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NITRIC ACID TRANSPORT FROM THE STRATOSPHERE TO THE TROPOSPHERE AND ICE SHEET IN ANTARCTICA THROUGH POLAR STRATOSPHERE

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Abstract: Growth and sedimentation of polar stratospheric clouds (PSCs) particles are examined using a numerical model named the 'Test Particle Sedimentation Model'.

PSCs particles transport stratospheric nitric acid (HNO_3) to the troposphere (maybe near the ice sheet) for several days by their sedimentation. The amounts of HNO_3 and H_2O removed by a particle depends on the trajectory of the particle (length of path and residence time). Usually the removed amount is larger in the higher part of the PSCs layer comparing with the lower part of the layer. The features of HNO_3 transport are consistent with the results of chemical analyses of the Antarctic ice sheet and of aerosols sampled at the surface of the ice sheet.

1. Introduction

Many chemical analyses of ice cores sampled in Antarctica suggested that non-sea salt components of anions were frequently not neutralized and that NO_3^- was the main component of anions (*e.g.*, DELMAS *et al.*, 1982). Two interpretations of the source of NO_3^- are proposed. One is NO_x production by tropospheric lightning in mid-latitudes (*e.g.*, LEGRAND and DELMAS, 1986) and the other is photochemical production in the middle atmosphere (*e.g.*, LAIRD *et al.*, 1982). However, transport processes of NO_3^- from the source region into the ice have not been fully investigated. There is no obvious evidence to determine what is the main source of NO_3^- in the ice sheet.

LAIRD *et al.* (1982) showed very good correlation between sun-spot number and NO_3^- flux to the ice sheet. They also pointed out that eddy diffusion in the stratosphere is not an effective transport process, but particle precipitation can be effective.

Recently, polar stratospheric clouds (PSCs) formation has been suggested as an important process causing the ozone hole (*e.g.*, CRUTZEN and ARNOLD, 1986). From recent field measurements and laboratory experiments, at least two different types of PSCs particles were proposed: Type-I PSCs composed of nitric acid trihydrate (NAT), and type-II PSCs composed of ice (*e.g.*, POOLE and MCCORMICK, 1988).

Concentrations of HNO_3 and/or H_2O vapors in the stratosphere are expected to

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be extremely higher than that of H_2SO_4 vapor forming the background stratospheric aerosol. High concentrations of condensable materials cause large growth rate of aerosols when atmospheric temperature becomes cooler than the frost point of the gas. PSCs particles may grow large to have large descending speed and may transport stratospheric HNO_3 and H_2O effectively under such atmospheric condition.

In this paper, stratospheric nitric acid transport is discussed in relation to the behavior of PSCs particles using a numerical model named the 'Test Particle Sedimentation Model', in which individual PSCs particle behavior is tested under various atmospheric conditions.

2. Numerical Model

The numerical model, 'Test Particle Sedimentation Model', has been developed to study the effect of particle sedimentation on change in chemical components of aerosol particles and to study transport and redistribution of vapor and particulate matter caused by particle sedimentation. Details of the model are described in another report (IWASAKA and HAYASHI, 1990). Here we give only an outline of the model.

2.1. Condensation

Growth and sedimentation of a PSCs particle are simulated in this numerical model. A particle grows through condensation (or evaporation) of vapors and coagulation with other aerosols. However, in the present study condensation is only taken into consideration, because contribution of coagulation to the growth of PSCs particles is negligible comparing with large growth rate by condensation of H_2O and HNO_3 vapors.

Condensation rate is given by the following equation for a spherical particle (TAKAHASHI, 1982).

$$dn/dt=4\pi r^2(C_i-C_s)VX \tag{1.1}$$

$$X=[4/\alpha+r^2V/\{(r+\Delta)D\}]^{-1} \tag{1.2}$$

$$\begin{aligned} \Delta&=l \quad \text{for} \quad r<l \\ \Delta&=2l/3 \quad \text{for} \quad r>l \end{aligned} \tag{1.3}$$

where n: number of molecules in a particle (molecules),
t: time (s),
r: radius of a particle (cm),
α: sticking coefficient of vapor (non-dimension),
l: mean free path of vapor (cm),
V: mean speed of vapor molecule (cm/s),
D: diffusion coefficient given by $(Vl)/3$ (cm^2/s),
C_s: concentration of vapor over particle surface (molecules/cm^3),
C_i: concentration of vapor in the surrounding atmosphere (molecules/cm^3).

When partial pressure of atmospheric H_2O is lower than the saturation vapor pressure over ice surface and partial pressures of atmospheric HNO_3 and H_2O are higher

than the saturation vapor pressures over NAT surface, HNO_3 and H_2O condense in the form of NAT. Growth rate of NAT particles (type-I PSCs) is mainly controlled by the rate of nitric acid condensation since the water vapor concentration is much higher than that of HNO_3 in the atmosphere.

Condensation rate of nitric acid (dn_n/dt) is given by eq. (1), and that of water (dn_w/dt) is given by the following equation.

$$dn_w/dt=(n_w/n_n)(dn_n/dt) \tag{2}$$

where subscripts w and n mean H_2O and HNO_3, respectively.

When H_2O partial pressure is higher than the saturation vapor pressure over ice surface, H_2O condenses in the form of ice, and HNO_3 is assumed to be contained as an impurity. Deposition of impurities on the ice surface may affect the condensation rate of H_2O. However, this process has not been fully investigated. Then, we assume that the growth rate of ice particles (type-II PSCs) is controlled by H_2O and HNO_3 condensation (these two condensation processes advance independently), and the condensation rate of each vapor is described by eq. (1).

2.2. *Particle sedimentation*

Particle growth rate changes as the particle descends. Settling speed is affected by particle shape, but particle shape is assumed to be spherical for simplicity.

2.3. *Atmospheric conditions*

Time-height cross section of temperature observed at Syowa Station (69°00′S, 39°35′E) in 1983 is shown in Fig. 1a, and super saturation region over NAT surface and ice surface are shown in Fig. 1b.

Two different type of atmospheric conditions are examined. Pressure profiles in both models follow the profile at 75°N in January of the US Standard Atmosphere (1966). Other parameters, HNO_3 and H_2O mixing ratios and temperature are different between two models on the basis of some observations, as described in following sections (2.3.1 and 2.3.2). These two atmospheric conditions are used to examine the behavior of two types of PSCs (hereafter we call them the NAT experiment and ICE experiment, respectively).

The atmosphere is separated into 16 layers with 1 km thickness in which physical parameters are supposed to be uniform, and the values of parameters are assumed to be held constant during particle descent.

2.3.1. Atmospheric conditions used for the NAT experiment

The atmospheric conditions used for this numerical experiment are summarized in Fig. 2. The temperature profile averaged in July in 1983 at Syowa Station is used. The mixing ratio profile of water vapor is based on obseravations at high latitudes (*e.g.*, HARRIES, 1976) and the HNO_3 profile from satellite observation at high latitudes in fall (*e.g.*, AUSTIN *et al.*, 1986). Super saturation layers appear in the range from 14 km to 22 km for the atmospheric conditions.

2.3.2. Atmospheric conditions for the ICE experiment

The atmospheric conditions used for this numerical experiment are summarized

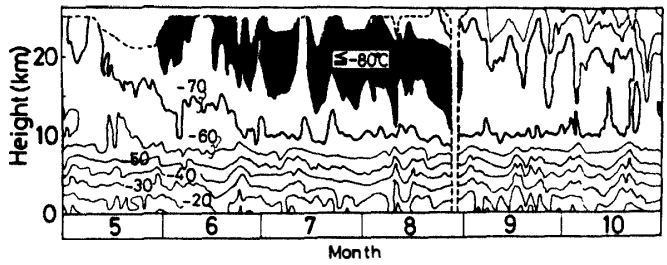

Fig. 1a. Time-height cross-section of temperature observed at Syowa Station (69°00′S, 39°35′E) in 1983. The region enclosed by the broken line shows no available data. The contour interval is 10°C. The black area shows the region with temperature less than −80°C.

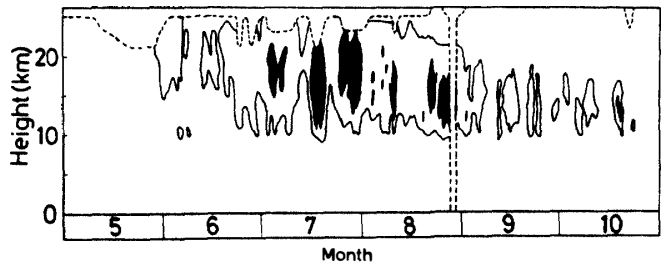

Fig. 1b. Time height cross section of super-saturated condition over nitric acid trihydrate (enclosed area by solid line) and over ice (black area). Temperature is given in Fig. 1a, and water vapor content is assumed to be 5 ppmv in the stratosphere and 35% relative humidity in the troposphere. Nitric acid vapor amount is according to the HNO_3 profile by satellite observation at high latitude in fall, from 1 ppbv to 10 ppbv in the stratosphere (e.g., AUSTIN et al., 1986).

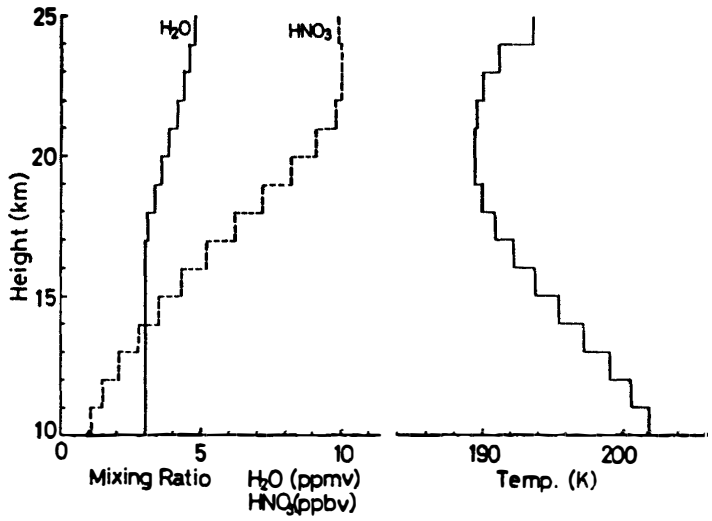

Fig. 2. Model atmosphere for NAT experiment (see text).

in Fig. 3. The temperature profile is based the average of observed data from July to 25, 1983 at Syowa Station. Mixing ratio (MR) of water and nitric acid vapors are given by the following relations for each of the 16 layers.

$$MR_{w,a} = 5 \text{ ppmv} \tag{3.1}$$

$$MR_{n,a}=MR_{n,i} \quad \text{for} \quad MR_{w,s}>5\ \text{ppmv} \tag{3.2}$$

$$MR_{w,a}=(1+S)MR_{w,s} \tag{3.3}$$

$$MR_{n,a}=MR_{n,i}(MR_{w,a}/5) \quad \text{when} \quad MR_{w,s}<5\ \text{ppmv} \tag{3.4}$$

where MR: mixing ratio in each layer (ppmv),
S: assumed super saturation ratio.

The subscript of w, n, a, i, and s meam H_2O, HNO_3, atmospheric conditions for ICE experiment, atmospheric conditions for NAT experiment, and ice surface, respectively.

The value of 5 ppmv for $MR_{w,a}$ is the maximum value observed in the lower stratosphere. Equation (3.3) is based on tropospheric cloud observation. According to many observations (WARNER, 1968), the super saturation ratio of water vapor is less than 0.01 in the tropospheric clouds, possibly because of precipitation. Then we assume that water vapor has been removed (eq. (3.3)) and nitric acid vapor also has been removed according to the ratio defined by eq. (3.4) in the super saturated layers. In this study the super saturation ratio, S, is assumed to be 0.01 from 11 km to 22 km; at other heights the super saturation ratio less than 0.01.

2.4. *Initial condition of test particle*

The initial radius of the test particle is assumed to be 0.5 μm. The time required for the particle to reach 0.5 μm radius is very short (on the order of 0.1 day) and settling velocity of the particle is very small (on the order of 10 m/day).

Initially test particles start sedimentation at heights from 22 km to 12 km at intervals of 2 km. Calculations are continued until a test particle reaches the troposphere (10 km) or shrinks to the initial radius (0.05 μm) by evaporation.

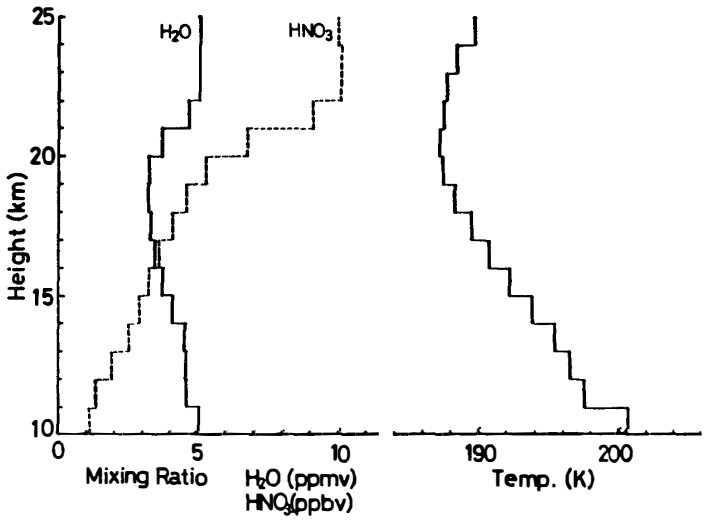

Fig. 3. Model atmosphere for ICE experiment (see text).

3. Results and Discussion

3.1. Three stages during NAT particle descending movement, and rapid transport of nitric acid

The results of the NAT experiment, in which the sticking coefficient of HNO_3 is assumed to be 1.0, are shown in Figs. 4 and 5. Figure 4 shows trajectories of test particles on a height-time plane (left) and on a height-radius plane (right). These results revealed that there are three growth stages of descending particles. In the early stage, growing NAT particles keep their initial altitudes. In the second stage, as the particle grows, the settling velocity becomes larger and the particle starts descending to the lower atmosphere. In the following stage, NAT particles evaporate and their radii decrease in the unsaturated layer (under 14 km). Finally particles reach the tropopause level (10 km) or shrink to their initial radii through evaporation. Particle

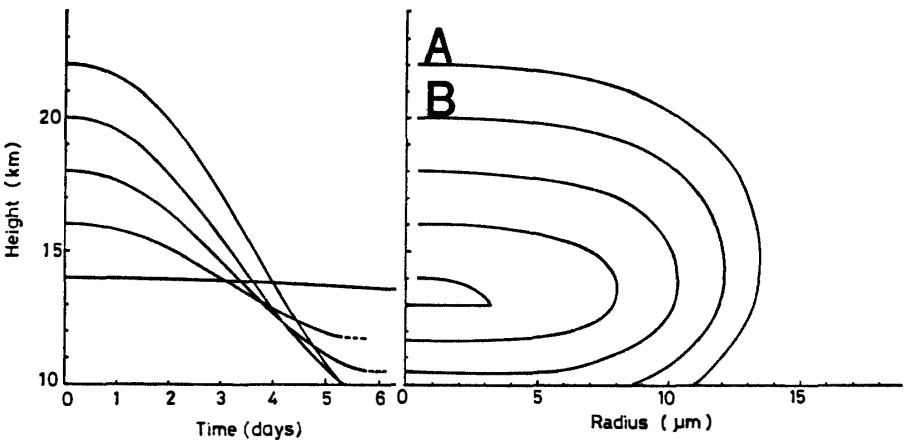

Fig. 4. Trajectories of test particles for NAT experiment on height-time plane and height-radius plane.

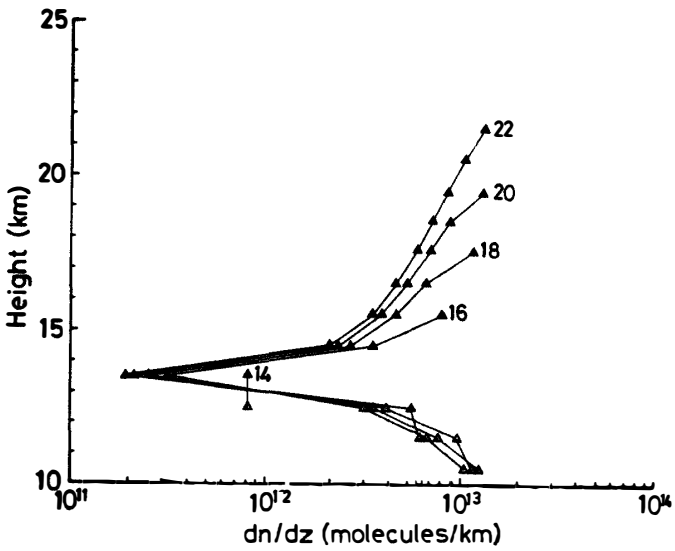

Fig. 5. The exchanged amounts (see text) of nitric acid of NAT test particle. Numbers denote the initial height. Closed triangle: condensation. Open triangle: evaporation.

growth is strongly controlled by growth rate and time during which the particle can pass through the high HNO_3 content region. For example, particle A grows larger than particle B, since particle A has a large growth rate and can stay in the high HNO_3 content region longer (see Fig. 4).

Particles which start at heights of 22 to 16 km reach the tropopause within 5 days. The time scale (several days) of transport of HNO_3 by PSCs particle sedimentation is much shorter than that of transport by diffusion, several months per 10 km in the vertical, in the stratosphere.

Water and nitric acid evaporate from NAT particles below the height of 14 km (unsaturated region). NAT particles can act as important carriers of HNO_3 and H_2O through condensation, sedimentation, and evaporation in the stratosphere and troposphere. Figure 5 shows the profiles of the amounts of HNO_3 condensing on (or evaporating from) the test particle during the particle sedimentation, defined by dn/dz (called 'the exchanged amount'). The exchanged amount of each test particle shows minimum near 14 km. This suggests that each NAT particle removes more HNO_3 from the higher part of the PSCs layer through condensation and adds more HNO_3 to the lower atmosphere through evaporation. Particles originating from 22 to 20 km can easily reach the tropopause.

3.2. *Large ice particle formation and descending motion*

The results of the ice experiment, in which sticking coefficients of HNO_3 and H_2O are assumed to be in 1.0 and 0.3 respectively, are shown in Figs. 6 and 7.

All particles descend to 11 km with in several days, and the travel time to reach the 11 km level depends on the initial heights of the particles. The maximum radii of all test particles is found in the narrow range from 14 μm to 18 μm at 11 km (Fig. 6). The particles of exchanged amount of HNO_3 (left side) is silimar to that of NAT particles, but that of H_2O (right side) is different from that of HNO_3. Water vapor is scavenged at all altitudes by each particle. Differences between the ICE experiment and NAT experiment are mainly due to the difference in profiles of vapor concentration for condensation (Figs. 2 and 3). However, general characteristics of HNO_3 transport, time scale and exchange mass profile are similar between the two experiments.

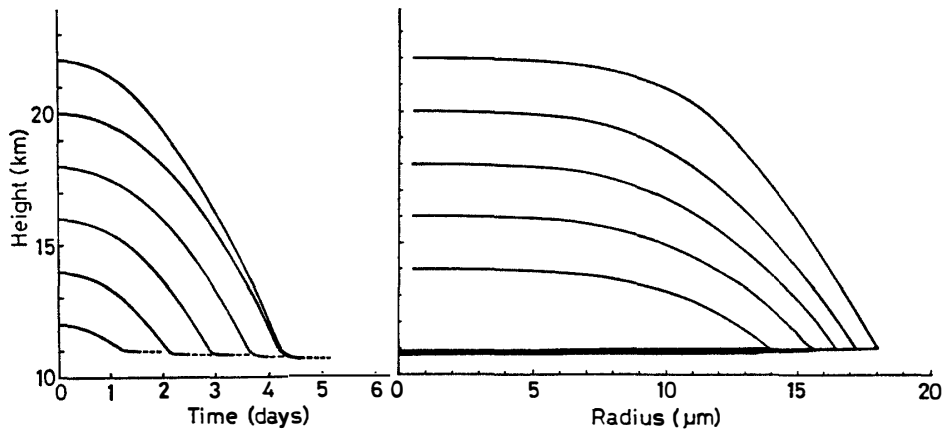

Fig. 6. Same as Fig. 4 but for ICE experiment.

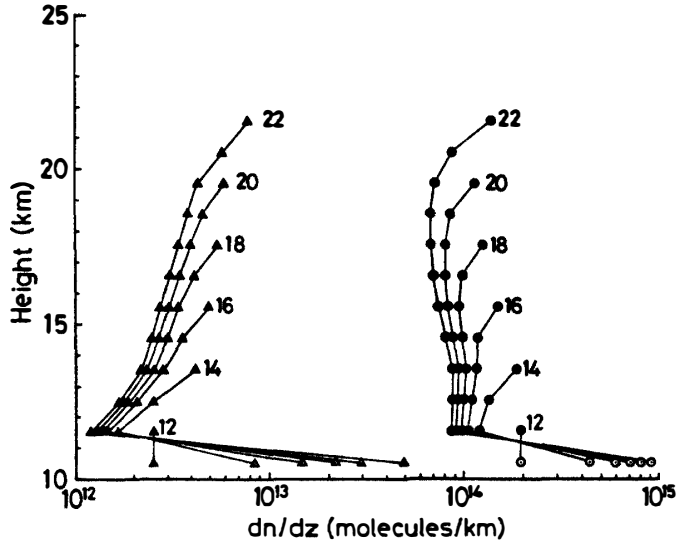

Fig. 7. Exchanged amount of nitric acid and water between ICE test particle and atmosphere. Numbers denote initial heights. Closed symbols: condensation. Open symbols: evaporation. Triangle: nitric acid. Circle: water.

3.3. Sedimentation and evaporation of PSCs particles in the troposphere

Particle sedimentation has been suggested as an important process of particulate matter during a PSCs event (IWASAKA and HAYASHI, 1990), but in the present experiments, type-II PSCs particles evaporate completely in the lower stratosphere within a few days. Only type-I PSCs particles which grow in the upper PSCs region can reach the tropopause.

The present results are obtained under the assumption that PSCs particles consist of pure NAT and pure ice. However, there are NH_3 originated from the troposphere (GRAS, 1983) and metal vapor originated in ablation of meteors (PRATHER and RODRIGUEZ, 1988) in the stratosphere. Parhaps these components are included in PSCs particles, and form salts (ex. NH_4NO_3) as the result of reaction with HNO_3. Equilibrium concentrations of NH_3 and HNO_3 over NH_4NO_3 are given by the thermal decomposition equation as follows (STELSON and SEINFELD, 1982),

$$NH_4NO_3(\text{solid}) \rightleftharpoons NH_3(\text{gas}) + HNO_3(\text{gas}) \tag{4.1}$$

$$K(\text{ppb}^2) = [NH_3][HNO_3] \tag{4.2}$$

$$\ln(K) = 84.6 - 24220/T - 6.1 \ln(T/298) \tag{4.3}$$

where K is the thermal decomposition coefficient (ppb^2), and square bracket denotes mixing ratio in ppb unit.

The calculated results using eqs. (4.1), (4.2), and (4.3) and values of $[NH_3][HNO_3]$ in the polar atmosphere are shown in Fig. 8. The equilibrium value of $[NH_3][HNO_3]$ is much smaller than that in the atmosphere. Then these salts are left on the PSCs surface and coat the surface through vaporization, which may decrease the evaporation rate of HNO_3. If this process is fully effective, PSCs particles can retain their size, about 10 μm radius, which is large enough to reach the ice sheet surface in several

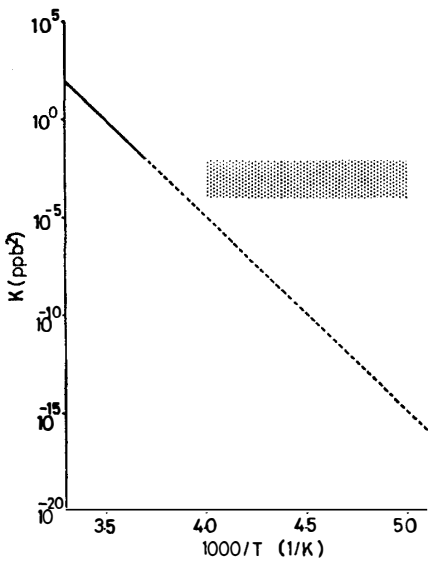

Fig. 8. Thermal decomposition coefficient (K) of NH_4NO_3, given as equilibrium coefficient by eqs. (4.1)–(4.3). These relations is obtained for temperatures higher than 0°C. Here it is extraporated to about −80°C (shown by broken line). The shadowed region shows conditions in the winter polar troposphere.

days sedimentation (IWASAKA and HAYASHI, 1990). Other processes of PSCs transport to the ice sheet surface may be snowing and cyclonic disturbance in the troposphere. The time required to transport PSCs particles to the ice sheet surface by these processes are from several days to a month, and longer than that by sedimentation with coating effect. Even if coating by salts is not effective enough to decrease the evaporation rate, stratospheric HNO_3 and H_2O in particulate matter may be transported to the ice sheet surface through snowing and/or cyclonic disturbances.

This coating effect is scarcely understood, although it is important as shown above. More research should be done on this effect.

3.4. Impacts of PSCs on the geochemical cycle of NO_3^- in ice sheet and the troposphere

Chemical analyses of aerosols obtained at Georg von Neumeyer Station (70°37′S, 8°22′W) from 1983 to 1985 show very low NO_3^- concentration in fall and high concentration in winter (WAGENBACH *et al.*, 1988). Sudden increase in NO_3^- concentration is also recognized in June, mid-winter. Moreover, LAIRD *et al.* (1982) show that the NO_3^- flux to the ice sheet becomes large in winter. These results indicate that an effective transport system operates in winter and that the NO_3^- transport system is controlled by some condition with critical stage, not fully identified in this study.

PSCs are formed during polar winter when stratospheric temperature becomes very low, below the temperature threshold. Moreover, lidar and satellite observations show sudden increase in the stratospheric content in several days (IWASAKA, 1986; MCCORMICK *et al.*, 1989). Now we can suppose that the sedimentation of PSCs particles is an important process for NO_3^- transport in the stratosphere, and from the stratosphere to the troposphere and ice sheet.

4. Conclusions

(1) The sedimentation of PSCs particles is an important process of stratospheric HNO_3 transport. Its time scale is several days and each PSCs particle effectively transports HNO_3 and H_2O in the upper part of PSCs layer.

(2) Transport of HNO_3 through PSCs sedimentation seems to be consist with some results of chemical analyses of ice sheet and surface aerosols. To better understand the HNO_3 transport process in the polar region, the following observational studies are necessary; vertical changes in size distribution and chemical composition of particles, profiles of HNO_3 and H_2O vapors, chemical composition of the snow and their temporal variations.

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