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In-situ Observations of an Antarctic Polar Stratospheric Cloud: Similarities with Arctic Observations

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Abstract. Measured particle volumes in a type I polar stratospheric cloud near the Antarctic polar vortex during ASHOE/MAESA show that the onset of the cloud occurred near 193 K, 3 degrees colder than nitric acid trihydrate (NAT) saturation. The onset temperature, the smooth increase of volume with decreasing temperature, the inverse correlation of particle volume and enhanced NO_y (HNO_3 in the particles) with temperature, and comparisons of observations with an equilibrium model of ternary droplet growth all support the notion that much of this type I PSC was ternary solution droplets. This provides confirmation of previous findings in the northern hemisphere. However, the ternary model does not fit the observations in all regions. This may be due to the presence of some solid phase growth in agreement with impactor observations.

Introduction

Since the realization that polar stratospheric clouds play an important role in the loss of polar ozone many papers have been written on PSC type I formation processes, but important questions remain. Observations in the Antarctic by *Fahey et al.*, [1989] showed that the particles did contain nitric acid and that the increases in particle volume and instrumentally enhanced NO_y indicating entry into the PSC occurred near 195 K, the temperature for saturation of HNO_3 over NAT. [*Hanson and Mauersberger*, 1988]. Thus they were broadly consistent with a NAT composition. However, Arctic observations by *Dye et al*, [1992], showed type I PSCs with onset temperatures of 192 to 193 K, several degrees colder than NAT saturation. They also observed growth of the sulfate aerosol outside of the cloud as temperature decreased, showing that most of the sul-

fate aerosols were not frozen, but were remaining liquid down past PSC formation temperatures.

Afterwards, laboratory work by [*Zhang et al*, 1993] showed large uptake of HNO_3 in $H_2SO_4/H_2O/HNO_3$ ternary solutions and modeling work by *Carslaw et al*, [1994], *Drdla et al*, [1994]; and *Tabazadeh et al*, [1994] showed that the ternary model fit the January 24 observations of *Dye et al*. much better than NAT. Recent laboratory results also show that ternary solutions do not readily freeze. [*Koop et al*, 1995; *Fox et al*, 1995].

A question then arises as to the cause of the different behaviors in the two hemispheres. *Dye et al*. suggested that in the late winter Antarctic vortex when the *Fahey et al*. observations were made, perhaps the sulfate particles were all frozen thus acting as nuclei for NAT formation. Flights from Christchurch, New Zealand during the Airborne Southern Hemisphere Ozone Experiment/Measurements for Assessing the Effects of Stratospheric Aircraft (ASHOE/MAESA) project gave an opportunity to address this question. In this paper we present the results from one flight of the NASA ER-2 into a PSC near the Antarctic polar vortex.

A New Instrument

The Multiangle Aerosol Spectrometer Probe (MASP), developed for the NASA High Speed Research Program, was flown for the first time on the ER-2 during ASHOE/MAESA. Like the FSSP 300 used in the Arctic ER-2 studies, the MASP counts and sizes individual particles in the size range of 0.4 to 10 μm diameter by measuring light scattered by individual particles. Sizing is based on Mie scattering for spheres of the appropriate index of refraction. The particle index of refraction also can be estimated over a size range of 0.4 to 0.7 μm by measuring the ratio of light scattered in the forward and backward directions [*Baumgardner et al.*, 1994]. Isokinetic flow is maintained in the sample inlet to eliminate volatilization of the particles. Herein we integrate the measured size distribution to determine particle volume. The index of refraction of supercooled stratospheric sulfate aerosols at normal stratospheric temperatures (220K) is thought to be 1.44. At temperatures below ~195 K the liquid aerosols take on water and nitric acid and the index of refraction decreases. In this paper we have used 1.40 as an approximate average over the temperature range seen during the PSC

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event. This smaller index of refraction gives 10-30 % larger volumes than for 1.44.

PSC Observations of July 28, 1994

Measurements from the MASP for the flight from Christchurch, New Zealand (43 S) to 68 S and return are shown in Figure 1 with ambient and NAT saturation temperatures superimposed. Because water vapor was not measured on this flight, a value of 4.9 ppmv of H_2O was used for NAT saturation in Figures 1 and 2, based on a fit of H_2O versus N_2O from later flights. HNO_3 was assumed to be 90% of NO_y^* (see below) giving 6.5 to 7.5 ppmv of HNO_3 near the PSC. At 2230 GMT (59S) near the vortex there is an air mass change (bold vertical bars in Figure 1) noted by a drop in particle volume and also N_2O (not shown). After the turn for the return leg at 2400 GMT, the temperature trace from 0005 to ~0035 reflects a descent from 20 to 15 km and reascent to 19.4 km, referred to as a dip. Temperature measurements from the Meteorological Measurement System on the ER-2 are thought to have an accuracy of about 0.3 K. [Gaines et al., 1992].

After the airmass change near 2230 GMT, the measured particle volume gradually increased as temperature decreased to a temperature of ~193K. Near 2330 both particle volume and NO_y-NO_y^* show large increases (Figure 2) indicative of entry into the PSC. Anisokinetic flow into the NO_y instrument enhances particle sampling and this enhancement (NO_y-NO_y^*) gives a measure of HNO_3 in the particles. [Fahey et al., 1989, for this PSC also see L. DelNegro, Evaluating the role of NAT, NAD, and liquid H_2SO_4/HNO_3/H_2O solutions in Antarctic polar stratospheric cloud aerosol, submitted to J. Geophys. Res.]. NO_y^* is a surrogate for NO_y based on a close linear correlation of N_2O and NO_y in regions without particle enhancements or deni-
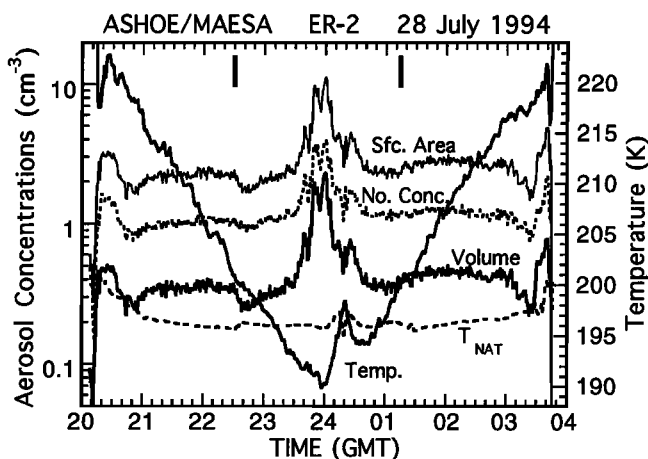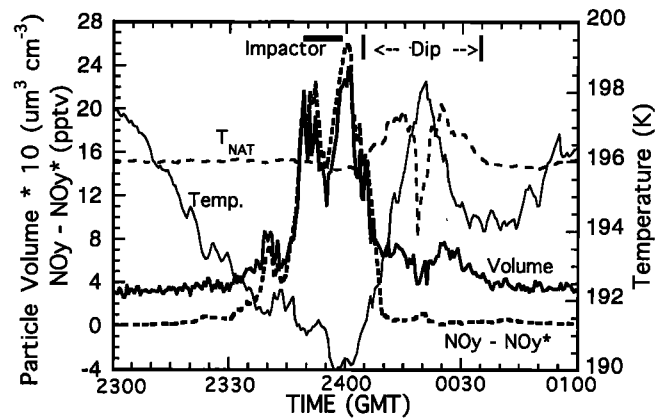

Figure 2. Measurements of particle volume, NO_y - NO_y^*, ambient temperature and NAT saturation temperature (Tnat) for a portion of the flight. The exposure of the AMES impactor is as indicated.

trification. Entry into the PSC occurs ~3 K colder than the temperature for saturation of HNO_3 over NAT and ~4 K warmer than ice saturation for 4.9 ppmv. There is an inverse correlation of particle volume and NO_y-NO_y^* with temperature before and after entry into the PSC. The similarity between volume and NO_y-NO_y^* shows that the PSC does contain substantial HNO_3. After ~0010 GMT (~ 18.5 km during the dive) NO_y - NO_y^* returns to near zero values, indicating that the ER-2 has descended below the PSC. The larger particle values from the MASP are caused by increases in sulfate burden below the 20 km cruise altitude of the ER-2, as can be seen during the ascent from and descent into Chrishchurch in Figure 1. As the ER-2 climbs back to 19km it is beyond the northern boundary of the PSC.

Ternary PSC

Particle volume and NO_y^* (reflecting the HNO_3 available for growth) are plotted in Figure 3 versus temperature for 2215 to 2405 GMT, the start of the dip. As with the January 24, 1989 Artic case reported by Dye et al., there is a relatively smooth volume increase with decreasing temperature, even during the entry into the PSC near 193 K. There are no abrupt transitions near 196 K, the saturation temperature of NAT, nor at 193 to 194 K, the temperature at which Fox et al., [1995] suggested that formation of a solid phase might begin based on their laboratory experiments. The smooth increase in volume with decreasing temperature outside and inside of the PSC and the close inverse correlation of both particle volume and enhanced NO_y with temperature (Figure 2) in the early phase of the PSC strongly suggest that in this region the particles are primarily ternary solution droplets which grow initially by water and then HNO_3/H_2O uptake.

An airmass change near 2352 can be seen in NO_y^* in Figure 3. As a result of the change in airmass and other factors as well, the volume versus temperature
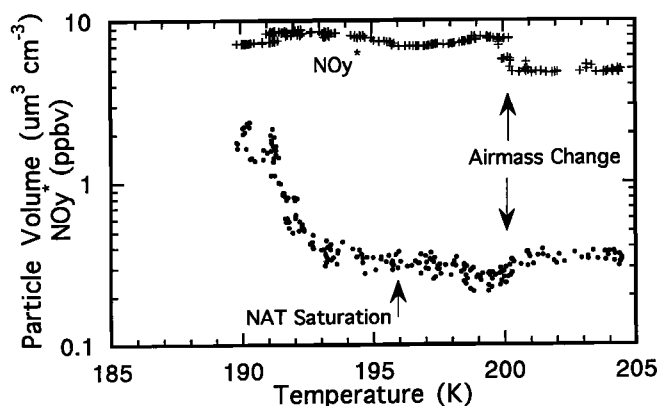

Figure 1. The concentration (cm^{-3}), surface area (μm^2 cm^{-3}) and volume (μm^3 cm^{-3}) of particles ≥ 0.4 μm from the MASP for July 28, 1994 with temperature and saturation temperature of HNO_3 over NAT.

Figure 3. Observed particle volume and NO_y^* averaged over 30 sec as a function of temperature for the southbound leg of the flight.

plot of Figure 3 is bifurcated at temperatures less than 191.5 K. After 2355 the inverse correlation of particle volume and temperature is not as clear (Figure 2). For example, the maximum in particle volume occurs near 2400, however the minimum in temperature (189.8 K) is 3 to 4 min earlier even though NO_y^* is relatively uniform. All of the points at temperatures less than 190.5 K in Figure 3 are associated with the broad maximum in volume centered on 2400 in Figures 1 and 2 and the cold temperatures between 2355 and 0005 at the very southernmost portion of the flight. Whereas most of the points between 191 and 191.5 K in Figure 3 are from the volume maximum centered on 2350 (Figure 2).

The observations are compared with growth expected for equilibrium ternary droplets and NAT in Figure 4. Calculations similar to those of *Drdla et al.*, [1994] were made for each point along the flight track, based upon measured temperature, NO_y^*, and sulfate volume measured by the Focussed Cavity Aerosol Spectrometer (FCAS) [*Jonsson et al.*, 1995]. Both the Aerosol Physical Chemistry Model (APCM) [*Tabazadeh et al.*, 1994] (Figure 4A) and the formulations of *Luo et al.*, [1995] (Figure 4B) were used for the ternary calculations. HNO_3 was assumed to be 0.9 NO_y^* and H_2O that given by the fit with N_2O. The sulfate mass used was 1.35 times that measured by the FCAS because from 2243 to 2320 in the pre-PSC background aerosol the MASP measured 1.35 times the volume of the FCAS in the 0.5 to 2.0 μm size overlap of the two instruments. Some of the increases in MASP volume in the PSC occur as a result of smaller sulfate particles growing into the size range of the MASP. This is taken into account in the model calculations. Because the FCAS draws the aerosol through an inlet into a warm cavity the highly volatile PSC particles are mostly evaporated, but the sulfate volume can be determined (see *Jonsson et al.*) and is shown in Figure 4. The FCAS values show the volume for no HNO_3/H_2O co-condensation by ternary droplets. There is uncertainty in the sulfate mass by at least as much as the factor of 1.35 difference between the

MASP and FCAS. This uncertainty will be discussed in *DelNegro et al.*, [1996].

The calculations of ternary growth fit the observations much better than those of NAT. The two ternary composition values are fairly close down to 192 K, but below 192 K the Luo formulation gives higher values than the APCM and better represents the observations, especially for the first maximum in volume (corresponding to the right fork in Figures 3 and 4) and in capturing the onset of the PSC. The difference between the two is perhaps an indication of the uncertainty in our knowledge of the ternary composition under stratospheric conditions. Both calculations capture a lot of the variation in measured volume caused by changes of HNO_3 in the airmass near 191.5 K, but the Luo values are closer to those observed. Note the drop in calculated NAT volume resulting from the change in airmass. At the coldest temperatures near 190 K (which were the furthest south and in the second major volume peak) the ternary models give volumes which are comparable to those measured, but neither match the widely forked nature of the observations very well.

The overall behavior agrees far better with ternary droplets than with NAT, but the observations at the
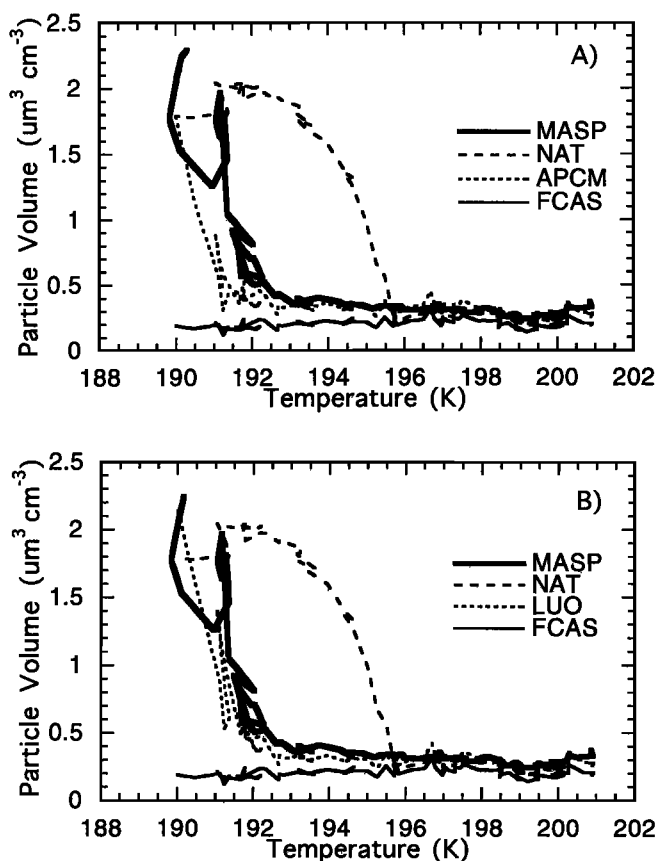

Figure 4. Comparison of 60 sec averages of observed particle volumes with volumes predicted for equilibrium growth of NAT particles and for growth of ternary solution droplets using both A) the APCM model and B) the Luo formulation. The sulfate volumes measured by the FCAS are also shown.

coldest temperatures are not entirely consistent with equilibrium ternary solution droplets and are more complicated, perhaps containing a mixture of ternary droplets and NAT or other solid phase. The Ames particle impactor which was exposed from 2349 to 2359 GMT (Figure 2) showed evidence of some solid particles and even type II PSC particles. (J. Goodman, Collection of type I and II PSC particles in the Antarctic stratosphere, unpublished manuscript, 1995) This includes parts of both major volume peaks seen by the MASP. They reported that the images of 30% of the particles >0.28 μm diameter (about 10% of the total sulfuric acid aerosol population) had irregular shapes and were thought to be solid. The remaining 70% were circular and inferred to be droplets. Ice-like particles up to 40 μm were observed in this PSC, but the numbers and volumes of the type II particles were small compared to those measured by the MASP. Thus, the impactor shows both liquid and solid particles were present over this time interval, but can not help us decipher what was happening in detail. It seems unlikely that non-equilibrium effects in the ternary growth are responsible for the complexity, because Meilinger et al., [1995] show that cooling rates >10 K per hour are needed. Backtrajectories for this day [Kawa et al., 1995] show cooling rates up to 1.4 K per hour. See DelNegro et al. for further discussion of non-equilibrium effects.

Summary

Observations in a PSC in the outer region of the Antarctic vortex show similarity with previous observations in the Arctic and the existence of PSCs composed of ternary droplets in the Antarctic, thus unifying our understanding of PSC formation processes in the two hemispheres. Although the behavior of the measured particle volumes as a function of temperature and comparison with two equilibrium ternary growth models suggest that most of this PSC was composed of ternary solution droplets, in some regions the composition is not clear and the AMES particle impactor showed solid particles were present.

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