

EFFECT OF POLAR STRATOSPHERIC CLOUDS
ON GEOCHEMICAL CYCLE OF STRATOSPHERIC MATERIAL
—STRATOSPHERIC PARTICLE PRECIPITATION—

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Abstract: A numerical calculation was done to see the effect of particulate matter sedimentation formed in the stratosphere on transport of atmospheric sulfuric acid and nitric acid to the troposphere and near the ground. Extremely large particle formed in the Antarctic winter stratosphere can produce large flux of these acids from the atmosphere to the ground.

1. Introduction

Volcanic materials originated in mid- and low-latitudes are frequently observed in the Antarctic ice sheet, and these materials have been speculated to be transported through the stratosphere (*e. g.*, MAENHAUT *et al.*, 1979; BOUTRON, 1980; HERRON, 1982; DELMAS *et al.*, 1985). In addition to volcanic materials, particulate matter produced in the Antarctic winter stratosphere can act as a carrier of stratospheric materials to the lower troposphere and/or the Antarctic ice sheet.

The cold stratosphere activates particle growth possibly through deposition of water vapor and nitric acid vapor in the Antarctic winter (*e. g.*, MCCORMICK *et al.*, 1982; STEELE *et al.*, 1983; IWASAKA *et al.*, 1985a; TOON *et al.*, 1986). STANFORD (1973) suggested that the Antarctic stratosphere was a possible sink of stratospheric water vapor through freeze-out of stratospheric particles, on the basis of eye-observations of clouds in Antarctica. A possibility of descending motion of the grown-up particles was suggested also from lidar measurements at Syowa, Antarctica (IWASAKA, 1986a, b). If a particle which grows large enough descends from the stratosphere to the troposphere, various stratospheric chemical elements, in addition to water, can move to the troposphere. Recently, LEGLAND and KIRCHNER (1988) speculated on the effect of stratospheric particle precipitation on NO_3^- content in particulate matter in the lower atmosphere from measurements in 1957–1983 in Antarctica.

In this paper, the effect of particle precipitation on transport of SO_4^{2-} and NO_3^- from the stratosphere to the troposphere is discussed in relation to the winter enhancement of Antarctic stratospheric aerosols (development of Polar Stratospheric Clouds) using a numerical model.

2. Numerical Model

2.1. Basic equation and atmospheric conditions

There have been very few observations of vertical change in water vapor mixing ratio, sulfuric acid vapor concentration, and nitric acid vapor content in the Antarctic stratosphere and troposphere. Here, we assume profiles of H_2O , H_2SO_4 , and HNO_3 vapor content of Fig. 1 on the basis of previous numerical calculations and measurements at low- and mid-latitudes.

There are insufficient data describing H_2SO_4 vapor content in the stratosphere (no measurement of Antarctic H_2SO_4). However, it should be reasonable to assume that the emission rate of sulfur compound containing gas and particulate in Antarctica is smaller than that in mid- and low-latitudes due to low human activities and the ice sheet covering the Antarctic continent and ocean. In winter, solar radiation is weak, so that photochemical reactions producing H_2SO_4 occur at a low rate. The mixing ratio of H_2SO_4 vapor used here corresponds to the lower limit of measurements of $\text{H}_2\text{SO}_4 + \text{HSO}_3$ in the stratosphere (*e. g.*, VIGGANO and ARNOLD, 1983). Concerning the mixing ratio of Antarctic tropospheric H_2SO_4 , we examined the atmospheric conditions with the mixing ratio of 1/10 of $\text{H}_2\text{SO}_4 + \text{HSO}_3$ estimated by TURCO *et al.* (1979). The concentration of HNO_3 was obtained from measurements in the winter atmosphere at 80°N by AUSTINE *et al.* (1986) and the numerical results of AIKIN *et al.* (1983). Water vapor content was based on the average value of measurements at high latitudes (IWASAKA *et al.*, 1985b; O'BRIEN and EVANS, 1981; HARRIES, 1976).

The temperature is based on meteorological sonde measurements made in mid-

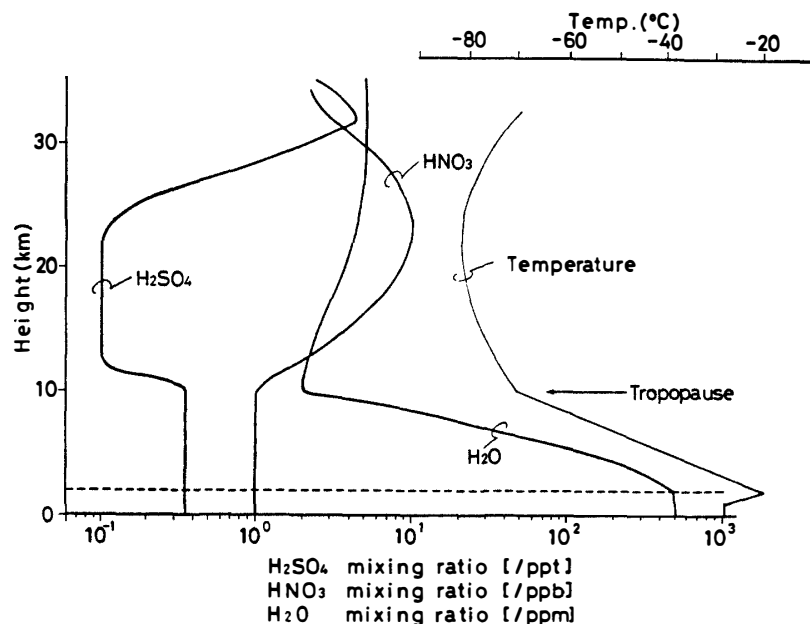


Fig. 1. Model atmosphere used for numerical calculation. An arrow ' \leftarrow ' shows the tropopause (10 km height) and the dotted line the averaged height of the Antarctic ice sheet surface. Temperature distribution is based on measurements in winter at Syowa Station, Antarctica. Profiles of H_2O , HNO_3 , and H_2SO_4 are assumed from measurements at mid- and low-latitudes and model calculations (see text).

winter at Syowa Station (69°00'S, 39°35'E). Tropopause height and height of ice sheet surface were assumed to be 10 km (winter average) and 2 km above sea level (approximate averaged heights), respectively.

Possible formation of extremely large particles was suggested by GOODMAN *et al.* (1988) and by HOFMANN *et al.* (1988) in the winter Antarctic stratosphere. If so, these particles seriously affect transport of stratospheric materials to the troposphere through particles sedimentation. According to lidar measurements at Syowa Station, the enhanced aerosol layer descends at the rate of 0.8 mm/s in winter (IWASAKA, 1986b).

Here we paid attention to following points;

1) Whether the extremely large particles formed in the cold stratosphere can transport stratospheric materials to the lower troposphere or not.

2) Whether a particle can change its chemical composition during sedimentation from the stratosphere to the lower troposphere.

From the measurements by GOODMAN *et al.* (1988) and HOFMANN *et al.* (1988), we assumed the following situations and initial conditions in the model calculation (Fig. 2):

1) Chemical composition of pre-existing stratospheric particles is sulfuric acid solution of 75 wt %.

2) Particles grow according to the ternary mixture model in the stratosphere and fall to the tropopause.

3) At the tropopause, all particles are solid.

4) During sedimentation in the troposphere, particles grow through condensation and coagulation (condensation growth only in the stratosphere).

The changes in descending particle size and chemical composition are numerically examined with the following relations (1)–(7).

The descending speed of a particle, U , is given by KASTEN (1968) (Details con-

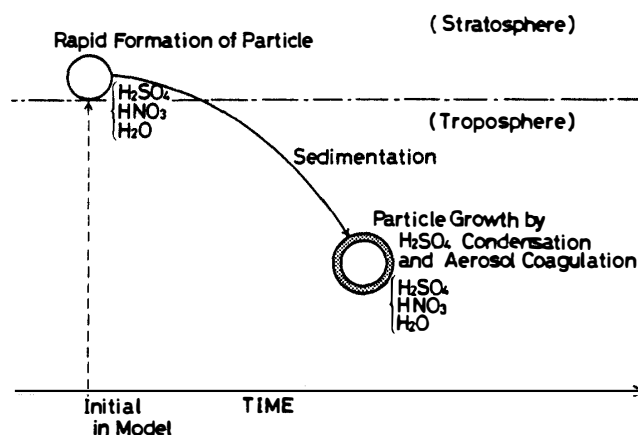


Fig. 2. Schematic diagram showing the effect of particle growth during its sedimentation. In the cold stratosphere, a particle grows according to the ternary mixture (H_2SO_4 - HNO_3 - H_2O) or binary mixture (HNO_3 - H_2O) model. In the troposphere, a solution layer of sulfuric acid grows over the solid state particle during its sedimentation. Coagulation with background aerosols with 75% sulfuric acid solution also contributes to particle growth. Detailed discussion is given in text.

cerning eqs. (1)–(7) are given in Appendix),

$$U = [Mg/(6\pi\eta r)][1 + AK_n + BK_n \exp(-C/K_n)] \quad (1)$$

where K_n : Knudsen number

M : mass of particle (g)

η : coefficient of viscosity (dyne s/cm²)

g : gravitational acceleration (cm/s²)

r : particle radius (cm)

$A=0.864$ (constant of correction)

$B=0.29$ (constant of correction)

$C=1.25$ (constant of correction)

During sedimentation, particle radius and chemical composition change through coagulation, and condensation of H₂SO₄ and HNO₃ vapors. We assume here that descending particles are rapidly coated in the troposphere by a thin film of sulfuric acid solution whose concentration corresponds to the equilibrium condition between partial pressure of H₂SO₄ in the surrounding atmosphere and H₂SO₄ concentration of solution. The change in number of H₂SO₄ molecules in aerosol through H₂SO₄ condensation and particle coagulation play the following relations:

$$dn_a/dt = (dn_a/dt)_{\text{cond}} + (dn_a/dt)_{\text{coag}} \quad (2)$$

$$r = f(r_c, n_a) \quad (3)$$

where n_a : number of H₂SO₄ molecules over the surface of particle (particles),

r_c : radius of particle core (cm),

f : function for radius estimation, which is determined under the condition of $P_{\text{H}_2\text{O}}$ in the atmosphere = $P_{\text{H}_2\text{O}}$ at the particle surface, and $P_{\text{H}_2\text{O}}$ is water vapor pressure.

The first term on the r. h. s. of eq. (2), change in number of H₂SO₄ molecules, is given at the surface by the following equation (FUCHS, 1959):

$$(dn_a/dt)_{\text{cond}} = 4\pi r^2 (C_{a\infty} - C_{as}) V_a X \quad (4)$$

and

$$X = [4/\alpha_a + r^2 V_a / \{(r + \Delta) D_a\}]^{-1} \quad (5)$$

where $\Delta = l_a$ for $r < l_a$
 $2l_a/3$ for $r \geq l_a$,

l_a : mean free path of H₂SO₄ (cm),

V_a : mean speed of H₂SO₄ molecule (cm/s),

D_a : diffusion coefficient given by $(V_a l_a)/3$ (cm²/s),

C_{as} : concentration of H₂SO₄ molecules at particle surface (particles/cm³),

and $C_{a\infty}$: concentration of H₂SO₄ molecules in the surrounding atmosphere (particles/cm³) (see Fig. 1).

The number of particles with radius of r_i , N_i , in the i -th bin of r in the size distribution function, which coagulate with descending particles of radius r during a unit time interval is given by:

$$N_i = 4\pi R_i^2 C_i V_i Y_i \quad (6)$$

where R_i : collision radius, $2R_i = (r + r_i)$ (cm),

V_i : velocity difference, $V_i = v_s - v_i$ where v_s and v_i are velocity of descending particle and velocity of particle of radius r_i (cm/s),

C_i : concentration of particles with radius r_i (cm⁻³)

Y_i : efficiency for collision between descending particle and particles in Brownian motion.

Therefore, the change in number of the H₂SO₄ molecules through coagulation due to particle sedimentation is given by the following relation:

$$(dn_a/dt)_{\text{coag}, i} = N_i x_i \quad (7)$$

where x_i : number of H₂SO₄ molecules in a particle of radius r_i and, given by $(4/3)\pi r_i^3 \rho_i w_i / m_a$ (molecules/particle),

w_i : weight ratio of H₂SO₄ to particle (no dimension),

m_a : mass of H₂SO₄ molecule (g),

and ρ_i : density of particulate matter (g/cm³).

Using eq. (7), the change in number of H₂SO₄ molecules through coagulation between descending particles and background particles, whose radius varies from r_1 to r_n , is given by the following equation:

$$(dn_a/dt)_{\text{coag}} = \sum_1^n N_i x_i \quad (8)$$

2.2. Distribution of HNO₃ and H₂SO₄ used in numerical calculation

Many investigators have suggested possible formation of HNO₃-H₂O binary mixture particles in the winter Antarctic stratosphere. In Fig. 3, we compare the density of atmospheric water vapor used here, which is from observations (*e. g.*, IWASAKA *et al.*, 1985b; HARRIES, 1976), with the water vapor content over the surface of the HNO₃-H₂O solid state mixture (50 wt %) and pure ice obtained from the diagram of CRUTZEN and ARNOLD (1986). The figure shows that super saturation of water vapor occurs for binary mixture HNO₃·3H₂O above 2 km.

In Fig. 4, atmospheric HNO₃ vapor content used in the model is compared with saturated HNO₃ vapor content over the solid state binary mixture of HNO₃-H₂O. Figures 3 and 4 suggest that the HNO₃·3H₂O mixture particles grow through deposition of HNO₃ and H₂O in the stratosphere and the upper troposphere. The growth rate of HNO₃·3H₂O particles should be larger than that of sulfuric acid droplets, since the concentration of HNO₃ is higher than that of H₂SO₄ in the stratosphere. Under such atmospheric conditions, particles which are large enough to descend can form in the stratosphere.

Active formation of particulate matter can cause serious change in chemical composition of surrounding air (for example: the extremely denitrified stratosphere was observed in spring in Antarctica; The denitrification is considered to be due to active production of HNO₃·3H₂O particles). This large growth rate of particles may decrease the residence time of particles in the stratosphere and interaction time between the particles and surrounding air. From the view point of denitrification and/or

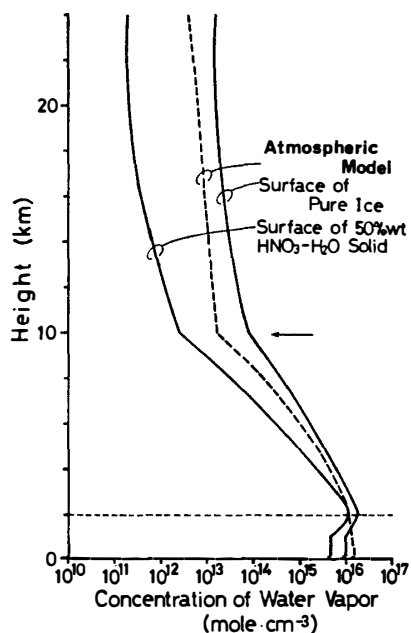


Fig. 3. Vertical profile of water vapor density used in numerical calculation (broken line). Profiles of water vapor saturated over the surface of pure ice, and over the surface of a solid mixture of $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (50 wt%) are compared. These profiles are estimated under the atmospheric conditions given in Fig. 1.

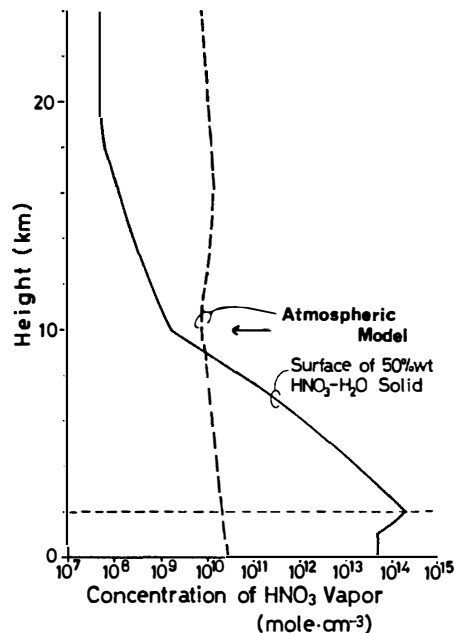


Fig. 4. Vertical profile of HNO_3 vapor concentrations used in numerical calculation and that saturated over the solid state $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ mixture. These profiles are estimated under the atmospheric conditions given in Fig. 1.

dehydration of the stratosphere, active particulate matter production is essential. From the stand point of transport of stratospheric constituents to the troposphere, the large sedimentation speed of particulate matter is interesting. Particles which descends from the stratosphere to the lower troposphere can be carriers of stratospheric constituents such as HNO_3 , H_2O , and so on.

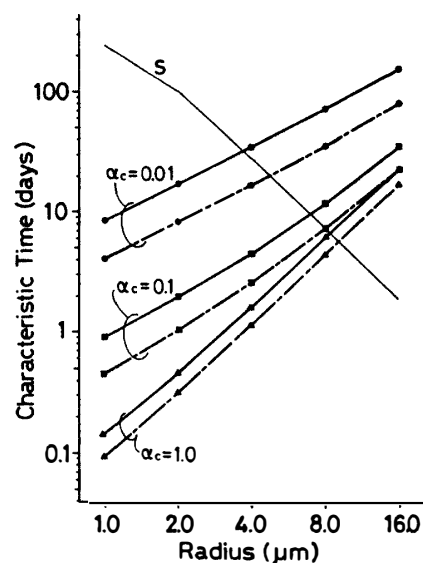
In this paper, deposition growth of $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ in the stratosphere is taken into consideration, but sublimation loss of HNO_3 in the troposphere is neglected, assessing coagulation growth including interception effect in the troposphere.

2.3. Growth of particles in the winter stratosphere

Figures 3 and 4 show that the particle of binary mixture $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ can form in the Antarctic winter stratosphere. Ternary mixture $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ condensation has been suggested as a possible particle growth process in the stratosphere since the frost point of the ternary system is expected to be noticeably lower than that of the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ mixture system (KIANG *et al.*, 1975).

Laboratory experiments on condensation of the ternary mixture and the binary mixture are insufficient, so it is impossible to come to a final conclusion about the particle condensation (or deposition) growth mechanism in the stratosphere. Here, in addition to particle growth of the binary mixture $\text{HNO}_3\text{-H}_2\text{O}$, the ternary condensation growth is also tested.

Fig. 5. Characteristic time scale of growth of a particle which is falling from 16 km to 15 km through condensing of HNO_3 and H_2O vapor. Growth time scale is estimated from the HNO_3 - H_2O binary mixture model (CRUTZEN and ARNOLD, 1986) (solid line) and the H_2SO_4 - HNO_3 - H_2O ternary mixture model (KIANG *et al.*, 1975). The region of 15 km–16 km is chosen, from lidar and meteorological sonde measurements at Syowa Station, as a good one to see whether the particle growth rate is considerable or not compared with descending motion of the particle. Initial chemical composition of the particle is assumed to be 75% sulfuric acid solution. The model calculation uses sticking coefficients = 1, 0.1, and 0.01 (see Discussion in text).



From Fig. 5, we can discuss whether stratospheric particles formed through these processes can descend to the troposphere or not. From the lidar data obtained at Syowa Station, the region from 15 km to 16 km is chosen as representative of the enhanced aerosol layer. We observe the behavior of test particles in the numerical model (eqs. (1)–(3)) where the lower and upper boundaries are 15 and 16 km, respectively. For initial conditions we use one trajectory of the test particle in space with time, vertical height, and particle radius (t - z - r space).

The time scale of particle growth defined by $r/(dr/dt=U)$ is calculated on the basis of analysis of particle growth on the r - t plane. The solid and dotted lines in Fig. 5 correspond to particle growth due to binary HNO_3 - H_2O solid mixture (50 wt %) growth (CRUTZEN and ARNOLD, 1986) and the ternary H_2SO_4 - HNO_3 - H_2O mixture (10–45–45 wt %) (KIANG *et al.*, 1975), respectively from, initial particles with H_2SO_4 - H_2O solution of 75 wt %. The time scale of travel in the stratosphere defined by $L/(dz/dt)$, in which L (1 km = 16 km – 15 km) is the vertical scale of travel, is calculated from analysis of test particle motion on the z - t plane. The value of α_c is the sticking coefficient. Owing to lack of laboratory experiment, we cannot say definitely what is the most appropriate value of α_c . Here we use values in the range 1–0.01.

The duration of winter enhancement of Antarctic stratospheric aerosols (Polar Stratospheric Clouds event) is about three months from lidar measurements (IWASAKA *et al.*, 1986) and satellite observations (McCORMICK *et al.*, 1985). Comparing the time of enhancement to time scales of particle travel and/or particle growth in the stratosphere, we discuss the possibility of sedimentation of stratospheric particles in the troposphere.

From Fig. 5, it can be concluded that particle actively sediment during winter enhancement if they are in the region of $L/(dz/dt) < 3$ months (=duration of winter enhancement). Particles which satisfy $L/(dz/dt) > r(dr/dt)$ grow rapidly during sedimentation. For the condition $L/(dz/dt) < r(dr/dt)$, particle sedimentation speed is so high that particles cannot actively grow further. Curves in the figure show that particles with about 4 μm are formed within their travel time in the stratosphere

(about 30 days) even if we assumed a low sticking coefficient $\alpha_c=0.01$. If we use a large sticking coefficient $\alpha_c=1$, particles with radius of about $8\text{ }\mu\text{m}$ are expected to form within the travel time, even residence time in the stratosphere is extremely short in the stratosphere (about 5 days).

From Figs. 3–5, it is expected that the Antarctic winter stratosphere can act as an important source of particulate matter to the troposphere. If so, it should be interesting to discuss the effect on the geochemical cycle of stratospheric constituents in Antarctica.

3. Transport of Stratospheric Particulate Matter into the Troposphere

Chemical analysis of ice cores sampled from the Antarctic ice sheet suggests that various atmospheric events affect the distribution of chemical elements in the ice core (*e. g.*, volcanic eruption, activity of the circulating cyclonic storm surrounding the continent). Particulate matter transport from the stratosphere to the troposphere also possibly plays an interesting role in the geochemical cycle in Antarctica. As described in Section 2.1, 2.2, and 2.3, it is quite possible that the Antarctic winter stratosphere accelerates downward transport of particulate matter. Here, we describe particle growth (or loss) and change in chemical composition of particles during sedimentation in the troposphere, and discuss the transport of atmospheric HNO_3 and H_2SO_4 due to sedimentation of particulate matter.

We illustrate particle sedimentation from the stratosphere to the troposphere in Fig. 6 considering the length of PSCs events. To simplify the problem, growth

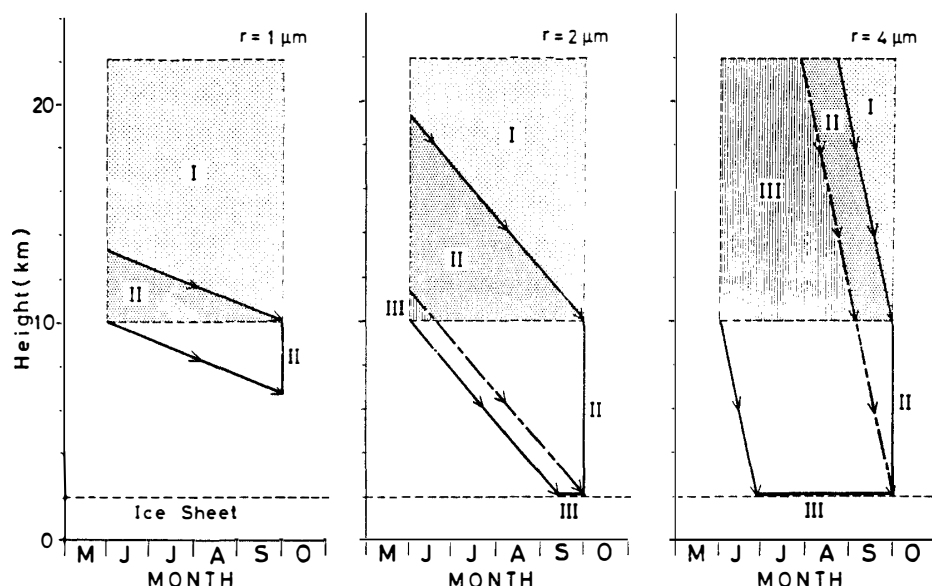


Fig. 6. Diagram of sedimentation of particle with radius = 1, 2, and $4\text{ }\mu\text{m}$. The region enclosed with broken line shows the region where aerosol enhancement appears. The number of I, II, and III in the shaded region mean: I: the area containing aerosol particles which cannot reach the tropopause within the period of the winter enhancement of stratospheric aerosols; II: the area containing aerosol particles which can enter the troposphere; III: the area containing aerosol particles which can reach the ground.

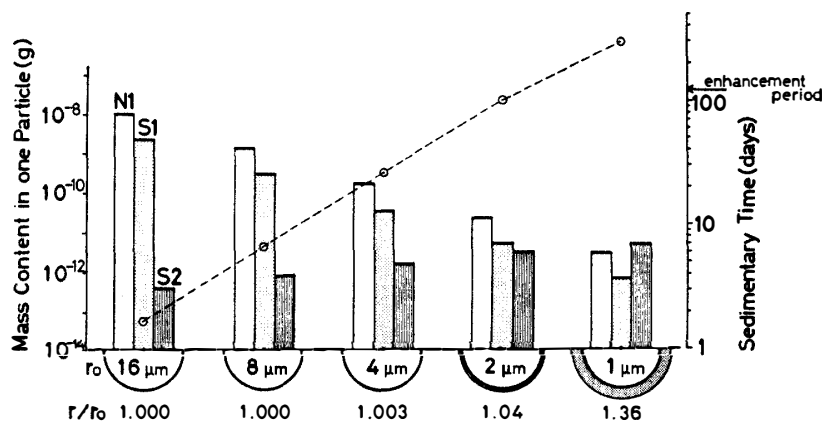


Fig. 7. Mass distribution contained in an individual particle which reaches the surface of the ice sheet. Value of N_1 denotes mass of HNO_3 which was transported from the stratosphere, S_1 the mass of H_2SO_4 transported from the stratosphere, and S_2 the mass of H_2SO_4 transported from the troposphere. Dotted curve shows travelling time of each particle. The value of r/r_0 is the ratio of final size (r) to initial size (r_0). The aerosol enhancement time scale is shown by an arrow.

and/or loss of particle size is neglected. The aerosol enhancement region and its active time are assumed to be heights from 10 to 22 km and the period from June to September, respectively, on the basis of lidar measurements at Syowa Station (IWASAKA *et al.*, 1986).

For particles having a radius of $1 \mu\text{m}$ at the beginning of winter enhancement of the aerosol layer, the particle sedimentation speed is not large enough to reach near the surface of the ice sheet within the period of winter enhancement. A particle with initial size of $2 \mu\text{m}$ can reach near the ground at the final stage of enhancement.

If a particle with radius $4 \mu\text{m}$ is formed during the period of enhancement, the particle may reach the ground in late June; and after that the transport of particulate matter to the lower troposphere continues until the end of the PSC events.

Figure 7 shows changes in chemical composition and radius of particles due to coagulation between descending particles and background sulfuric acid droplets (interception effect is taken into consideration). During the sedimentation in the troposphere, chemical composition as well as particle size changes through condensation, evaporation, and coagulation (eqs. (1)–(8)). In the figure mass content of HNO_3 transported from the stratosphere (N_1), H_2SO_4 transported from the stratosphere (S_1), and H_2SO_4 from the troposphere (S_2) through sedimentation of individual particles are shown in units of g. Change in particle size is indicated by the ratio r/r_0 ; r is size at the ground (ice sheet) and r_0 is size at the tropopause.

We indicate the contributions of coagulation of tropospheric aerosol to mass growth of descending particles by radius growth of semicircles (relative units). The shaded part indicates size growth due to coagulation of tropospheric aerosols. The sediment time in the troposphere is indicated by a dotted line.

Chemical composition of the test particle is assumed to be HNO_3 45%, H_2O 45%, and H_2SO_4 10% at the tropopause considering the results of our numerical

calculation on the growth of background aerosols in the stratosphere (Fig. 5). For a particle with initial size of $16\text{ }\mu\text{m}$, travel time from the tropopause to the ground is at most 2 days. Therefore these particles can easily transport stratospheric particulate matter to the lower troposphere, but the travel time is so short that the effects of condensation (H_2SO_4) and coagulation with background aerosol (sulfuric acid droplets) are apparently smaller than in the case of particles of 2 and $1\text{ }\mu\text{m}$. The size ratio r/r_0 does not show meaningful change ($r/r_0=1$). A $1\text{ }\mu\text{m}$ particle at the tropopause can grow to about $1.36\text{ }\mu\text{m}$ through condensation of H_2SO_4 and coagulation during sedimentation from the tropopause to near the ground. In this particle, the mass content of H_2SO_4 obtained in the troposphere becomes larger than those of H_2SO_4 and HNO_3 transported from the stratosphere.

4. Discussion and Conclusion

Formation of extremely large particles has been suggested in the winter (or spring) Antarctic stratosphere by direct sampling (GOODMAN *et al.*, 1988) and photoelectric measurements (HOFMANN *et al.*, 1988). The particles collected by airborne wire-sampler were about $100\text{ }\mu\text{m}$ and larger in the lower stratosphere. According to the balloon measurements by HOFMANN *et al.* (1988), the number-size distribution function of stratospheric aerosols showed a noticeable peak at about $2\text{ }\mu\text{m}$. Such large particles seem to be important in controlling the circulation and budget of various atmospheric constituents in the Antarctic atmosphere.

Descending motion of the aerosol layer was clear in the winter Antarctic stratosphere from lidar measurements at Syowa Station (IWASAKA, 1986b). According to IWASAKA (1986b), the Antarctic winter stratosphere could act as an important sink of stratospheric water vapor if the descending motion is due to particle sedimentation. As shown in Fig. 5, the particle growth rate is large enough to form particles a few micron in diameter within a very short time under the conditions of the winter Antarctic stratosphere. When large particles are formed in winter according to the HNO_3 - H_2O binary mixture particle growth model or the H_2SO_4 - HNO_3 - H_2O model, the particles may become effective carriers of stratospheric HNO_3 and H_2SO_4 (Figs. 5, 6, and 7). Furthermore the particles can transport tropospheric H_2SO_4 (Fig. 7).

Figures 6 and 7 suggest the possibility that the fully grown particles in the winter stratosphere affect the chemical composition of particles near the ground. There is a large possibility that such aerosol is contained in snow and ice sheet. These figures also suggested the possibility that sedimentation of stratospheric particles causes seasonal change in the particulate matter near the ground, especially NO_3^- and SO_4^{2-} . Chemical analysis of ice core sampled from the Antarctic ice sheet suggests that severe volcanic eruptions at mid- and low-latitudes disturbed the content of various chemical elements in the ice core through the stratospheric transport of these elements. It should be interesting to discuss the effect of active particle formation in the Antarctic winter stratosphere on volcanic materials transported into the Antarctic stratosphere.

The relation between particle sedimentation and various dynamical air motion is also interesting. However, the numerical model used here is extremely simplified

in order to see the effect of gravitational sedimentation of large particles observed in winter and spring. The effect of other possible transports such as eddy diffusion and large-scale air circulation are not discussed here. There is no discussion of details of nucleation processes of PSCs particles owing to lack of measurements. At present the conclusions are speculative and it is necessary to obtain much more information about particle growth processes, phase changes, and particle transport.

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Appendix

The procedure used here is briefly described.

The parameters in eq. (1) are given by the following relations. The Knudsen number K_n in eq. (1) is defined by

$$K_n = l_g / r$$

where l_g is the mean free path in the surrounding gas and r is the particle radius. l_g is determined as a function of height, z on the basis of a given atmospheric model (number concentration of air molecules, and averaged radius of air molecules). The coefficient of viscosity η is given by

$$\eta = \xi n_g m_g G_g l_g$$

where n_g is the number concentration of air molecules, m_g mass of air molecules, and G_g thermal velocity. The value of ξ is assumed to be 0.499. The thermal velocity is a function of height since it depends on atmospheric temperature.

The gravitational acceleration constant g is assumed to be 980.665 cm/s², and vertical change in acceleration due to gravity is neglected.

An aerosol particle changes its size through H₂SO₄ vapor condensation and

coagulation during descent as shown by eq. (2). For condensation growth, it is assumed that the descending particle is always in equilibrium with water vapor pressure in the surrounding air, but not with sulfuric acid vapor (see discussion in IWASAKA, 1986a). Therefore a particle whose size is at first determined on equilibrium condition with partial pressure of H_2O (eq. (3)) gains its mass (or volume) according to eq. (4).

Mean free path and mean speed of H_2SO_4 molecule in eq. (4) are defined by

$$l_a = 1 / [\sqrt{(1 + m_a/m_g)} n_g \pi \sigma_a^2]$$

and

$$V_a = \sqrt{8kT/\pi m_a}$$

where k is the Boltzmann constant, σ_a diameter of an H_2SO_4 molecule, T atmospheric temperature, and m_a mass of an H_2SO_4 molecule. Therefore, these are functions of height.

In the coagulation process, a descending particle of radius r coagulates with background particles of radius r_i . The number of particles which coagulate with the descending particle in unit time, N_i , is equal to the number of particles in the space $4\pi(R_i)2XV_i$, where $2R_i (=r+r_i)$ is the collision radius and V_i the sweeping speed of a particle of radius $(r+r_i)$. Here $V_i=U$ is assumed since the speed of background particle is small compared with U . Therefore the most simplified estimation leads to the relation;

$$N_i = 4\pi(R_i)2V_i C_i$$

where C_i is the number concentration of particles of radius of r_i . However, in the atmosphere, the value of N_i is disturbed through various interception effects. It is necessary to modify this relation. In eq. (6), Y_i is the modification factor showing the interception effect. In Y_i , D_i is the diffusion coefficient of particles of radius r_i , and α_i is a constant (here $\alpha_i=1$ is assumed).

The change in number of H_2SO_4 molecules per unit time due to coagulation with particles of radius r_i is given by eq (7), and summation over i in eq. (7) shows the total effect of coagulation on change in the number of H_2SO_4 particles (eq. (8)).