Proc. NIPR Symp. Polar Meteorol. Glaciol., 1, 24–30, 1987

COMMENT ON AEROSOL EFFECT ON ANTARCTIC OZONE

Yasunobu IWASAKA[1] and Guang-Yu SHI[2]

[1]*Water Research Institue, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464*
[2]*Atmospheric Environmental Research, Inc., Cambridge, MA 02139, U.S.A.*

Abstract: The structure of the aerosol layer disturbed by a cold air was suggested from the lidar measurements at Syowa Station (69°00′S, 39°35′E). The particle layer containing sublayers of spherical or nonspherical aerosols was frequently observed in Antarctic spring. It is a point one sholud not ignore when he discusses aerosol effects on "Antarctic ozone depletion" through radiative processes and heterogeneous chemical reactions.

1. Introduction

Lidar measurements at Syowa Station (69°00′S, 39°35′E) suggested a noticeable enhancement of aerosols in the winter stratosphere (IWASAKA, 1985; IWASAKA *et al.*, 1985). The rapid grwoth of ice crystals under the cold stratosphere was suggested by STEELE *et al.* (1983). Large depolarization ratio measured at Syowa Station suggested that nonspherical particles were formed in the winter stratosphere (IWASAKA, 1986a). A production of many hydrates from diluted sulfuric acid acts as a possible site where water vapor molecules can nucleate (IWASAKA, 1986b).

SOLOMON *et al.* (1986) and MCELROY *et al.* (1986) emphasized the importance of heterogeneous reactions including Antarctic stratospheric aerosols to explain Antarctic ozone depletion in spring, since such a large ozone depletion as pointed by many investigates (*e.g.*, FARMAN *et al.*, 1985) cannot be explained only by homogeneous chemical reactions. HATAKEYAMA and LEU (1986) and FRIEDL *et al.* (1986) suggested that the heterogeneous reactions presented by SOLOMON *et al.* (1986) and MCELROY *et al.* (1986) were the adsorption reactions of the Langmuir type.

Rate of chemical reactions on particle surface is expected to depend on the surface area, chemical composition, structure of surface, spot of surface, and spatial distribution of particles. At present the information on these features is limited.

Some investigators pointed out that the dynamical air motion driven by solar radiation absorption by aerosols was important for the formation of "ozone hole" (TUNG, 1986; PYLE, 1986). The detailed calculation on the radiative balance suggested that the heating rate was too small to make effective upwelling motion (SHI *et al.*, 1986). However, the estimation was based on an incomplete data set; the aerosol number concentration, particle size, and some other parameters were assumed from the atmospheric turbidity measured at the ground.

In this short paper we comment on the correspondence of aerosol transformation to temperature, and the formation of a multilayer structure in the aerosol layer due to the transformation, which appeared frequently in spring.

2. Temperature Profiles and Appearance of Nonspherical Particles

Large depolarization ratio of the aerosol layer was measured at Syowa Station in winter (IWASAKA, 1985). According to STEELE *et al.* (1983), active ice particle formation was expected in the Antarctic winter stratosphere. IWASAKA (1986b) pointed out that hydrates formed from dilute sulfuric acid droplets could act as a nucleation site for water vapor under the cold atmospheric conditions.

CRUTZEN and ARNOLD (1986) suggested the possibly that HNO_3 vapor, in addition to H_2O, condenses on the pre-existing particles in the winter Antarctic stratosphere. If so, as pointed out by them, the condensation of HNO_3 vapor can cause a rise of the temperature at which the winter enhancement of aerosols starts.

IWASAKA and KONDOH (1987) suggested that the region having a large loss rate of ozone was near the height of 150 mb in September and October at Syowa Station. In their measurements it is worth to notice the following:

1) The large ozone-loss region was corresponding to the cold region in the stratosphere.

2) The height of the loss region seems to decrease during the period from late winter to spring.

According to Iwasaka (1986b) the descending motion of the center of the aerosol layer also was corresponding to the movement of the cold region. From these results, it would be surmised that the knowledge about the vertical changes in aerosol content and their temporal changes in useful to resolve the "ozone hole" problem.

Figure 1 shows typical temperature distribution of each season at Syowa Station. The most striking point is that the temperature decrease starts in the upper region of

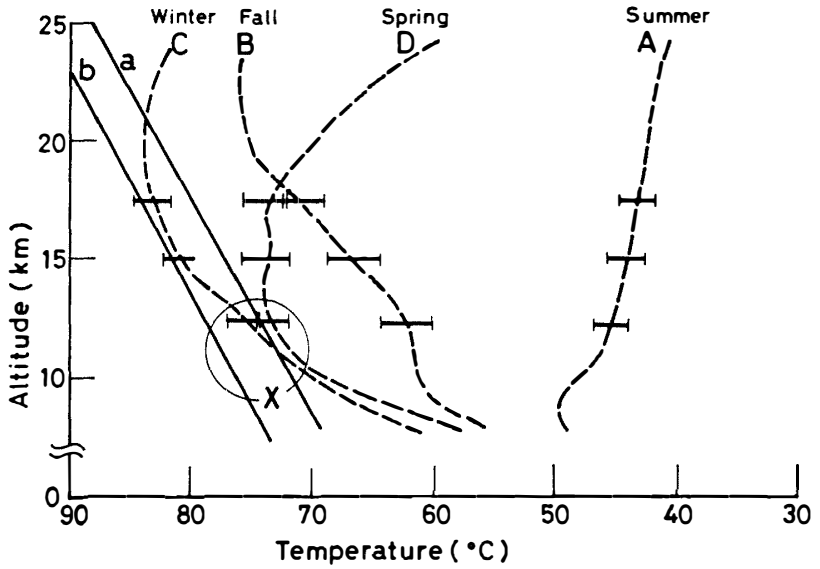

Fig. 1. Seasonal changes in temperature profiles measured at Syowa Station (69°00′S, 39°35′E). Curves A, B, C and D are the atmospheric temperatures which are half-monthly averaged; A: February 1–15 (summer), B: May 16–31 (fall), C: July 1–15 (winter), D: September 16–30 (spring). Frost point temperature for water vapor=5 ppmv (curve a) and 10 ppmv (b) are compared.

the aerosol layer from fall to winter, and the warming starts also in the upper aerosol region from winter to spring. As the result, cold area (see circle X in Fig. 1) remains in the lower region until spring.

According to the Clausius-Clapeyron equation the frost point temperature of water vapor, T_f is given by

$$T_f = T_0/[1-[kT_0/(L_v m)] \ln (P/P_0)\,, \tag{1}$$

where P_0 is the known saturation vapor pressure at temperature T_0, L_v the latent heat of vaporization, m the mass of water vapor, k Boltzmann's constant.

The frost point temperature for water vapor mixing ratios of 5 and 10 ppmv are estimated (Fig. 1). At present there are no information on the water vapor content in the Antarctic stratosphere. If we assume that the water vapor content of the Antarctic stratosphere is comparable with the measurements obtained in mid and low latitudes, the content may be in the range from 2 to 7 ppmv. However, the air having large humidity, although its physical processes are not clear, is frequently observed on the tropopause (*e.g.*, ELLSAESSER, 1983). Considering this point, the temperature distribution in spring can produce ice crystal particles.

3. Aerosols and Ozone

3.1. Aerosol surface

Many investigators pointed out the importance of heterogeneous reactions including stratospheric aerosols for the Antarctic ozone depletion (*e.g.*, SOLOMON *et al.*, 1986). If so, the area of particle surface is an important parameter to assess the loss rate of ozone. As described by IWASAKA (1986b), there are many ice crystals in the stratosphere during the main phase of the winter enhancement. The shape of ice crystals at low atmospheric temperature was observed by many investigators (*e.g.*, (THUMAN and ROBINSON, 1954; OHTAKE, 1970).

KOBAYASHI (1965) made intensive laboratory experiments on the growth of ice crystals at low temperature. From the observations and experiments, it seems likely that the "droxtals" and faceted crystals found in the field present a low-temperature quasi-stable state. In view of KOBAYASHI's experiments on the shape of ice crystals, it might be expected, as suggested by HOBBS (1974), that stratospheric ice particles, which are just a few μm in diameter, will develop pyramidal faces. Apparently the surface of such a particle is larger than that of the spherical particle even if those two particles have the same volume and mass (order of 10).

However, this discussion is speculative since we have no definite observations on the shape of the Antarctic stratospheric particles expect for the depolarization ratio obtained by lidar measurements.

3.2. Radiative energy transfer

The annual increase in heating rate of the Antarctic stratosphere was speculated by some investigators since recent active volcanism could cause the increase in particulate matter in the polar region and the volcanic particles absorb solar radiation (*e.g.*, TUNG, 1986). If the heating rate is sufficiently large, a diabatic upwelling motion

in the Antarctic stratosphere may cause ozone depletion in spring. In order to clarify the effect, vertical profile of aerosol concentration, size distribution, and chemical composition of particles are needed. As described by SHI *et al.* (1986), information about those parameters is limited. In addition to the previous estimations, temperature distributions were assumed without paying attention to the correspondence of temperature with aerosol content and shape.

Lidar measurements at Syowa Station suggest that there is a complex structure in the aerosol layer from late winter to early spring. In Fig. 2, we compare the aerosol scattering ratio (particle mixing ratio=scattering ratio −1) and depolarization ratio measured on 5 October 1985. The vertical profile of scattering ratio gives the aerosol layer and existence of nonspherical particles produces a large depolarization ratio. If we assume that the region with a large depolarization ratio is composed of ice crystals, it is natural to speculate that the aerosol layer is composed of sublayers of sulfuric acid droplets and ice crystals.

From the temperature distribution in spring shown in Fig. 1, we can assume that one possible interpretation for the inhomogeneity of the depolarization ratio in the

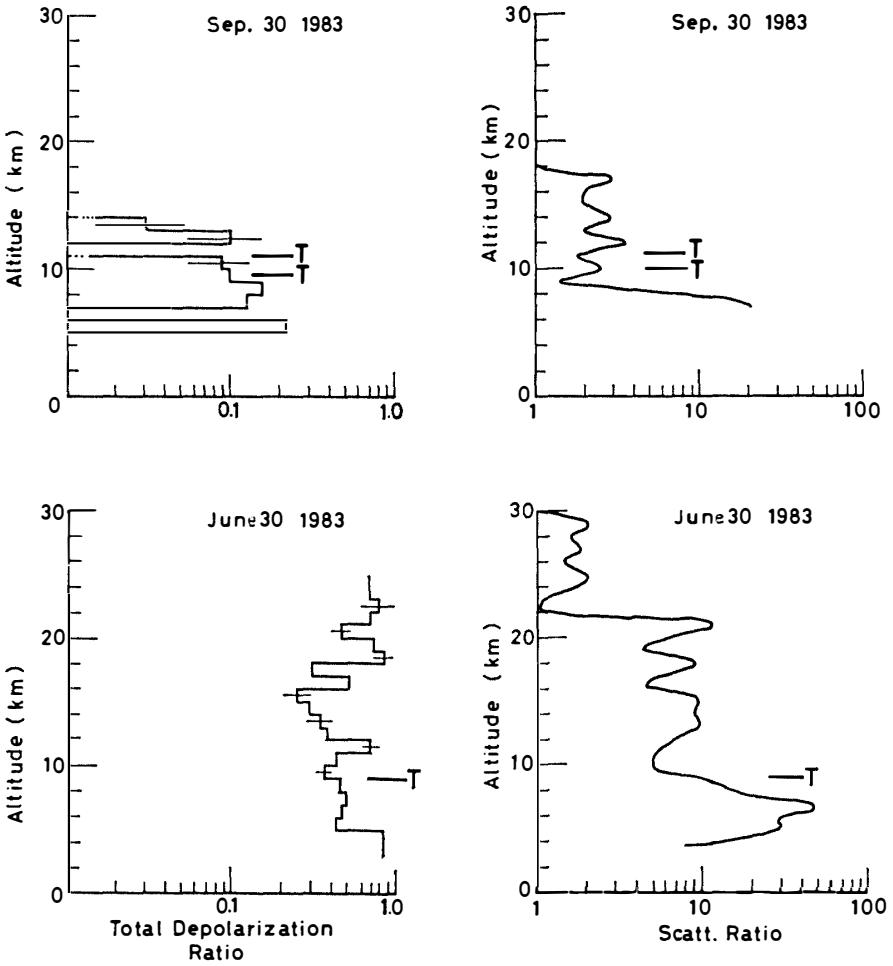

Fig. 2. Fine structure in the aerosol layer. The depolarization ratio measured in spring shows inhomogeneity of chemical composition of aerosols. Layer "a" contains a lot of nonspherical particles, but layer "b" spherical ones.

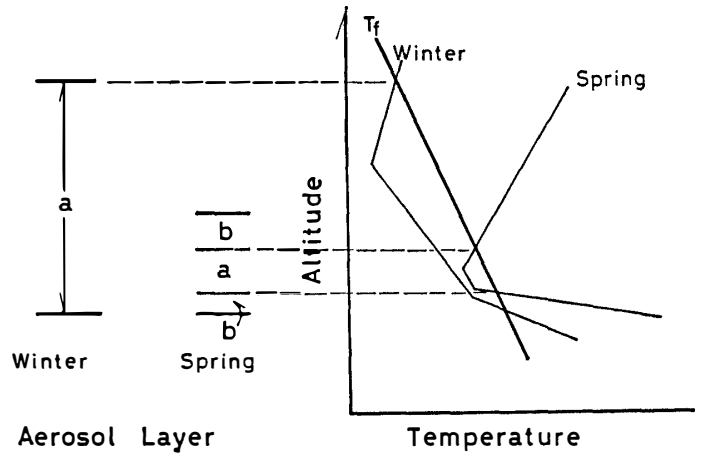

Fig. 3. Schematic picture showing multilayer structure of the spring aerosol layer. Temperature distribution (left) and layer structure (right) are compared. In winter the aerosol layer contains nonspherical particles (possibly ice crystals), but the spring aerosol layer has multiple layer structure of spherical (possibly sulfuric acid droplet) and nonspherical particle (ice crystal). As discussed in text, the cold region remains on the tropopause during the period when the stratosphere is warmed up by solar radiation. This can produce the crystal particle region (region "a") in the lower aerosol layer in early spring when the temperature is lower than the frost point of particle matter. If we assume the frost point of water, the condition shown in the figure is frequently observed (IWASAKA, 1986b). Region "b" shows the layer containing sulfuric acid droplets.

aerosol layer is the temperature distribution having a cold region above the tropopause. In Fig. 3, we show a representative temperature distribution of spring. In spring the relatively cold air remains on the local tropopause. If we assume the existence of the air with a relatively high humidity (about 10 ppmv) on the tropopause, the frost point temperature can be below the atmospheric temperature on the tropopause. This aera possibly shows an extremely large depolarization ratio.

Region "a" in Fig. 3 shows a large depolarization area in the aerosol layer. As shown in the schematic figure, the spring aerosol layer can contain a sublayer of ice crystal particles on the tropopause. In midwinter, the cold area expands and all of aerosols are composed of ice crystals (or HNO_3-H_2O crystals).

It may be necessary to take an inhomogeneity of optical constants in the aerosol layer into consideration for discussing the radiative effect of particles. In these previous investigations, the model of aerosol is extremely simplified and the relation between aerosol and temperature is not treated on a realistic basis.

3.3. Other possible processes forming particles in the winter stratosphere

Some investigators pointed out the importance of the condensation of HNO_3 and HCl gases for particle growth in the winter stratosphere (*e.g.*, CRUTZEN and ARNOLD, 1986). IWASAKA (1986a, b) pointed out that the increase in particulate matter content did not accompany increase in depolarization ratio during an early phase of the winter enhancement. If the winter enhancement is due to only transformation of pre-existing sulfuric acid droplets to ice crystals. It is expected that the rapid increase in particle content corresponds to the increase in depolarization ratio

(STEELE *et al.*, 1983). At present we are not informed of any data relating to the partial vapor pressures or freezing points of mixtures of water, NHO_3, HCl, and sulfuric acid. Thus it is impossible to give a definite conclusion about it, but it is worth to consider that at temperatures below 200 K, HNO_3 and HCl can condense on the sulfuric acid droplet.

In addition to the pre-existing models, new particle formation may contribute to the winter enhancement. According to the particle growth hypotheses, it is expected that the size of all particles becomes larger and the value of $N(r \geq 15)/N(r \geq 25)$, where $N(r \geq 15)$ and $N(r \geq 25)$ are number density of particles with the radius larger than 0.15 and 0.25 μm respectively, decreases rapidly during the enhancement. The aerosol sonde measurements gave evidence that the ratio was $\sim 5 - \sim 15$ in winters of 1983 and 1985 at Syowa Station (MORITA *et al.*, 1985; IWASAKA, 1986b). IWASAKA speculated the new particle formation in winter from this measurements (1986b).

4. Conclusion

In order to assess the aerosol effect on the ozone depletion in Antarctic spring, one should consider that the stratospheric temperature influences the vertical distribution of aerosol concentration, chemical composition of particles, aerosol shape, and area of aerosol surface. Therefore, it is essential to study the relationship between temperature and these parameters in order to solve the "Antarctic ozone" problem. In addition, it is necessary to know the concentration of HNO_3 and HCl and the thermodynamical parameters of mixture of HNO_3, HCl, H_2SO_4 and water to clarify the effect of HNO_3 and HCl gases on the winter aerosol enhancement.

References

CRUTZEN, P. J. and ARNOLD, F. (1986): Nitric acid cloud formation in the cold Antarctic stratosphere; A major cause for the springtime "ozone hole". Nature, **324**, 651–655.

ELLSAESSER, H. W. (1983): Stratospheric water vapor. J. Geophys. Res., **88**, 3897–3906.

FARMAN, J. C., GARDINER B. G. and SHANKLIN, J. D. (1985): Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction. Nature, **315**, 207–210.

FRIEDL, R. R., GOBLE, J. H. and SANDER, S. P. (1986): A kinetics study of the homogeneous and heterogeneous components of $HCl + ClONO_2$ reaction. Geophys. Res. Lett., **13**, 1351–1354.

HATAKEYAMA, S. and LEU, M.-T. (1986): Reactions of chlorine nitrate with HCl and H_2O. Geophys. Res. Lett., **13**, 1343–1346.

HOBBS, P. (1974): Ice Physics. Oxford, Clarendon Press, 837 p.

IWASAKA, Y. (1985): Lidar measurement of the stratospheric aerosol layer at Syowa Station (69°00'S, 39°35'E), Antarctica. J. Meteorol. Soc. Jpn., **63**, 283–287.

IWASAKA, Y. (1986a): Large depolarization ratio of the winter Antarctic stratospheric aerosol layer; Lidar measurement at Syowa Station (69°00'S, 39°35'E), Antarctica. J. Meteorol. Soc. Jpn., **64**, 303–309.

IWASAKA, Y. (1986b): Non-spherical particles in the antarctic polar stratosphere—increase in particulate content and stratospheric water vapor budget. Tellus, Ser. B, **38**, 364–374.

IWASAKA, Y. and KONDOH, K. (1987): Depletion of Antarctic ozone; Height of ozone loss region and its temporal changes. Geophys. Res. Lett., **14**, 87–90.

IWASAKA, Y., HIRASAWA, T. and FUKUNISH, H. (1985): Lidar measurement on the Antarctic stratospheric aerosol layer; [I] Winter enhancement. J. Geomagn. Geoelectr., **37**, 1087–1095.

KOBAYASHI, T. (1965): Vapour growth of ice crystal between −40 and −90°C. J. Meteorol. Soc.

Jpn., **43**, 359–367.
McELROY, M. B., SALAWITCH, R. J., WOFSY, S. C. and LOGAN, J. A. (1986): Reductions of Antarctic ozone due to synergistic interactions of chlorine and bromine. Nature, **321**, 759–762.
MORITA, Y., TAKAGI, M., IWASAKA, Y. and ONO, A. (1985): Balloon measurements of aerosol in the Antarctic stratosphere. Handb. MAP, **18**, 482–485.
OHTAKE, T. (1970): Unusual crystal in ice fog. J. Atmos. Sci., **21**, 509–511.
PYLE, J. A. (1986): Large ozone losses in Antarctica; The role of heating perturbations. Geophys. Res. Lett., **13**, 1320–1322.
SHI, G.-Y., WANG, W.-C., KO, M. K. W. and TANAKA, M. (1986): Radiative heating due to stratospheric aerosols over Antarctica. Geophys. Res. Lett., **13**, 1335–1338.
SOLOMON, S., GARCIA, R.R., ROWLAND, F. S. and WUEBBLES, D. J. (1986): On the depletion of Antarctic ozone. Nature, **321**, 755–758.
STEELE, H. M., HAMILL, P., MCCORMICK, M. P. and SWISSLER, T. J. (1983): The formation of polar stratospheric clouds. J. Atmos. Sci., **40**, 2055–2067.
THUMAN, W. C. and ROBINSON, E. (1954): Studies of Alaskan ice-fog particles. J. Meteorol., **11**, 151–156.
TUNG, K. K. (1986): On the relatioinship between the thermal structure of the stratosphere and the seasonal distribution of ozone. Geophys. Res. Lett., **13**, 1308–1311.

(Received February 10, 1987; Revised manuscript received May 18, 1987)