Polar stratospheric clouds due to vapor enhancement: HALOE observations of the Antarctic vortex in 1993

M. E. Hervig¹, K. S. Carslaw², T. Peter², T. Deshler¹, L. L. Gordley³, G. Redaelli⁴, U. Biermann², and J. M. Russell III⁵

Abstract. Aerosol measurements from the Halogen Occultation Experiment (HALOE) during the Antarctic spring of 1993 are compared with calculations of the volume of different types of polar stratospheric clouds (PSCs) at equilibrium. The observed volumes increased by a factor of ~30 coincident with water vapor enhancements of ~3 ppmv, suggesting that the enhancement of water vapor was important in determining PSC growth. The enhanced water vapor was coincident with increased methane mixing ratios, and trajectory analysis suggests that the vapor enhancements were consistent with transport from lower latitudes. The nitric acid distribution was not measured and is treated either as constant or as positively correlated with the observed water. Comparing the observed volumes with model calculations assuming constant nitric acid suggests that the PSCs were composed of liquid ternary H₂SO₄-H₂O-HNO₃ aerosols (LTA) rather than solid nitric acid trihydrate (NAT). However, if the water vapor intrusions were accompanied by enhanced nitric acid, the observations closely match predictions for solid NAT, and those for LTA. These comparisons highlight the importance of the vapor distributions for modeling PSC growth and suggest that vapor resupply is important for late spring PSC growth. This work also highlights some inherent limitations of large field of view limb-viewing instruments for the observation of PSCs.

1. Introduction

Stratospheric temperatures during the polar winter and spring are often sufficiently low to allow the formation and growth of particles that can attain volumes 5–100 times greater than the background sulfuric acid–water aerosol, to form polar stratospheric clouds (PSCs). The current understanding of particles within PSCs suggests various possible compositions and phases [Koop et al., 1997]. The most likely forms are liquid ternary H₂SO₄-H₂O-HNO₃ aerosols (LTA), solid nitric acid trihydrate (NAT), and water ice. Liquid H₂SO₄-H₂O aerosols can grow by the uptake of nitric acid and water vapors at temperatures below ~196 K [Molina et al., 1993; Carslaw et al., 1994; Tabazadeh et al., 1994; Carslaw et al., 1997] to form LTA. Molina et al. [1993] have suggested that solid NAT particles nucleate from the LTA droplets when supersaturation with respect to crystallization of NAT occurs. Carslaw et al. [1994] and later Koop et al. [1995, 1997] showed that the LTA probably remain liquid to temperatures at least as low as the ice frost point. The mechanism for nucleation of NAT remains a subject of debate [e.g., Tolbert, 1996]. For cooling below the water frost point, growth as water ice becomes the dominant process, regardless of the preexisting particle phase and composition.

PSC observations in the Arctic and Antarctic are consistent with the presence of both solid and liquid particles at different times. For example, analysis of in situ particle volume measurements made in the Arctic [Dye et al., 1992] revealed that some PSCs were very likely composed of LTA droplets to the ice frost point (about 189 K) [Carslaw et al., 1994; Drdla et al., 1994; Tabazadeh et al., 1994]. Other measurements, however, have been explained in terms of hydrates of nitric acid [Dye et al., 1992; Adriani et al., 1995; Peter, 1997] or solid solutions [Tabazadeh and Toon, 1996].

In this work, aerosol and water vapor measurements from the Halogen Occultation Experiment (HALOE) (version 18) during the austral spring of 1993 are compared with the calculated volumes for LTA, solid NAT, and ice. The calculations show that significant growth of either liquid or solid particles requires not only low temperatures but also mixing ratios of H₂O and HNO₃ that are higher than generally available in the spring Antarctic vortex.

2. HALOE Measurements

The HALOE instrument uses the principle of satellite solar occultation and the instrumental techniques of gas filter radiometry and broadband radiometry to measure profiles of solar attenuation by the atmosphere’s limb as the Sun rises or sets relative to the spacecraft. Measurements in eight spectral bands (from 2.45 to 10.01 μm) are used to retrieve the profiles of HF, HCl, CH₄, NO, NO₂, H₂O, and O₃ mixing ratios, temperature, and aerosol extinction at 2.45, 3.40, 3.46, and 5.26 μm wavelengths. HALOE measurements cover two longitude sweeps each day (15 profiles each): one at the latitude of sunsets and one at the latitude of sunrises. Each HALOE sunrise (or sunset) measurement is separated by 1.6 hours and 24° longitude (which is 911 km at 70°S). HALOE sampling covers the Antarctic spring from roughly September 20 to October 20 reaching latitudes near 78°S.

The HALOE sample volume dimensions are determined by the instantaneous field of view (FOV) and the geometry of the atmospheric limb path. The vertical resolution of the measurements is ~2 km for retrievals of aerosol, NO₂, H₂O, and O₃, and ~4 km
for retrievals of HF, HCl, CH₄, and NO. The FOV length (along the limb) is determined mainly by the vertical resolution, and the width (across the limb) is determined mainly by the angle between the orbit plane and the satellite–Sun vector. The HALOE across–limb resolution (between 6 and 50 km) is close to the FOV width, and the along–limb dimension (320 km) is the limiting factor for observations of small–scale features. A complete description of the experiment is given by Russell et al. [1993a]. Of particular importance to this work are the HALOE retrievals of water vapor and aerosol extinction.

2.1 Aerosols

This work uses profiles of aerosol extinction retrieved from gas filter measurements in the 5.26 μm NO band [Hervig et al., 1995]. A validation of the aerosol measurements by Hervig et al. [1996a] reports uncertainties of the order of ±15% for measurements in the middle and lower stratosphere. Growth of aerosol particles is most easily quantified in terms of the volume density (particle volume per unit volume of air). A theoretical relationship between volume density and extinction has been calculated from Mie theory based on a large number of aerosol size distributions measured using balloon–borne optical particle counters (OPCs). Thus the volume–extinction relationship is determined independently of HALOE and is used to convert HALOE extinctions to volumes. This work uses profiles measured in sulfate aerosols over Laramie, Wyoming (41°N), covering the complete cycle of the Mount Pinatubo volcanic aerosol cloud, and profiles measured in sulfate aerosols and PSCs over McMurdo Station, Antarctica (78°S) [see, for example, Hofmann and Deshler, 1991; Deshler et al., 1994].

To determine the relationship for sulfate aerosols we have used 50 size distribution profiles measured over Laramie between August 1991 and March 1995. The balloonborne sampling did not include water vapor, and a constant 5 ppmv was assumed to compute the sulfate aerosol composition [Steele and Hamill, 1981]. The refractive index versus composition was determined according to Palmer and Williams [1975]. The results show a compact relationship between the extinctions and volumes (Figure 1) which were fit according to a power law relationship: \( V = 1678.8 \beta^{0.937} \), where \( \beta \) is the 5.26 μm extinction coefficient (km⁻¹) and \( V \) is the volume density (μm³ cm⁻³). The relationship between extinction and volume is almost linear (\( V \propto \beta^{0.937} \)), as expected for a strongly absorbing medium.

Since the size distributions and refractive indices of PSC particles are different from those of sulfate aerosumes, the volume–extinction relationship given above is expected to change for measurements in PSCs. The effect of inferring the volume in PSCs was investigated using size distributions measured in PSCs using OPCs over McMurdo Station during each Austral spring from 1990 to 1995. Using these size distributions, we assigned the refractive indices for either NAT [Toon et al., 1994] or for ternary solutions to recalculate the volume–extinction relationships. The balloonborne sampling did not include water or nitric acid vapors, and constant mixing ratios were assumed (2 ppmv H₂O and 5 ppmv HNO₃) to determine the equilibrium temperature of NAT (\( T_{NAT} \)) [Hanson and Mauersberger, 1988] and the equilibrium composition of LTA [Carslaw et al., 1995]. The calculations assuming NAT used all aerosol observations where the temperature was below \( T_{NAT} \) with the NAT refractive indices reported by Toon et al. [1994]. Thus, the relationship between 5.26 μm extinction and volume density was derived for NAT: \( V = 1570.4 \beta^{0.991} \), with units as above.

Refractive indices for ternary solutions have not yet been measured in the infrared region. To obtain them from existing indices for binary H₂O–H₂SO₄ [Palmer and Williams, 1975] and H₂O–HNO₃ [Boone et al., 1980] solutions, we have used the Lorenz–Lorenz (L–L) mixing rule, which describes the refractivity for a mixture of different components. Luo et al. [1997] have shown that this technique can be applied successfully to typical stratospheric LTA compositions for wavelengths up to 2 μm. However, the strong absorption features of the ternary H₂SO₄–H₂O–HNO₃ system in the middle infrared region determine that application of the L–L rule is not straightforward. The L–L mixing rule assumes first, that the refractivity of a mixture can be obtained directly from a linear combination of the refractivities of the individual components, and second, that the refractivity is a function of the solution density, thereby allowing extrapolation to lower temperatures in terms of changes in the density alone. These assumptions certainly apply to the real part of the refractive index, as shown by Luo et al. [1997], but the imaginary component is seldom a linear combination of the component indices due to interactions between the absorbing molecules. In addition, these molecular interactions can change with decreasing temperature, and, in stratospherically relevant acids, the absorption features are also dependent on the dissociation constants of the acids, which change with aerosol composition and temperature.

Recent Fourier transform infrared (FTIR) thin film experiments [U. Biermann, dissertation in preparation, 1997] show that for the H₂SO₄–H₂O–HNO₃ system the L–L rule can be applied at least at certain wavelengths in the middle infrared. Specifically, the L–L rule can be applied in the 6.25 to 20 μm region (the sulfate and nitrate absorption regions of the ternary mixtures) and also with good reliability at 5.26 μm. The physical basis for this finding is that the absorption features are dependent on the overall acidity of the mixture and not on the precise composition. Extrapolation of the refractive index to lower temperatures according to the change in solution density is also more difficult to apply in the middle infrared, particularly since the H₂O–H₂SO₄ absorption spectra are strongly temperature dependent. However, at 5.26 μm the
absorption is small, thus allowing a reliable extrapolation to be made. We therefore use the 5.26 μm channel for our analysis, rather than the 3.46 μm channel. The relationships for LTA were determined from data where the calculated equilibrium nitric acid content of the droplets was greater than 10 wt % (typically temperatures less than about 194 K), with the appropriate (calculated) LTA index. Thus the relationship between 5.26 μm extinction and volume density was derived for LTA: V=1940.990.9656, with units as above.

The inferred PSC volumes calculated assuming either NAT or LTA are estimated to be within ±30% of those calculated by assuming sulfate aerosol. Instead of attempting to identify the correct refractive index, in the results below, extinctions were converted to volumes using the sulfate relationship with the nominal uncertainty of ±15–20% in volume increased to ±50%, to account for additional uncertainties in the volume determination. By doing so, we do not make an a priori assumption about the phase or composition of the particles, which would bias the results. As we show below, such an approach is necessary for cases where the PSC type cannot be determined unambiguously. Test calculations using either NAT or LTA indices reveal our assumption of ±50% uncertainty to be a true upper limit.

Aerosol measurements in PSCs probably contain signal from both cloud and background aerosol existing simultaneously in the sample volume. However, extinctions add linearly and PSC attenuation is typically a factor of 30 or more greater than for background aerosol, so the total extinction is essentially due to the PSC. When both targets fill the field of view (FOV). A more important concern, however, is that the PSCs could have spatial dimensions that are smaller than the HALOE sample volume. Since the retrieved extinction (cross section per unit volume) is spatially smoothed over the FOV, degradation of the actual PSC extinction can occur when the cloud is nonuniform in the sample volume. We return to this issue later.

2.2. Water Vapor

Profiles of water vapor mixing ratio are retrieved from broadband radiometer measurements in the 6.62 μm H2O band. These measurements are contaminated by aerosol absorption and are corrected using aerosol information retrieved independently at 5.26 μm wavelength. A major concern for the water vapor measurements in PSCs is the extrapolation of extinction from 5.26 μm to the water band—pass wavelength. The aerosol correction assumes sulfate aerosol size distributions and refractive indices but does not consider PSCs [Hervig et al., 1995]. Test calculations using measured PSC size distributions and NAT refractive indices suggest that using the sulfate extrapolations in PSC contamination introduces errors of less than ±20% in the water vapor retrievals. A validation of the HALOE H2O measurements by Harries et al. [1996] reports uncertainties of ±10% in the lower stratosphere, and increased uncertainties are considered below to account for the additional errors for retrievals in PSCs.

2.3. Temperature

HALOE transmission measurements in the 2.80 μm CO2 band are used to retrieve profiles of temperature and pressure at altitudes above 35 km [Hervig et al., 1996b]. For each HALOE measurement below 35 km altitude, a temperature profile is taken from the U.K. Meteorological Office (UKMO) record by interpolating the UKMO data to the HALOE measurement location and time. Manney et al. [1996] have shown that for the southern hemisphere under cold conditions (T < 200 K), the UKMO temperatures are generally unbiased with respect to radiosonde temperature observations and that the UKMO—radiosonde RMS temperature differences are less than 2 K.

3. HALOE Observations and Meteorological Situation

The HALOE aerosol, water vapor, and CH4 measurements and the UKMO temperatures for the 1993 Antarctic spring are shown as orthographic projections on the 390 K potential temperature (Θ) surface (Plate 1). The HALOE measurement latitude progressed from 50°S on October 4 to 75°S on October 9, giving a quasi-synoptic picture of the Antarctic region (since the measurements for different locations are at different times, such maps cannot be considered as truly synoptic). Each polygon in Plate 1 represents the true orientation and length of the HALOE FOV. The data are not contoured, as is typically done, since this would artificially introduce sub-FOV-scale gradients.

Aerosol measurements in PSCs probably contain signal from both cloud and background aerosol existing simultaneously in the sample volume. However, extinctions add linearly and PSC attenuation is typically a factor of 30 or more greater than for background aerosol, so the total extinction is essentially due to the PSC alone when both targets fill the field of view (FOV). A more important concern, however, is that the PSCs could have spatial dimensions that are smaller than the HALOE sample volume. Since the retrieved extinction (cross section per unit volume) is spatially smoothed over the FOV, degradation of the actual PSC extinction can occur when the cloud is nonuniform in the sample volume. We return to this issue later.
Plate 1. Orthographic projections from 50°S to 90°S on the 390 K potential temperature surface of temperature, 5.26 μm aerosol extinction, water vapor mixing ratio, and methane mixing ratio. The data are HALOE sunsets from October 4 (50°S) to October 9 (75°S), 1993. Each polygon represents the true orientation and length (along the limb) of the HALOE sample volume. The actual sample volume width (across the limb) was increased from ~50 to ~100 km for visual clarity.

4. Comparisons of Measured and Modeled PSC Volume

The measured volume densities are compared with the calculated volumes of different types of PSCs at equilibrium. Since only equilibrium states are considered, we do not require the specific temperature history of each air parcel, and it is therefore reasonable to include all PSC observations from this period (October 7–9) for these comparisons. In Figures 2 and 5, the measured and calculated volumes are shown versus temperature. However, it should be noted that this representation does not mean that each point is related to the others by a physical process.

Plate 2. Potential vorticity (K m² kg⁻¹ s⁻¹) on the 390 K θ surface for October 7, 1993. The bold green dashed line shows the vortex boundary. The data are from the National Center for Environmental Protection (NCEP, formerly NMC) analysis.
Plate 3. Results of 670 ten-day isentropic back-trajectories ending in the PSC region on October 8, on the 390 K θ surface. The colors indicate (a) the latitude of each air parcel 10 days earlier, and (b) the potential vorticity (PV) (K m² kg⁻¹ s⁻¹) 10 days earlier. (c) The location of these air parcels 10 days earlier, with colors indicating the associated PV.
the stoichiometry of NAT is fixed and HNO₃ is the limiting species. For the liquid aerosols, however, the amount of H₂O absorbed into the condensed phase is variable, and changes in H₂O content affect the uptake of HNO₃ and hence the aerosol volume. These initial comparisons suggest that temperature alone would be a good predictor of NAT particle growth but a very poor predictor for liquid aerosol growth. Model calculations considering a possible ±30% systematic uncertainty in the measured water vapor (with a constant 10 ppbv HNO₃) resulted in a range of LTA volumes similar to the range obtained for 5 and 15 ppbv HNO₃ (see Figure 2b). Even when considering the possible uncertainties in measured water vapor and aerosol volume (calculations not shown), the comparison suggests that with the assumption of constant HNO₃ mixing ratios, the HALOE volumes would be consistent with LTA but not with NAT. To clarify these comparisons, Figures 2c and 2d show the observed volumes versus calculated volumes for the NAT and LTA models.

4.2. Scenario 2

In a second comparison we consider that the observed increases in water vapor could be accompanied by increases in HNO₃ and H₂SO₄. Although nitric acid measurements were not available for the period studied here, a positive correlation between H₂O and HNO₃ can be expected in the spring Antarctic vortex since both species are removed from the gas phase during PSC growth and sedimentation [Fahey et al., 1989]. Microwave Limb Sounder (MLS) H₂O and HNO₃ observations [Lahoz et al., 1996] from the 1992 Antarctic spring on constant pressure surfaces ranging in latitude from 50°S to 79°S on each day show a persistent positive H₂O–HNO₃ correlation. Figure 3 shows a representative comparison of H₂O and HNO₃ mixing ratios on September 9, 1992, with a linear fit overlain. Although there is a great deal of scatter, the clear correlation between H₂O and HNO₃ strongly suggests that intrusions of H₂O–rich air are likely to be associated with enhanced HNO₃. To test the effect of this on PSC growth, in the following calculations the amount of HNO₃ in an air parcel was determined from the observed water using the H₂O–HNO₃ correlation in Figure 3.

The total amount of total H₂SO₄ is also reduced within the vortex due to diabatic descent of aerosol–poor air during the winter, as indicated by the low aerosol extinctions in Plate 1. In addition, the H₂SO₄ abundance may be further reduced due to large scale gravitational sedimentation of H₂SO₄-containing particles (e.g., loss of H₂SO₄ particles contained within sedimenting ice crystals). The total H₂SO₄ should therefore increase in the intrusion region, thus contributing to the increase in aerosol volume density that is observed in the PSC. The amount of additional H₂SO₄ in the intruded air parcels cannot be determined from the aerosol volume under PSC conditions (T less than about 195 K), since the major contribution to the volume increase is the uptake of H₂O and HNO₃.
To estimate the possible increase in $H_2SO_4$ abundance, we therefore use the correlation between total $H_2SO_4$ and $H_2O$ vapor, determined under non-PSC conditions (see Figure 4). Clearly, there is a correlation between these two species, albeit weak; $H_2SO_4$ varies between about 2.5 ppbv for high $H_2O$ mixing ratios outside the vortex and 0.5 ppbv for low $H_2O$ values typical of inner vortex conditions. We use the correlation shown in Figure 4 with the observed water to determine the amount of $H_2SO_4$ in the following calculations. Although the uncertainty in $H_2SO_4$ is large (up to ±100%), the effect on calculated aerosol volume densities is relatively small (±30%), since the main contribution to aerosol growth is the uptake of $H_2O$ and $HNO_3$.

The NAT and LTA volumes were recalculated using the $HNO_3$ and total $H_2SO_4$ mixing ratios determined from the measured water vapor using the correlations given in Figures 3 and 4. The resulting $H_2SO_4$ and $HNO_3$ mixing ratios are shown in Figure 5a, and the calculated and measured volumes are compared in Figure 5b. The NAT volumes are directly modulated by the nitric acid amount, resulting in volume fluctuations that are now consistent with the observations. The resulting LTA volumes are similar to the calculations using constant $HNO_3$ (Figure 2b) but with sharpened peaks and troughs. Changes in NAT volume due to enhanced $H_2SO_4$ in the intrusion air are small compared with the effects of enhanced $HNO_3$. Comparing the observed volumes versus calculated volumes demonstrates the drastic changes in the NAT simulations for incorporating variations in $HNO_3$, as the RMS HALOE-model differences are decreased from 200% to 44% (compare Figures 5c and 2c). The RMS HALOE-model volume differences for LTA decreased from 39% to 28% (compare Figures 5d and 2d). It is difficult to identify the phase of the PSC from these comparisons, however, due to the uncertainties in the mixing ratios of $HNO_3$ and $H_2SO_4$.

5. Discussion

In the preceding analysis, the inherent limitations of a large FOV were not considered. For example, observed fluctuations in water vapor could be due to the averaging of vapor–rich elements (extravortex air) and vapor–poor elements (vortex air), both within the same FOV. HALOE observations provide only an FOV–averaged $H_2O$ signal, which, due to the nonlinear response of PSC growth to $H_2O$ mixing ratio, cannot be used to calculated an FOV–averaged PSC volume density. However, the maximum and minimum $H_2O$ mixing ratios are well defined, and some observations can be identified as most likely homogeneous within the FOV. Specifically, measurements of about 1.5 ppmv $H_2O$ represent the maximum value observed over a wide area of the vortex and are therefore likely to be homogeneous on the scale of the FOV. Measurements of about 4 ppmv $H_2O$ represent pure extravortex air, and similar arguments apply. Additionally, the limiting $H_2O$ values observed by HALOE (about 1.5 and 4 ppmv) are consistent with other observations at different times at the same altitudes [e.g., Fahey et al., 1989; Abbas et al., 1996].

Similar arguments apply to the lower limit of extinction, which is bounded by the background value observed within the vortex.
(about 1×10⁻⁴ km⁻¹, or 0.4 μm³ cm⁻³ in volume). An upper bound of aerosol extinction can also be identified as approximately 4×10⁻³ km⁻¹ (or 10 μm³ cm⁻³ in volume), which corresponds to near-complete removal of HNO₃ to the condensed phase by growth of either NAT or LTA PSCs (which are FOV-filling). Higher extinctions are possible for observations in ice clouds, which can reach volume densities near 100 μm³ cm⁻³. The possibility of ice can be excluded for observations above ~189 K; however, at lower temperatures it is possible that sub-FOV-scale ice PSCs caused an overall increase in the FOV-averaged aerosol extinction.

The large FOV causes the greatest concerns for observations of small-scale features or where strong gradients exist (such as the vortex edges). In Figures 2 and 5, the observations between the extremes are likely to fall into this category. There are justifiable arguments, however, to validate the observed maximum and minimum mixing ratios and the minimum volumes, and it is reassuring that both model and measurement have produced the same volume extremes.

6. Conclusions

HALOE observations over the eastern Weddell Sea during October 7–9, 1993, show factor of ~30 increases in aerosol volume coincident with water vapor enhancements of ~3 ppmv. The enhancement of H₂O and the coincident enhancement of HNO₃ and H₂SO₄ were considered in model calculations of PSC volume which closely match the observed volumes, suggesting that vapor resupply was an important factor in determining PSC growth. The particle type within this PSC is uncertain, however, due to uncertainties in the mixing ratios of HNO₃ and H₂SO₄.

The HALOE sunset measurements progressed northward after October 9 (75°S), reaching 50°S by October 25 (Plate 4). For this period, the HALOE water and methane fields show no evidence of enhancement, with uniformly low mixing ratios in the vortex. Although stratospheric temperatures remained low (192 K) over the Weddell Sea, there is no evidence of PSCs after October 9, which is consistent with the lack of condensable vapors. This would imply that the reformation of PSCs during October 7–9 was only temporary and that there was not an irreversible mixing of low-latitude air into the vortex.

The comparison of HALOE observations with model calculations for the growth of liquid or solid PSCs confirms the importance of the vapor distributions for the formation of late spring PSCs, as suggested by McKenna et al. [1989] and Watterson and Tuck [1989]. Watterson and Tuck [1989] have shown from SAM II satellite data that resupply of condensible material was important for PSC formation late in the Antarctic spring, particularly over the Weddell Sea region (longitudes from 270° to 0°E). They also observed that the incidence of PSCs diminished close to the pole even before the seasonal minimum temperatures were reached, resulting from strong dehydration and denitrification. McKenna et al. [1989] have also suggested that resupply of vapor from lower latitudes was important for late spring PSC formation, in a study of observations over the Weddell Sea. More specifically, our results show that the PSC volume density is strongly modulated by water vapor in the case of liquid aerosols and by nitric acid vapor in the case of NAT PSCs. The periodic resupply of vapor may lead to periods of PSC development late in the Antarctic spring, which could lead to continued heterogeneous chemistry.

Acknowledgments. We thank the HALOE science team for providing a high-quality data set, Paul Crutzen for initiating collaborations with the Max Planck Institute, and P. Newman and NCEP/CPC for providing the meteorological data. This work was supported through funding from the NASA Langley Research Center.

References
Adriani, A., T. Dehler, G. Di Donfrancesco, and G. P. Gobbi, Polar


