

POLAR STRATOSPHERIC CLOUDS AND THE OZONE HOLE

Clouds of frozen nitric acid particles that form in the polar winter stratosphere are a crucial element in the massive springtime ozone depletion over Antarctica.

Patrick Hamill and Owen Brian Toon



During the winter clouds appear in the Arctic and the Antarctic stratospheres. These clouds have been observed for over a century, and during most of that time they were considered an interesting and beautiful but relatively unimportant phenomenon. Recently, however, atmospheric scientists have found a critical relationship between the massive springtime ozone depletion over Antarctica and the formation of polar stratospheric clouds. (See figure 1.) In this article we outline the general properties of the three main types of stratospheric aerosols, and we show how changes in the levels of stratospheric nitrogen and chlorine species required for ozone depletion are dependent upon the formation of polar stratospheric clouds.

Ozone is generated in the stratosphere when solar ultraviolet radiation is absorbed by molecular oxygen, breaking the molecular bond and yielding two free oxygen atoms. A free oxygen atom can then combine with an oxygen molecule to form ozone, O_3 . Ozone itself undergoes photodissociation (as well as other loss processes), yielding a net balance between ozone formation and ozone destruction. This balance leads to a quasi-steady-state concentration of atmospheric ozone that is greatest in the lower stratosphere, between about 15 and 30 km of altitude. The absorption of solar radiation in both the formation and the destruction of ozone heats the atmosphere, so the temperature increases with altitude from the tropopause up to about 50 km, as illustrated in figure 2.

During the polar winter night the stratospheric air mass over Antarctica is effectively isolated from the rest of the atmosphere by a very strong circulation centered over

the pole. This polar vortex forms as polar air cools, contracts and descends. Air moving poleward from lower latitudes is deflected by the Coriolis effect, and a strong, nearly circular vortex is produced over a region roughly corresponding to the Antarctic continent. In the Northern Hemisphere the temperatures are not as low, and so the Arctic vortex is weaker and tends to be disrupted one or more times during the winter. The Antarctic vortex, however, is quite stable and lasts until spring, when the sun rises and warms the air. A rapid and dramatic change in the circulation pattern results as air from lower latitudes flows into the southern polar region.

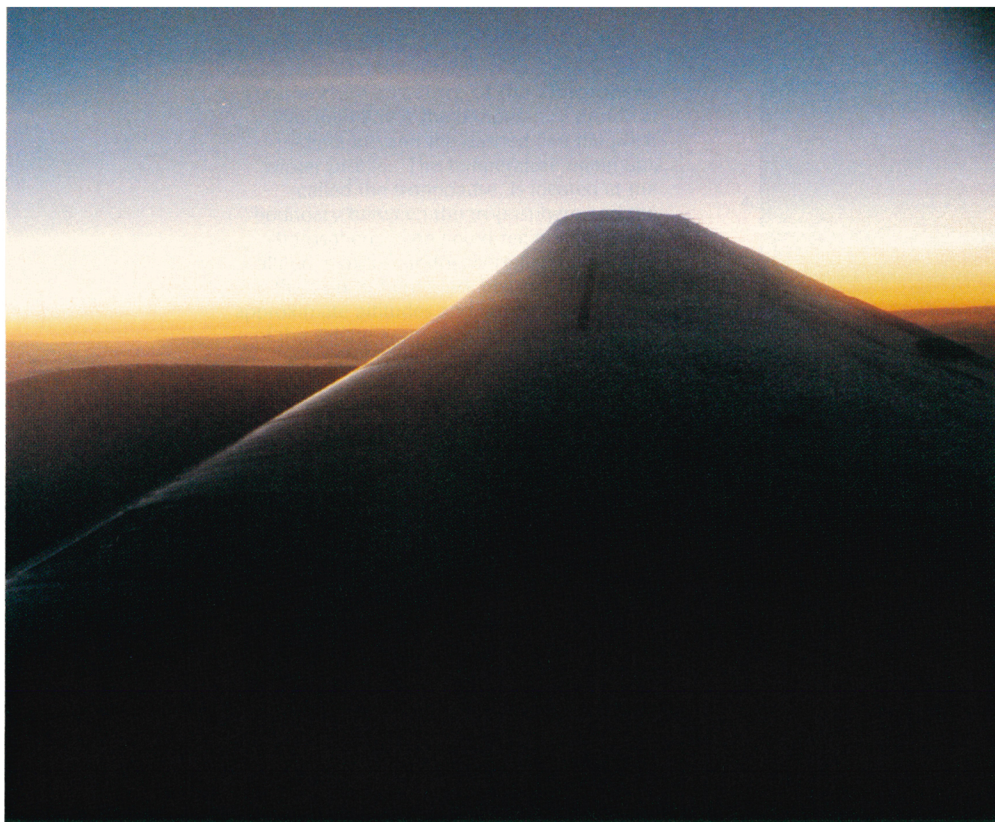
Antarctic ozone depletion

In a 1985 paper in *Nature*, Joseph Farman and his coworkers with the British Antarctic Survey described ozone measurements made at Halley Bay, Antarctica.¹ They used ground-based spectrophotometers to evaluate the total amount of ozone in a vertical column extending upward from the instrument. (The results of such measurements are usually presented in milliatmosphere-centimeters, or Dobson units. When multiplied by the number of air molecules in 1 cubic centimeter at standard temperature and pressure a measurement in DU gives the total number of molecules of ozone in a cross-sectional area of 1 cm^2 rising from the surface of the Earth.)

British observations of ozone and other atmospheric gases began in 1957, so long-term trends are well established. Farman and his coworkers found that since 1968 the ozone column in October had a downward trend, as shown in figure 3. The daily value for mean total ozone in October prior to 1968 was greater than 300 DU, but by 1984 it had fallen to less than 200 DU. The daily low value over Antarctica in October 1991 was less than 150 DU.

This springtime ozone depletion is observed to take place over a period of six weeks. It represents the destruction of about 3% of the total stratospheric ozone.

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Stratospheric ice clouds
(type II) over the Arctic
Ocean appear as white
streaks over the wingtip of
a NASA airplane. This
photo was taken during the
1989 Arctic
expedition. **Figure 1**

The catastrophic loss of so much ozone over such a short time demonstrates that global-scale atmospheric changes can occur very rapidly. The ozone hole contributes to a general worldwide decrease in stratospheric ozone because when the polar vortex breaks down in spring, the ozone-depleted air is transported to lower latitudes.

Farman and his colleagues postulated that the observed ozone decrease was caused by reactions involving chlorine in a catalytic cycle. Measurements made at Halley Bay indicated (in agreement with measurements made worldwide) that the amount of certain chlorofluorocarbons such as Freon 11 (CFCl_3) and Freon 12 (CFCl_2) had increased by a factor of about 3 between 1970 and 1980. These measurements suggested a link between CFCs and the depletion of the stratospheric ozone.¹

Since the discovery of the ozone hole, a number of scientific expeditions have gone to Antarctic research bases to measure ozone and other atmospheric chemical species with ground-based and aircraft- and balloon-borne instruments. Measurements made with balloon-borne sensors in 1986 by David Hofmann showed that the maximum ozone depletion occurred between 14 and 22 km altitude² (see figure 4), indicating that ozone depletion occurs at the altitude of maximum ozone concentration.

The possibility that chlorofluorocarbons could destroy stratospheric ozone through catalytic cycles involving chlorine had originally been suggested by Mario Molina and Sherwood Rowland.³ And it is now believed⁴ that at least 95% of the chemically catalyzed ozone loss can be attributed to two chemical schemes (shown in the table on page 38): About 75% of the ozone loss results from reactions involving the ClO dimer,⁵ and most of the remaining ozone is destroyed in reactions involving bromine.⁶

The simple scenario of chlorine release by photodissociation of CFCs does not explain why severe ozone depletion is limited to the Antarctic region or why it is ob-

served only during the spring. Furthermore, in model calculations of the atmospheric chemistry done shortly after the discovery of the ozone hole, aeronomers were not able to reproduce the observed rapid ozone decreases when they used the expected concentrations of reactive (or free) chlorine in the stratosphere.⁷ The photodissociation of the CFCs is ordinarily followed by gas-phase reactions of gaseous chlorine monoxide with nitrogen dioxide, leading to the formation of chlorine nitrate, ClONO_2 . In fact, most of the chlorine in the stratosphere should be bound up in the less reactive compounds ClONO_2 or HCl , referred to as "reservoir" species. Consequently, the models predicted that only a small fraction of the chlorine is present in reactive forms such as Cl or ClO . However, these early model calculations were based on the assumption that only gas-phase reactions occur; they did not include the possibility of *heterogeneous* reactions—that is, reactions on the surfaces of particles—and thus may have used incorrect rates in accounting for reactions that compete with reactions involved in the formation of reservoir species.

An earlier discovery based on satellite data had shown that the Antarctic winter stratosphere is a region of extensive cloud formation.⁸ Susan Solomon, Michael McElroy and others⁹ suggested that these polar stratospheric clouds might provide surfaces for heterogeneous chemical reactions. However, modelers later found that even when they accounted for a higher rate of chlorine production by including heterogeneous reactions, they still could not model the observed ozone destruction using known stratospheric NO and NO_2 concentrations. Some mechanism for removing these nitrogen species was not being considered.

At about this time, Toon and coworkers and, independently, Paul Crutzen and Frank Arnold¹⁰ suggested that some polar stratospheric clouds were composed of small, frozen nitric acid particles and others were formed of

water ice. Shortly thereafter Molina¹¹ and other atmospheric chemists found that chlorine nitrate reacts very rapidly with HCl adsorbed on ice surfaces, releasing chlorine. Chlorine nitrate also reacts with water ice to produce HOCl, an unstable molecule. Both of these reactions generate nitric acid, so they not only lead to the production of active chlorine but also suppress the amount of available NO₂ in favor of HNO₃, which does not readily react with Cl. As we show below, the nitric acid clouds supply a mechanism not only for removing nitrogen compounds from the gas phase but also for the overall denitrification of the Antarctic stratosphere. Over the course of the Antarctic winter, the polar stratospheric clouds are responsible for a significant reduction in the NO and NO₂ levels.

In addition other reactions, such as N₂O₅ + H₂O → HNO₃, occur on particle surfaces. These reactions were proposed many years ago to explain various aspects of the nitric acid budget of the stratosphere. They tend to remove nitrogen from active NO_x forms such as NO₂ and N₂O₅ and convert them to HNO₃. These processes are said to *denoxify* the stratosphere. (Thus it is possible to denoxify the stratosphere without denitrifying it.)

To understand the interactions between the clouds and the ozone destruction mechanisms, it is helpful to review some of the physical processes governing the formation of stratospheric particles.

Formation of stratospheric cloud particles

Although the stratosphere is much cleaner than the troposphere, it contains a significant amount of suspended particulate matter. Some of this material, for example, the debris from meteoritic ablation, is of natural origin, and some, like the aluminum oxide spherules from space shuttle launches, is anthropogenic. The most important gaseous source of particles is sulfur dioxide injected into the stratosphere by violent volcanic eruptions. Through photochemical reactions the sulfur dioxide is converted to sulfuric acid, which subsequently condenses to form a subvisible mist of sulfuric acid solution droplets. The concentration of this aerosol is enhanced after large volcanic eruptions, but even during volcanically quiescent periods it is maintained by the upward transport of naturally occurring, sulfur-bearing gases. Under normal midlatitude stratospheric conditions (say, 20 km altitude and 220 K temperature) the sulfate aerosol, with a number density of some 10 particles/cm³, is made up of particles with an average radius of about 0.07 μm and a composition of about 75% H₂SO₄ and 25% H₂O. It is believed that these particles are in a supercooled liquid state.

In addition to this permanent stratospheric sulfate aerosol layer, which envelops the Earth at altitudes between about 12 and 30 km, one occasionally finds clouds in the stratosphere. Reports of these clouds have been

published sporadically in the scientific literature over the past 150 years, and their appearance was considered a rather uncommon phenomenon. Many of these observations were of the so-called nacreous or mother-of-pearl clouds, which form when air is lifted and cooled in passing over mountain ranges.

About ten years ago Patrick McCormick and coworkers,⁸ using satellite data, identified a different type of stratospheric cloud and showed that there are extensive stratospheric cloud formations over Antarctica during the winter months. This finding came as a surprise, because the stratosphere is extremely dry: It is believed that tropospheric air enters the stratosphere through the tropical tropopause, which, with temperatures as low as 185 K, is the coldest part of the lower atmosphere. As the humid tropospheric air passes through this "cold trap," water condenses and presumably rains out, thus dehumidifying the air entering the stratosphere. Another source of stratospheric water vapor is the oxidation of methane at higher altitudes.

Although these processes are not yet completely understood, it is well known that the water content of the stratosphere is seldom greater than 5 parts per million by volume. At 20 km altitude and 220 K this amount of water corresponds to a relative humidity of less than 1%. It is easy to show that the environment must cool to about 188 K before 5 ppmv of water vapor can condense (to form ice crystals). Ice clouds, or type-II polar stratospheric clouds, formed under these conditions have been observed in the winter Antarctic stratosphere. However, the satellite record also shows the presence of clouds at temperatures between 190 and 200 K, too warm for water ice to form. These clouds, now called type I, were the subject of considerable speculation until it was suggested¹⁰ that the cloud particles were composed of condensed nitric acid, possibly in the crystalline form of HNO₃·3(H₂O), nitric acid trihydrate or NAT.

Cloud physicists use the term "microphysics" to refer to the mechanisms that determine the properties of cloud particles. For stratospheric particles the most important microphysical processes are nucleation, condensation and evaporation, coagulation and sedimentation. Figure 5 illustrates how these processes lead to the formation of polar stratospheric cloud particles.

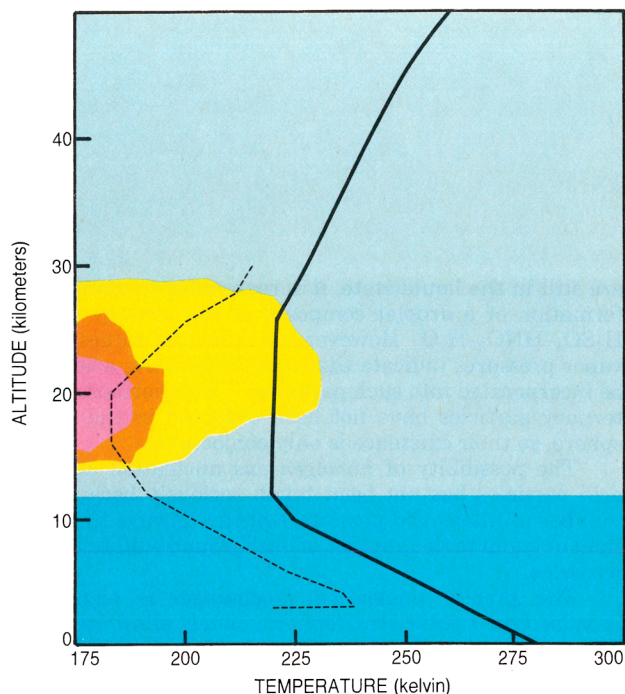
Nucleation

Nucleation usually refers to the formation of a liquid droplet from a supersaturated vapor, but it can also refer to the formation of a solid particle in vapor or to the formation of a frozen grain in a supercooled liquid.

Nucleation theory is rather controversial. For water vapor there is reasonable agreement between theoretical and measured nucleation rates, but for many substances the disagreement is quite severe. Frequently, however, one is interested not in the actual number of particles

Temperature structure of the atmosphere.

The solid line is the temperature profile at midlatitude and the dashed line the polar winter profile. The temperature minimum, called the tropopause, is located at the boundary between the troposphere and the stratosphere. The tinted regions show the altitudes of the stratosphere (light blue) and the troposphere (dark blue) as well as the approximate altitudes and temperature ranges of the sulfate aerosol (yellow) and the polar stratospheric clouds (orange and red). **Figure 2**



formed per unit time but rather in the conditions of temperature and gas-phase concentration at which nucleation will proceed at a significant rate. These factors are predicted fairly well by a simple classical theory.

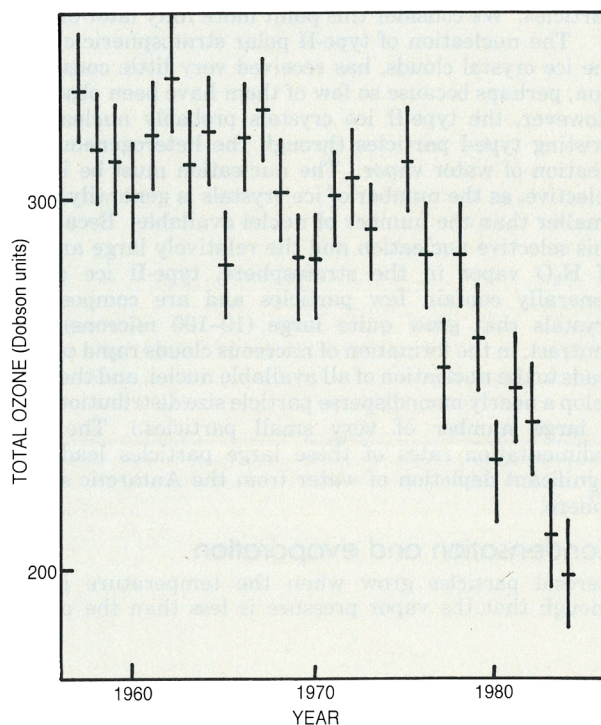
In the stratosphere we are interested primarily in the nucleation of solution particles formed by the simultaneous condensation of two vapors, a process known as heteromolecular nucleation. Although the theory of heteromolecular nucleation was developed over 15 years ago, mainly by C. S. Kiang and Dietrich Stauffer,¹² it has had little experimental verification.

In the lower atmosphere, the nucleation of water drops (as in the formation of rain or dew) always takes place on foreign surfaces, such as minute grains of salt suspended in the air or blades of grass. This process is called heterogeneous (as opposed to homogeneous) nucleation. Because the troposphere has an abundance of foreign surfaces to serve as nucleation sites, heterogeneous nucleation is the dominant mode of particle formation there. Furthermore, heterogeneous nucleation will take place at relative humidities very near 100%, whereas homogeneous nucleation requires roughly 300% relative humidity.

The actual mechanism for the formation of the stratospheric sulfate particles is uncertain, but it is fairly clear that they are generated *in situ*. Atmospheric physicists have suggested that sulfate particles may nucleate heterogeneously on the surfaces of micrometeorites, on tropospheric particles that have been transported into the stratosphere, or on ions. Our own calculations of the rate of particle formation onto solid surfaces show that for midlatitude conditions these nucleation processes could lead to particle formation in the lower stratosphere, at about 13 km.

The stratosphere is very clean, and therefore *homogeneous* nucleation may occur if the temperature is low enough. Our calculations¹³ indicate that in the polar winter stratosphere, homogeneous nucleation of sulfuric acid-water solutions may take place at altitudes from the tropopause up to about 28 km. This result suggests that another source of the background stratospheric aerosol particles may be homogeneous nucleation over the poles in the winter, with subsequent dispersal throughout the stratosphere by dynamical processes. This explanation agrees with measurements showing high numbers of particles in the polar stratospheres.¹⁴

The nucleation of the nitric acid particles in polar stratospheric clouds is far from understood. Type-I cloud formation is estimated to occur at temperatures between 191 and 195 K. If the nucleation is heterogeneous onto the surface of preexisting sulfuric acid particles, then it takes place at a supersaturation of about 10 (with respect to nitric acid vapors over solid nitric acid trihydrate). However, the nucleation process may involve the formation of supercooled nitric acid solution particles rather



Average total column ozone measured over Halley Bay, Antarctica, during October decreased between 1957 and 1984. (Adapted from ref. 1.) **Figure 3**

than NAT. In this case, the supersaturation would be less extreme because the vapor pressure of water and nitric acid over a supercooled liquid solution is higher than it is over the frozen solution at the same temperature.

To complicate the problem even further, there is evidence that sulfuric acid particles do not freeze at temperatures above about 195 K. At this temperature they would be highly supercooled. If the sulfate particles

are still in the liquid state, it is reasonable to assume the formation of a droplet composed of the ternary system $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O}$. However, extrapolated values of the vapor pressures indicate that very little nitric acid could be incorporated into such particles.¹⁵ Furthermore, these ternary particles have not been observed in the stratosphere, so their existence is only conjectural.

The possibility of *homogeneous* nucleation of nitric acid particles has not been taken seriously because the number of nitric acid particles appears always to be less than or equal to the number of background sulfate aerosol particles.

The precise nucleation mechanism is significant because type-I polar stratospheric clouds allow for ozone destruction through denitrification of the stratosphere. Denitrification depends on particle size, which in turn is controlled by the nucleation mechanism for nitric acid particles. We consider this point more fully later on.

The nucleation of type-II polar stratospheric clouds, the ice crystal clouds, has received very little consideration, perhaps because so few of them have been observed. However, the type-II ice crystals probably nucleate on existing type-I particles through the heterogeneous nucleation of water vapor. The nucleation must be highly selective, as the number of ice crystals is generally much smaller than the number of nuclei available. Because of this selective nucleation and the relatively large amount of H_2O vapor in the stratosphere, type-II ice clouds generally contain few particles and are composed of crystals that grow quite large (10–100 microns). (By contrast, in the formation of nacreous clouds rapid cooling leads to the nucleation of all available nuclei, and these develop a nearly monodisperse particle size distribution with a large number of very small particles.) The high sedimentation rates of these large particles lead to a significant depletion of water from the Antarctic stratosphere.

Condensation and evaporation

Aerosol particles grow when the temperature is low enough that the vapor pressure is less than the partial

pressure. If the reverse is true, the particles will evaporate. The process seems simple enough, but in the stratosphere it is complicated by the fact that for both the sulfuric acid particles and the nitric acid particles, the condensed phase is a two-component solution. For the background sulfate aerosol, the two vapors are water and sulfuric acid; for type-I clouds the two vapors are water and nitric acid. For type-II clouds, however, the condensing species is simply water vapor.

Let us consider sulfate particle growth in more detail. Under our nominal stratospheric conditions of 220 K at 20 km such a particle is 75% H_2SO_4 and 25% H_2O . The particles are continuously bombarded by vapor-phase sulfuric acid and water molecules, some of which are absorbed. At the same time both sulfuric acid and water evaporate from the droplets. When the rate of evaporation equals the rate of condensation, the droplet is in equilibrium. It would be quite fortuitous for a solution droplet to be in equilibrium with both vapors simultaneously. In the stratosphere the sulfate particles quickly reach equilibrium with water, which is much more prevalent than sulfuric acid. (Some 10^8 water vapor molecules collide with the particle before a single sulfuric acid molecule impinges on it.) For a particle in equilibrium with water vapor, each time a water molecule is absorbed another water molecule is evaporated. However, when a sulfuric acid molecule is absorbed, the composition of the particle changes slightly. To regain its equilibrium composition the particle absorbs water molecules, leading to slow growth by condensation. Because there are so few sulfuric acid molecules available in the vapor phase, the growth process is slow.

The equilibrium composition of a droplet of sulfuric acid solution depends on temperature. If the environment grows colder, the droplet becomes more dilute—that is, it absorbs water and grows larger. As the temperature falls during the polar night, the droplets swell up to nearly twice their original radii and change in composition from 75% to about 50% sulfuric acid.

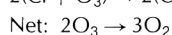
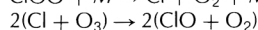
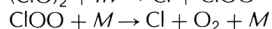
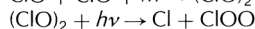
Closely related to the growth by condensation of sulfuric acid droplets is their evaporation. As shown in figure 2, the temperature of the midlatitude stratosphere increases with altitude. At about 30 km the temperature is high enough that the sulfuric acid particles begin to evaporate. Cloud physicists believe that this evaporation accounts for the upper altitude limit on the sulfate layer. The lower altitude limit of the aerosol layer is somewhat above the tropopause, suggesting that particles are “washed out” by incursions of tropospheric air into the lower stratosphere.

The growth of type-I polar stratospheric clouds is probably much the same as for the sulfate aerosols. That is, they are most likely in equilibrium with water vapor and grow only when nitric acid molecules impinge on them.

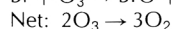
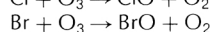
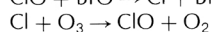
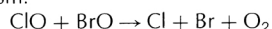
Another interesting question concerns the evaporation of polar stratospheric cloud particles as they fall during the polar night. These descending particles pass through a region of higher temperature and higher relative humidity, and it is not clear that they survive

Ozone-destroying catalytic cycles

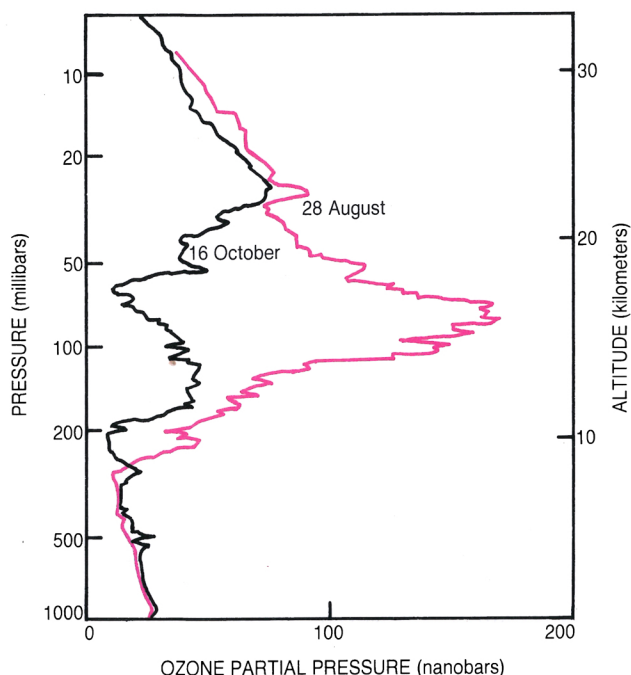
CIO dimer mechanism:



Br mechanism:



M represents a neutral molecule that has some momentum.



Ozone partial pressure as a function of altitude before and after ozone depletion. Maximum depletion occurs in the altitude range where ozone concentration is highest. Essentially all of the ozone has disappeared over this range. (Adapted with permission from ref. 2.) **Figure 4**

Sedimentation and coagulation

The gravitational sedimentation of small particles depends on particle size and air density. The terminal velocity of particles with radii between 0.5 and 10 μm can be calculated from a modified Stokes relation and is approximately linear with particle radius.

A 1- μm -radius particle will fall from 20 km to 10 km altitude in less than a year, whereas a 0.1- μm -radius particle requires 10 years to fall the same distance. On the other hand, a particle of radius 9.5 μm will fall 10 km in one week. The sulfate particles are so small that gravitational sedimentation is far too slow to account for their removal. However, gravitational sedimentation has a significant effect on polar stratospheric clouds, and gives rise to dehumidification and denitrification, particularly in the Antarctic stratosphere.

Atmospheric particles tend to stick together when they collide. In general this leads to changes in the particle size distribution. However, these changes are quite slow unless the number of particles is very large (as it is, for example, immediately following a burst of nucleation). Thus coagulation has little effect on polar stratospheric clouds: A characteristic time for coagulation to affect the size distribution of stratospheric particles is on the order of a year, whereas the characteristic lifetime of polar stratospheric clouds is measured in weeks.

Observing polar stratospheric clouds

Although much is yet to be understood, airborne, satellite and other studies are revealing the nature and the formation mechanisms of both the nitric acid and water-ice polar stratospheric clouds.

Nitric acid (type I) polar stratospheric clouds were initially postulated on theoretical grounds based on an extrapolation of high-temperature vapor-pressure data that indicated that in the stratosphere frozen NAT would form from nitric acid and water vapor at about 195 K. Laboratory experiments by David Hanson and Konrad Mauersberger on the vapor pressure of nitric acid trihydrate confirm that NAT should be stable at stratospheric conditions.¹⁷

There is now considerable evidence that the polar stratospheric cloud particles are indeed made of nitric acid. In 1987 NASA aircraft flew through stratospheric clouds over Antarctica and collected particles on filters and impactors. Bruce Gandrud and coworkers analyzed the filters and found particulate nitrate.¹⁸ R. Pueschel at NASA Ames Research Center analyzed stratospheric particles collected on impactors coated with nitron, a precipitating agent for nitrates. The reaction of the nitron with nitric acid led to the growth of nitron nitrate crystals, like the one shown in the scanning electron micrograph of figure 6. David Fahey and colleagues,¹⁹ using an NO_y detector (where y is 1 or 2), found enhanced NO_y when particles were detected by optical probes. They concluded that the temperatures at which the enhanced total nitrogen compounds were first observed were consistent with the temperatures at which

their fall. Even if they do evaporate, however, the nitric acid vapor might be incorporated into falling tropospheric snowflakes. If this happens, or if the particles fall to the ground intact, then ice-core samples of the Antarctic ice shelf should show an increase in nitrate corresponding to spring precipitation. Indeed, these records do give an indication of such a nitrate ion maximum. It has been suggested that recent increases in the spring nitrate maximum seen in the South Polar ice-core record result from the "rain out" of polar stratospheric clouds.¹⁶ Although this hypothesis has not yet been supported by other evidence, it is interesting because it implies that the extent and persistence of polar stratospheric clouds may be increasing.

The time scales for growth and evaporation determine the relative importance of various processes. For example, the stratospheric sulfate aerosol is in equilibrium with water vapor and grows by the absorption of sulfuric acid molecules. The number of vapor-phase sulfuric acid molecules in the stratosphere is very low (on the order of 4×10^4 molecules/ cm^3 at 20 km) because most of the sulfuric acid is in the condensed phase. Therefore the rate at which H_2SO_4 molecules impinge on a sulfate particle is quite low, and its characteristic growth rate is on the order of 0.1 micron per year.

In late autumn, prior to the formation of polar stratospheric clouds, the amount of nitric acid in the vapor phase is about 5 parts per billion by volume, some five orders of magnitude larger than the gas-phase concentration of sulfuric acid. The growth rate of type-I clouds is correspondingly larger than the sulfate particle growth rate. Because the water-vapor concentration is 2–5 ppmv, type-II clouds grow even faster. In fact, the growth times for type-I and type-II clouds are so short (hours or less) that their sizes are controlled mainly by rates of temperature change. One can assume for most practical purposes that as the temperature decreases the particles attain their equilibrium size instantaneously. Because the total condensable mass is relatively constant, the ultimate size of the particles is controlled by the number of particles that actually form. Therefore, as mentioned above, it is the nucleation mechanism that directly determines the final particle size.

NAT particles are formed. The particles probably have the NAT crystal structure, although they could possibly have the structure of other hydrates or even of super-cooled solutions.

The stratosphere has about 10 times as much nitric acid as sulfuric acid, so NAT particles grow considerably larger than do sulfate particles. If every sulfate particle served as a nucleation site, the resultant NAT particles would have a radius of about $0.33\text{ }\mu\text{m}$. On the other hand, if one-tenth of the sulfate particles provided a site for nucleation, the NAT particles would grow to roughly $0.7\text{ }\mu\text{m}$ in radius, and if only one out of a hundred sulfate particles were nucleated, the NAT particle radius would be about $1.5\text{ }\mu\text{m}$. Particles of this size have a fall velocity large enough to significantly deplete nitric acid from the stratosphere.

An interesting but not completely understood property of the nitric acid clouds is that when observed with polarized laser light, some of them reflect a highly depolarized signal whereas others reflect a signal whose polarization is unchanged.²⁰ These clouds are distinguished by the names type-Ia and type-Ib polar stratospheric clouds, respectively. Most likely the difference in polarization is related to differences in particle size, but variations in particle shape may also be involved. Size variations could result from selective nucleation under different environmental conditions, as described above. Indeed, on one Arctic mission flight, the two types of clouds were observed at the same temperature but in air masses that had different cooling-rate histories. This observation supports selective nucleation as the underlying cause for the difference between type-Ia and type-Ib cloud particles.

A probable scenario for the formation of the type-I polar stratospheric clouds involves the heterogeneous nucleation of nitric acid onto the surfaces of frozen sulfate particles. Because heterogeneous nucleation rates are a function of the radius of curvature of the substrate, this process may be the mechanism for selective nucleation. The number of NAT particles formed cannot exceed the number of sulfate particles but may be much less, depending on other factors. For example, if the temperature decreased slowly, the first nitric acid particles to form would absorb the excess nitric acid and prevent the formation of other particles, whereas rapid cooling would lead to high supersaturations and the nucleation of NAT particles on every available surface. It is also possible that only a fraction of the sulfuric acid droplets are frozen, limiting the subsequent number of nitric acid particles.

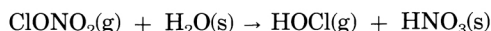
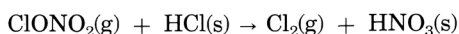
Water-ice (type II) polar stratospheric clouds appear when the temperature falls below the frost point—

typically 188 K for stratospheric conditions. On flights over Antarctica in 1987 ice crystals were picked up on wire impactors mounted on the wing tip of an ER-2 airplane.²¹ These crystals, collected in subsaturated air, may have been the remnants of previous type-II clouds. The crystals were mainly columnar and ranged from 6 to $50\text{ }\mu\text{m}$ in length and from 5 to $16\text{ }\mu\text{m}$ in width. The number densities were quite low for this particular set of observations: on the order of 100 particles per cubic meter, four orders of magnitude less than the number of sulfate particles.

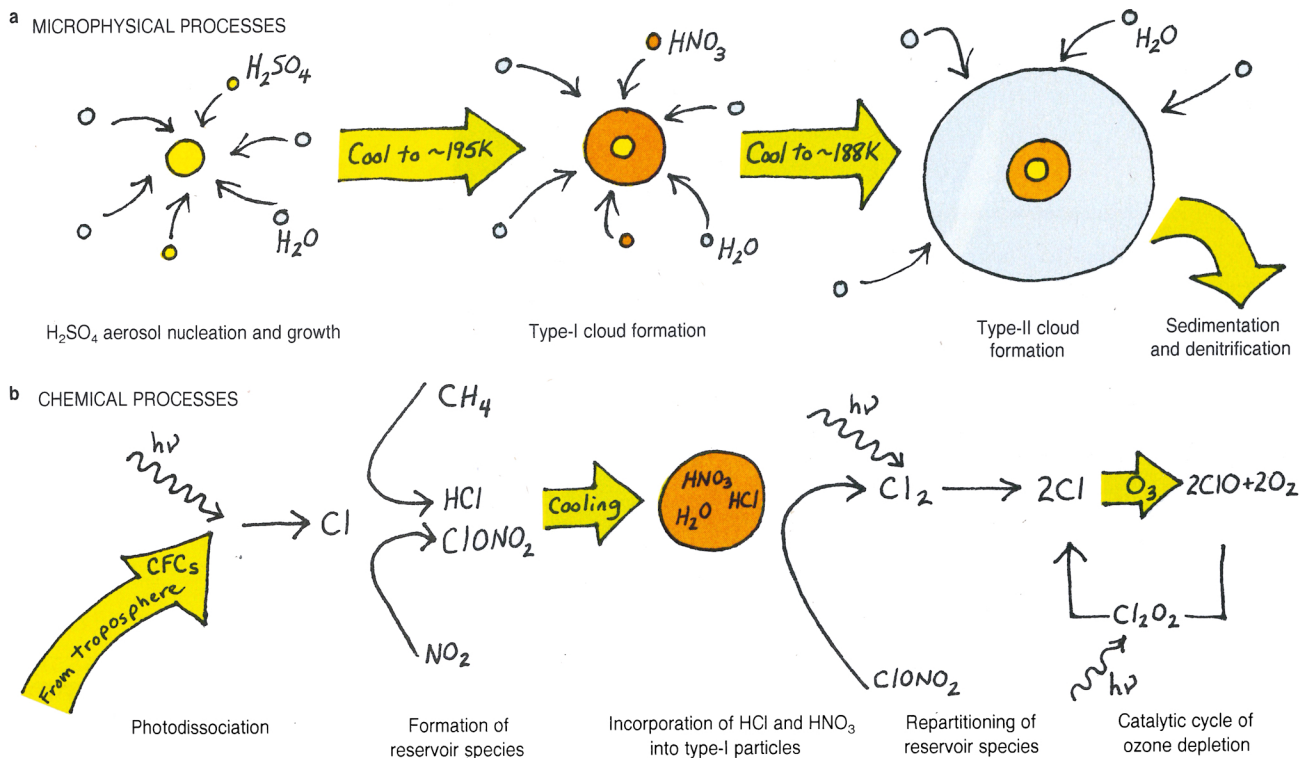
Because large ice crystals have significant net downward velocities (about 1 kilometer per day), if the ice crystals either form on the preexisting type-I particles or scavenge them, they will efficiently denitrify the stratosphere. Of course, the sedimentation of ice crystals also dehumidifies the stratosphere. This explains why the Antarctic stratosphere has some 5 ppmv water vapor in autumn but only about 2 ppmv in the spring. Because the Arctic stratosphere is warmer than the Antarctic, the Arctic has few type-II polar stratospheric clouds and dehumidification does not take place there. The Arctic stratosphere does undergo denitrification, implying either that over the North Polar region some sort of selective nucleation of NAT particles occurs, leading to larger NAT particles, or ice crystals falling from above the region of observation scavenge nitric acid droplets or vapor as the crystals pass through the region.

How the clouds affect the ozone

The currently accepted explanation for the formation of the ozone hole begins with the release of chlorofluorocarbons from ground level. On a time scale of decades these compounds are transported into the stratosphere, where they undergo photodissociation and release chlorine atoms. The chlorine may react with methane to form HCl. Alternatively, the chlorine may react with O_3 to form ClO, which then reacts with NO_2 to yield ClONO_2 . In either case, chlorine released by the dissociation of the CFC molecule is diverted into one of the nonreactive reservoirs, HCl or ClONO_2 , and little or no ozone destruction takes place. However, in the polar winter stratosphere, when cloud particles form, HCl dissolves into the particles, probably along grain boundaries. When ClONO_2 molecules collide with such a particle, the following chemical reactions take place:²²



where “g” and “s” indicate gas and solid, respectively.



Cloud particles may contribute to ozone destruction by depleting the stratosphere of nitrogen compounds and providing sites for heterogeneous reactions. **a:** Frozen sulfate particles in the stratosphere seed the heterogeneous nucleation of nitric acid particles. When the temperature drops to about 188 K, water-ice particles form. These particles can grow quite large and, through gravitational sedimentation, fall from the stratosphere. **b:** Chlorofluorocarbons photodissociate to form highly reactive chlorine. Chlorine can react with nitrogen compounds and methane to form less reactive "reservoir species." Sedimentation of the cloud particles denitrifies the polar stratosphere, eliminating this sink for reactive chlorine. Reactions of reservoir species reintroduce reactive chlorine, which at high levels enters a nonlinear catalytic cycle that destroys ozone. **Figure 5**

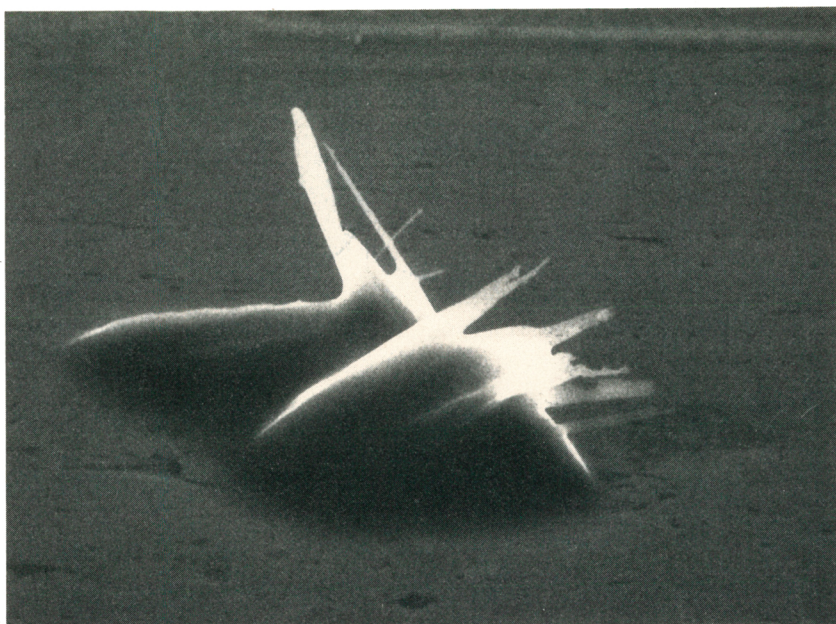
Thus polar stratospheric clouds become the source of chlorine, the agent of ozone destruction. As a result there is considerable interest in the effect of different substrates (ices of sulfuric acid, nitric acid and water) on the relevant chemical reaction rates. Numerous laboratory experiments are being carried out to evaluate absorption and reaction rates on these substrates.

Another effect of the polar stratospheric clouds is to denitrify the Antarctic stratosphere by the transformation of $ClONO_2$ to HNO_3 and by the subsequent sedimentation and removal of the particles. Nitric acid is also produced by the heterogeneous reaction $N_2O_5 + H_2O \rightarrow 2HNO_3$. This reaction reduces the amount of N_2O_5 in the environment, and because N_2O_5 is in a dynamic balance with NO and NO_2 , it reduces the concentrations of those species. This denoxification, which occurs at the surfaces of NAT particles, is crucial to ozone depletion because, as mentioned previously, NO_2 reacts with ClO to produce the reservoir species $ClONO_2$. During the polar spring low NO_2 concentrations allow the amount of free chlorine to remain high.

Recall that the repartitioning of chlorine from reservoir species to Cl_2 and $HOCl$ takes place during the polar night. These compounds do not affect ozone, so ozone levels remain high until the end of the polar night. Then in springtime the reappearance of the Sun leads to the photodissociation of $HOCl$ and Cl_2 into the reactive forms Cl and ClO . But springtime also brings the evaporation

of the polar stratospheric clouds. If all of the HNO_3 were once again released to the environment, photolysis would raise the NO_2 levels and the ozone destruction would be suppressed by the subsequent repartitioning of the Cl into $ClONO_2$. But the removal of nitric acid from the stratosphere, through the sedimentation of the polar stratospheric clouds, eliminates this sink for reactive chlorine, greatly enhancing ozone depletion. (There is some uncertainty as to whether or not *denitrification* is necessary for Antarctic ozone depletion, as *denoxification* may be sufficient for ozone destruction to take place. Nevertheless, it is clear that denitrification would greatly amplify the process.) In general the only way type-I (NAT) cloud particles can have sedimentation rates large enough to denitrify the stratosphere is for them to undergo selective nucleation so that only a very small percentage of the sulfate particles become NAT particles. However, type-II (ice) clouds always have a high sedimentation rate and could contribute to denitrification through scavenging.

One of the most interesting facets of the ozone hole phenomenon is that there is such a wholesale depletion of ozone in the Antarctic, whereas Arctic ozone is not depleted nearly as much. The 1989 NASA expedition to Norway determined that the Arctic atmosphere was chemically primed for ozone depletion, with levels of reactive chlorine as high as those observed in the Antarctic vortex. In fact about 25% of the ozone in the



Polar stratospheric cloud particles (shown enlarged 2000 times) collected on an impactor having a nitron substrate. The exfoliation of the particles seen in this scanning electron micrograph is an indication that they contain nitric acid, which reacts with the substrate. (Courtesy of R. Pueschel, NASA Ames Research Center.) **Figure 6**

Arctic vortex at and just above 18 km had been destroyed.

One reason that more substantial ozone loss did not occur may be that the stratospheric clouds of the Arctic vortex do not remain intact long enough for the chemical processes affecting ozone destruction to go to completion. The number of polar stratospheric clouds observed by satellite in the Arctic is less than a tenth the number observed in the Antarctic, and they tend to be found at higher altitudes.

Although reaction rates on polar stratospheric clouds are so rapid that even a brief appearance of the clouds can lead to the chemical alteration of the form of chlorine in the air mass, at ambient chlorine levels the rate of ozone loss is $\frac{1}{2}$ –1% per day. So a more probable explanation for the relatively small Arctic ozone depletion is that the North Polar stratospheric clouds do not last long enough to denitrify the region of the stratosphere where ozone is most abundant.

It was good fortune indeed that the polar stratospheric clouds were observed before the discovery of the ozone hole. Had it not been for our knowledge of them it is doubtful that our understanding of the mechanisms of Antarctic ozone depletion would have developed so quickly.

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