

CHEMICAL STATE OF POLAR STRATOSPHERIC AEROSOLS

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Abstract: Electron microscopic observation of individual particles collected in the winter Arctic stratosphere with a balloon-borne impactor showed the possibility that particles containing nitric acid were formed above the background sulfate particle layer during the cold winter season. External mixing of nitric acid and sulfate particles was observed in the region of 18.8–19.6 km (the upper part of the sulfate particle layer) during the measurements of January 31, 1990. One possible explanation of this phenomenon is sedimentation of nitric acid particle, which has been speculated as an important process causing denitrification of the polar stratosphere and polar ozone depletion.

1. Introduction

Dramatic ozone depletion in the Antarctic spring (ozone hole) was first observed by FARMAN *et al.* (1985), who suggested an increase in chlorofluorocarbon content in the atmosphere as the most important cause of the ozone hole. Since such large ozone depletion in the Antarctic spring cannot be explained only by gas phase chemical reactions, SOLOMON *et al.* (1986) and others suggested potential contribution of heterogeneous processes to the ozone loss.

Lidar measurements have showed noticeable enhancement of stratospheric aerosol during winter at Syowa Station, Antarctica (*e.g.*, IWASAKA *et al.*, 1985). Satellite measurements also showed winter enhancement of stratospheric aerosols in the Antarctic and Arctic regions (*e.g.*, MCCORMICK *et al.*, 1982). From thermodynamic studies, it has been suggested that formation of ice particles and/or nitric acid trihydrate particles is the main cause of the winter enhancement of polar stratospheric aerosols (*e.g.*, MCELROY *et al.*, 1986; TOON *et al.*, 1986; HANSEN and MAUERSBERGER, 1988). Formation of such particles can cause a seriously dehydrated and denitrified stratosphere (*e.g.*, CRUTZEN and ARNOLD, 1986). Additionally, the surfaces of these particles are expected to serve as catalysts for reactions which convert reactive nitrogen gases to HNO₃ and chlorine reservoir gases to photolytically active chlorine-containing

gases, from which chlorine atoms can easily be liberated after the sun returns to the polar region (*e. g.*, SOLOMON *et al.*, 1986; MOLINA *et al.*, 1987).

Recent observations have suggested that these heterogeneous processes produce large disturbances in ozone in the Antarctic spring stratosphere (*e. g.*, special issue of *J. Geophys. Res.*, **94**, 1989, describing results during the Airborne Antarctic Ozone Experiment). However, there are few observations of the chemical state of individual particles which disturb the chemistry of the polar stratosphere.

Electron microscopic observations of individual particles which are collected on surfaces of vapor (calcium, carbon, and nitron) deposited thin films have been frequently made for studies of particles near the ground surface (*e. g.*, BIGG *et al.*, 1974; ONO *et al.*, 1983; YAMATO *et al.*, 1987; WEISWEILER and SCHWARZ, 1990). This chemical test technique is very effective for identifying the molecular state of individual particles and mixing state of particulate chemical composition (externally mixed or internally mixed). However, concerning stratospheric particles, such chemical tests are very scarce since only few collections of particles were made.

Here, we made electron microscope measurements of particles collected with a balloon borne impactor in the winter Arctic stratosphere, and discuss the effect of nitrate particle formation on the winter enhancement of polar stratospheric aerosols.

2. Particle Collection in the Winter Arctic Stratosphere

Stratospheric particles were collected on an electron microscope screen of which the surface was coated with a thin film of carbon or nitron on January 18 and 31, 1990 at Kiruna, Sweden, with a balloon-borne impactor. The height interval of particle sampling was about 0.7 km in the range from the upper troposphere (about 10 km for measurements of January 18, and about 13 km for measurements of January 31) to the mid-stratosphere (about 23 km for measurements of January 18, and about 30 km for measurements of January 31). Thirty one collections were made during one balloon flight. The impactor used had a 2-mm diameter jet nozzle, and the flow rate of sampled air was 10 l/min. The value of 50% cut-off radius was 0.09 μm at 15 km height.

In measurements of January 31, many nitrate particles were collected. Figures 1–4 show vertical changes in the molecular state of individual particles collected at 18.1–21.0 km on January 31. Figure 1 is an electron micrograph of particles collected on carbon deposited thin film at a height of 18.1–18.8 km. Most of the particles show typical features which have been frequently observed for sulfate particles (*e. g.*, GRAS and LABY, 1978; YAMATO *et al.*, 1987). Some particles have a ‘satellite structure’ which has been recognized as a characteristic sulfuric acid morphology. Sulfate particles and/or sulfuric acid droplets are considered to be major constituents of the stratospheric aerosol layer (*e. g.*, TURCO *et al.*, 1982).

Figure 2 is an electron micrograph of particles collected on a nitron thin film at height of 18.8–19.6 km. Only one particle produced needle-like crystals through reaction between nitron film and nitrate in particulate matter; other particles did not. Figure 3 is an electron micrograph of particles collected on carbon at 19.6–20.2 km. The particles in Fig. 3 are very similar in morphology to the particles in Fig. 1. Figure

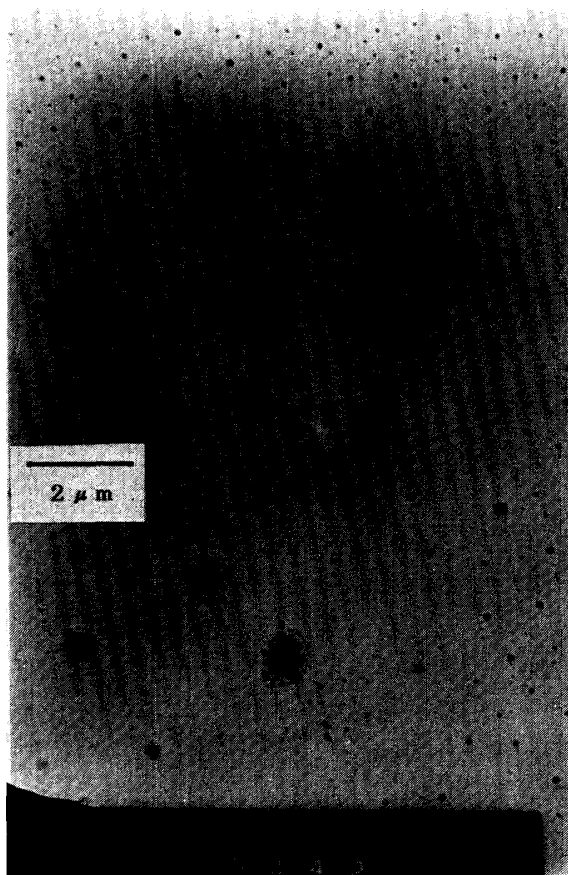


Fig. 1. Electron micrograph showing the particles collected on carbon deposited screen of electron microscope at 18.1–18.8 km, on January 31, 1990 at Kiruna (68°N, 21°E), Sweden.

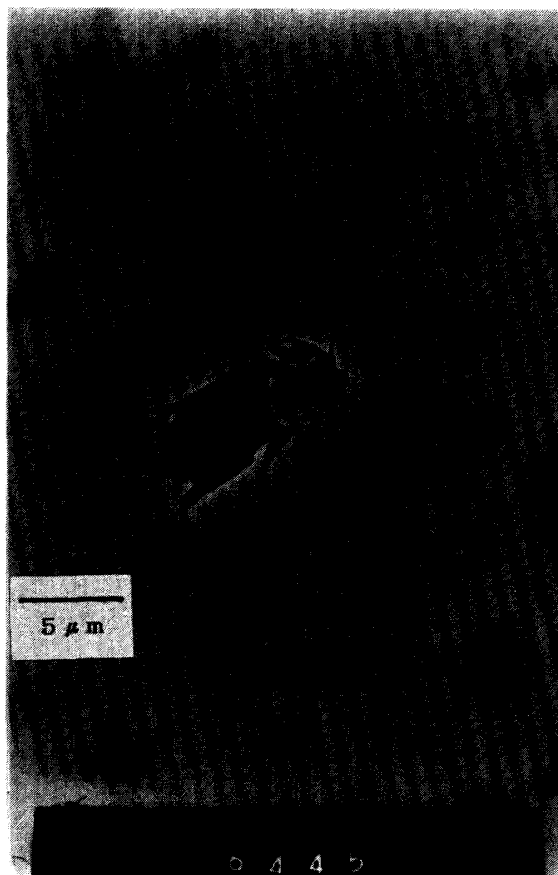


Fig. 2. Same as Fig. 1 but for 18.8–19.6 km. The particle in the center of the figure has needle-like crystals formed reaction between nitron film and nitrate containing particulate matter.

4 shows an electron micrograph of particle collected on nitron thin film at a height of 20.2–21.0 km. In this case, all particles have a needle-like structure which forms through reaction between nitron and nitrate.

Although few previous reports have described the existence of particles containing nitrate in the Arctic stratosphere, recent individual particle measurements clearly suggested that the nitric acid particles were formed in the winter Arctic stratosphere.

3. Discussion

Electron microscope observations of collected particles suggested the formation of nitrate particles in the winter Arctic stratosphere. From the morphology of needle-like crystals surrounding the particles collected on nitron thin film, these particles possibly contain nitric acid. In the cold winter polar stratosphere, an extremely enhanced aerosol layer (Polar Stratospheric Clouds; PSCs) was frequently observed (*e. g.*, McCORMICK *et al.*, 1982; IWASAKA *et al.*, 1985). From thermodynamic studies these particles were suggested to be ice crystals (type-II PSCs particles) and nitric

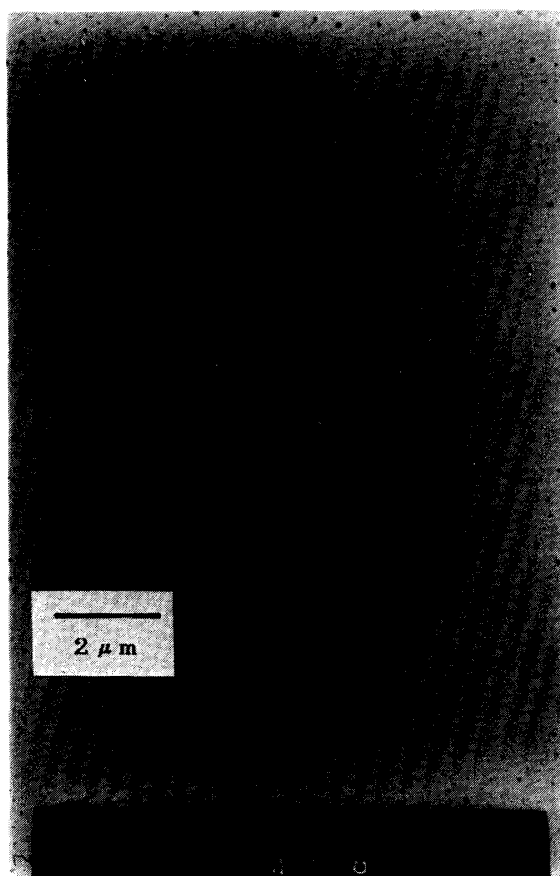


Fig. 3. Same as Fig. 1 but for 19.6–20.2 km. Particles show very similar morphology to the particles in Fig. 1.

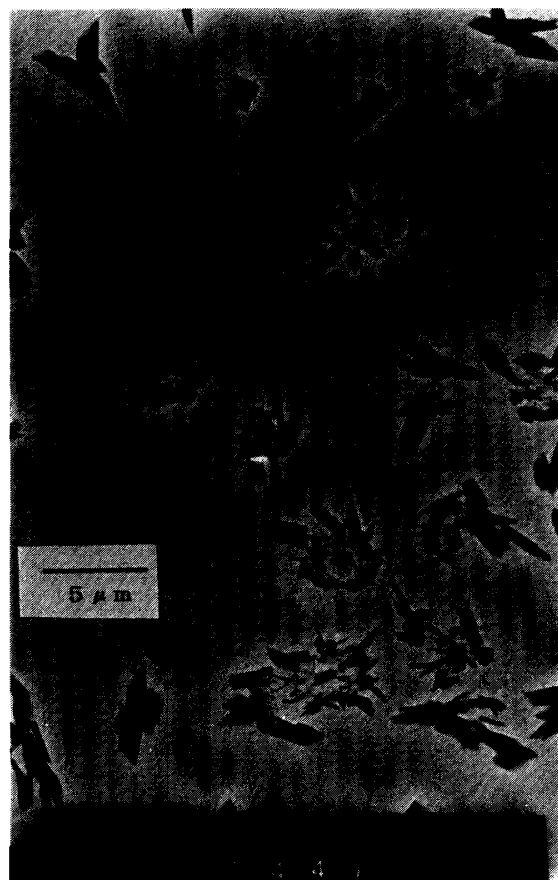


Fig. 4. Same as Fig. 1 but for 20.2–21.0 km. All particles in this figure have needle-like crystals.

caid trihydrate crystals (NAT; type-I PSCs particles) (*e. g.*, HANSEN and MAUERSBERGER, 1988).

In Table 1 we summarize the molecular state of particles collected at 15.5–24.4 km during the measurements of January 31, 1990. Sulfate particles were dominant below 20.2 km; this layer certainly corresponded to the stratospheric aerosol layer which is mainly composed of background sulfate particles. NAT particles were detected above this sulfate layer. Some investigators suggested that the preexisting sulfate particles acted as nuclei for PSCs particles (*e. g.*, FAHEY *et al.*, 1989; ROSEN *et al.*, 1988). The clear separation of the sulfate particle layer and NAT particle layer suggests that nuclei of NAT particle are not always typical sulfate particles. HOFMANN *et al.* (1989) reported large increase in $r \geq 0.20 \mu\text{m}$ particles, reaching a concentration of more than 50% of the concentration of condensation nuclei in the cold layer at 19–22 km. Condensation nuclei above the background sulfate layer can act as nuclei of NAT particles.

Lidar measurements have suggested that the upper aerosol layer is frequently enhanced in the early polar winter; the enhancement expanded to the lower aerosol layer in mid-winter (IWASAKA, 1986). This tendency was suggested to be the result of downward motion of a cold region which appears at about 25 km in early winter.

Table 1. Molecular state of particulate matter (January 31, 1990: Kiruna, Sweden).

Hight (km)	Type of film ^{a)}	SO ₄ ²⁻	NO ₃ ⁻	Fine particle	Comment
13.2-13.7	C	⊙		×	Sulfuric acid droplets are major constituents.
13.7-14.2	N		×		
14.2-14.8	C	⊙		×	Sulfuric acid droplets are major constituents.
14.8-15.5	N		×		
15.5-16.1	C	⊙		×	Sulfuric acid droplets are major constituents.
16.1-16.7	N		×		
16.7-17.4	C	⊙		○	Partially neutralized particles are major constituents.
17.4-18.1	N		×		
18.1-18.8	C	⊙ ^{b)}		○	Partially neutralized particles are major constituents.
18.8-19.6	N		△ ^{c)}		Nitrate particles are externally mixed.
19.6-20.2	C	⊙ ^{d)}		○	Partially neutralized particles are major constituents.
20.2-21.0	N		⊙ ^{e)}		
21.0-21.6	C	○ ^{f)}		○	Partially neutralized particles are major constituents.
21.6-22.2	N		⊙		
22.2-22.9	C	○ ^{f)}		⊙	Fine particles are major constituents.
22.9-23.6	N		⊙		
23.6-24.4	C	○ ^{f)}		⊙	Fine particles are major constituents.
24.4-25.0	N		⊙		
25.0-25.5	C			⊙ ^{f)}	
25.5-26.1	N		×		
26.1-26.6	C			⊙	
26.6-27.0	N		△		Soil-like particles are found.
27.0-27.5	C			⊙	
27.5-28.0	N		×		
28.0-28.5	C			⊙	
28.5-28.8	N		×		
28.8-29.2	C			⊙	
29.2-29.4	N		×		
29.4-29.6	C			⊙	
29.4-29.6	N		×		
29.6-29.8	C			⊙	

⊙: Most particles are this type. ○: Some particles are this type. △: External mixing situation is suggested. ×: This type particle cannot be identified.

^{a)}: C and N mean carbon film and nitrate film used to collect particles, respectively. ^{b)}: See Fig. 1. ^{c)}: See Fig. 2. ^{d)}: See Fig. 3. ^{e)}: See Fig. 4. ^{f)}: Size of particles identified as sulfate particle is apparently smaller than the size of sulfate particles collected in the range of 13.2-20.2 km.

However, the importance of nitric acid vapor profile was not discussed. Figure 5 schematically shows the relation among atmospheric temperature, frost point of water vapor, and frost point of mixture HNO₃·H₂O.

When we assume mixing ratios of 3 ppmv water vapor and 10 ppbv nitric acid vapor (or 5 ppbv nitric acid vapor) in the lower stratosphere, NAT particles are expected to form in the region from 18 km to 24.5 km (Fig. 6). The nitrate particle

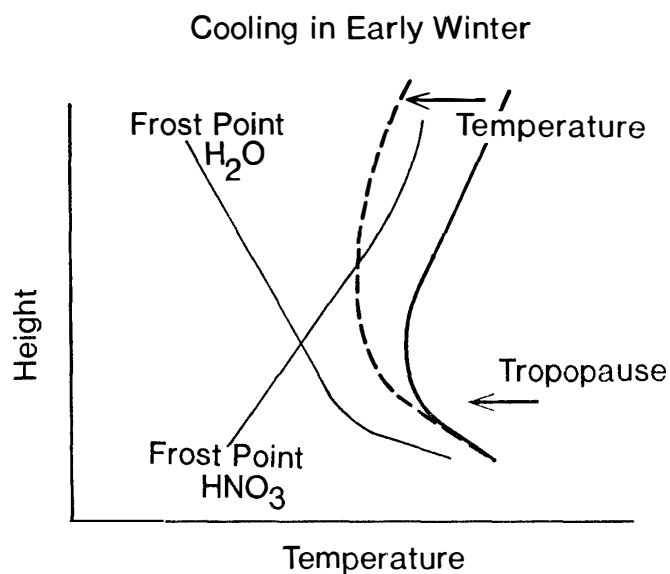


Fig. 5. Schematic figure showing relation among temperature of early winter, frost point temperature of water vapor, and frost point of nitric acid vapor on NAT surface on assumption of usual vertical profiles of water vapor and nitric acid vapor distribution.

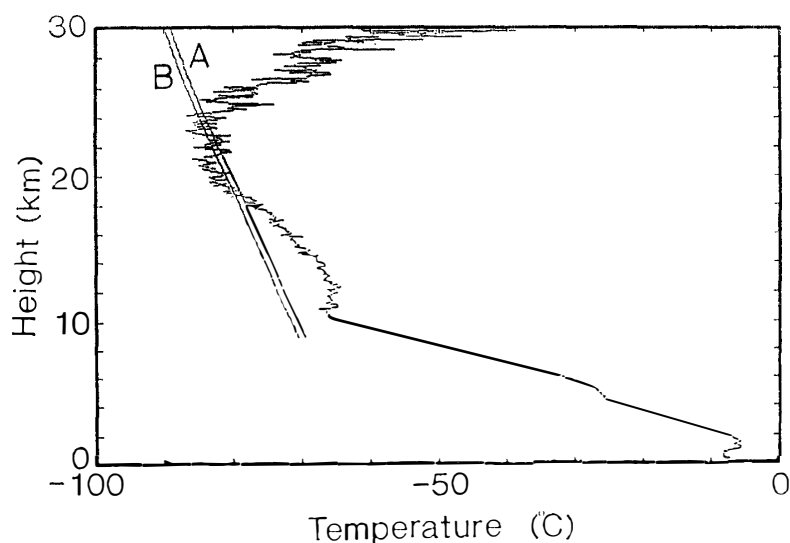


Fig. 6. Temperature distribution measured on January 31, 1991 at Kiruna ($68^\circ N$, $21^\circ E$), Sweden and saturation point temperature of nitric acid trihydrate particles estimated for 3 ppmv water vapor and 10 ppbv nitric acid vapor mixing ratio (curve A), and for 3 ppmv water vapor and 5 ppbv nitric acid vapor mixing ratio (curve B).

distribution in Table 1 shows good correspondence with the region where NAT particles are expected to form. Therefore it is reasonable to conclude that the particles shown in Fig. 2 are possibly type-I PSCs particles, and that this good correspondence suggests that the concentrations of water and nitric acid vapors were about 3 ppmv and 5–10 ppbv at 20–25 km during this period.

The external mixing of NAT particles in sulfate particles shown in Fig. 2 is very interesting in light of NAT particle behavior in the winter stratosphere. The following

three explanations are possible,

- (1) NAT particles formed in the region of 18.8–19.6 km,
- (2) A very thin NAT particle layer, thickness was smaller than the vertical resolution of particle sampling, 700 m, existed between 18.8 and 19.9 km, and
- (3) The NAT particle in Fig. 2 was the particle descending from the active NAT particle forming region.

If we assume NAT particle formation in the region of 18.8–19.6 km, we must face the fact that only few sulfate particles in this region can act as nuclei for NAT particles.

HOFMANN *et al.* (1989) observed that a cloud layer composed of PSCs had many tenuous layers. However, present situation was apparently different from their observations since their measurements did not show that tenuous layers of PSCs were in the sulfate particle layer. Therefore it is impossible to use their results to support assumption (2).

Of those three assumptions, process (3) seems to be the most probable one since NAT particles can grow to several μm through condensation of nitric acid vapor, and coagulation of these NAT particles, in addition to this, can produce larger particles. Such size particle can easily descend from the NAT particle forming region to the sulfate particle layer.

No nitrate particles were observed during the balloon measurements on January 18, 1990, although the temperature distribution on January 18 was very similar to that on January 31. Most particles collected on January 18 were sulfuric acid particles and sulfate particles (possibly ammonium sulfate or partially neutralized sulfate particles). This difference suggests the importance of studies on overall evolution of PSCs event. After the atmosphere is fully denitrified through PSCs activity, it is impossible to detect NAT particles even if the atmosphere is very cold, since the atmosphere has no nitric acid vapor. The time lag between starting the time of cooling and that of NAT formation is also an important factor. Too early particle collection cannot detect NAT particles.

4. Conclusions

Nitrate particles (possibly nitric acid particles) were detected in the winter Arctic stratosphere from electron microscopic measurements of individual particles. This type particle is expected to exist in a little higher region than usual background aerosol layer, from temperature measured during the observation period. Most nitrate particles were detected above the sulfate aerosol layer. A high aerosol layer is frequently observed in early winter at Syowa Station. This may be due to formation of nitrate particles above the sulfate aerosol layer.

The external mixing of nitrate particles in the background sulfate particle layer suggests a possibility of NAT particle descent.

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