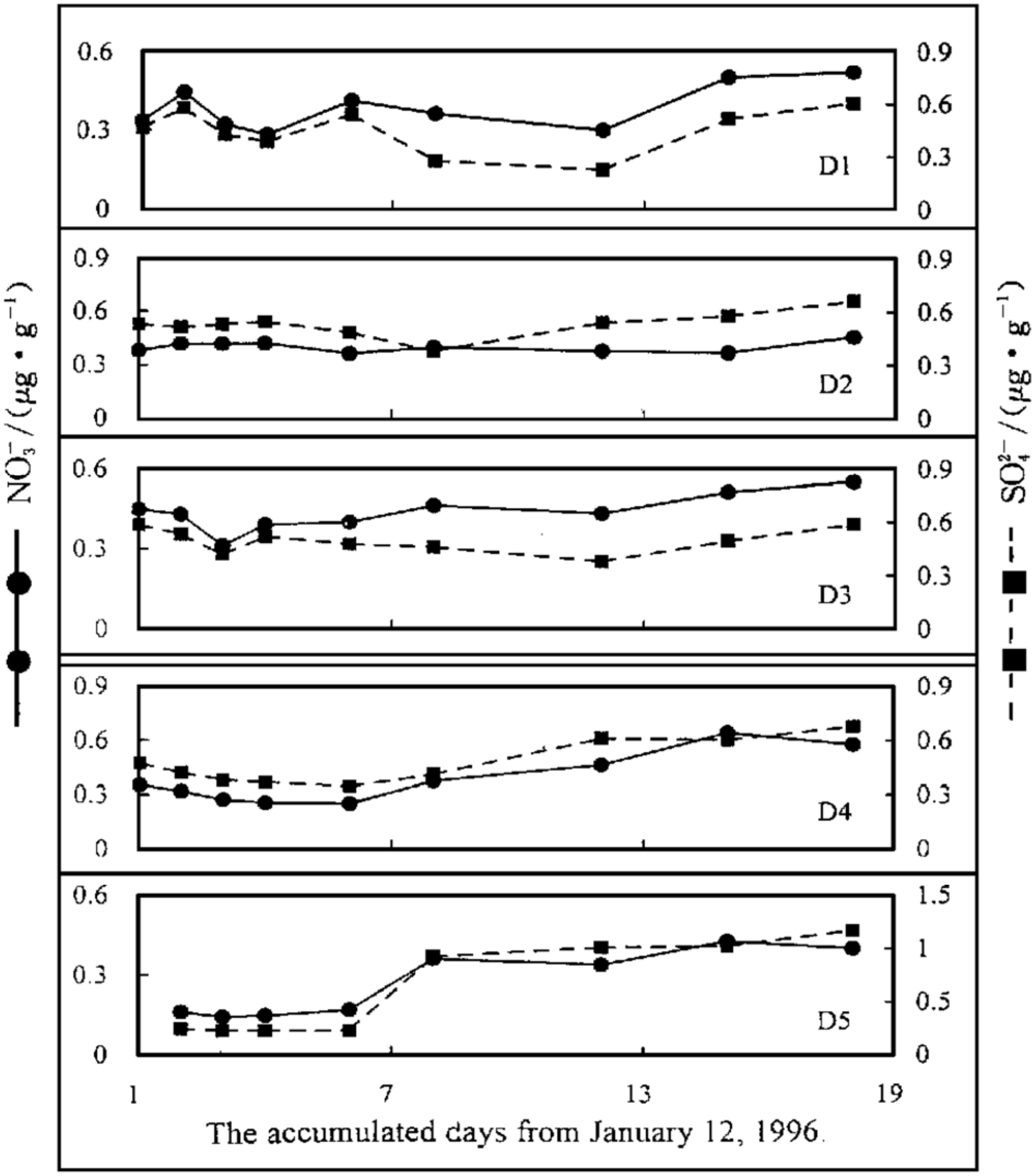

Fig. 4. The nitrate and sulphate profiles of the surface winter snowpacks at the head of Ur•mqi River.

uary 17 to 19 at the sampling sites (especially at site of D5). Furthermore, local mineral dust may be also deposited on the surface snowpack by wind, and radiation crust can be observed at the sampling sites (which implies the existence of liquid water). So the dissolution of mineral dust might also increase the ionic content in the surface snowpack.

4 Discussion and conclusions

Legrand and Kirchner (1990) studied the firn and ice cores collected at the South Pole, and concluded that nitrate in Antarctic snow mainly existed in the form of nitric acid (an ultimate product of atmospheric NO_x reactions). The linear regression equation between annual nitrate deposition fluxes (Φ) and snow accumulation (A) was proposed as follows:

$$\Phi = 0.82A + 0.99 \qquad r = 0.92$$

The rather low y-intercept (0.99), as compared with the mean deposition flux (9.5), suggests that nitrate in the Antarcitc snow and ice is mainly accumulated by wet deposition processes (scavenging by snowfall). Wolff *et al*. (1998) discussed the scavenging of air chemistry at coastal Antarctic sites and concluded that for the major aerosol species, dry deposition is responsible for less that 10% of the total deposition and that wet deposition dominates the deposition processes.

To the contrary, Williams *et al*. (1992) performed a comprehensive research on the sources and spatial variation of the chemical content of winter snowpack at the head of Ur•mqi River, and believed that terrestrial dust may be the primary source of nitrate in the snowpack. Their ANOVA tests showed that nitrate was grouped with calcium and ANC (acid-neutralizing capacity, representing primarily carbonate/bicarbonate). Since the primary source of calcium and ANC in the snowpack may be from aeolian dust, the grouping of nitrate with calcium and ANC suggests that nitrate should have a similar source. Crustal dust in the form of $CaSO_4$ is a potential source of sulfate, and is consistent with the high correlation of calcium with sulfate (Williams *et al*. 1992). Similar changing feature for the nitrate and sulfate concentrations in our surface winter snowpacks (Fig. 4) conforms further the co-deposition of nitrate with neutral associated dust.

Sun *et al*. (1998) conducted simultaneous sampling of aerosol and snow at Glacier No. 1 at the head of Ur•mqi River between May 19 and June 29, 1996. They suggested that anthropogenic emissions are a more important source for nitrate than dust. However, under an alkaline atmospheric environment, gaseous HNO_3 can be absorbed on the surface of mineral particles and react to form salts (Mamane and Gottlieb 1992). Sun *et al*. (1998) also propose the presence of NH_4NO_3 in snow samples because the equivalence ratio of ammonium to sulfate exceeds 1 in some cases. At the same time, neutralization of nitric acid by ammonia was observed to have the effect of fixing nitrate and preventing re-emission from surface snowpack (Mulvaney *et al*. 1998).

Though there is no data available for the contribution of dry deposition to the total nitrate in snow at our study site, Li (1994)* found that at least 66% of the nitrate preserved in the snow and ice at Guliya ice cap, Northwest Qinghai-Tibetan Plateau, is due to dry deposition. Since our study site is bordered by large deserts on three sides: the Gobi desert to the east, the Taklamakan desert to the south, the Junggar, Resk Sary Ishikotran and Muyum Kum deserts to the north, this guarantees that nitrate is mainly incorporated into snow predominantly by dry depositional processes, as what is observed at Guliya ice cap.

In summary, we believe that the different depositional processes and the different nitrate ion forms at East Antarctica and at the headwater of Urumqi River may account for the post-depositional difference of the study sites.

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* Li ZQ (1994): Aerosol records in the glaciers of Qinghai-Tibetan Plateau. Dissertation of Lanzhou Institute of Glaciology and Geocryology, Chinese Academy of Sciences.

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