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## **Group Report**

# **Changes in Antarctic Ozone**

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### **INTRODUCTION**

Since the discovery by Farman et al. (1985) of a sharp drop in the springtime ozone column over Halley Bay starting in the mid-1970s, there has been a great deal of speculation about the causes of this dramatic and probably unprecedented change. Several theories have been proposed invoking solar cycle effects, changes in circulation patterns, or the possible effects of chlorofluorocarbons (CFCs). At the time of the discovery, observations of atmospheric parameters needed to validate or reject these theories were either not available or too sparse to provide the required information. A first expedition was organized to collect measurements from the U.S. station of McMurdo in spring 1986. A larger campaign took place in August and September 1987, during which measurements were taken from two aircraft based in Punta Arenas, Chile, and flying at about 11 and 18 km. Again, measurements were made from the McMurdo station. Additional observations made at the Japanese station of Syowa, the British station of Halley Bay, the U.S. station of South Pole, the Forster station of the German Democratic Republic, the Scott Base of New Zealand, as well as ozone and meteorological data provided from satellite instruments such as TOMS, SBUV, SAGE II, and operational meteorological satellites are also available.

In this report, we discuss some of the key issues as well as some important unresolved problems related to the rapid ozone change over the Antarctic continent in August, September, and October. The morphology of ozone and temperature changes will first be discussed, as will the formation and morphology of polar stratospheric clouds (PSCs) because of their potential importance for the release of active chlorine from chlorine reservoirs. Recent observations of trace gases, which provide useful information to validate chemical as well as dynamical theories, will then be discussed. It is important to determine whether the chemistry is sufficiently perturbed to destroy ozone in periods of the order of one month or less and to establish what processes are responsible for the ozone reduction. In particular, the role of heterogeneous processes, which are believed to be important in the cold polar stratosphere, will be discussed. Also, the present status of dynamical theories in light of the recent observations will be addressed. Two questions will be raised in conclusion: (a) Do we now understand the time evolution of Antarctic springtime ozone over the last 20 years? and (b) What are the implications of the observed depletion for the global Earth system, today and in the future?

## THE MORPHOLOGY OF THE ANTARCTIC OZONE DECREASE

The primary ozone decrease since the mid-1970s has occurred in the cold southern polar vortex region in the early spring. There is evidence from satellite measurements of total ozone that the decrease is not entirely confined to the cold polar vortex but that lesser changes extend outward to about 45°S through the warm circumpolar ring of higher total ozone (Stolarski, this volume).

Measurements from McMurdo in 1986 (Hofmann et al. 1987) indicated that the altitude of the ozone-depleted region ranged from 12–22 km. Measurements in 1987 over Halley Bay (Farman 1987), shown in Fig. 1b, indicate that the main depletion region was slightly higher in altitude. SAGE II measurements (McCormick, private communication) show a clear difference between inside and outside the vortex at altitudes up to 1 mb (Fig. 1a) but show no significant year-to-year change within the vortex above approximately 30 km. A question related to the altitude dependence is whether there is an ultimate lower limit for column ozone amounts. If the effect is confined to a 10 km band near the ozone peak, the 1987 minimum data within much of this region are almost as low as possible. Unless the effect spreads to include higher and/or lower altitudes, it will be difficult to find significantly lower total ozone amounts. Although the major ozone decrease occurs during the spring, there is evidence of smaller changes during other seasons. They may be related to dilution effects following the breakdown of the polar vortex (discussed later in this chapter) and need to

be confirmed to the extent possible by an intercomparison of all available sonde, satellite, and Dobson data. In September, when measurements in the sunlight just outside the polar night are beginning to show a significant decrease in the total ozone, polar night measurements at the South Pole (Komhyr et al. 1987) seem to indicate that ozone there has not yet changed. This needs confirmation as it clearly seems to indicate the role of solar radiation.

The beginning of the decrease appears to be in August when "mini-holes" appear at latitudes just outside of the polar night. These usually last a few days and then disappear. Eventually, by about mid-September, several of these holes appear together and seem to conglomerate into one large region of low ozone within which the ozone levels continue to decline through the first week in October. It is not yet clear whether or not there is any causal connection between the mini-holes and the overall pole-centered ozone hole. More evaluation of the meteorological data in relation to their formulation is needed.

All of these changes are superposed on an uncertain and highly variable background ozone distribution. Measurements prior to the mid-1970s were limited. From the available measurements it appears that the latitude distribution of total ozone always had a springtime polar minimum in the South, although it was very shallow. This was surrounded by a highly variable circumpolar maximum.

## TEMPERATURE VARIATIONS OVER ANTARCTICA

The existence of interannual variations in mean polar temperatures in winter is now well established. However, the cause of these changes and their consequences on the polar ozone variations remain an open question. For example, there is clear evidence that the northern stratosphere was colder and the polar vortex stronger during the winters following the volcanic eruption of Mount St Helens and El Chichon. The intrusion of particles of volcanic origin might have played a role in also delaying the timing of the final warming over the South Pole. There also appears to be a relationship between the decreased ozone values in the mid-1980s and declining October mean temperatures (Mahlman and Fels 1986; Fig. 2). No evidence is available for corresponding temperature decreases in August and September.

The correlation between total ozone and 50 mbar October temperatures is known from recent observations to be very high (e.g.,  $r = 0.8$  for Syowa, or  $r = 0.6$  for the South Polar station) but the slope of the correlation changes after 1981. Since 1982, the total ozone values are clearly lower than expected from the correlation suggested by the earlier measurements (Labitzke 1987); see Fig. 2. This abnormal behavior provides indirect evidence for perturbed chemistry.



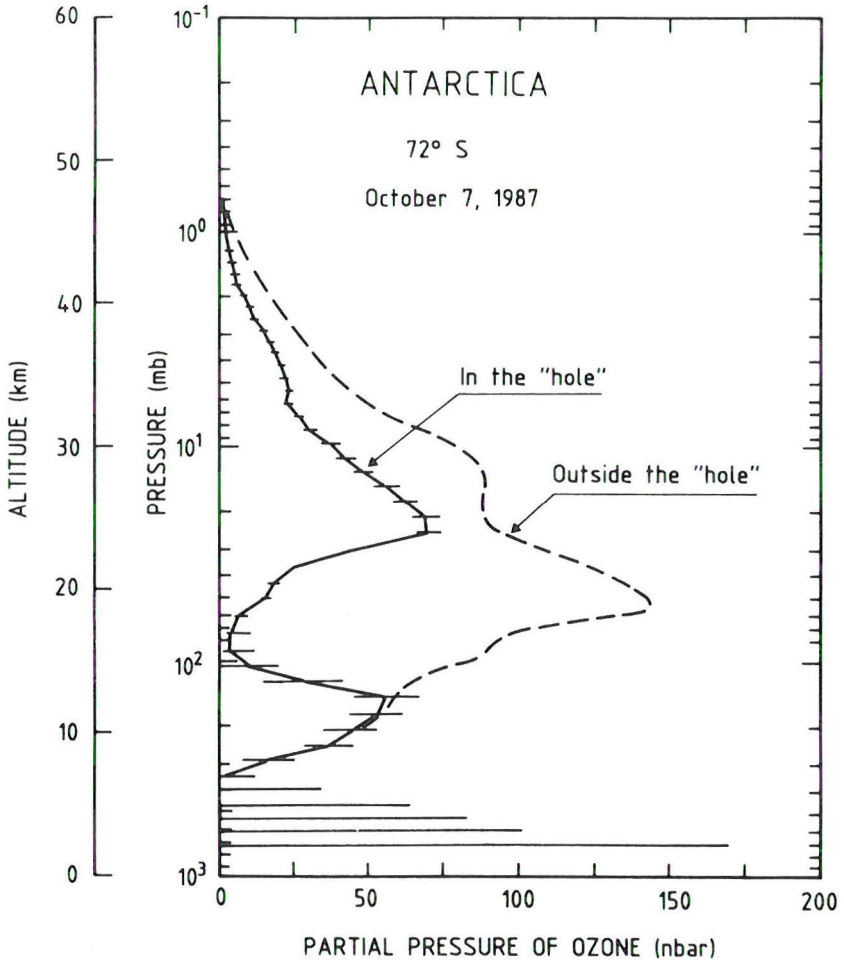


Fig. 1a—Vertical profile of the ozone partial pressure (nbar) observed by the SAGE II instrument on October 7, 1987. The curve labelled "in the hole" represents the lowest abundance of ozone measured at 72°S, and the curve labelled "outside the hole" shows a profile measured at the same latitude but outside the region of highly depleted ozone (McCormick, personal communication, 1987).

## THE MORPHOLOGY OF POLAR STRATOSPHERIC CLOUDS

Remote sensing measurements made by the satellite sensor SAM II starting in late 1978 have shown that more stratospheric clouds exist in both winter polar regions than had been realized by earlier visual sightings. They were named polar stratospheric clouds (PSCs) (McCormick et al. 1982) and found not to be just confined to the lee side of mountain ranges, but were strongly associated with synoptic-scale regions of very cold stratospheric temperatures.

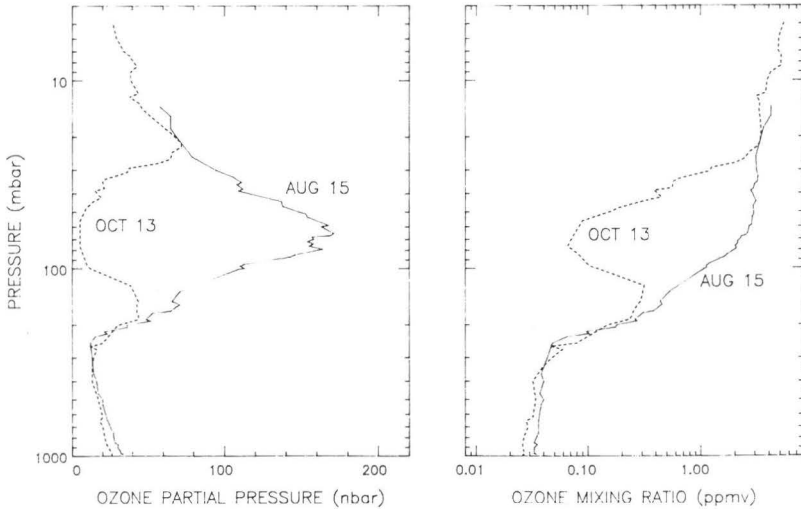


Fig. 1b—Vertical distribution of the ozone partial pressure (nbar) and volume mixing ratio observed at Halley Bay station on August 15, 1987 (high values) and October 13, 1987 (low values) respectively (Farman, personal communication, 1987).

The first idea put forth to describe the initial data was that the clouds were probably formed by the deposition of water vapor into the preexisting stratospheric aerosol droplets (made of sulfuric acid and water) at temperatures below the frost point. Recent studies have proposed that PSCs form initially at temperatures above the frost point as solid solutions of nitric acid and water rather than as solely pure water ice (Toon et al. 1986; Crutzen and Arnold 1986). McElroy et al. (1986) supported this idea of PSC formation by co-deposition of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  vapors but suggested that the cloud particles would be acid-rich or acid-poor  $\text{HNO}_3$  hydrates. Figure 3, from McCormick and Trepte (1987), shows the SAM II weekly averaged polar stratospheric optical depth record at  $1 \mu\text{m}$  wavelength for the years October 1978 to December 1986. Both polar regions clearly show that the overall aerosol trend is driven by major volcanic eruptions, which are annotated on the abscissa with their eruption times. The largest increase in this record was caused by the April 1982 eruption of El Chichon. In addition, the Antarctic record clearly shows yearly enhancements in austral winter caused by the presence of PSCs. (See, for example, the large order of magnitude enhancement from June to September, 1979.) This signature is repeated each year even in the presence of the strong volcanic levels after the El Chichon eruption.

Another feature shown in the Antarctic record of Fig. 3 is the noticeable minimum occurring each year in October. At this time the vortex is still

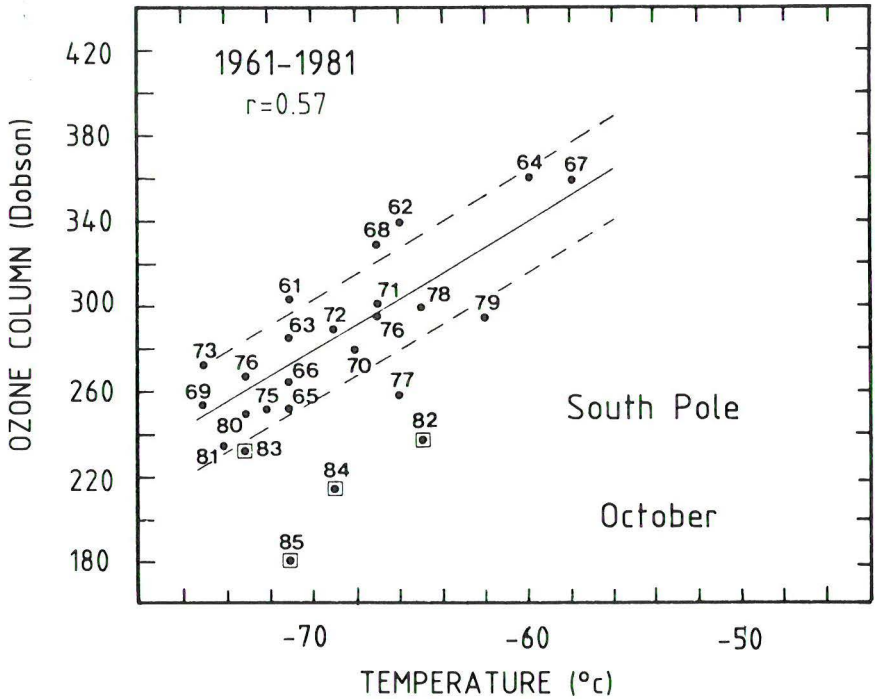


Fig. 2—Relation between the monthly average ozone column and the 50 millibar temperature over the South Pole in October between 1961 and 1985.

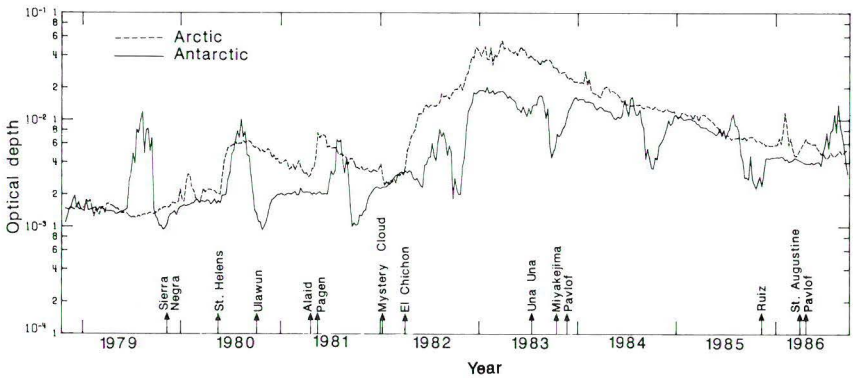


Fig. 3—SAM II weekly averaged polar stratospheric optical depth at 1  $\mu\text{m}$  over the Arctic and Antarctic regions from October 1978 to September 1986 (McCormick and Trepte 1987).

well-formed with SAM II measurements occurring within the vortex—the minimum indicating that a cleansing has occurred between the pre- and post-PSC period. Subsidence of the air in the major altitude region of aerosols and PSCs (10–25 km) is probably not strong enough to cause this cleansing over this period, nor could the sedimentation of aerosols of PSCs normally thought to be less than or equal to about  $1\ \mu\text{m}$ . Recent studies by Poole (1987) and Poole and McCormick (1988a) with experimental evidence given by Poole and McCormick (1988b), however, support the suggestion that these particles have more than one growth mode delineated by temperature. A stage of nitric acid trihydrate deposition is interposed between the two stages of cloud growth assumed in earlier PSC studies; that is, between the aerosol droplet precursors and ice particles. Figure 4 shows the calculations for three specific temperatures: the end of the precursor stage at about 195 K; just prior to the end of the  $\text{HNO}_3/\text{H}_2\text{O}$  deposition stage at about 191 K; and below the frost point at about 189 K. About 80% of the nitric acid and 30% of the water vapor supplies may be sequestered in the relatively large  $8\ \mu\text{m}$  diameter PSC particles formed at and below the frost point temperature. These large particles would fall at a rate of about 2 km per week, fast enough to produce the October cleansing shown in Fig. 3, also suggesting that PSCs may act as a sink for stratospheric trace gases, in this case  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ . It might be possible for other gases to condense like HCl and, at a minimum, to redistribute in altitude certain stratospheric gases.

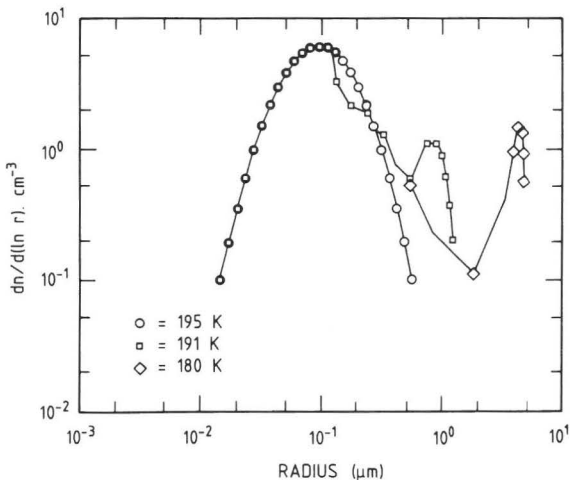


Fig. 4—Evolution of the nonvolcanic particle size distribution at 70 mbar with temperature. Cooling rate  $-0.5\text{K/day}$  (McCormick, personal communication, 1987).



Figure 5 shows the SAM II weekly averaged aerosol extinction ratio (aerosol extinction divided by molecular extinction) for Antarctica as a function of time for the years 1980, 1982, and 1984 (McCormick and Trepte 1986). As previously described, it also shows the vertical extent of PSCs correlated with cold temperatures, the subsidence/sedimentation that takes place during each wintertime period, the relative minimum in October, and the large overall increase in stratospheric aerosols after the April 1982 eruption of El Chichon in the Southern Hemisphere starting in approximately November 1982.

A number of measurements would further the understanding of PSCs and the mechanisms involved in their formation. Accurate temperature, water vapor, compositional measurements, and vertical velocity measurements would all be helpful, as would of course more measurements of their spatial and time variability. There are a lot of studies that can be done, however, without obtaining new data, but rather by using the data already obtained by SAM II and lidar measurements. These would include studies attempting to determine if there has been (a) an increase of Antarctic PSCs over the past winters; (b) an increase in the vortex period before vortex breakdown; (c) an increase in low altitude PSCs; and (d) a change in altitude distribution of PSCs. Because of the correlation of PSCs and cold temperature, areal maps of temperatures less than ca.  $-80$  and  $-85^{\circ}\text{C}$  at 70 and 50 mb would also be useful in determining the area versus time where PSCs are probable.

## OZONE DESTRUCTION

The destruction of ozone in the stratosphere is catalyzed by the presence of nitrogen oxides and chlorine oxides. Generally, these processes are slow in the lower stratosphere so that the rapid destruction of ozone, appearing in the polar region after the return of solar light, becomes possible only if the abundance of these catalysts is several orders of magnitude larger than observed at midlatitudes. Observations of odd nitrogen species in 1986 and 1987 suggest that the densities of  $\text{NO}_y$ ,  $\text{HNO}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  are so low that the rapid destruction of ozone cannot be attributed to active nitrogen produced in the thermosphere and transported into the lower stratosphere in the very stable polar vortex. This possible explanation was invoked to link the springtime ozone depletion to solar activity, which affects the production of odd nitrogen above 100 km altitude.

If active chlorine is released from reservoirs, such as  $\text{ClONO}_2$  and  $\text{HCl}$  (which are the most abundant odd chlorine species in the lower stratosphere under "standard" conditions), different catalytical cycles could be responsible for the destruction of ozone. Below approximately 25 km, where the concentration of atomic oxygen is very low, several possible cycles have been considered. The efficiency of the following cycle

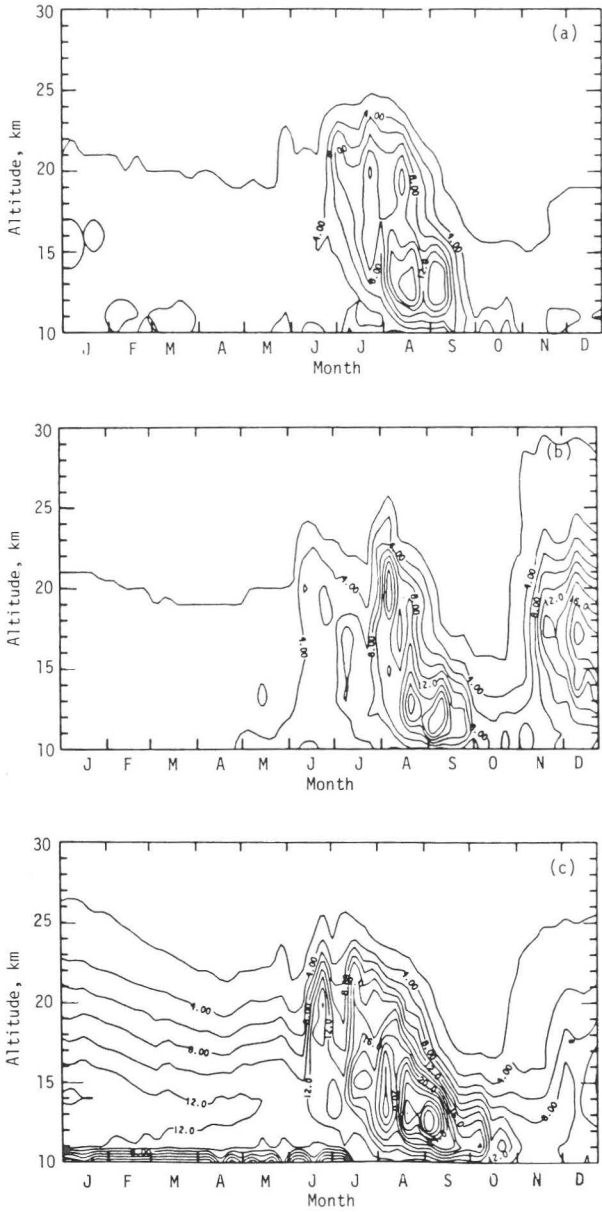
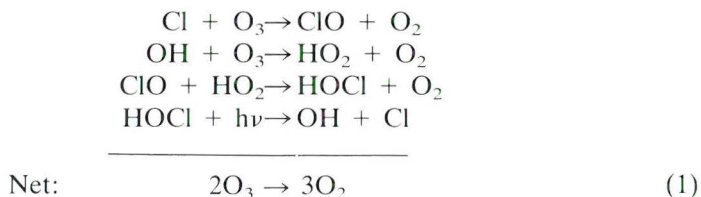
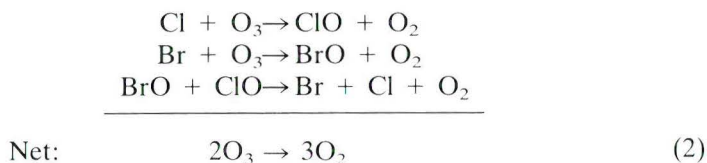


Fig. 5—Contour plots of SAM II weekly averaged extinction ratio at 1  $\mu\text{m}$ . (a) 1980; (b) 1982; and (c) 1984 (McCormick and Trepte 1986).



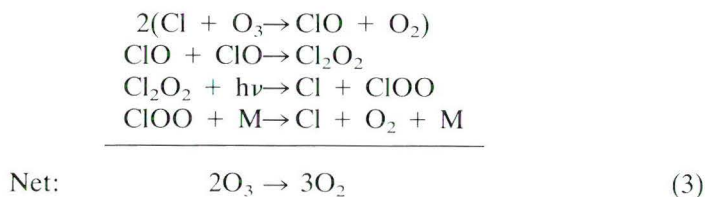
is difficult to assess since the abundance of HO<sub>2</sub> in the polar stratosphere in spring is not known. With HO<sub>2</sub> densities similar to the midlatitude values, and even with ClO concentrations as large as 1 ppbv, this cycle alone cannot account for the observed ozone trend in spring near 15–20 km. But if the amount of odd hydrogen radicals is significantly enhanced, it could play a major role.

A second cycle (McElroy et al. 1986)

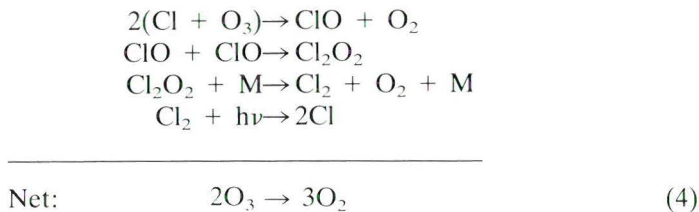


requires the presence of bromine. With the recent measurements of BrO, suggesting a mixing ratio of only a few pptv at 18.5 km altitude, this cycle could contribute to at most 10% to 20% of the ozone destruction at 18.5 km but cannot be the dominant loss mechanism at this level.

Finally, the following cycles (Molina and Molina 1987)



and (Molina et al., submitted)



are other potential ozone destruction mechanisms which can, within a factor of two, explain the observed ozone destruction if the abundance of ClO is of the order of 0.5–1 ppbv and if the measured value of the rate constant for the rate limiting step (i.e.,  $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2\text{O}_2$ ) is correct. Measurements of lower stratospheric ClO by deZafra et al. (1987) and P. Solomon et al. (1987), with a millimeter wave spectrometer during the 1986 Antarctic spring, showed that the ClO mixing ratio in the region around 20 km was close to 1 ppb. These measurements further showed that the lower stratosphere ClO remained high during most of September but declined (see Fig. 6) substantially by mid-October, providing further evidence for a coincidence between excess ClO and the time of ozone depletion. Measurements of OClO (S. Solomon et al. 1987) showed additional evidence of peculiar chlorine chemistry. More recent measurements, made by Anderson during the 1987 aircraft campaign, indicate that the ClO abundance reaches these high values at 18.5 km altitude inside a sharply defined region, appearing to be a "chemical containment vessel" (CCV). Outside this region, the mixing ratio of ClO is a factor of approximately 100 lower than inside the CCV, but is still a factor of about 10 higher than at midlatitudes at the same level. No data of ClO from this experiment is available above 18.5 km. Below 18 km, the mixing ratio of this radical decreases rapidly, so that the cycles described above cannot quantitatively explain the observed ozone loss at much lower altitudes. The rapid falloff in ClO with altitude is not understood and suggests that the processes involved in controlling the abundance and partitioning of chlorine need to be more fully studied. One problem that needs to be addressed is the behavior of OClO. OClO is one of the products resulting from the  $\text{ClO} + \text{BrO} \rightarrow \text{Br} + \text{OClO}$  reaction. Day-to-night ratios observed in 1986 at McMurdo appear to be significantly lower than suggested by model calculations. Since the observed abundance of BrO is only a few ppt, another production mechanism of OClO may need to be suggested. The photolysis of  $\text{Cl}_2\text{O}_2$  could result in the formation of Cl and OClO if the structure of the dimeric  $\text{Cl}_2\text{O}_2$  is ClOClO rather than ClOOCl. The formation of OClO would lead to a null cycle, and thus no ozone destruction would take place through this cycle. The formation of  $\text{Cl}_2 + \text{O}_2$  as products of the dissociation of  $\text{Cl}_2\text{O}_2$  should also be considered. Laboratory work dealing with these questions is urgently needed.

Despite these uncertainties, strong negative correlations between ClO and  $\text{O}_3$ , observed at 18.5 km on a macro- as well as on a microscale during the second half of September, strongly suggest that chlorine plays a major role in the formation of the "ozone hole."

Measurements of chlorine reservoirs have also become available. The abundance of HCl in the CCV, as measured by infrared techniques, appears to be extremely low, so that the existence of a strong transformation mechanism of HCl into free chlorine or the eventual condensation of HCl vapor onto particles must be considered. There is no measurement of HOCl

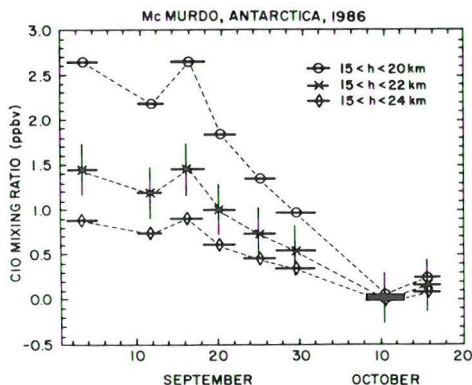


Fig. 6—Observed trend in lower stratospheric ClO over McMurdo Station (Solomon et al. 1987) during September and October 1986. The mixing ratios are assumed to be constant over the altitude range from 15–20 km (circles), 15–22 km (crosses), and over 15–24 km (diamonds). The dashed lines connecting the data are meant only as a guide.

available, but relatively high column values of  $\text{ClONO}_2$  compared to midlatitudes have been observed (Farmer et al. 1987).

Inside the CCV, it is observed that the lower stratosphere appears to be highly dehydrated and denitrified. In this region, chlorine can thus very efficiently attack ozone molecules if reservoirs such as HCl and  $\text{ClONO}_2$  are converted into active chlorine. We still need to understand why high ClO amounts are produced in the chemical containment vessel which is close to, but does not exactly coincide with, the meteorological polar vortex. This question will be addressed in the next section.

## FORMATION OF ACTIVE CHLORINE

The measurement of high ClO concentrations suggests that chlorine atoms are liberated in the chemical containment vessel. Solomon et al. (1986) proposed that surface catalyzed reactions on ice particles of HCl with  $\text{ClONO}_2$  and of  $\text{ClONO}_2$  with  $\text{H}_2\text{O}$  would produce the required quantities of active chlorine to destroy ozone over less than a month. Solomon et al. (1986) and McElroy et al. (1986) also suggested that nitrogen oxides could be efficiently converted to gaseous  $\text{HNO}_3$  through reactions of  $\text{N}_2\text{O}_5$  (and  $\text{ClONO}_2$ ) with  $\text{H}_2\text{O}$  on the surface of these ice particles. More recently, however, Molina et al. (1987) showed that photolytically active chlorine ( $\text{Cl}_2$ ) is liberated in the gas phase from a collisional reaction of  $\text{ClONO}_2$  on the surface of ice containing dissolved HCl, whereas the other product,  $\text{HNO}_3$ , remains in the condensed phase. Since HCl molecules dissolve



readily in the ice, this mechanism (which will be considered with further details in the next section) could play a significant role in the formation of active chlorine.

It was also recognized by Toon et al. (1986) and by Crutzen and Arnold (1986) that the aerosol particles in the polar stratospheric clouds could be composed of nitric acid and water in roughly the same mass fraction. If  $\text{HNO}_3$  condenses on background atmospheric aerosols and disappears from the gas phase, the most efficient OH destruction mechanism is suppressed and the OH density in the lower stratosphere could reach values as high as  $10^7 \text{ cm}^{-3}$ . The presence of these large OH abundancies should lead to a rapid transformation of HCl into free chlorine and subsequently to the formation of ClO. This latter mechanism does not involve chlorine reservoir species in the surface catalyzed reactions but introduces a critical dependence of the ozone destruction efficiency on atmospheric temperatures. Also, as in the case of the Solomon et al. (1986) mechanism, it restricts the ozone destruction to about 10–25 km altitude. Several questions need to be addressed to validate these theories. For example, it is important to determine if  $\text{HNO}_3$  effectively disappears from the gas phase (or is significantly reduced) during the polar winter season and if large OH densities are produced as soon as the sun returns over the pole. Furthermore, the mechanisms involved must become efficient as early as late August and early September since most of the ozone is destroyed before early October. A definitive validation of these proposed explanations requires a clear understanding of the details involved in the different potential heterogeneous processes occurring in the polar stratospheric clouds.

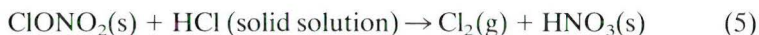
## THE ROLE OF HETEROGENEOUS PROCESSES

All of the contending theories of ozone hole formation implicitly or explicitly involve “heterogeneous” chemical processes (as distinguished from homogeneous gas-phase processes). However, the treatments have been largely qualitative in nature, without complete simulations of the physical and chemical steps leading to heterogeneous effects. This is a practical result of the fact that the heterogeneous processes of interest are not well defined by fundamental experimental measurements or physical models. Accordingly, treatments employed in atmospheric chemistry models must be rather speculative.

The possibility of heterogeneous chemical effects is strongly supported by a variety of observations and analyses, none of which are individually decisive. Observations of highly perturbed chemistry within the southern winter polar vortex strongly suggest unusual precursor processes outside the normal range of behavior of known homogeneous atmospheric chemical systems. Much new, and perhaps more conclusive, data will soon be available

from the 1987 Ozone Hole research project. However, even without this critical data, a relatively consistent and logical argument for substantial heterogeneous reactions can be made. These arguments have been expressed or developed to varying degrees in numerous papers (Solomon et al. 1986; McElroy et al. 1986; Crutzen and Arnold 1986; Toon et al. 1986; Hamill et al. 1986; Poole and McCormick 1988a). The basis for our present confidence in these possibilities derives from the following information:

1. the clear establishment of PSC formation in the winter polar vortex (in both hemispheres) by satellite and aircraft observations;
2. plausible thermodynamic arguments on the condensation of multicomponent solid compounds of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  under conditions representative of the polar winter stratosphere;
3. the broad consistency of a PSC nitric acid ice formation mechanism with observed PSC morphology and physical properties, polar meteorological parameters, air composition data, and aerosol microphysical principles;
4. laboratory measurements of ice-catalyzed chemical reactions that would otherwise occur very slowly under stratospheric conditions. Molina et al. (1987) have delineated the following key reactions:



where  $\gamma$  is the  $\text{ClONO}_2$  "collision efficiency" for the reaction (roughly 0.05 for the first reaction and 0.02 for the second reaction), s = surface adsorbate, and solid solution of  $\text{HCl}$  in ice represents an absorption of  $\text{HCl}$  molecules into the crystal lattice;

5. the consistency between observed and estimated PSC particle sedimentation rates and observed  $\text{H}_2\text{O}$ ,  $\text{NO}_y$ , and  $\text{HNO}_3$  depletions in the lower winter polar stratosphere.

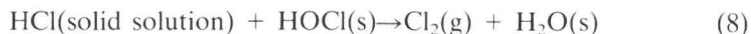
The existence of widespread clouds in the polar winter stratosphere has been established by data from the SAM II satellite system launched in 1978 (McCormick et al. 1979). (Details of the cloud morphology are discussed elsewhere in this report and in the scientific literature.) When the "ozone hole" problem was discovered in 1985, it became apparent that the clouds might have a role in modifying stratospheric chemistry, leading to accelerated ozone destruction (e.g., Solomon et al. 1986).

Based on estimates of thermodynamic parameters for binary ices, Toon et al. (1986) and Crutzen and Arnold (1986) independently concluded that nitric acid/water crystals might condense in the extremely cold winter polar vortex at temperatures above the frost point of water, explaining the appearance and properties of PSCs under certain conditions. Nevertheless,

vapor pressure data on  $\text{HNO}_3/\text{H}_2\text{O}$  ices are lacking, and definite conclusions on the precise composition of the condensates cannot be determined. Also, HCl probably condenses under polar winter conditions (Toon et al. 1986) as "solid solutions" of HCl in water ice (Molina et al. 1987). Although details of the properties of these solid solutions are unknown, under polar stratospheric conditions they would probably be composed of a few percent or less of HCl in ice (M. Molina, personal communication, 1987). The formation of nitric acid/ice aerosols and consistency with PSC observations are discussed by a number of authors (McCormick and Trepte 1986; Hamill et al., submitted; Rosen et al., submitted; Poole and McCormick 1988b). The evidence for nitric acid ice PSCs includes lidar backscatter depolarization measurements (Poole and McCormick 1988b), which indicate the formation of relatively small PSC particles in regions with temperatures from about 190–195 K (the solid nitric acid/water ice regime) and large ice crystals in regions with temperatures below about 185–190 K (the water frost point). The direct measurement of efficient  $\text{ClONO}_2 + \text{HCl}$  and  $\text{ClONO}_2 + \text{H}_2\text{O}$  reactions on ice surfaces (Molina et al. 1987) constitutes a major step in developing theories of heterogeneous chemistry for the ozone hole. Questions remain about other potential heterogeneous processes. Rowland (this volume) and others speculate that a number of similar reactions may occur in the polar winter stratosphere, e.g.,



P.J. Crutzen (private communication) also emphasized that the exothermic process mentioned by Rowland (this volume),



could play a significant role.

Rudimentary evidence exists for the catalysis of such types of reactions on surfaces in a laboratory setting. However, there is no data available for stratospheric conditions, and at the present time these additional mechanisms remain speculative.

Uncertainties in the heterogeneous chemical mechanisms result from a lack of information on the thermodynamics of condensation and the absorption/adsorption of various compounds on ice at temperatures below 200 K, the quantitative rate coefficients and mechanisms for specific heterogeneous reactions that may affect ozone concentrations, and the actual composition and properties of polar stratospheric aerosols and clouds. The role of heterogeneous chemistry in controlling ozone photochemistry during the polar ozone hole season depends in a complex way on the evolution of gaseous species concentrations; the formation, settling, and evaporation of

PSCs; and the unique variation in solar radiation levels during the period of the ozone hole appearance. The processes involved are often competitive, and therefore careful rate determinations are necessary to resolve potential pathways. Moreover, the polar regions of interest are not homogeneous, and substantial variation with altitude, geographical locations, and time must be considered in analyses.

## PRESENT STATUS OF DYNAMICAL THEORIES

It has been suggested that changes in the strength of the atmospheric circulation and formation of transient rising motions over the pole with the return of the sun in spring could explain the sudden decrease of ozone in September over Antarctica. For dynamics to play a role, a necessary requirement is that the tropospheric dynamical forcing of the lower stratosphere has decreased since the mid-1970s. The consequences of lower forcing, as hypothesized by Mahlman and Fels (1986), can be characterized by (a) colder temperature in the polar winter region and a longer-lived polar vortex (longer Southern Hemisphere winter); (b) higher zonal winds; (c) weaker diabatic circulation and reduced downward high latitude mass flow; (d) decrease in Southern Hemisphere mean ozone; and (e) formation of a more efficient polar vortex containment vessel. As discussed by Tung (1986), assuming the above conditions, a transient high latitude circulation cell could be formed with rising motions over the pole as the sun returns after the long polar night period. For such a circulation to occur the Antarctic lower stratosphere must be near its radiative temperature at the end of the winter.

Analysis of meteorological data as well as observations of trace species recently made over Antarctica have produced some information about potential climatological and dynamical changes relative to the above-hypothesized changes. For example, there is evidence that the lower tropospheric forcing of the stratosphere has decreased since, as shown by Nagatani and Miller (1987), the vertical component of the Eliassen-Palm flux observed in September has been reduced since 1979. Such a September decrease might be expected to result in a corresponding decrease in the October polar temperatures, given a typical time lag of a few weeks for the stratosphere to respond to such a change. There is evidence that the temperature over the South Pole has decreased in the 1980s, at least in October (Mahlman and Fels 1986; Labitzke 1987), but the existence of a year-to-year trend is less clear for August and September. A significant trend in the zonal winds and in the meridional circulation has not been clearly established. However, reduced ozone amounts from year to year, not only in the polar region but also at midlatitudes in the Southern Hemisphere, have been observed by space-borne instruments (SBUV and



TOMS). More importantly, there is now clear evidence that systematic slow rising motion does not occur in spring inside the polar vortex. On the contrary, the very low concentrations of source gases measured at 18.5 km in August and September 1987, consistent with the reanalyzed millimeter emission spectra recorded at McMurdo (Parrish et al. 1988), suggest weak but persistent downward motions in the lower stratosphere in September and October. The observed seasonal temperature increase during this period has therefore to be of dynamical rather than of radiative origins required by the Tung (1986) and Mahlman and Fels (1986) hypotheses. This is because the Punta Arenas high altitude aircraft data provides indirect evidence for net diabatic cooling inside the polar vortex as the temperature slowly warms up in September.

This conclusion provides strong indirect support for the view that the formation of the "ozone hole" arises from efficient chemical mechanisms. The late September-October ozone decreases are consistent with dynamical control in the sense that the ozone integral poleward of 45°S is nearly conserved as the "hole" goes through its last deepening. As the hole deepens further, the ozone "high" associated with the midlatitude warm belt experiences a virtually simultaneous ozone increase (Stolarski and Schoeberl 1986). In addition, observations of rapid transient ozone decreases in the lower stratosphere have been associated with transport from middle latitudes. These processes may play a role in reducing the lower stratospheric ozone.

To summarize, dynamics appear to play an important role in setting up the cold, PSC-containing vortex, which is required for heterogeneous processes to occur. The significant differences in the dynamical and temperature conditions between the Northern and the Southern Hemisphere are consistent with the springtime ozone decrease being unambiguously observed at the South Pole rather than at the North Pole. The failure of the transient rising motions hypothesis argues in favor of the chemical ozone destruction in late August and September. However, the final ozone drop may be influenced by three-dimensional dynamical phenomena not yet well explained. For example, recent observations of lower stratospheric intrusions from lower latitudes suggest a role in desiccation and import of lower ozone air.

### **CAN WE EXPLAIN THE OBSERVED SPRINGTIME OZONE TREND OVER ANTARCTICA IN THE LAST 20 YEARS?**

The year-to-year variation of the mean ozone column in October over the Antarctic station of Halley Bay (see Fig. 2 of Rowland, this volume) exhibits a weak downward trend in the 1970s followed by a substantially faster decrease after 1980. The reason for this highly nonlinear behavior is not clearly understood. A doubling of the  $\text{Cl}_x$  abundance, which probably



occurred in the last 15 years or so, cannot itself explain a 50% ozone reduction without invoking other mechanisms not yet included in current atmospheric chemical models. Even if the amount of odd chlorine becomes similar or larger than the abundance of odd nitrogen, the nonlinear chemical processes occurring under such conditions cannot entirely explain the amplitude of the observed year-to-year decrease in springtime ozone or its sudden occurrence after 1979. Another cause for the abrupt reduction in polar ozone in the early 1980s could have been a cooling of the winter polar vortex. The consequence of even a slightly climatological temperature change could be increased polar stratospheric cloudiness, since heterogeneous nucleation of gases such as  $\text{HNO}_3$  occurs only if the temperature becomes sufficiently low. Below a certain "threshold,"  $\text{NO}_x$  and  $\text{HNO}_3$  should start to disappear from the gas phase and heterogeneous processes should become efficient, contributing to the formation of ozone-destroying agents. Cold winters have been observed repeatedly in the past. In addition, the mean polar temperature appears to change with the QBO and probably also with solar activity. The amount of particles in the stratosphere has varied by several orders of magnitude on different occasions after the eruption of volcanoes. The persistence of PSCs has increased in 1985 and 1987 with PSCs at 18 km lasting into the first week of October, 1987. There is also substantial evidence that the temperatures of the lower Antarctic stratosphere in October and November are now colder than in 1979, even though the August and September temperatures show little or no change from 1979–1986. Model calculations, even those including the effects of some heterogeneous processes, do not quantitatively predict the observed nonlinear ozone response when the only change is an increasing abundance of odd chlorine related to the amounts of chlorofluorocarbons released into the atmosphere over the last 20 years. However, the models have not yet fully treated the nonlinear behavior of the heterogeneous component of the chemical system. Further model investigations considering plausible changes in the atmospheric environment should thus be pursued. We need to understand, for example, why the observed rate at which ozone is depleted during the month of September does not seem to increase from year to year, while the rate of change predicted by atmospheric models becomes larger as the amount of chlorine increases.

In conclusion, although the preliminary findings from the most recent field experiments have provided much insight about the mechanisms involved in the Antarctic ozone depletion, it remains difficult at this time to provide a global and definitive explanation for the causes of this dramatic phenomenon and to understand quantitatively the long-term nonlinear ozone trend. In order to study the year-to-year evolution of Antarctic ozone, the relative contributions of chemistry and dynamics in the formation of the "ozone hole" need to be accurately determined, in particular, below 16 km where

the abundance of ClO is not particularly high and where the classical chlorine catalytic mechanisms do not appear to be able to account for the observed ozone changes.

### **WHAT ARE THE IMPLICATIONS FOR THE GLOBAL EARTH'S SYSTEM OF THE OZONE CHANGES OBSERVED OVER ANTARCTICA?**

Besides its dramatic character and its sudden appearance, a reason for concern about the "ozone hole" is that the processes, which appear to play a decisive role in the polar environment and which are neither fully understood nor included in atmospheric models, could be important at other latitudes and contribute to a global ozone depletion.

Since particles are present in the stratosphere at all latitudes, it is important to be able to estimate whether the processes involving heterogeneous reactions and possibly leading to ozone destruction could also occur in other regions of the atmosphere, particularly near the North Pole. In addressing this problem, it is useful to note that the polar temperatures of the Southern Hemisphere are, on the average, nearly 10 K colder than those of the Northern Hemisphere although the composition and physical properties of the aerosols should not be qualitatively different. For example, in the Antarctic polar stratosphere, where the temperature reaches 180–190 K at 10–20 km altitude, the frost point of water vapor can be reached, and large ice particles are formed. These may subside and disappear from the stratosphere. In Arctic polar regions, where the temperatures are less often in the 180–190 K range, a haze of relatively small (HNO<sub>3</sub>) PSC particles is expected to be formed more often than the larger PSC particles. Since the Arctic temperature increases at the end of the winter, essentially as a result of adiabatic processes, the PSCs should disappear before the sun returns over the North Pole. However, because of the high planetary wave activity in the Northern Hemisphere during winter, the vortex might be significantly displaced from the pole and reach an illuminated environment where photochemistry starts to play an efficient role and could initiate ozone destruction processes. Except for very special configurations where small regions of low temperature are formed, such events might not produce dramatic ozone changes, since the particles are not large enough to subside and remove active nitrogen from the northern polar vortex and since the time required for elevated ClO abundances to destroy ozone is probably larger than the time during which the vortex is illuminated. Finally, because of high dynamical activity and frequent breakdowns of the vortex, substantial transport of ozone from midlatitudes to the polar region occurs during a large portion of the winter, so that any "mini-hole" formed should rapidly disappear. Measurements of key chemical constituents in the polar region

of the Northern Hemisphere should nevertheless confirm these hypotheses and establish whether eventually ozone is substantially changed in limited cold and dynamically undisturbed areas.

The question of possible ozone depletion at midlatitudes as a result of heterogeneous chemistry must also be considered since a substantial number of particles is present at all latitudes inside the so-called Junge layer. These particles, which are small liquid drops, are composed of a mixture of sulfuric acid and water and are thus significantly different from the  $\text{HNO}_3/\text{H}_2\text{O}$  particles in the polar stratospheric clouds (or haze). The catalytic efficiencies of the particles in the Junge layer are thought to be lower than in the PSCs. Furthermore, the mass density of the aerosols in the Junge layer is one or two orders of magnitude smaller than in the PSCs. Finally, the temperature of the lower stratosphere outside the polar regions is significantly higher (220 K) than in the polar vortex (190–210 K), except over the tropics where the Hadley cell produces strong upward motions. Processes similar to those hypothesized to explain the formation of the “ozone hole” over Antarctica are thus very unlikely to appear at midlatitudes although some heterogeneous processes might periodically become important and lead to ozone destruction after large volcanic eruptions, when the amount of particles in the stratosphere may be enhanced by one or two orders of magnitude.

The possibility of a “dilution effect” of the polar anomaly observed in spring over Antarctica must be considered as another possible global implication of the Antarctic ozone hole. Since the chemical restoration time of ozone in the lower stratosphere is on the order of a year, air masses, with depleted ozone amounts, move toward the equator as soon as the winter vortex ceases to exist (November and December). As volumes of air with extremely low ozone are transported toward lower latitudes every year, the effects might partly accumulate, and a limited change in the total hemispheric ozone content could become noticeable.

Finally, an interesting but highly speculative positive feedback mechanism in the evolution of the atmosphere must be considered. The reduction in the ozone amount at high latitudes produces a net radiative cooling. If the lower ozone is still present the following autumn, a cooler vortex could be maintained throughout the next winter. Assuming a larger area of PSCs, a larger amount of ozone might be depleted during the second year. The size of the CCV might grow, assuming that the region where the temperature has decreased is now larger than during the previous year. The zonal flow would likewise be increased, so that the propagation of planetary waves is modified so as to enhance the stability of the polar vortex. Accordingly, the colder polar regime with lower ozone might tend to maintain itself. The southern high latitude region could conceivably change from a partially dynamically controlled regime into a purely radiative equilibrium state.



## QUESTIONS FOR THE FUTURE

The understanding of the mechanisms involved in the rapid decrease of ozone over Antarctica each spring since the mid-1970s requires a continuous intense international research effort, involving additional field experiments (in the Antarctic and Arctic regions), laboratory work (dealing with homogeneous chlorine chemistry and heterogeneous processes), and modeling studies (involving coupled chemical, dynamical, and radiative models). The following questions should be urgently addressed:

1. How is the Antarctic atmosphere preconditioned before ozone is depleted in late winter and early spring? Does the chemical composition change during the polar night?
2. Do the observed abundancies of ClO and BrO “quantitatively” explain the observed ozone decrease as a function of height and time?
3. Are the mechanisms for the formation of polar stratospheric clouds and the subsequent role of PSCs in heterogeneous processes understood?
4. Is the dynamical morphology of the “ozone hole” understood? Is the relative role of chemistry and dynamics explained?
5. Can the ozone decrease be explained within a given year? Are the year-to-year changes understood?
6. Can the region of depleted ozone become wider and deeper?
7. Can mechanisms similar to those occurring in Antarctica destroy ozone at other latitudes (e.g., at the North Pole)? To what extent will the region of low ozone be diluted toward other latitudes in the Southern Hemisphere?

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