Simultaneous observations of Polar Stratospheric clouds and HNO3 over Scandinavia in January, 1992


Abstract. Simultaneous observations of Polar Stratospheric Cloud aerosol extinction and HNO3 mixing ratios over Scandinavia are examined for January 9-10, 1992. Data measured by the Microwave Limb Sounder (MLS), Cryogenic Limb Array Etalon Spectrometer (CLAES), and improved Stratospheric and Mesospheric Sounder (ISAMS) experiments on the Upper Atmosphere Research Satellite (UARS) are examined at locations adjacent to parcel trajectory positions. Regression coefficients, obtained from Mie calculations, are used to transform aerosol extinctions into aerosol volume densities. Graphs of temperature versus volume density, and importantly, temperature versus HNO3 mixing ratio, show volume increases and simultaneous loss of HNO3 consistent with the presence of ternary solution droplets.

introduction

Polar Stratospheric Cloud (PSC) formation processes can be studied with data measured by the Upper Atmosphere, Research Satellite (UARS), UARS instruments simultaneously observe both aerosol extinction and gas phase HNO3, and thus it is possible to study the interconversion of gas phase HNO3 into PSC particles. PSCs are thought to be composed of either ice crystals (Type I), nitric acid trihydrate (NAT) solid particles (Type Ia), or ternary
solution (HNO$_3$/H$_2$SO$_4$/H$_2$O) droplets (Type lb). Studies of forward scattering spectrometer probe (FSSP), balloonborne backscattersonde, and lidar data, have indicated the presence of ternary and NAT particles (Tabazadeh et al., 1994a, Carslaw et al., 1994, Drdla et al., 1994, Larsen et al., 1996).

Simultaneous UARS observations of aerosol extinction, measured by the Cryogenic Limb Array Spectrometer (CLAES) and Improved Stratospheric and Mesospheric Sounder (ISAMS) experiments, and gas phase HNO$_3$, measured by the CLAES and Microwave Limb Sounder (MLS) experiments, are used to study the formation of a PSC over Scandinavia during January 9-10, 1992. UARS observations on January 9 and 10 are used only if they are adjacent to specific parcel trajectories. The parcel positions originate over Greenland on January 9, and then proceed to a region of cold temperature, low HNO$_3$, and high aerosol extinction, located over Scandinavia on January 10.

Carslaw et al. (1994) used an equilibrium ternary model to show that the aerosol growth measured by the FSSP was consistent with HNO$_3$ uptake by ternary liquid droplets. The UARS extinction data are transformed into volume density values using regression coefficients, obtained from Mie calculations. Graphs of temperature versus volume density, and temperature versus gas phase HNO$_3$, reveal the interconversion between the gas and aerosol phase. The data are compared to equilibrium, and time dependent calculations, for PSCs of several compositions.

UARS Data

This study uses UARS observations at 46 and 68 hPa. CLAES and ISAMS aerosol extinction precision and accuracies for this range of pressure are on the order of 20 and 35% (Massie et al., 1996a, Lambert et al., 1996). Kumer et al. (1996) discuss the CLAES (version 7) data, and Santee et al. (1996) discuss the MLS (version 4) HNO$_3$ data, which are accurate
to 2 and 3 ppbv, respectively, at 46 hPa. MLS data at 68 hPa are obtained by interpolation of 46 and 100 hPa retrieved measurements.

Since PSC microphysics is quite temperature dependent, it is important to assess the accuracy of the United Kingdom Meteorological Office (UKMO) temperatures used in this study. Comparisons between the UKMO and radiosonde temperatures at pressures near 46 hPa for January 9-11, 1992 show that the UKMO temperatures are 1 K warmer than the radiosonde temperatures for the 190 to 195 K temperature range, with an rms deviation of 2 K about the bias. UKMO temperatures were therefore decreased by 1 K.

To transform the UARS extinction data into volume densities, Mie calculations are used to establish linear regression coefficients for each of the CLAES and ISAMS observational wavelengths. The Mie calculations use FSSP particle size distributions measured during the AASHII flights of the ER-2 (Dye et al., 1992) and sulfate aerosol size distributions measured over Laramie, Wyoming (Deshler et al., 1993). Regression coefficients were established for several sets of refractive indices (e.g., HNO3/H2O, H2SO4/H2O and NAT) for various weight concentrations of HNO3 and H2SO4. Binary HNO3/H2O indices approximate the HNO3/H2O/H2SO4 ternary indices, since the weight percent of H2SO4 is small in a ternary droplet for temperatures less than 195 K. For each extinction data point, the weight percent of H2SO4 and HNO3 is calculated, the composition is specified to be either sulfate, ternary or NAT, and the appropriate set of regression coefficients are then used to transform extinction to volume density. Details of the transformation calculations are discussed elsewhere (Massie et al., 1996b).

UARS Data on January 9 - 10

Plate 1 displays mapped versions of UKMO temperatures (decreased by 1 K), CLAES HNO3 mixing ratios, and ISAMS 12.1 µm extinction data, on the 460 K potential temperature surface for January 10, 1992. 1.OW mixing ratios and high extinction values are
associated with a region of cold temperature over Scandinavia (see Figure 3 of Taylor et al., 1994, for maps of temperature and aerosol extinction on adjacent days). Also displayed are specific parcel trajectories, calculated using UKMO wind field data. The parcels are located on the 460 K surface (corresponding to 19-20 km altitude over Scandinavia). Westernmost parcel positions, located over Greenland on January 9, have temperatures near 215 K, and easternmost positions over Norway on January 10 have temperatures near 190 K.

The volume densities presented in Figure 1 are an average of volume densities derived from ISAMS 12.1, ISAMS 6.23, CLAES 12.65, and CLAES 12.82 pm extinction data. UARS aerosol extinction and HNO3 data at 46 and 68 hPa were linearly interpolated in pressure, to the pressure value of the nearest parcel trajectory point. The assigned temperature is that of the nearest trajectory point. Horizontal arrows indicate the ±2 K rms deviation between the UKMO temperatures and that of the radiosondes.

Time progresses from January 9 to January 10 from right to left for the observations displayed in Figure 1. An observation was used if the data point was within 400 km of a parcel trajectory position, on either the 9th or 10th. Figures 1a and 1b display pairs of aerosol and HNO3 data which were measured during the same 65 second UARS observation time period, i.e. the volume densities and HNO3 mixing ratios are simultaneous. Graphs (not shown) of only the data observed on the same day as the trajectory points, show the same structure as in Figure 1, but contain fewer points.

In Figure 1 the aerosol is assumed to be sulfate (H2SO4/H2O droplets) for temperatures greater than 196 K, and assumed to be ternary droplets at temperatures less than 196 K. If the NAT composition is assumed at temperatures less than 196 K, then the volume densities are 20% lower than in the ternary case. The temperature versus volume density graph (not shown), based upon the NAT indices, however, has a visual appearance similar to Figure 1a. The differences in refractive index do not alter the fact that the rise in volume density (with decreasing temperature) in Figure 1a occurs at a temperature less than that expected for a
The structure of Figure 1a is controlled primarily by the relationship between temperature and aerosol extinction (e.g. see Figure 5 of Taylor et al., 1994).

**Theoretical interpretation**

Theoretical equilibrium curves, for NAT, nitric acid dihydrate (NAD) and ternary particles, are presented in Figures 1a-b, and are derived from the programs and data of Tabazadeh et al. (1994b), Carslaw et al. (1995), and Worsnop et al. (1993). The four ternary theory curves were initialized with volume density values of 0.4 and 0.9 $\mu$m$^3$cm$^{-3}$, and HNO$_3$ values of 9 and 13 ppbv. The NAT and NAD curves were initialized with 0.9 $\mu$m$^3$ cm$^{-3}$ and 13 ppbv. It is apparent that increases in volume density are accompanied by decreases in gas phase HNO$_3$, that the four ternary curves for the HNO$_3$ gas phase overlap at colder temperatures, and that the theoretical curves for the NAT, NAD, and the ternary solutions have different temperature thresholds for uptake of HNO$_3$, and subsequent increases in the aerosol volume density.

Most of the data points in Figure 1 are consistent with the existence of ternary solution droplets. The increase in volume density in Figure 1a, and the decrease in HNO$_3$ in Figure 1b, do not take place at the temperature threshold (i.e. 196 K) of the NAT equilibrium curve. These results are in agreement with those of Tabazadeh et al. (1994a), Carslaw et al. (1994) and Drdla et al. (1994).

A chemical box model is used to investigate the effects of heterogeneous reactions upon the gas phase HNO$_3$ mixing ratio. The box model uses the SMVGEAR solver (Jacobson et al., 1994), and contains 50 species, 150 reactions, and 16 heterogeneous reactions. The aerosol physical chemistry model (APCM) of Tabazadeh et al. (1994b) is used to calculate the equilibrium value of the volume density for the ternary solution droplets, which is used to estimate the area density (assuming a particle density of 2.5 particles/cm$^3$). For calculations
of the NAT particles, the mechanism of Chipperfield et al. (1993) is used. The volume and area densities are updated every 15 minutes.

Figure 1c presents theoretical curves of HNO$_3$ versus temperature. Time is indicated at the top of the figure. The time dependent values in Figure 1c were calculated using the temperatures and times from the parcel trajectory in Plate 1 which is closest to the equator, initial conditions for the calculations were derived from 2d model results, and the UARS observations. The calculations in Figure 1c start with 5 ppmv H$_2$O, 7 ppmv HNO$_3$, 2.4 ppbv N$_2$O$_5$, 14 ppbv NO$_y$, 1.7 ppbv ClONO$_2$, 1.7 ppbv HCl and 3.5 ppbv Cl$_2$.

The heterogeneous reactions

\begin{align*}
    \text{N}_2\text{O}_5 + \text{H}_2\text{O} &\rightarrow 2\text{HNO}_3 \\
    \text{ClONO}_2 + \text{H}_2\text{O} &\rightarrow \text{HNO}_3 + \text{HOCl} \\
    \text{ClONO}_2 + \text{HCl} &\rightarrow \text{HNO}_3 + \text{Cl}_2
\end{align*}

are influential in determining the gas phase HNO$_3$ mixing ratio. The “Ternary, all reactions” curve between 0 and 24 hours illustrates that reactions 1-3 enhance polar HNO$_3$ with a time scale of one day. The other theoretical curves show the results of the box model with and without heterogeneous reactions. Reaction (1) is the largest source term of gas phase HNO$_3$. Note that the equilibrium curves of Figure 1b do not incorporate chemical reactions, and are based upon thermodynamic (laboratory vapor pressure) data. The HNO$_3$ “Ternary, all reactions” solid curve values in Figure 1c, at temperatures less than 195 K, are somewhat larger than the topmost ternary curve values in Figure 1b. The “Ternary, all reactions” curve is supportive of the conclusion that the decrease of the observed HNO$_3$ is due to the uptake of gas phase HNO$_3$ into PSC droplets.

Comparison with other observations

The January period over Scandinavia has been studied by ground, aircraft, and satellite instrumentation. A comparison of UARS ClO, ClONO$_2$, HCl, and aerosol data on January
10, 1992 with a three dimensional model is discussed by Geller et al. (1995). Geller et al. (1995) demonstrate that heterogeneous processing transformed HCl and ClONO2 into reactive chlorine (ClO).

Airborne FTIR observations, on January 9, of low HNO3 column amounts west of Norway (67.6 °N, 9.5°E) by Hopfner et al. (1996) arc consistent with NAT particles, i.e. the observed HNO3 column and the ECMWF temperature profile arc more consistent with the theoretical equilibrium HNO3 column for NAT, than with that of the ternary solution. It is interesting to note that the lowest HNO3 mixing ratios in Figure 1b are within 600 km of the location of the Hopfner observations, and the data points arc closer to the NAT curves than to the ternary solution curves.

Schafer et al. (1994) report lidar observations at Andoya Island (69 °N, 16 °E), which is located along the coast of Norway, on January 5, 8, 9 and 19. The depolarization and perpendicular backscatter data on January 9 support the presence of nonspherical PSC particles at altitudes above 20 km, and spherical particles below 20 km. Since the data presented in Figure 1b apply to the pressure range between 46 and 68 hPa, the data comes from the altitude range for which the lidar reports spherical particles. It is commonly held that nonspherical particles are solid "Type la NAT" particles, while spherical particles arc liquid "Type lb Ternary" droplets. The Schafer data at altitudes below 20 km, and the majority of the data points in Figures 1a and 1b, arc consistent with the presence of ternary droplets.

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References.


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**Figure and Plate captions.**
Plate 1. Mapped fields on the 460 K potential temperature surface for January 10, 1992. a) UKMO temperature (decreased by 1 K). b) CLAES gas phase HNO₃ mixing ratios (ppbv). c) ISAMS 12.1 pm extinction (in units of 10⁻⁴ km⁻¹). d) Parcel trajectories on the 460 K surface. Parcel positions are over Greenland on January 9, and over Scandinavia on January 10.

Figure 1. Profile data which are adjacent to parcel trajectory positions on January 9 and January 10, 1992. a) Average values of ISAMS and CLAES volume densities. Equilibrium curves for ternary solution (solid lines), NAD and NAT solid particles (dashed lines) are also presented. b) CLAES and MLS HNO₃ mixing ratios which correspond to the data points displayed in Figure 1a. The equilibrium curves for ternary solution (solid lines), NAD and NAT solid particles (dashed lines) are obtained from the same calculations which produced the theory curves in Figure 1a. c) Time dependent HNO₃ mixing ratios, calculated with and without heterogeneous reactions. Curve A incorporates all heterogeneous reactions, curve B only includes the N₂O₅ + H₂O -> 2HNO₃ reaction, curve C excludes all heterogeneous reactions, and curve D includes all heterogeneous reactions for the h⁷AT composition. Time values, indicated at the top of the graph, are those of the parcels of the trajectory in Plate 1 which is closest to the equator.

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Theory (50 hPa, 9-13 ppbv HN03, 5 ppmv H2O)

(a) Volume density (micron^3 cm^-3)

(b) HNO3 (ppbv)

(c) Time dependent calculations

A, Ternary, all reactions
B, no N2O5 + H2O -> 2HN03
C, no heterogeneous reactions
D, NAT, all reactions