

Studies of Polar Stratospheric Cloud Formation

ANTHONY J. PRENNI AND
MARGARET A. TOLBERT*

Department of Chemistry and Biochemistry and CIRES,
University of Colorado, Boulder, Colorado 80309

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ABSTRACT

Stratospheric ozone depletion was first reported in 1985. Early on, researchers identified polar stratospheric clouds (PSCs) as being important in chemistry related to ozone depletion. PSCs exist as crystalline water–ice particles (type II), and as crystalline (type Ia) or liquid (type Ib) particles stable above the water–ice frost point. Uncertainty remains concerning the composition and formation mechanism of the most common PSC, type Ia. Here, we consider likely formation mechanisms for type Ia PSCs.

Introduction

The role of stratospheric ozone in absorbing solar ultraviolet (UV) radiation has been known for more than a century.¹ Other things being equal, a decrease in stratospheric ozone will cause an increase in the amount of UV radiation that reaches the Earth's surface. This is of biological interest, because exposure to increased UV radiation can detrimentally affect the health of plants, animals, and humans.² In this Account, we present a brief outline of polar ozone observations, focusing on those studies which have led to the current understanding of ozone depletion. Solomon³ provides a more in-depth review on this topic. We then focus on field and laboratory studies of polar stratospheric clouds (PSCs), key players in the ozone depletion story.

While ozone exists throughout the atmosphere, there is a concentrated ozone layer at altitudes of 12–40 km. The thickness of this layer has natural variations. However, in recent decades there has been a decline in springtime polar ozone that falls outside of natural variability. First reported by Farman et al.,⁴ the trend in polar stratospheric ozone is clearly observable in Figure 1.⁵ Here, the average springtime ozone column is shown for both poles for the past three decades, as determined from satellite measurements.

Bates and Nicolet⁶ first suggested that hydrogen oxide species play a role in ozone chemistry. These compounds participate in catalytic cycles that deplete ozone and

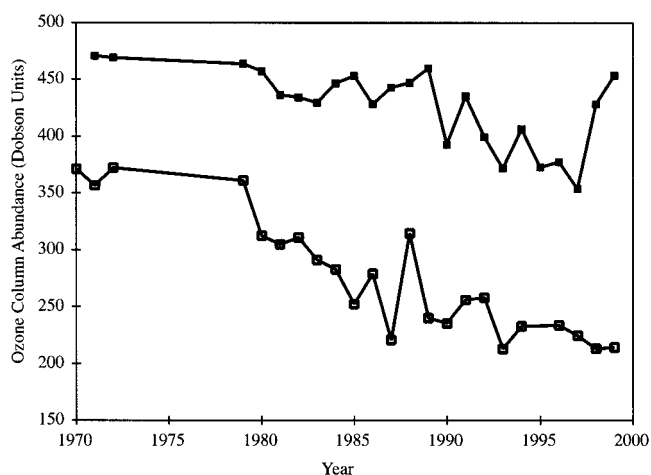
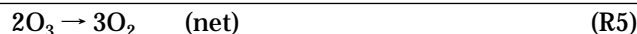
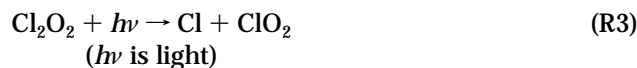
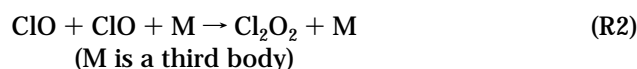


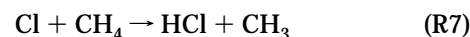
FIGURE 1. Average ozone column abundance determined from satellite measurements for 63–90°N (■) in March and 63–90°S in October (□).

regenerate reactive hydrogen species. It was later suggested that nitrogen oxides play a similar catalytic role in the stratosphere.⁷ The nitrogen and hydrogen species which destroy ozone form naturally in the atmosphere. However, their abundances may also be affected by anthropogenic emissions.

Chlorine emissions pose a much greater anthropogenic threat to ozone. Like hydrogen and nitrogen species, chlorine compounds participate in catalytic ozone depletion cycles.⁸ Molina and Rowland⁹ identified chlorofluorocarbons (CFCs) as a source of stratospheric chlorine. Because CFCs are not reactive in the lower atmosphere and are not sufficiently water soluble to be rained out, there is no known mechanism to remove them in the troposphere. Upon reaching the stratosphere, CFCs are broken down photolytically to produce Cl radicals, which can then react catalytically to destroy ozone. One polar ozone loss mechanism in regions with high chlorine and low NO_x (NO + NO₂) concentrations is



Reactive Cl species can also react to form the reservoir species HCl and ClONO₂, which do not destroy ozone:



Bromine compounds can also deplete ozone¹⁰ through

* Address correspondence to this author at University of Colorado, Campus Box 216, CIRES Room 318, Boulder, CO 80309. Phone: (303) 492 3179. E-mail: tolbert@spot.colorado.edu.

Anthony Prenni received his B.S. from Emory University in 1992 and his Ph.D. from the University of Colorado in 2000. Anthony began a postdoctoral position at Colorado State University in August 2000.

Margaret Tolbert received her B.A. from Grinnell College in 1979, her M.S. from the University of California, Berkeley, in 1985, and her Ph.D. from Cal Tech in 1986. After postdoctoral work at SRI International, she joined the faculty at the University of Colorado in 1992. Her interests are in the area of heterogeneous atmospheric chemistry, cloud microphysics, and planetary atmospheres. She is the recipient of numerous awards, including the 1993 MacElwane Medal of the American Geophysical Union.

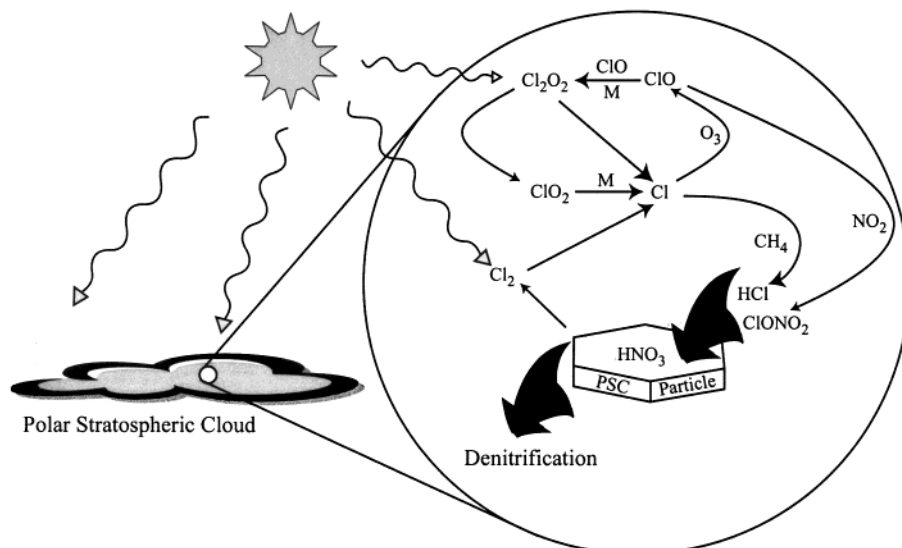
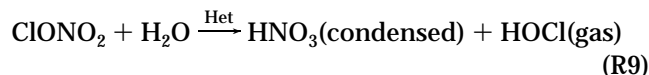
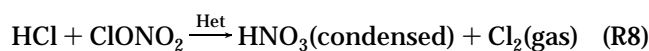


FIGURE 2. Schematic diagram of chlorine activation and one catalytic ozone depletion mechanism in the stratosphere.

their own catalytic cycles and through cycles in which both Cl and Br participate.

Gas-phase chemistry models ozone in the upper polar stratosphere reasonably well. However, it does not effectively describe the lower polar stratosphere. Here, gas-phase chemistry predicts minimal ozone depletion. In 1985, however, much larger depletions were reported over Antarctica.⁴ The “ozone hole”, as it was later named, was originally confined to the southern polar region during springtime. Ozone loss has subsequently been observed in the Arctic winter and springtime as well. Solomon et al.¹¹ suggested that the reservoir species HCl and ClONO₂ react on PSC surfaces to liberate Cl₂. Cl₂ is then readily photolyzed in even dim sunlight and can participate in catalytic ozone destruction. These heterogeneous reactions also remove HNO₃ from the gas phase. As cloud particles grow, they can settle out of the stratosphere, causing “denitrification”. In doing so, the amount of NO₂ available to pacify active chlorine via R6 is reduced, thereby promoting efficient ozone depletion.^{12,13} This process is shown schematically in Figure 2 and has been reported in the Arctic¹² and Antarctic¹⁴ stratosphere.

A number of heterogeneous reactions have proven to be important in chlorine activation:



While R11 does not produce an active halogen compound, it serves to remove nitrogen oxides from the gas phase, promoting denitrification. Other halogens, most notably bromine, participate in similar reaction schemes.

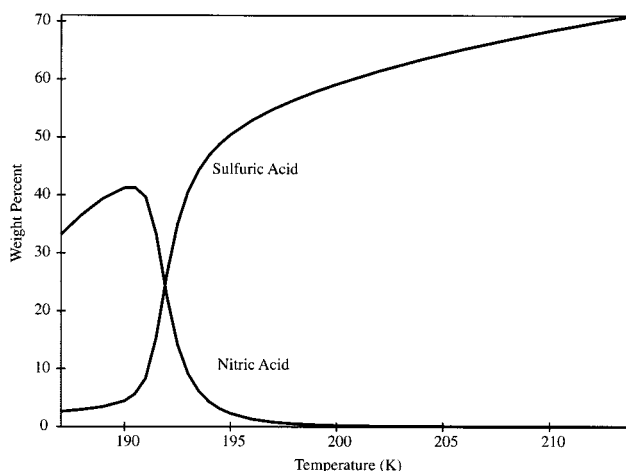


FIGURE 3. Modeled composition of liquid PSC particles for a pressure of 50 mbar, with 0.5 ppbv H₂SO₄, 10 ppbv HNO₃, and 5 ppmv H₂O.²⁰ Water makes up the remaining weight percent of the solution.

Polar Stratospheric Clouds

PSCs can exist as solids (type II and type Ia) and liquids (type Ib). Reviews on the chemistry and microphysics of PSCs^{15,16} and on theoretical concepts related to nucleation¹⁷ have been presented. Spherical liquid particles were first recognized based on lidar measurements,¹⁸ and there are measurements from the field which indicate liquid particles in the Arctic and Antarctic.^{18,19} At altitudes of approximately 15–20 km over the poles, PSCs form on background stratospheric aerosol, composed primarily of H₂SO₄/H₂O at temperatures > 200 K. As the background aerosol cools, H₂O and HNO₃ condense onto the particles, forming a supercooled H₂SO₄/HNO₃/H₂O ternary solution (type Ib PSCs). The equilibrium composition of these particles has been modeled,^{20,21} and their thermodynamic properties have been described in detail.²² Figure 3 shows expected concentrations in type Ib particles as a function of atmospheric temperature for a pressure of 50 mbar, for total amounts of H₂SO₄, HNO₃, and H₂O of 0.5 ppbv

H_2SO_4 , 10 ppbv HNO_3 , and 5 ppmv H_2O .²⁰ Water makes up the remaining weight percent in the solution particles. It can be seen that the background aerosol takes up significant amounts of HNO_3 below 195 K, and HNO_3 becomes the dominant acid below ~ 193 K. Laboratory studies have shown that heterogeneous reactions R8–R11 are fast on $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosols more dilute than 50 wt%. This indicates that ozone depletion may not require the presence of solid PSCs, but merely low temperatures (< 195 K) to form sulfuric acid droplets of this composition.

If cooled 3–4 K below the ice frost point, crystalline water–ice clouds (type II PSCs) can form.²³ Crystalline particles have also been observed at temperatures above the ice frost point in the Arctic and Antarctic.¹⁸ These crystalline, non-water–ice particles are denoted type Ia PSCs. Toon et al.²⁴ first suggested that type Ia PSCs may be composed of nitric acid trihydrate (NAT), which is stable at temperatures warmer than the water–ice frost point,²⁵ and field studies have demonstrated that particles do contain HNO_3 .¹⁴ However, the exact composition of these particles has yet to be determined.

While crystalline particles are regularly observed above the water–ice frost point, it is difficult to collect PSC particles to determine their exact composition. One recent study did successfully collect stratospheric particles, but in that case type Ib PSCs were found.²⁶ Although NAT is a stable crystalline substance under stratospheric conditions, NAT has not proven to be kinetically favored due to a nucleation barrier for crystallization. This barrier results due to the difficulty in forming an ordered crystalline substance from a disordered solution. Because of this, a number of metastable acid hydrates have been suggested as alternative type Ia PSCs, or as important intermediates in the formation of stable type Ia particles;^{27–32} e.g., nitric acid dihydrate (NAD) forms readily at stratospheric temperatures and may be important in type Ia PSC formation.

Determining the composition and formation mechanisms of PSCs is important for a number of reasons. First, while water–ice, NAT, and supercooled ternary solutions can all play a role in activating chlorine, reaction efficiencies vary somewhat based on the phase and composition of the particles.³³ Also, denitrification due to particle settling depends largely on particle size which, in turn, depends on particle composition and phase. For example, if PSCs remain as supercooled droplets, the particles will take up enough H_2O and HNO_3 to reach their equilibrium composition. Because all the particles grow without a nucleation barrier, the supercooled droplets typically remain smaller than $1 \mu\text{m}$ in diameter. This growth is not sufficient to cause significant sedimentation. Alternatively, selective nucleation of a few NAT particles will lead to a small number of low-vapor-pressure solids. This, in turn, supports growth of large particles which can sediment rapidly. Indeed, in the lower stratosphere, type II PSCs often reach diameters greater than $10 \mu\text{m}$,³⁴ and Fahey et al.³⁵ report type Ia PSC particles with diameters larger than $10 \mu\text{m}$ in the Arctic.

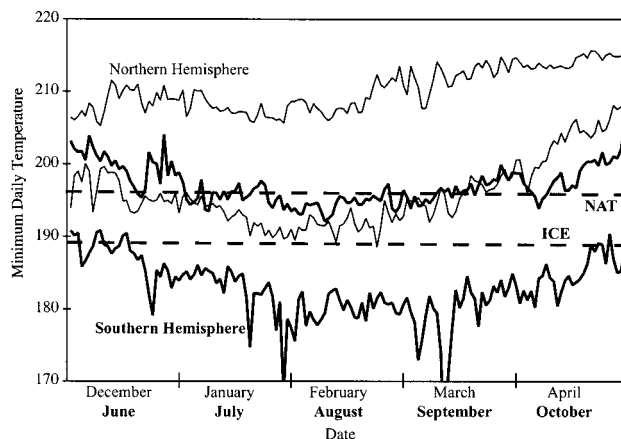


FIGURE 4. Daily minimum temperatures observed at 100 hPa for $50\text{--}90^\circ\text{N}$ (range falls within thin lines) and $50\text{--}90^\circ\text{S}$ (range falls within thick lines) from December 1978 to April 2000 (Paul Newman, personal communication). Water–ice and NAT frost points are also shown.

While ozone has decreased throughout much of the stratosphere, complete destruction of ozone occurs primarily in the southern polar stratosphere. Such isolated depletion results for a number of reasons. First, due to the low partial pressure of water in the stratosphere, extremely low temperatures are required for water–ice PSC formation (< 189 K). During the Antarctic winter, a strong polar vortex forms, thereby hindering mixing of polar air with warmer, low-latitude air and enabling the Antarctic stratosphere to reach temperatures < 189 K. A weaker, warmer vortex also occurs over the Arctic, but temperatures reach 189 K much less frequently. Figure 4 illustrates the range of minimum stratospheric temperatures for the two poles from December 1978 through April 2000. It can be seen that, at the low temperatures of the Antarctic, type II PSCs and type I PSCs, which form at higher temperatures, can both readily form and provide the surfaces necessary for the aforementioned heterogeneous chemistry. The presence of both low temperatures and springtime sunlight (to photolyze Cl_2) allow for nearly complete destruction of lower stratospheric ozone in the southern hemisphere. In contrast, temperatures in the Arctic are usually too warm for type II PSC formation and are often too warm for type I PSCs. Furthermore, there are few of any type of PSC present in the northern hemisphere spring, where the sunlight needed for ozone depletion is available. Consequently, ozone losses in the Arctic are not nearly as severe as losses in the Antarctic. However, future climate changes may cause a decrease in polar stratospheric temperatures, leading to more frequent PSC formation in the Arctic and perhaps Arctic PSCs extending to the springtime.

Laboratory Experiments To Measure Type Ia PSC Formation

Laboratory studies have been performed to investigate the freezing behavior of model stratospheric particles. In our laboratory, we use Fourier transform infrared (FTIR) spectroscopy to monitor thin films and aerosols repre-

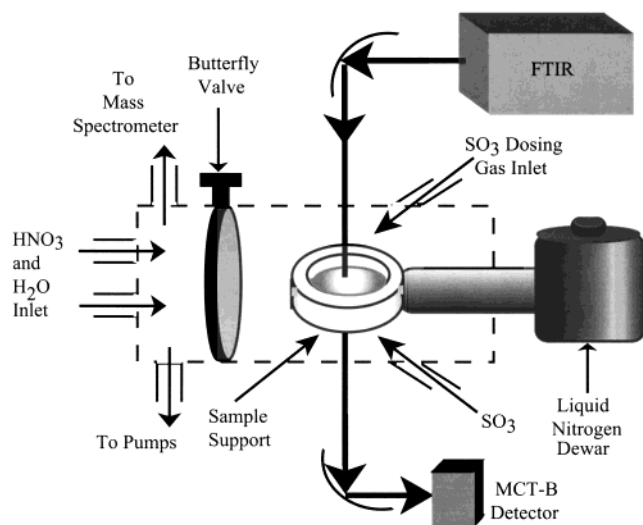


FIGURE 5. Experimental apparatus for FTIR spectroscopy studies using a thin-film chamber.

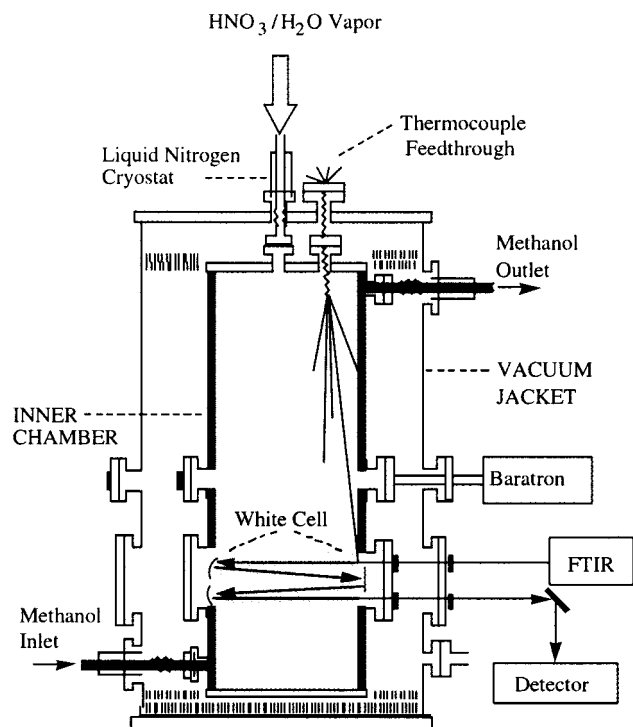


FIGURE 6. Experimental apparatus for FTIR spectroscopy studies using an aerosol settling chamber.

sentative of PSCs. A schematic diagram of the thin-film apparatus is shown in Figure 5. Here, a thin film with a model PSC composition is deposited on a cold silicon wafer. Phase and composition of the film are monitored using FTIR spectroscopy, while the gas phase is monitored using mass spectrometry. For aerosol studies, micrometer-sized particles are introduced into a temperature-controlled settling chamber and are monitored using FTIR spectroscopy, as shown in Figure 6. Constant particle composition during an experiment suggests that the particles are in equilibrium with the gas phase. The chamber is temperature-controlled to ± 2 K, with a lower temperature limit of ~ 188 K. Particle settling limits the

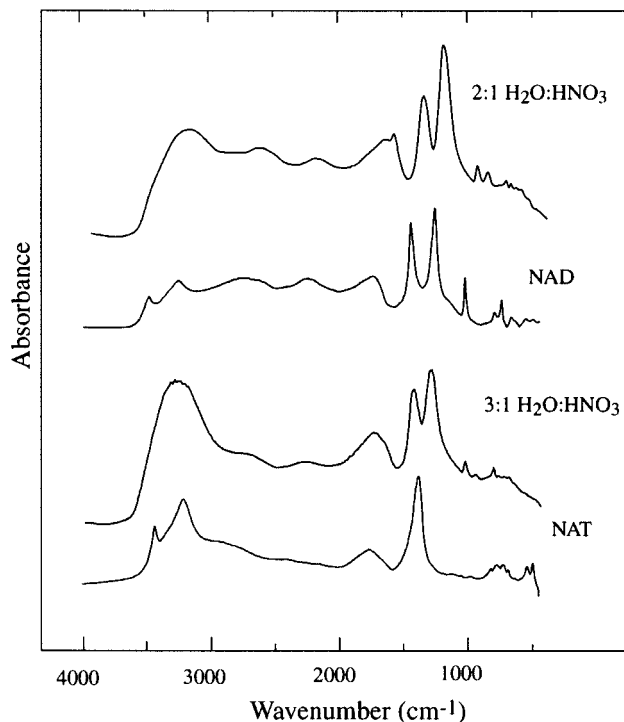


FIGURE 7. Thin-film reference spectra of amorphous and crystalline $\text{HNO}_3/\text{H}_2\text{O}$.³⁶

lifetime of the aerosol in the chamber. This lifetime varies with particle size but can be as long as 4 h for small particles. Aerosol phase and composition can be determined using reference spectra obtained from the thin-film chamber. For example, Figure 7 shows infrared spectra for supercooled 2:1 and 3:1 $\text{H}_2\text{O}:\text{HNO}_3$, NAT, and NAD.³⁶ It can be seen from Figure 7 that the spectrum for each hydrate is unique, and that the relative peak heights for the supercooled spectra change with composition, allowing for both phase and composition to be accurately determined using FTIR spectroscopy.

Type Ia PSC Formation

Type Ia Formation Due to Lee Waves. Light detection and ranging (lidar) has been used to assess the role of lee waves in PSC formation.^{23,37} Lee waves occur when an air parcel passes over a large topographical feature, causing the air to rise and cool rapidly. Figure 8 shows lidar data which follow the development of particles as an air parcel passes over an extended mountain range.²³ The white line in the figure represents an air parcel trajectory moving from left to right through the mountain wave. In lidar measurements, backscattered light from particles is used to determine their size and shape. Figure 8a shows the total backscatter ratio, S , and Figure 8b shows the backscatter depolarization, S_{\perp} . The total backscatter ratio is proportional to particle size, with larger S corresponding to larger particles. Backscatter depolarization is related to particle shape. Particles with low depolarization are spherical and are thought to be liquid droplets. Particles with high depolarization are not spherical and are thought to be crystalline. The aircraft encounters the lee wave at

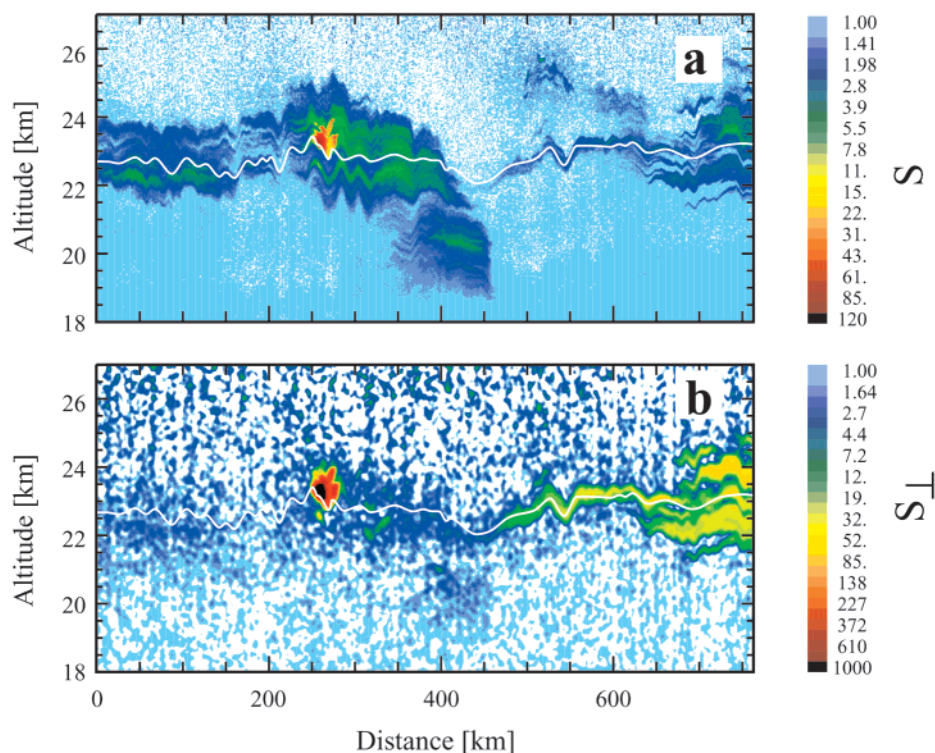


FIGURE 8. Lidar data which follow the development of particles in a lee wave. (a) Total backscatter ratio, S , and (b) backscatter depolarization, S_{\perp} .²³ The white line is a trajectory of an air parcel passing through the lee wave. A more detailed description is found in the text.

~250 km. Prior to passing through the lee wave, the temperature remains below the NAT frost point but above the ice frost point. Here, the particles are relatively small, supercooled liquid particles, as indicated by the low backscatter ratio and the low depolarization. At ~250 km, the rapid cooling caused by the lee wave causes the temperature to fall below the water–ice frost point, and larger, crystalline type II PSCs are observed, as indicated by the high backscatter ratio and high depolarization. These ice particles begin to evaporate upon warming above the ice frost point at ~300 km, as indicated by the lower values for backscatter ratio and depolarization. Finally, there is a gradual increase in backscatter ratio and depolarization after 500 km, indicating the growth of crystalline type Ia PSCs.

The ice particles formed in the mountain wave appear to have nucleated type Ia PSCs downwind of the lee wave. Type Ia particles are thought to form on ice through two potential mechanisms. Ice particles which are in an environment supersaturated with respect to NAT may have additional nitric acid condense onto the surface. In support of this mechanism, Zondlo et al.³⁸ used an apparatus similar to the one shown in Figure 5 to show that an ice film exposed to nitric acid will, indeed, form a layer of supercooled $\text{HNO}_3/\text{H}_2\text{O}$. Upon lowering the relative humidity (or warming), this supercooled layer crystallized to NAT. Alternatively, water and nitric acid may condense simultaneously as the ice particles grow, and NAT clusters may become embedded in the ice. Subsequent preferential evaporation of water molecules leaves behind an ice core with a NAT coating.³⁹ In support of this mechanism, Barton et al.⁴⁰ observed ice formation

followed by NAT formation in the residual solution in $\text{H}_2\text{O}/\text{HNO}_3$ clusters with compositions of $>5:1$ $\text{H}_2\text{O}:\text{HNO}_3$. Furthermore, Middlebrook et al.⁴¹ showed that heating an ice film with a NAT coating resulted in preferential evaporation of water.

Other field studies of lee wave PSCs give indirect evidence of HNO_3 uptake by ice. Deshler et al.⁴² observed ice particles to persist downwind of a lee wave, even though the air was subsaturated with respect to ice. Peter et al.³⁹ explained the observations by suggesting HNO_3 coated the ice, lowering the ice evaporation rate and allowing the particles to persist for a longer time. Laboratory studies show that NAT formed from a supercooled $\text{HNO}_3/\text{H}_2\text{O}$ solution does, indeed, slow the ice evaporation rate.⁴³ In contrast, NAT clusters in the ice allow for preferential evaporation of H_2O .

Lee waves may also induce type Ia PSC formation by allowing NAT or NAD to nucleate directly from concentrated $\text{HNO}_3/\text{H}_2\text{O}$ particles. Meilinger et al.⁴⁴ and Tsias et al.⁴⁵ suggest that the smallest particles in a lee wave may reach compositions which are nearly binary solutions of $\text{HNO}_3/\text{H}_2\text{O}$ with compositions as concentrated in nitric acid as 2.5:1 $\text{H}_2\text{O}:\text{HNO}_3$. To determine whether these particles can crystallize, laboratory experiments have been carried out on submicrometer particles with compositions of 2:1, 2.5:1, and 3:1 $\text{H}_2\text{O}:\text{HNO}_3$. Data for 2:1 $\text{H}_2\text{O}:\text{HNO}_3$ aerosol are shown in Figure 9, which shows FTIR spectra for a typical crystallization experiment in the aerosol settling chamber described earlier. Here, a 2:1 $\text{H}_2\text{O}:\text{HNO}_3$ aerosol is introduced into the chamber at 191 K, and the aerosol is monitored over time. Spectrum a in Figure 9 is at the onset of the experiment, when the aerosol is entirely

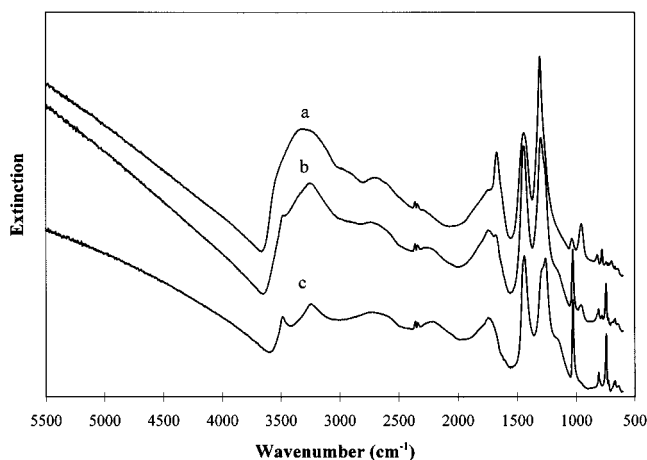


FIGURE 9. FTIR spectra for an aerosol settling chamber freezing experiment at 191 K. (a) Supercooled 2:1 H₂O:HNO₃ aerosol at the onset of the experiment. (b) The aerosol begins to crystallize to NAD, and (c) the aerosol is completely converted to crystalline NAD.

supercooled. The aerosol begins to crystallize to NAD, and by 625 s changes in the spectrum are clearly evident, as shown in spectrum b. After 2100 s, shown in spectrum c, the aerosol is completely converted to NAD. These data are used to determine the conditions under which nitric acid solutions form a crystalline hydrate, the hydrate which forms most readily for a given temperature and aerosol composition, and the freezing kinetics for the particles.⁴⁶ For 3:1 H₂O:HNO₃, Prenni et al.⁴⁶ used the apparatus shown in Figure 6 and found that NAT does not form on the time scale of the experiment at stratospheric temperatures. From these measurements, they placed a limit of more than 35 h for 1 μm diameter aerosol to crystallize in the atmosphere. Bertram and Sloan⁴⁷ also did not observe freezing of NAT at stratospheric temperatures. Rather, NAT formation was observed only when the aerosol was cooled to temperatures below 170 K followed by rapid warming. Salcedo et al.⁴⁸ recently measured nucleation rates of NAT from ~3:1 H₂O:HNO₃ particles at temperatures <180 K. Extrapolating their results to warmer temperatures and assuming that sulfuric acid in the particles does not slow the nucleation rate, their measurements suggest that if the stratosphere remains below the NAT freezing temperature for more than 1 day, NAT could form from 1 μm particles.

For the most concentrated particles expected in lee waves, 2.5:1 H₂O:HNO₃, Tsias et al.⁴⁵ observed NAD formation from submicrometer particles. However, it is unclear whether NAD will form fast enough from 2.5:1 H₂O:HNO₃ particles for significant type Ia PSC formation in lee waves by this mechanism. If so, NAD particles are stable at temperatures above the ice frost point and so are a possible alternative to NAT as type Ia PSCs. NAD may also serve as an intermediate to NAT formation. For example, Barton et al.⁴⁰ observed NAD formation in H₂O/HNO₃ clusters with compositions of 2.5–4:1 H₂O:HNO₃, followed by conversion of NAD to NAT, and Middlebrook et al.⁴⁹ reported that NAD films convert to NAT upon exposure to stratospheric water pressures. A number of

groups have also measured NAD formation from 2:1 H₂O:HNO₃ solution particles,^{46,50–52} finding that NAD forms readily from the stoichiometric solution particles.

Type Ia Formation throughout the Arctic Stratosphere. Lidar data suggest that type Ia PSCs are prevalent throughout the Arctic stratosphere, and not only downwind from lee waves.⁵³ Figure 10a shows the flight track for an Arctic research flight during the 1989 Airborne Arctic Stratospheric Experiment. Figure 10b shows the interpretation of the resulting lidar data, where blue areas indicate large, nonspherical particles. These measurements were taken at temperatures above the ice frost point, and so these particles are type Ia PSCs. Although lee waves provide a likely mechanism for PSC formation, for such extensive type Ia PSC coverage, an alternative mechanism is needed.

Because the Arctic stratosphere rarely reaches the water–ice frost point but regularly reaches the NAT frost point, NAT is believed to be the predominant form of type Ia PSCs in the Arctic. Further, while NAT formation may be relatively slow at stratospheric temperatures, particle studies suggest that NAT may form if stratospheric temperatures remain below the NAT frost point for more than 1 day,⁴⁸ and concentrated bulk samples indicate homogeneous nucleation of NAT.⁵⁴ However, there is no overwhelming field evidence to confirm that type Ia particles are composed of NAT rather than an alternative acid hydrate. Further, bulk studies revealed that even very small amounts of H₂SO₄ could inhibit NAT nucleation.⁵⁴

Sulfuric acid tetrahydrate (SAT) is thermodynamically favored under stratospheric conditions. However, in settling chamber experiments at stratospheric temperatures, Anthony et al.⁵⁵ used the apparatus in Figure 6 to show that SAT does not crystallize from 35–95 wt % H₂SO₄, nor from ternary H₂SO₄/HNO₃/H₂O under stratospheric temperature and composition conditions.⁵⁶ Other laboratory measurements⁵⁷ confirmed these findings, and theoretical⁵⁸ and bulk⁵⁴ experiments have shown that homogeneous nucleation of SAT from H₂SO₄/H₂O is a very slow process. However, SAT may form via heterogeneous nucleation on ice. As the temperature drops below the water–ice frost point to form ice in stratospheric particles, a residual, concentrated sulfuric acid solution remains. Martin et al.⁵⁹ showed that ice served as an effective heterogeneous nucleus for SAT formation. Similarly, Koop et al.⁵⁴ added a crystalline ice seed to supercooled H₂SO₄/H₂O solutions and observed crystallization in the supersaturated solutions. In contrast, Clapp et al.⁶⁰ found that ice was not an effective nucleus for sulfuric acid hydrate formation at stratospheric temperatures. If SAT can form, its relatively high melting temperature of 215 K suggests that crystalline particles could exist for long time periods in the Arctic stratosphere.⁶¹ If cooled to temperatures below 192 K, SAT will deliquesce in the ternary H₂SO₄/HNO₃/H₂O system.⁶² Using the apparatus shown in Figure 5, Iraci et al.⁶³ showed that upon exposure to HNO₃ and H₂O and initiation of SAT deliquescence, NAT may nucleate on SAT from the resulting solution, providing a possible pathway for NAT formation.

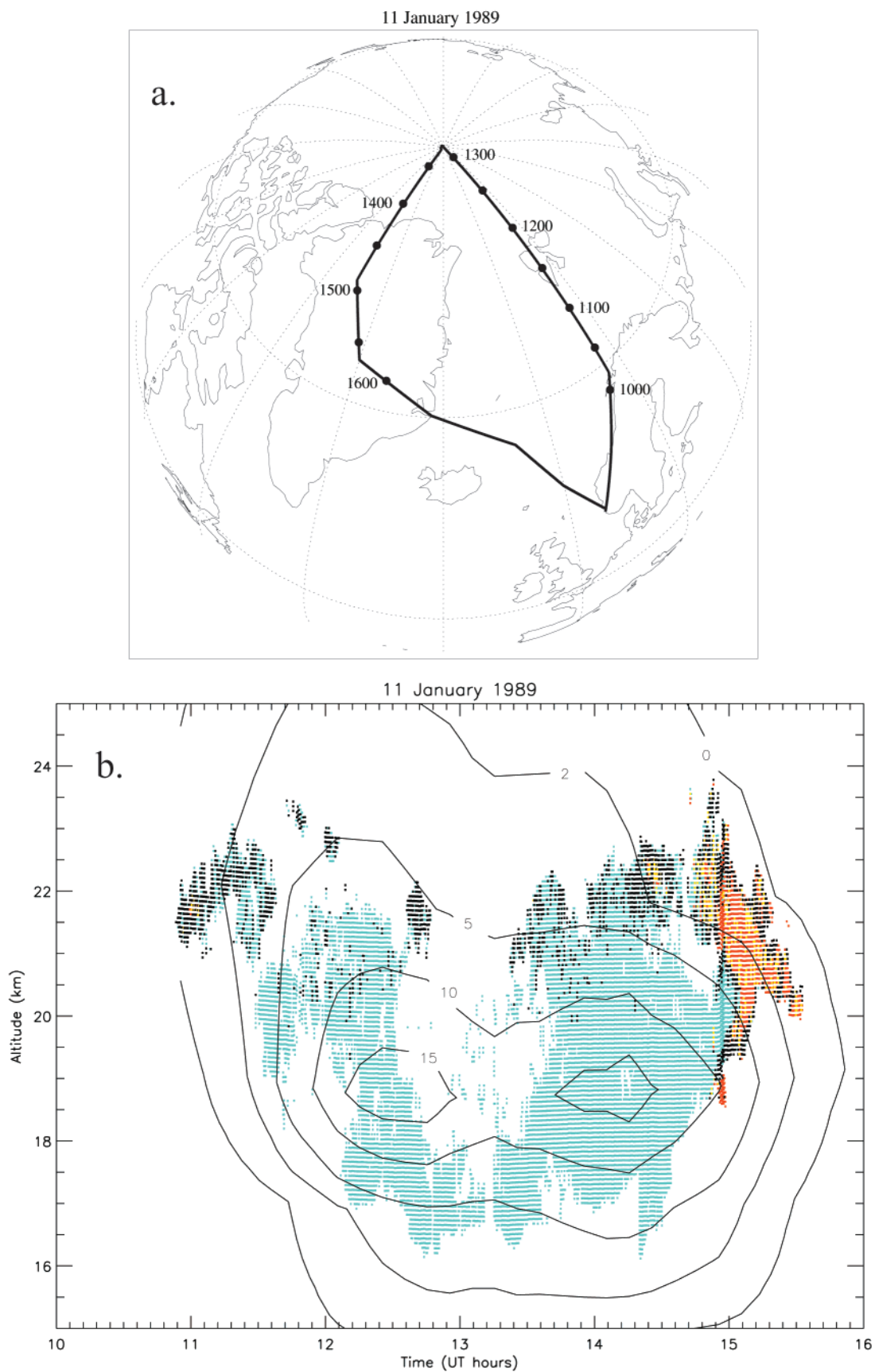


FIGURE 10. (a) Flight track of an Arctic research aircraft in which PSCs were observed using lidar. (b) Interpretation of the corresponding backscatter and depolarization data, which indicate size and shape. Blue areas indicate large, nonspherical particles above the ice frost point: type Ia PSCs.⁵³

Heterogeneous Pathways for Type Ia Formation.

Currently, there is not a well-established mechanism for type Ia PSC formation. Laboratory studies of PSC formation may not be representative of atmospheric aerosols because nucleation may be initiated by impurities present in real aerosols which are missing in the laboratory. For example, Murphy et al.⁶⁴ recently reported that iron is present in about half of the stratospheric particles that they sampled using a single-particle mass spectrometer system. Further, Bogdan and Kulmala⁶⁵ demonstrated that H₂O/HNO₃ microdroplets crystallized readily to NAT due to heterogeneous nucleation on silica. In contrast, Koop et al.⁶⁶ and Biermann et al.⁶⁷ performed heterogeneous experiments using a number of potential heterogeneous nuclei and found no significant increase in nucleation rates. These contradictory results suggest that the effects of heterogeneous nuclei still need to be fully explored.

Conclusions

While the importance of PSCs in ozone depletion is well documented, uncertainty remains in the composition and formation mechanism of type Ia PSCs. Field and laboratory studies have shown that lee waves may induce type Ia formation, most likely by the nucleation of NAT on ice particles. Once formed, these NAT particles can survive at temperatures higher than the temperature of the ice particles on which they formed. This process is clearly important on a local scale; however, it is unclear whether it can explain the extent of type Ia PSCs observed throughout the Arctic.

Type Ia PSCs may also form by some other mechanism. First, NAT may form homogeneously if stratospheric temperatures remain below the NAT frost point for an extended period of time. Second, a number of metastable crystalline phases have been suggested as playing an important role in the formation of type Ia PSCs. Further, if SAT can form in the stratosphere, there is evidence that suggests NAT may nucleate on SAT upon SAT deliquescence. Finally, there is laboratory evidence for heterogeneous nucleation. Determining the relative importance of each of these mechanisms remains open and is needed for accurate modeling of PSC formation and Arctic ozone depletion.

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