

A study of Type I polar stratospheric cloud formation

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Abstract. Mechanisms for the formation of Type I (nitric acid-based) polar stratospheric clouds (PSCs) are discussed. If the pre-existing sulfate aerosols are liquid prior to PSC formation, then nitric acid particles (Type Ib) form by HNO₃ dissolution in aqueous H₂SO₄ solution droplets. This process does not require a nucleation step for the formation of HNO₃ aerosols, so most pre-existing aerosols grow to become relatively small HNO₃-containing particles. At significantly lower temperatures, the resulting supercooled solutions (Type Ib) may freeze to form HNO₃ ice particles (Type Ia). If the pre-existing sulfate aerosols are initially solid before PSC formation, then HNO₃ vapor can be deposited directly on the frozen sulfate particles. However, because an energy barrier to the condensation exists a nucleation mechanism is involved. Here, we suggest a unique nucleation mechanism that involves formation of HNO₃/H₂O solutions on the sulfate ice particles. These nucleation processes may be highly selective, resulting in the formation of relatively small number of large particles.

Introduction

It is believed that stratospheric sulfate aerosols serve as condensation nuclei for the formation of Type I PSCs. Toon *et al.* [1986] and Crutzen and Arnold [1986] independently suggested that Type I PSCs are composed mainly of HNO₃ and H₂O, possibly in the form of thermodynamically stable nitric acid trihydrate (NAT). Two mechanisms have been suggested for the formation of NAT particles in the stratosphere. The first mechanism is the heterogeneous nucleation of HNO₃ and H₂O vapors on frozen sulfuric acid aerosols [e.g., Turco *et al.*, 1989]. This process requires, as an initial step, the freezing of the background aerosols. The second mechanism is the nucleation of NAT crystals from ternary solutions of H₂SO₄/HNO₃/H₂O [Molina *et al.*, 1993], with subsequent growth of these crystals by condensation of HNO₃ and H₂O vapors. This latter mechanism does not require freezing of the background aerosols as the initial step. Moreover, analyses of 1989 AASE (Airborne Arctic Stratospheric Expedition) lidar data [Browell *et al.*, 1990] reveal two subclasses of Type I PSCs (Type Ia and Ib), both appearing at temperatures at, or below, the equilibrium threshold temperature of NAT; however, the Type Ib particles exhibit physical characteristics (i.e., low depolarization, associated with a spherical shape), which is consistent with a liquid state. Here, we describe a mechanism for the formation of Type Ib PSCs that does not require nucleation. Also, in the case of frozen sulfate nuclei, we suggest a possible formation mechanism that involves nucleation of aqueous HNO₃ embryos on the solid sulfate particles.

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Type I PSC Formation Mechanism

Figure 1 illustrates the various processes discussed in this work. The transitions between the different phases shown in Figure 1 are controlled mainly by variations in the ambient temperature and humidity. However, the thermal history of the air mass is also important since it determines the physical state of the pre-existing sulfate aerosols. NAT particle nucleation rates can be roughly estimated using classical binary heterogeneous nucleation theory for the HNO₃/H₂O system. Unfortunately, nucleation parameters, such as interfacial energies, densities, and contact parameters have not been determined experimentally for HNO₃ and H₂O solutions and solid phases at low temperatures. Here, an alternative method based on thermodynamic arguments is used to describe formation of HNO₃ aerosols in the stratosphere.

HNO₃ Dissolution

Recently, we developed an aerosol physical chemistry model (APCM) to study the uptake of HNO₃ (and H₂O) by H₂SO₄ solutions [Tabazadeh *et al.*, 1994; Jacobson *et al.*, 1994]. Briefly, the APCM is an equilibrium model which calculates the composition of stratospheric aerosols as a function of ambient temperature, relative humidity, and the total amounts of HNO₃ and H₂SO₄ present per unit volume of

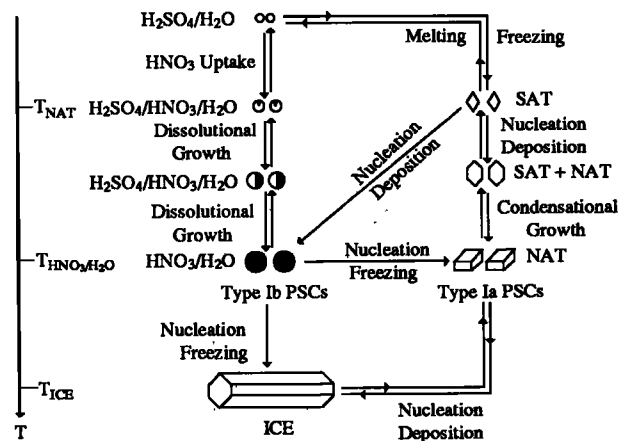


Figure 1. Type I PSCs formation. Temperature decreases from the top to the bottom of the chart. An approximate range for the condensation point and the frost points shown in the chart are $T_{\text{HNO}_3/\text{H}_2\text{O}} \sim 191\text{-}193\text{ K}$, $T_{\text{NAT}} \sim 195\text{-}197\text{ K}$, and $T_{\text{ICE}} \sim 188\text{-}190\text{ K}$, respectively. The melting temperature of sulfuric acid tetrahydrate (SAT) can vary from 210-220 K. Arrows in the upward direction indicate evaporation. Note that Type Ia and Ib PSCs contain trace amounts of H₂SO₄, and ice contains trace amounts of both HNO₃ and H₂SO₄. See Iraci *et al.* [1994] for a possible pathway of freezing H₂SO₄ solutions at higher temperatures ($T \sim 198\text{ K}$).

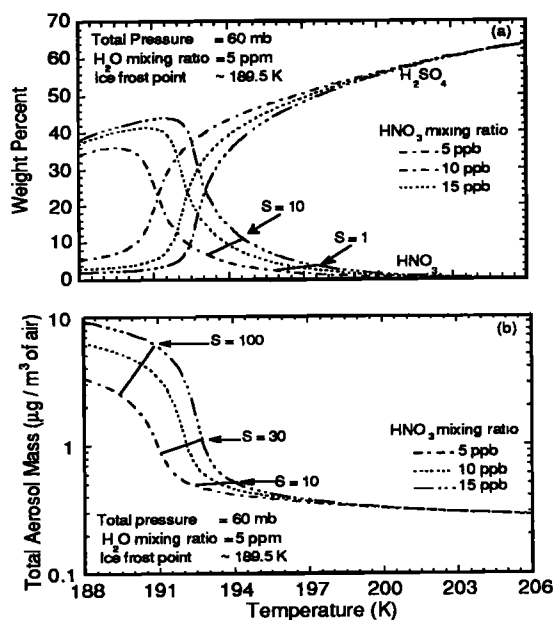


Figure 2. Type Ib PSC composition calculated from the APCM. S is the supersaturation of HNO₃ over NAT. (a) Weight percent of H₂SO₄ and HNO₃ in a pure H₂SO₄/HNO₃/H₂O solution as a function of temperature. (b) Total aerosol mass calculated as a function of temperature. For computations, the total sulfate aerosol mass was set at 0.18 µg / m³ of air.

air. APCM results are depicted in Figure 2, for a constant water and varying HNO₃ mixing ratios, under background sulfate aerosol loadings.

If the background aerosols are liquid when the NAT frost point is reached ($S_{NAT} = 1$; where S_{NAT} refers to the supersaturation of HNO₃ over NAT), then HNO₃ vapor dissolves in the background aerosols, accompanied by H₂O vapor absorption, which results in the growth of the existing aerosols. Such a mechanism does not involve a nucleation barrier; therefore, most existing aerosols, excluding the smallest, can grow to become cloud droplets. Hence, the background aerosol size distribution simply shifts to a larger mode, and the observed cloud particle size distribution will be unimodal [Hofmann *et al.*, 1990]. Thus, Type Ib particles have similar number concentration as, and are relatively larger than, background aerosols, while their composition varies as a function of relative humidity (Figure 2a).

Under the conditions shown in Figure 2, the NAT frost point ($S_{NAT} = 1$) varies between 196 - 197 K. When liquid aerosols grow from $S_{NAT} = 1$ to $S_{NAT} = 10$ in Figure 2, the total aerosol mass per unit volume of air increases by a factor of 2 at most. This mass increase is insufficient to match the observed physical properties of Type Ib PSCs, as described by Toon *et al.* [1990a; i.e., spherical with a mode radius of ~ 0.2 µm to 0.5 µm]. In growing from $S_{NAT} = 10$ to the ice frost point ($T \sim 189.5$ K) in Figure 2, the total aerosol mass per unit volume of air can increase by a factor of 10 to 100 (Figure 2b). Hence, the dissolutional growth stage of the ternary system (from $S_{NAT} = 10$ to the ice frost point) can result in the presence of particles ($r \sim 0.2 - 0.5$ µm) with an appropriate size and shape consistent with the definition of Type Ib PSCs given by Toon *et al.* [1990a]. Arctic field investigations [e.g., Dye *et al.*, 1992] indicate that significant particle growth is not evident until S_{NAT} is about 10. These NAT supersaturations are consistent with the APCM results shown in Figure 2 because significant particle growth is expected to occur when $S_{NAT} > 10$.

Lidar observations show that Type Ib PSCs exhibit low depolarization [Browell *et al.*, 1990], indicating that they are probably spherical in shape and may be composed of liquid droplets [Toon *et al.*, 1990a]. Even for $T < 192$ K, where the APCM predicts an almost pure HNO₃/H₂O composition for these aerosols (see Figure 2a, for 10 ppb of HNO₃), lidar data yields low depolarizations, indicating that the observed particles are probably still supercooled droplets.

We compared APCM results to an ER2 (890124) in-situ measurement taken during the 1989 AASE (Arctic Airborne Stratospheric Expedition) mission. To calculate a HNO₃ volume aerosol mixing ratio (AMR) from Kawa *et al.*'s [1992] data, we used the equations derived by Fahey *et al.* [1989]. The inferred HNO₃ volume AMR, $[HNO_3]_{aer}$, for an ER2 measurement is given by

$$[HNO_3]_{aer} = \frac{[NO_y]_{meas} - [HNO_3]_{gas}}{A_{eff}} \quad (1)$$

where $[NO_y]_{meas}$ is the total measured HNO₃ volume mixing ratio (note that we assumed all the available NO_y was present as HNO₃, or $R = 1$ in Equation (12) of Fahey *et al.*) and $[HNO_3]_{gas}$ is the equilibrium HNO₃ volume vapor aerosol mixing ratio (VMR) over the condensed phase. The A_{eff} is an enhancement factor which increases the observed NO_y by a factor of about 6 to 9 (see Kawa *et al.* for more detail). The data used for comparison to model calculations are given in Table 1, along with the computed values of $[HNO_3]_{gas}$ over STS (supercooled ternary solution) droplets and NAT particles. The $[HNO_3]_{gas}$ was calculated assuming typical values of 10 ppbv and 5 ppmv for the HNO₃ and H₂O mixing ratios, respectively. Table 1 shows that, for similar conditions, NAT particles are more efficient in depleting HNO₃ from the vapor phase as compared to STS droplets.

APCM and NAT results are shown as solid lines in Figures 3a and 3b, respectively. The measured points are shown as circles in Figure 3, and were calculated using values given in Table 1 in Equation (1). The error bars were calculated assuming A_{eff} values ranging from 6 to 9. Figure 3a shows that, assuming an STS composition for cloud particles, the predicted aerosol mass agrees with observed data over the temperature range shown in the figure. However, assuming a NAT composition (Figure 3b) does not allow the data to be fit. Figure 3 can also explain the large supersaturations observed during the AASE mission [e.g., Dye *et al.*, 1992]. For instance, at a temperature of 192 K, which is ~ 4 K cooler than the NAT frost point, significant incorporation of HNO₃ into liquid aerosols has not yet occurred.

Heterogeneous Nucleation

Here, we generically refer to NAT as the main HNO₃ ice particle that can form under stratospheric conditions. Browell *et al.*'s [1990] lidar observations show the presence of Type Ia PSC layers with high depolarization ratios at temperatures above the ice frost point. Calculations indicate that the average mode radius for these cloud particles would exceed 1.0 µm [Toon *et al.*, 1990a]. This size is significantly larger than

Table 1. Temperature and Inferred HNO₃ Mixing Ratios

T (K)	$[NO_y]_{meas}$	$[HNO_3]_{STS}$	$[HNO_3]_{NAT}$
189	70	0.79	0.25
190	60	1.87	0.58
191	45	4.04	1.25
192	20	8.21	2.67

Values in the first two columns were taken from Kawa *et al.* [1992]. The mixing ratios are given in ppbv.

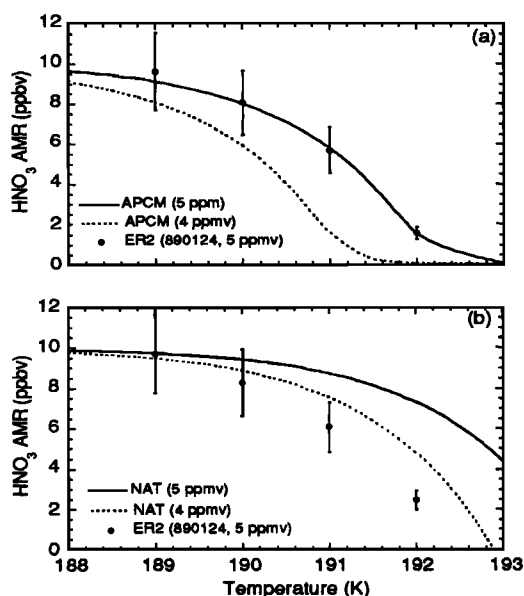


Figure 3. Variations in the HNO_3 volume aerosol mixing ratio (AMR) with temperature. (a) Solid lines are APCM results calculated for 10 ppbv and 5 ppmv HNO_3 and H_2O mixing ratios, respectively, at ~ 20 km altitude. Dashed lines were calculated for a water mixing ratio of 4 ppmv. Circles with error bars are measured HNO_3 volume AMR's taken from *Kawa et al.* [1992] (see text for more detail). (b) Same as (a), except AMR's were calculated assuming a NAT composition for the particles using the vapor pressures of *Hanson and Mauersberger* [1988].

the mode radius estimated for Type Ib particles, as discussed above. *Hofmann and Deshler* [1991] noted that NAT particles observed in the Antarctic form selectively on the larger background sulfate aerosols ($r > 0.3 \mu\text{m}$), indicating that a size-selective growth was involved in the formation of these clouds. They also reported a bimodal size distribution for the observed Type I PSC particles. The larger mode results from the growth of NAT particles (with $r \sim 1 - 3 \mu\text{m}$), and the smaller mode results from the water absorption by smaller-sized particles, which are not nucleated into NAT. Below, we discuss several possibilities for the formation of HNO_3 ice particles in the stratosphere via a nucleation mechanism.

Laboratory studies indicate that bulk ternary solutions ($\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$) with similar compositions to those depicted in Figure 2a freeze under laboratory conditions to form NAT [*Molina et al.*, 1993]. However, freezing of bulk solutions under such conditions does not prove that micron-sized aerosols of the same composition will freeze in the stratosphere. Large volumes and the presence of heterogeneous wall surfaces greatly increase the freezing probability of samples studied. If NAT (Type Ia) clouds form by the freezing of a few of the largest Type Ib particles (ternary solutions) in the stratosphere, then NAT can grow at the expense of the remaining unfrozen solution particles due to the difference in the HNO_3 vapor pressure over the condensed phases (see Table 1). This selective growth can also result in the formation of a bimodal size distribution for PSC particles as observed by *Hofmann and Deshler* [1991].

Browell et al. [1990] and *Kawa et al.*'s [1992] observational data point to the fact that aerosols formed from HNO_3 dissolution in H_2SO_4 solutions remain supercooled instead of nucleating into NAT particles. In the stratosphere, nucleation of NAT crystals from supercooled solutions probably occurs at temperatures near the ice frost point. However, more work is

needed to demonstrate such freezing of aerosols as suggested by *Molina et al.* [1993]. Moreover, some droplets contain solid cores [*Turco et al.*, 1981]. Therefore, it is possible that two droplets having the same size, liquid composition, and thermal history would freeze at different temperatures.

Arnold [1992] studied the binary gas phase heterogeneous nucleation of NAT on SAT surfaces using macroscopic parameters (surface tension and density) in a classical binary heterogeneous nucleation theory. From *Arnold's* calculations, nucleation is only possible if the contact parameter is large ($m > 0.95$). [m ranges from 0 to 1; for $m = 1$, there is no nucleation barrier for the formation of the condensate, and for $m = 0$, the free energy barrier for the nucleation will be the same as that of homogeneous nucleation.] However, laboratory studies indicate that SAT is not a good nucleating agent for NAT, implying that m is probably much smaller than 0.95 [*Molina et al.*, 1993]. Therefore, it is unlikely for NAT to nucleate directly onto SAT surfaces.

Recently, *Marti and Mauersberger* [1993] have shown that, if vapor containing stratospheric molar ratios of HNO_3 to H_2O is cooled to $T \sim 192$ K, a hydrate or a solution with a $\text{H}_2\text{O}:\text{HNO}_3$ ratio of about 5-6 to 1 is formed. The condensation point of $\text{HNO}_3/\text{H}_2\text{O}$ solutions under their laboratory conditions would be about ~ 196 K [*Tabazadeh et al.*, 1994]. Therefore, the metastable phase detected by *Marti and Mauersberger* may have consisted of aqueous HNO_3 solutions, which may freeze and grow over time to form NAT or metastable phases.

We suggest that HNO_3 and H_2O vapors may first nucleate on SAT particles as liquid embryos. The condensation point of $\text{HNO}_3/\text{H}_2\text{O}$ solutions in the stratosphere is about 191 - 193 K [*Tabazadeh et al.*, 1994], which is lower than the NAT frost point by about 3 - 4 K. Note that at the condensation point of aqueous HNO_3 solutions, the supersaturation of HNO_3 over NAT is > 20 . Therefore, if PSC formation initially involves nucleation of liquid embryos, then cloud formation will occur well below the expected NAT frost point. However, it is possible to nucleate liquid embryos of HNO_3 and H_2O on SAT surfaces because the surface and condensate are both hydrophilic (wettable) and therefore a large contact parameter may be assumed for this nucleation process [*Pruppacher and Klett*, 1978]. Heterogeneous $\text{HNO}_3/\text{H}_2\text{O}$ droplets will have a better chance of freezing to form NAT compared to pure solution droplets that originate from HNO_3 dissolution in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions. The presence of a SAT core in a small drop could increase the freezing probability of the droplet.

The Role of Freezing and Melting of SAT

Laboratory measurements indicate that it might be necessary to go down to the ice frost point for H_2SO_4 in stratospheric aerosols to freeze as SAT [*Middlebrook et al.*, 1993; *Zhang et al.*, 1993; *Iraci et al.*, 1994]. The melting temperature of SAT in the stratosphere can be estimated as: T_m (K) = $3236 / (11.502 - \log P_{\text{H}_2\text{O}})$, where $P_{\text{H}_2\text{O}}$ is the ambient water vapor pressure in units of torr [*Zhang et al.*, 1993; *Middlebrook et al.*, 1993]. For typical stratospheric water vapor mixing ratios [*Kelly et al.*, 1990] SAT melting temperatures of about 210 - 220 K are predicted. Temperature measurements by *Arnold* [1992] during the Arctic winter showed that stratospheric aerosols may go through freezing/melting cycles. However, under Antarctic winter conditions, temperature fluctuations after the autumn are seldom large enough to melt SAT once it freezes, and PSCs may form by a nucleation mechanism, as described above.

Discussion

In many Antarctic observations, PSCs have been observed when $S_{\text{NAT}} \sim 1$ [e.g., *Fahey et al.*; 1989, *Rosen et al.*, 1993].

However, these observations do not indicate that PSCs nucleate when $S_{NAT} \sim 1$. For instance, Rosen *et al.* [1993] observed no PSCs in one Antarctic measurement taken near the beginning of the winter season, when temperatures dropped to ~ 194 K ($\sim 1 - 2$ K lower than the NAT frost point). This observation suggests that, in the Antarctic, as in the Arctic, the initial onset for PSC formation requires $S_{NAT} \gg 1$. Thus, the apparent hemispheric differences in the supersaturations at which PSCs were observed may simply be an observational artifact. The few Antarctic PSC observations discussed by Fahey *et al.* [1989] may have been in clouds that were previously at lower temperatures than the ones at which the measurements were taken. If Type Ia PSCs are already present, then they will be observed at $S_{NAT} \sim 1$. Whereas, if PSCs have not yet formed, then $S_{NAT} > 1$ will be observed. In addition, lidar observations of Antarctic PSCs [Deshler *et al.*, 1990; Rosen *et al.*, 1993] also indicate the presence of both Types Ia and Ib clouds similar to the ones observed by Browell *et al.* [1990] in the Arctic, indicating that similar mechanisms are involved in the formation of PSCs in both hemispheres.

A final point to consider is the observations discussed by Browell *et al.* [1990] and Toon *et al.* [1990a] of adjacent Type Ia and Ib clouds occurring at temperatures within 1 K of each other over vast areas of the Arctic. Toon *et al.* [1990a] attributed the formation of the Type Ia and Ib clouds to nucleation in air masses having cooled slowly and rapidly, respectively. A drawback to this hypothesis is the nearly constant presence of short time-scale temperature fluctuations in the Arctic, which expose all air masses to large cooling rates. Here, we propose two alternative explanations for the presence of different cloud types at similar temperatures. In this hypothesis, cooling rates will not control the selective formation of PSC particles. If the pre-existing sulfate aerosols are liquid, then Type Ib clouds would form. These liquid aerosols are present either because the air mass has never been exposed to temperatures cold enough for H_2SO_4 in the aerosols to freeze as SAT or the air mass has recently sampled temperatures high enough for SAT to melt. The Type Ia clouds (NAT) can form either because SAT particles are present in the air mass or enough time has passed for HNO_3 -containing solution droplets to freeze as NAT. Further examination of observational data may distinguish between these postulates and shed light on different denitrification mechanisms [Toon *et al.*, 1990b], which affect ozone loss.

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