

STRATOSPHERIC OZONE DEPLETION: A REVIEW OF CONCEPTS AND HISTORY

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Abstract. Stratospheric ozone depletion through catalytic chemistry involving man-made chlorofluorocarbons is an area of focus in the study of geophysics and one of the global environmental issues of the twentieth century. This review presents a brief history of the science of ozone depletion and describes a conceptual framework to explain the key processes involved, with a focus on chemistry. Observations that may be considered as evidence (fingerprints) of ozone depletion due to chlorofluorocarbons are explored, and the related gas phase and surface chemistry is described. Observations of ozone and of chlorine-related trace gases near 40 km provide evidence that gas phase chemistry has indeed currently depleted about 10% of the stratospheric ozone there as predicted, and the vertical and horizontal structures of this depletion are fingerprints for that process. More striking changes are observed each austral spring in Antarctica, where about half of the total ozone column is depleted each September, forming the Antarctic ozone hole. Measurements of large amounts of ClO, a key ozone destruction catalyst, are among the finger-

prints showing that human releases of chlorofluorocarbons are the primary cause of this change. Enhanced ozone depletion in the Antarctic and Arctic regions is linked to heterogeneous chlorine chemistry that occurs on the surfaces of polar stratospheric clouds at cold temperatures. Observations also show that some of the same heterogeneous chemistry occurs on the surfaces of particles present at midlatitudes as well, and the abundances of these particles are enhanced following explosive volcanic eruptions. The partitioning of chlorine between active forms that destroy ozone and inert reservoirs that sequester it is a central part of the framework for our understanding of the 40-km ozone decline, the Antarctic ozone hole, the recent Arctic ozone losses in particularly cold years, and the observation of record midlatitude ozone depletion after the major eruption of Mount Pinatubo in the early 1990s. As human use of chlorofluorocarbons continues to decrease, these changes throughout the ozone layer are expected to gradually reverse during the twenty-first century.

1. INTRODUCTION

The unique role of ozone in absorbing certain wavelengths of incoming solar ultraviolet light was recognized in the latter part of the nineteenth century by *Cornu* [1879] and *Hartley* [1880]. Interest in ozone stems from the fact that such absorption of solar radiation is important in determining not only the thermal structure of the *stratosphere* [e.g., *Andrews et al.*, 1987] but also the ecological framework for life on the Earth's surface. (Terms in italic type are defined in the glossary following the main text.) Decreased ozone results in increased ultraviolet transmission, which can affect the health of humans, animals, and plants [e.g., *van der Leun et al.*, 1995, and references therein].

Observations of the total integrated column ozone based on ultraviolet absorption began in the first few decades of the twentieth century [e.g., *Fabry and Buisson*, 1913; *Dobson*, 1968, and references therein; *Dütsch*, 1974]. Systematic measurements of this type have re-

vealed that the total ozone abundances over many regions of the globe have decreased markedly since about 1980, as is illustrated in the data presented in Figure 1. Indeed, the depletion of the global ozone layer has emerged as one of the major global scientific and environmental issues of the twentieth century.

Downward trends are evident in the time series of spatially or time-averaged spring column ozone observations shown in Figure 1. Ozone varies from year to year at all locations, but the behavior seen in recent decades in Antarctic spring lies very far outside of the historical variability. The longest available high-quality record is that of Arosa, Switzerland, which dates back to the 1920s [*Stahelin et al.*, 1998a, b]. The record at this site agrees well with the larger-scale changes observed by satellite since 1979. Figure 1 shows that the observed ozone changes in the 1990s compared with earlier decades are large enough that sophisticated statistical treatments are not needed to discern them, not only over Antarctica but also in the Arctic and at midlatitudes. For

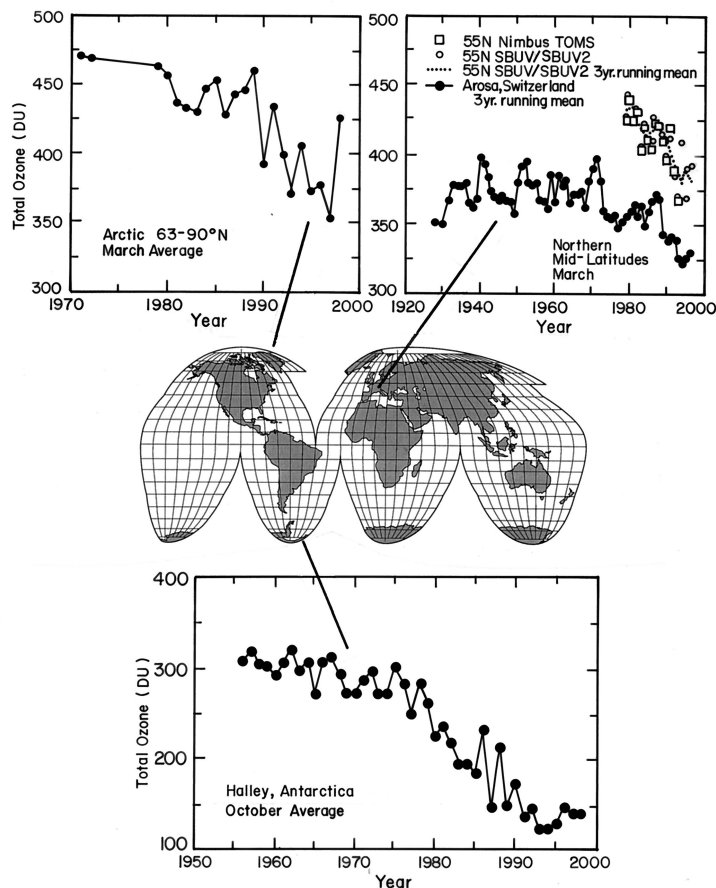


Figure 1. Observations of total ozone at various locations. The Antarctic data are from Halley [Farman *et al.*, 1985; Jones and Shanklin, 1995] and updated courtesy of J. Shanklin. The Arctic data are from satellite observations described by Newman *et al.* [1997], updated courtesy of P. Newman. The Arosa, Switzerland dataset is the longest running in the world [Stahelin *et al.*, 1998a, b]. Satellite observations from a slightly higher midlatitude region are shown for comparison [Hollandsworth *et al.*, 1995], updated courtesy of R. Nagatani. The satellite data are zonally and monthly averaged, while the ground-based data at each site have also been averaged over time as indicated in each case.

detailed discussions of data quality and ozone trend detection approaches, see the recent reviews by Harris *et al.* [1998] and J. Stahelin *et al.* (Observations of ozone trends, submitted to *Reviews of Geophysics*, 1998, hereinafter referred to as Stahelin *et al.*, submitted manuscript, 1998).

The aim of this review is to describe a framework for a conceptual and historical understanding of the processes controlling stratospheric ozone depletion, particularly the role played by human use of *chlorofluorocarbons* (CFCs). Key historical and illustrative recent references will be cited. Such a review is by design limited in scope and is intended to be accessible to the nonspecialist. It focuses strictly on ozone depletion processes rather than on the broader aspects of the current, highly detailed understanding of stratospheric ozone chemistry, radiative transfer, dynamics, and meteorology. For recent in-depth treatments of those topics, see, for example, *World Meteorological Organization/United Nations Environment Programme (WMO/UNEP)* [1994, 1999, and references therein], Andrews *et al.* [1987], and Holton *et al.* [1995].

Section 2 of this paper briefly discusses the general theoretical understanding of the vulnerability of ozone to chemical change, particularly the depletions that were predicted to occur in the distant future based upon gas phase chlorine and bromine chemistry [Molina and Rowland, 1974]. The transformation of this theory to the remarkable reality depicted by the ozone decline illus-

trated in Figure 1 is the focus of sections 3–6. Section 3 describes how the discovery and explanation of the Antarctic ozone hole radically altered the gas phase chemical picture by revealing the key role played by reactions of chlorine compounds on and within surfaces (heterogeneous chemistry), particularly under very cold conditions in polar regions. The chemical nature of stratospheric surfaces capable of driving such chemistry is the focus of section 4, where it is shown that water ice, nitric acid hydrates, and liquid sulfuric acid/water surfaces all must be considered. Laboratory studies, observations of mid-latitude ozone trends, and measurements of stratospheric chemical composition have underscored the need to consider both gas phase and heterogeneous chemistry not only under extreme cold but also under relatively warm conditions, as is discussed in sections 3, 4, and 5. Recent changes in Arctic ozone have further illustrated the strong coupling between heterogeneous chemistry and extensive polar ozone depletion and have raised important questions regarding meteorological trends (section 6). A key framework for understanding that is emphasized throughout this review is the concept of chemical *partitioning* of chlorine between forms that are inert with regard to ozone (HCl, ClONO₂) and others that can destroy it (Cl, ClO). Major conclusions are briefly summarized in section 7. A glossary of terms used follows the main text.

2. GAS PHASE CHEMISTRY AND RELATED CONSIDERATIONS

2.1. Catalytic Cycles and Chemical Families

A photochemical theory for formation and destruction of ozone based on an oxygen-only chemical scheme was first proposed by *Chapman* [1930]. An updated version of this framework is shown by the first seven reactions presented in Table 1. Perhaps most importantly, Chapman noted that ozone and atomic oxygen rapidly interchange with each other, while the sum of the two is linked to much slower chemical processes. This work laid the foundation for the understanding of “odd oxygen” chemistry. Such a conceptual picture allows a clear distinction to be drawn between net and gross production and loss of ozone over a chosen timescale which will be briefly summarized here (see the seminal review by *Johnston and Podolske* [1978] for further details).

Ozone photolysis below ~ 50 km represents a gross but not net loss process over timescales of the order of minutes or more, since nearly all of the atomic oxygen thus produced reforms ozone (through the reaction of $O + O_2$ with a third body, M ; see (R2) in Table 1) in just a few seconds or less. Ozone and atomic oxygen thereby cycle very rapidly between one another in the stratosphere. A very small fraction of the oxygen atoms produced from ozone photolysis can react with ozone ($O + O_3 \rightarrow 2O_2$), yielding a net loss of the sum of the two over extended timescales. Hence it is conceptually useful to consider atomic oxygen and ozone together as an odd oxygen family distinct from the much longer-lived form of “even oxygen,” O_2 (for further discussion see, e.g., *Brasseur and Solomon*, 1986).

In the 40 years following Chapman’s groundbreaking paper, it became clear that stratospheric ozone was chemically destroyed not solely by reaction with atomic oxygen, but also by hydrogen [*Bates and Nicolet*, 1950; *Hampson*, 1964] and nitrogen oxide chemistry [*Crutzen*, 1970, 1971; *Johnston*, 1971]. Each of these species may also be considered in terms of their own odd hydrogen and odd nitrogen families, the members of which can interchange chemically with one another [see, e.g., *Brasseur and Solomon*, 1986]. Table 1 illustrates the fact that hydrogen and nitrogen oxides can destroy odd oxygen in a catalytic fashion wherein the initiating active species (e.g., OH, NO) are regenerated, so that even small amounts of these gases can influence the much greater ozone abundances. Table 1 also presents some illustrative reactions that couple one family of gases to another (such as the formation of $ClONO_2$ through reaction of ClO with NO_2 ; $ClONO_2$ is thus a member of both the odd chlorine and odd nitrogen families) and processes that form relatively long-lived *reservoirs* (HCl, $ClONO_2$, HNO_3), which can strongly influence the abundances of the ozone-destroying gases (e.g., ClO, NO_2), as is discussed further below.

Perturbations to the natural abundances of odd hy-

drogen may arise through human modifications of source gases such as H_2O and CH_4 , while natural odd nitrogen can be perturbed through direct emissions of high-flying aircraft, by nuclear explosions, or by changes in its primary source gas, N_2O . *Heath et al.* [1977] demonstrated that large solar proton events can lead to transient perturbations in upper stratospheric ozone due to a natural modulation of odd nitrogen chemistry. This verified the nitrogen-catalyzed ozone destruction cycle in a dramatic fashion (see also the review by *Jackman and McPeters* [1987]). Refinements to measured laboratory kinetic rates allowed the numerical model estimates of the impacts of such perturbations upon ozone to be gradually improved over a period of several decades [e.g., *Ko and Sze*, 1983]. While the study of possible ozone depletion due to hydrogen and nitrogen chemistry remains an area of active research (see *WMO/UNEP* [1998] for current studies and *Johnston* [1992] for an historical review), the weight of evidence shows that the bulk of the observed recent depletion depicted in Figure 1 is due to other processes, particularly the chlorine-related chemistry that is the primary subject of this review.

In 1974 it was shown that chlorine could also engage in a catalytic cycle resulting in ozone destruction [*Stolarski and Cicerone*, 1974]. Of particular importance was the identification of man-made chlorofluorocarbons as the major source of ozone-destroying stratospheric chlorine [*Molina and Rowland*, 1974]. Like the nitrogen and hydrogen oxides, chlorine can destroy ozone in catalytic cycles such as those shown in Table 1. *Wofsy et al.* [1975]; *Yung et al.* [1980], *Tung et al.* [1986], and *McElroy et al.* [1986] showed that bromocarbons could also contribute to ozone depletion, particularly through the coupling of bromine and chlorine chemistry. Collectively, the depletion of ozone by chlorine, bromine, and the interactions between them will be referred to herein as halogen chemistry.

2.2. Processes Controlling Chlorocarbon Lifetimes

Molina and Rowland [1974] and *Rowland and Molina* [1975] pointed out that the chlorofluorocarbons hypothesized as ozone depletors have very long atmospheric residence times, so that if these gases were to be depleting stratospheric ozone, they would continue to do so well into the twenty-first century. This critical point merits a brief elucidation (expert readers may wish to skip to section 2.3). Figure 2 is a schematic diagram of the key processes that contribute to and control chlorofluorocarbon lifetimes in the Earth’s atmosphere. As was emphasized by *Molina and Rowland* [1974], the chlorofluorocarbons are not significantly soluble in water; nor do they react with ocean or soil surfaces or with any chemical species present in the lower atmosphere (below ~ 12 – 15 km, the *troposphere*). Their chemical destruction depends upon the ultraviolet light found in the upper atmosphere (between ~ 12 – 15 and 50 km, the stratosphere). This radiation breaks up the chlorofluo-

TABLE 1. Key Chemical Processes and Catalytic Cycles

<i>Chemical Process</i>	<i>Reaction Number</i>
<i>Chapman Chemistry^a</i>	
$O_2 + h\nu \rightarrow 2O$	R1
$O + O_2 + M \rightarrow O_3 + M$	R2
$O_3 + h\nu \rightarrow O_2 + O(^1D)$	R3
$O(^1D) + M \rightarrow O + M$	R4
$O_3 + h\nu \rightarrow O_2 + O$	R5
$O + O + M \rightarrow O_2 + M$	R6
$O + O_3 \rightarrow 2O_2$	R7
<i>Illustrative Odd Hydrogen Catalytic Cycles^b</i>	
$O + OH \rightarrow O_2 + H$	R8
$H + O_2 + M \rightarrow HO_2 + M$	R9
$O + HO_2 \rightarrow O_2 + OH$	R10
Net Cycle 1: $O + O + M \rightarrow O_2 + M$	R6
$OH + O_3 \rightarrow HO_2 + O_2$	R11
$HO_2 + O_3 \rightarrow OH + 2O_2$	R12
Net Cycle 2: $2 O_3 \rightarrow 3O_2$	R13
<i>Illustrative Odd Nitrogen Catalytic Cycle^c</i>	
$NO + O_3 \rightarrow NO_2 + O_2$	R14
$O + NO_2 \rightarrow NO + O_2$	R15
Net Cycle 3: $O + O_3 \rightarrow O_2$	R7
<i>Illustrative Odd Chlorine Catalytic Cycles^d</i>	
$Cl + O_3 \rightarrow ClO + O_2$	R16
$ClO + O \rightarrow Cl + O_2$	R17
Net Cycle 4: $O + O_3 \rightarrow O_2$	R7
$Cl + O_3 \rightarrow ClO + O_2$	R16
$Cl + O_3 \rightarrow ClO + O_2$	R16
$ClO + ClO + M \rightarrow Cl_2O_2 + M$	R18
$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2$	R19
$ClO_2 + M \rightarrow Cl + O_2 + M$	R20
Net Cycle 5: $2 O_3 \rightarrow 3O_2$	R13
<i>Illustrative Cl-Br Catalytic Cycle^e</i>	
$Cl + O_3 \rightarrow ClO + O_2$	R16
$Br + O_3 \rightarrow BrO + O_2$	R21
$BrO + ClO \rightarrow Br + ClO_2$	R22
$ClO_2 + M \rightarrow Cl + O_2 + M$	R20
Net Cycle 6: $2 O_3 \rightarrow 3O_2$	R13
<i>Some Important Coupling and Reservoir Reactions</i>	
$ClO + NO \rightarrow Cl + NO_2$	R23
$Cl + CH_4 \rightarrow HCl + CH_3$	R24
$HO_2 + ClO \rightarrow HOCl + O_2$	R25
$ClO + NO_2 + M \rightarrow ClONO_2 + M$	R26
$OH + NO_2 + M \rightarrow HNO_3 + M$	R27
<i>Key Heterogeneous Reactions</i>	
$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$	R28
$N_2O_5 + H_2O \rightarrow 2HNO_3$	R29
$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$	R30
$HCl + HOCl \rightarrow H_2O + Cl_2$	R31
$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr$	R32
$HCl + BrONO_2 \rightarrow HNO_3 + BrCl$	R33
$HCl + HOBr \rightarrow H_2O + BrCl$	R34

^aChapman [1930].^bBates and Nicolet [1950]; Hampson [1964].^cCrutzen [1970]; Johnston [1971].^dStolarski and Cicerone [1974]; Molina and Molina [1987].^eMcElroy et al. [1986]; Tung et al. [1986].

rocarbon molecules, yielding Cl atoms that can go on to destroy ozone in catalytic cycles such as those shown in Table 1 as they move through the stratosphere.

A review of the fluid mechanical principles underlying the dynamics and meteorology that is responsible for the

movement of air from the troposphere to the stratosphere is provided, for example, by Andrews et al. [1987] and Holton et al. [1995]. It is interesting to note that long before the fluid dynamical underpinnings of stratospheric transport were fully established, a broad concep-

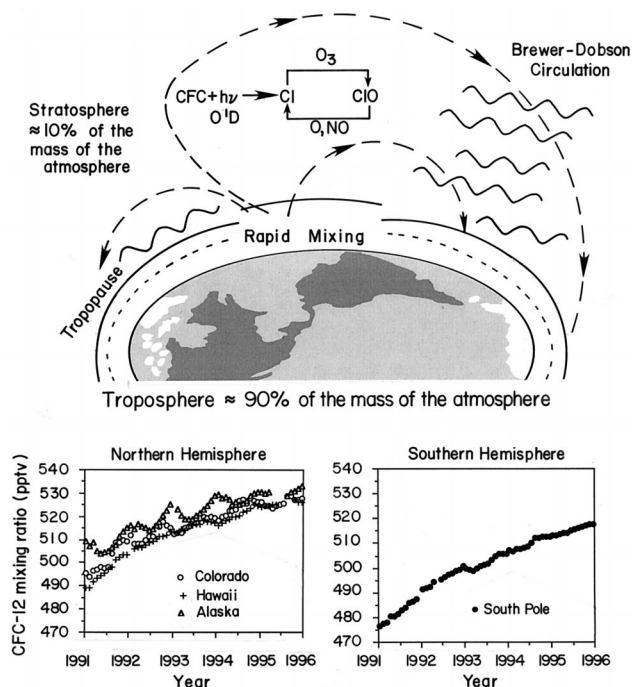


Figure 2. Schematic diagram illustrating the breakdown of CFCs and catalytic destruction of ozone in the middle and upper stratosphere. Because the stratosphere contains only 10% of the mass of the total atmosphere, the atmosphere must turn over many times to destroy all of the CFCs present, resulting in long atmospheric residence times for these gases. The simplified cartoon illustrates only the key net processes that transport CFCs and other gases in a zonally averaged sense. The Brewer-Dobson circulation illustrates a typical average flow pattern. Waves mix trace gases when they break down, particularly in the winter hemisphere (Southern Hemisphere in this illustration). The long CFC lifetimes are reflected in the surface observations of CFC-12 at stations, such as South Pole, that are far removed from the emission regions in the industrialized Northern Hemisphere.

tual framework had been deduced from chemical observations that remains basically intact today. *Dobson* [1930] inferred the existence of a large-scale stratospheric circulation cell characterized by rising motion in the tropics and descending motion at mid and high latitudes on the basis of his observations of the latitude gradients in ozone. He pointed out that greater ozone column abundances observed at higher latitudes must be the result of downward, poleward motion. *Brewer* [1949] reached a similar conclusion based upon an elegant analysis of early measurements of water vapor. Recent studies have, for example, used observations of very long-lived gases with known tropospheric trends such as CO_2 [e.g., *Schmidt and Khedim*, 1991; *Boering et al.*, 1996] to show that the timescale for the overturning of this “Brewer-Dobson” circulation cell is ~ 5 years. About 90% of the total atmospheric mass resides in the troposphere, and $\sim 10\%$ resides in the stratosphere.

Consider the fate of 1 kg of CFC-11 released in today’s atmosphere, using Figure 2. Rapid mixing in the

lower atmosphere distributes the CFC-11 throughout the troposphere. Observations of chlorofluorocarbons from surface stations as far apart as the South Pole and Colorado as indicated in Figure 2 (data taken from *Montzka et al.* [1996]) show that the mixing ratios of CFCs in the Southern Hemisphere lag those of the Northern Hemisphere by about a year. However, the fact that the abundances of chlorofluorocarbons are so large at a remote site like the South Pole, far removed from their emission in the industrialized parts of the Northern Hemisphere, attests to the fact that their destruction in the troposphere must be extremely slow or nonexistent. Key factors are the near-insolubility of CFCs in water (which makes them resistant to the rain-out and washout processes that remove some other gases emitted by industrial activities, such as those that form the local pollution of acid rain) and their chemically inert character.

A fraction of the tropospheric mass enters the stratosphere and is slowly transported upward, poleward, and back to the troposphere. Rapid horizontal mixing in the troposphere, coupled with the fact that the primary point of entry to the stratosphere is in the tropics (as sketched in simplified form in Figure 2; see *Holton et al.* [1995] for a more detailed picture), implies that the chlorine content of stratospheric air will not depend substantially upon proximity to local sources. Ozone depletion is therefore a global phenomenon, since the amount of total chlorine (also called *chlorine loading*) both at and above the South Pole is nearly the same as that above industrialized regions. The observed spatial and temporal variations in ozone loss are closely tied to chemical processes that partition this total chlorine loading among its various forms and thereby modulate ozone destruction in space and time, as is discussed below.

Within ~ 5 years, air will have cycled through the mid to upper stratosphere. Most of the CFC-11 contained in this air breaks down in the upper stratosphere to release its chlorine (which in turn destroys ozone) and returns to the troposphere largely in the form of hydrochloric acid (which ultimately rains out and removes the chlorine from the system). Since only $\sim 10\%$ of the mass of the troposphere exchanges with the upper stratosphere in each 5-year period, the process will have to be repeated approximately 10 times to destroy the bulk of chlorofluorocarbon initially released. In the case of CFC-11, this leads to a lifetime of ~ 50 years. For some of the other chlorofluorocarbons, stratospheric photodissociation destroys a smaller fraction of the parent compound within a single circuit through the Brewer-Dobson circulation, extending the lifetimes considerably (in the case of CFC-115, for example, the lifetime is about 500 years [*WMO/UNEP*, 1994]). If all emissions of these chlorofluorocarbons were to cease immediately, these gases would be slowly removed from the atmosphere on such timescales according to the processes depicted in Figure 2. A concise review of global emissions and future projections is provided by *Prather et al.* [1996].

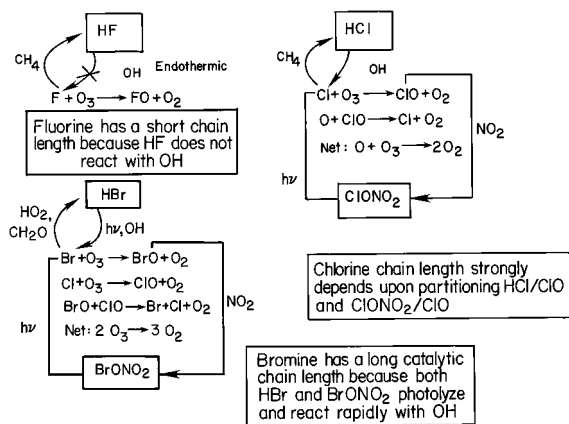


Figure 3. Key contrasts between F, Cl, and Br for ozone loss are linked to their gas phase partitioning processes illustrated here.

The challenges facing geoengineering strategies to mitigate ozone losses by, for example, making more ozone, have been recognized for decades. The energy required to break the O₂ bond in order to make two ozone molecules is about 5.1 eV, so that the power input required to produce the ozone layer is about 2×10^{13} W [Hunten, 1977]. This power is provided on a natural and continuing basis by the Sun but was estimated at ~ 3 times mankind's total artificial power generation in 1970 [Hunten, 1977]. Making enough ozone to artificially replace even a small fraction of the global burden would still be an extremely expensive proposition today. Alternative schemes involving interference with chlorine chemistry have also been shown to be impractical [see, e.g., Viggiano *et al.*, 1995]. Hence the reduction of global emissions and the resulting gradual removal of atmospheric chlorine is the only known practical approach to future recovery of the ozone layer.

2.3. Chemical Partitioning, Chlorine Sources, and Gas Phase Chemistry Fingerprints

The foregoing discussion and the references therein outline the dominant catalytic processes that control ozone chemistry and describe in general terms why compounds such as chlorofluorocarbons released at ground level reside in the global atmosphere over timescales of decades to centuries. Along with these catalytic cycles, chemical partitioning processes play a major role in ozone destruction that is dramatically illustrated by the contrasts between F, Cl, and Br gas phase chemistry shown in simplified form in Figure 3. Briefly, the halogen atoms released in the stratosphere from chlorocarbon, bromocarbon, and fluorocarbon source gases can form acids (through abstraction of a hydrogen atom) and nitrates (through reaction with NO₂). In the case of fluorine, the acid HF is quickly formed and so tightly bound that essentially all fluorine released from fluorine source gases in the stratosphere is irreversibly and rapidly "neutralized" as HF [Rowland and Molina, 1975;

Stolarski and Rundel, 1975; Sze, 1978]. The amount of atomic fluorine and FO available to participate in ozone-destroying catalytic cycles (or, in chemical terms, the catalytic chain length [see Johnston and Podolske, 1978]) is hence extremely short, and fluorine has a negligible impact on ozone (see the recent analysis by D. J. Lary *et al.* (Atmospheric fluorine photochemistry, submitted to *Journal of Geophysical Research*, 1998)). Chlorine forms both HCl [Stolarski and Cicerone, 1974] and ClONO₂ reservoirs [Rowland *et al.*, 1976]. These gases can, however, be reconverted to chlorine atoms by gas phase chemistry (i.e., by reaction with OH and photolysis, respectively). The amount of Cl and ClO available to participate in ozone-destroying catalytic chemistry therefore is critically dependent on the partitioning of chlorine between these "active" chlorine radicals and the non-ozone-destroying "reservoirs," HCl and ClONO₂. The rates of chemical formation and destruction of the reservoirs control this partitioning. Bromine is less tightly bound than chlorine, so that relatively little of the bromine released from bromocarbons is tied up in HBr and BrONO₂, rendering this atom quite effective for ozone loss [Wofsy *et al.*, 1975; Yung *et al.*, 1980; Lary, 1996], especially in combination with chlorine [Tung *et al.*, 1986; McElroy *et al.*, 1986]. Although there are significant human sources of bromine, the contemporary abundances of total stratospheric bromine are about 200 times smaller than those of chlorine [e.g., Schauffler *et al.*, 1993; Wamsley *et al.*, 1998]. Iodine may also participate in ozone-destroying catalytic cycles with bromine and chlorine [Solomon *et al.*, 1994, 1997] but its stratospheric abundance is believed to be much smaller than those of bromine and chlorine, and its primary sources are believed to be natural rather than largely or partly man-made as in the case of fluorine, chlorine, and bromine.

While many natural processes produce chlorine at ground level (including for example, sea salt and volcanic emissions of HCl), these compounds are efficiently removed in precipitation (rain and snow) owing to high solubility. The removal of HCl emitted, for example, by volcanoes is extremely efficient [see, e.g., Tabazadeh and Turco, 1993], rendering even the most explosive volcanic plumes ineffective at providing significant inputs of chlorine to the stratosphere (as was demonstrated in direct observations of volcanic plumes by Mankin *et al.* [1992] and Wallace and Livingston [1992]).

In contrast, airborne observations of the suite of chlorofluorocarbons at the base of the tropical stratosphere [see, e.g., Schauffler *et al.*, 1993] show that the total chlorine content in air entering the lowermost stratosphere due to chlorofluorocarbons in 1992 was about 3.0 ppbv, compared with only ~ 0.1 – 0.2 ppbv from concurrent measurements of HCl and ~ 0.5 – 0.6 ppbv from CH₃Cl, which is the sole stratospheric chlorocarbon that has significant natural sources. Observations such as those in Figure 2 have confirmed that the temporal trends in global surface level abundances of chlo-

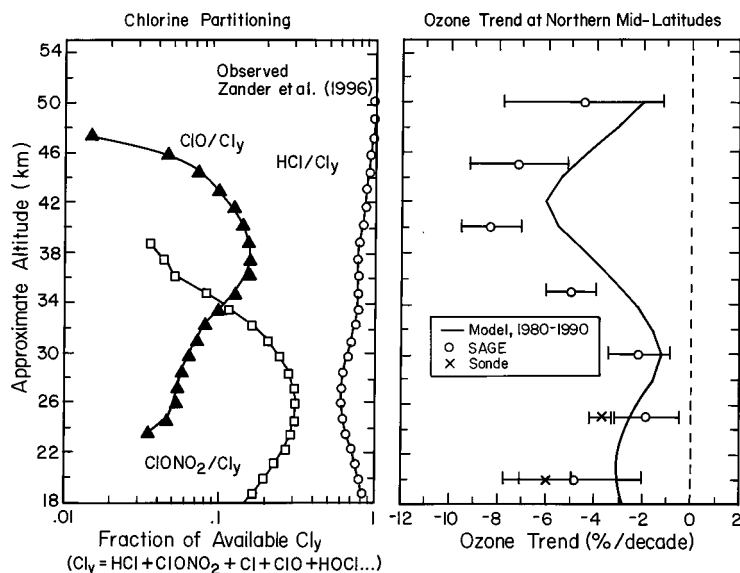


Figure 4. (left) Observations of chlorine partitioning as a function of altitude from an instrument on board the space shuttle [Zander et al., 1996]. (right) Observed vertical profile of the ozone trend at northern midlatitudes [Harris et al., 1998], together with a current model estimate [from Solomon et al., 1997].

rofluorocarbons are consistent with the known industrial emissions [e.g., Montzka et al., 1996; Prinn et al., 1995; WMO, 1985; WMO/UNEP, 1991, 1994, 1999], both in terms of the buildup of these gases in past decades and the slower accumulation in the 1990s following reductions in global use (see also Plate 5 below).

Observations of HCl, ClO, ClONO₂, and other chlorine-bearing gases by infrared spectroscopy onboard the space shuttle [Michelsen et al., 1996; Zander et al., 1996] or from satellites [Dessler et al., 1995, 1998] allow study of how chlorine is chemically partitioned in the middle and upper stratosphere in some detail, as shown in the left-hand side of Figure 4. In the uppermost stratosphere above ~45 km, nearly all of the chlorine released from source molecules such as CFCs (hereinafter referred to as Cl_y) is sequestered in the HCl reservoir, owing largely to the efficacy of the reaction of Cl + CH₄ at warm temperatures and high Cl/ClO ratios there. Recent models [Michelsen et al., 1996], stratospheric observations [Stachnik et al., 1992; Chandra et al., 1993], and laboratory measurements [Lipson et al., 1997] (see *Jet Propulsion Laboratory (JPL)* [1997]) suggest that a small yield of HCl in the reaction of ClO with OH also affects the HCl/ClO partitioning in this region.

Because nearly all of the chlorine and fluorine released from chlorofluorocarbons resides as HCl and HF in the stratosphere near 50 km, observations of these two gases in this region provide key verification of their attribution to CFC sources. Recent global data by Russell et al. [1996] display abundances and trends in both HCl and HF near 50 km that are quantitatively consistent with observations of the chlorofluorocarbons at ground level; these observations therefore confirm that CFCs are the key sources for stratospheric chlorine and fluorine. Taken together, the global measurements of HCl, HF, other chlorine compounds, and the CFC source gases both at the surface and in the *tropopause*

region [e.g., Russell et al., 1993; Zander et al., 1996; Montzka et al., 1996; Schauffler et al., 1993] provide direct evidence that the chlorine content of the contemporary stratosphere has been greatly perturbed, with about 85% of the 1992 stratospheric chlorine burden attributable to human activities.

Crutzen [1974] and Crutzen et al. [1978] carried out some of the first detailed chemical models of ozone depletion, building upon the studies of Stolarski and Cicerone [1974], Molina and Rowland [1974] and Rowland and Molina [1975] and including the chemical understanding outlined above. Crutzen [1974] predicted a relative maximum in ClO near 40 km, which was broadly confirmed a few years later by observations of ClO by Anderson et al. [1977], Parrish et al. [1981], and Waters et al. [1981]. Largely because of this relative maximum in ClO, Crutzen [1974] predicted a maximum in ozone depletion in the same region (although other factors such as the availability of atomic oxygen also contribute to the vertical profile of ozone depletion). The left-hand side of Figure 4 shows that current observations of the ClO/Cl_y profile in the middle and upper stratosphere agree with those early predictions and observations.

While there have been indications of ozone depletion in the upper stratosphere for more than a decade [e.g., *Ozone Trends Panel*, 1988], only within the past few years has it been well quantified [e.g., Miller et al., 1995; Harris et al., 1998]. Sample observations of the northern mid-latitude ozone profile trends as shown in the right-hand side of Figure 4 display a maximum near 40 km, just as predicted more than 2 decades ago. The close agreement between the vertical shapes of the observed and predicted ozone changes in the upper stratosphere provides strong evidence for gas phase chlorine-catalyzed ozone depletion chemistry. Further, the correspondence between the shapes of the vertical profiles of the observed ozone depletion and of the ClO/Cl_y ratio attests

to the role of partitioning processes in modulating this chemistry. Indeed, this is the first of several “fingerprints” that can be used to establish the role of chlorine in ozone depletion.

Plate 1 presents another fingerprint illustrating the role of gas phase chemistry and chlorine partitioning in ozone depletion, namely, the latitudinal gradients in upper stratospheric ClO and ozone depletion. In the early 1980s, global measurements of methane by satellite illustrated that the strong upwelling of the Brewer-Dobson circulation in the tropical upper stratosphere (see Figure 2) gives rise to a maximum in methane there [Jones and Pyle, 1984]. The enhanced methane, in turn, was predicted to lead to a tropical minimum in ClO through its dominant role in ClO/HCl partitioning and hence in ozone depletion [Solomon and Garcia, 1984]. Current global satellite observations of ClO [Waters et al., 1993; Waters et al., 1999], as shown in the left panel of Plate 1, indeed display a strong latitudinal gradient with a pronounced minimum in the tropics. Satellite observations of the latitudinal variation of the ozone trends over the past 15 years (right panel of Plate 1) reveal a similar spatial pattern in the upper stratosphere as predicted. Thus not only the vertical profile but also the latitudinal structure of the ozone depletion above ~25 km parallels the patterns observed in ClO. These spatial variations in ozone depletion point towards gas phase chlorine chemistry and highlight the role of chemical partitioning in modulating ozone depletion. For further discussion of other factors influencing upper stratospheric ozone (including, for example, the roles of temperature, water vapor, and other factors) see Müller et al. [1999] in the WMO/UNEP [1999] ozone assessment. Plate 1 also shows very high ClO abundances in the lower stratosphere (below 30 km) over the Antarctic in austral spring, where gas phase chemical partitioning would not predict it. These are a focus of the next section.

3. HETEROGENEOUS CHEMISTRY UNDER COLD CONDITIONS: THE ANTARCTIC OZONE HOLE

3.1. Discovery and Verification of the Ozone Hole

Measurable ozone depletion was first documented in the Antarctic spring at the British Antarctic Survey station at Halley [Farman et al., 1985]. Farman et al. showed that the ozone hole is confined to particular seasons (i.e., spring) and to south polar latitudes. These pioneering findings were quickly confirmed by space-based measurements [Stolarski et al., 1986] and by observations at other Antarctic sites [e.g., Komhyr et al., 1986]. Observations of total column ozone using infrared [Farmer et al., 1987] and visible spectroscopy [Mount et al., 1987] provided further support for the seasonal depletion of springtime ozone using independent methods. As the satellite measurements confirmed that the depletion extended over roughly the entire continent, the

phenomenon became known as the Antarctic ozone “hole.”

While the Antarctic ozone hole is not a true hole, in the sense that some column ozone remains even in the most extreme depletions observed in the mid 1990s (when October ozone minima were near 100 Dobson units (DU) over the South Pole, or depletion of about two thirds of the historical levels [see Hofmann et al., 1997]), the descriptor captures the fact that the peak depletion is sharply limited to Antarctic latitudes. Dobson [1968 and references therein] noted that there is less ozone naturally present over Antarctica than over the Arctic in winter and spring, but this climatological difference between the natural ozone levels over the poles of the two hemispheres should not be confused with the abrupt decline that began near the mid-1970s as depicted in Figure 1. Newman [1994] discusses these and other historical measurements of total ozone and shows that the Antarctic ozone hole began in the last few decades.

The latitudinal gradients in Antarctic ozone depletion are related to the dynamical structure of the polar winter stratosphere, whose circulation can be viewed as a vortex [see, e.g., Schoeberl et al., 1992a; Holton et al., 1995]. Briefly, the absence of solar illumination in high-latitude winter leads to cooling over the poles and hence a large temperature gradient near the polar terminator. This thermal gradient implies rapid zonal (west-east) flow characterizing the “jet” at the edge of the vortex, while the air within the vortex is relatively isolated in comparison with surrounding midlatitude regions, allowing deep depletion to develop. Differences in the pre-1970s ozone abundances in the two polar vortices first noted by Dobson [1968] are related to differences in atmospheric waves and circulation patterns, which are in turn driven by factors relating to surface topography (e.g., distribution of mountains, oceans, and continents). In brief, the north polar vortex is generally more disturbed by atmospheric waves forced from beneath by flow over a more variable surface topography. These lead to greater mixing and faster downward motion, which both increases the natural wintertime Arctic ozone abundances (by bringing down ozone-rich air from above) and warms the lower stratosphere (through adiabatic compression). Temperatures in the Antarctic vortex are both colder and less variable than those of the Arctic, which strongly influences the polar ozone depletion in the two hemispheres (sections 3.3 and 6 below).

Plate 2 shows measurements of the seasonal cycle of ozone at Halley in historical and recent data, which show that the depletion occurs only over a limited portion of the year. These observations demonstrate that contemporary observations of ozone at Halley in late August (end of austral winter) are near historical levels, while the bulk of the ozone loss there occurs rapidly during the month of September. The ozonesonde data [e.g., Hofmann et al., 1987] further underscore this point.

Farman et al. [1985] presented evidence for large

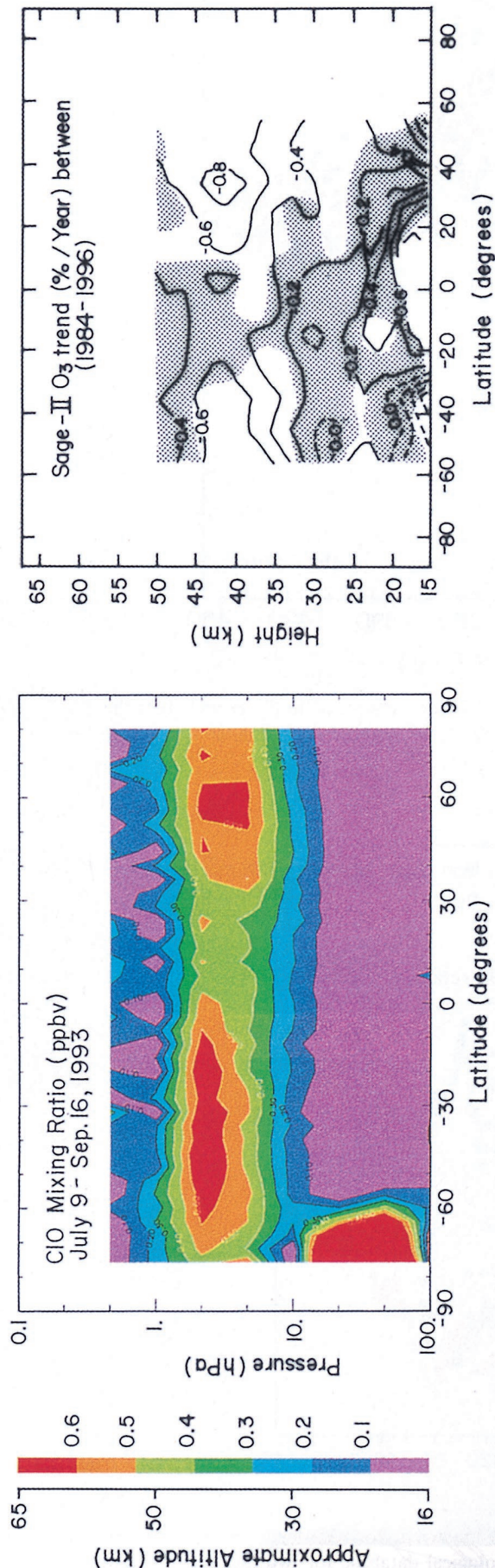


Plate 1. (left) Observations of the global distribution of zonally averaged daytime ClO abundance from satellite-based microwave remote sensing [Waters *et al.*, 1999] together with the zonally averaged ozone trend deduced from satellite-based visible spectroscopy [Harris *et al.*, 1998] (see McCormick *et al.* [1992]).

trends in October Antarctic total ozone that were completely unanticipated at the time. They suggested chlorofluorocarbons as the likely cause. This assertion was remarkable because the observed depletion was far larger than was ever anticipated up to that point. Scientific understanding of the behavior of the ozone layer prior to Farman *et al.*'s discovery suggested that trends of a few percent in total ozone might begin to become observable sometime in the twenty-first century if chlorofluorocarbon emissions continued [see, e.g., Wuebbles *et al.*, 1983]. The reason that the predicted changes were relatively small and far in the future is reflected in the discussion of gas phase chemistry outlined in section 2. Figures 3 and 4 show that a gas phase chemical understanding predicts that chlorine's greatest impact on ozone occurs in the upper stratosphere near 40 km. Since the bulk of the total ozone column lies in a layer at much lower altitudes near 10–30 km, the integrated impact on the total ozone column is small with such a depletion profile. Further, this framework does not identify Antarctica as a site of particular significance for ozone depletion. As Figure 1 illustrates, the Antarctic ozone depletion was the earliest to be observed and remains the most extreme on Earth at the time of this writing [see Jones and Shanklin, 1995].

Measurements of the vertical profile of the depletion within the ozone hole were first presented by Chubachi [1984] and were rapidly followed by other data such as those of Hofmann *et al.* [1987], Gardiner [1988], and Iwasaka and Kondoh [1987], and more recently in satellite studies such as that of Bevilacqua *et al.* [1997]. Hofmann *et al.* [1997] presented a detailed analysis of many years of ozonesonde measurements at the South Pole. Figure 5 summarizes a key result of that study, showing that the depletion of the Antarctic ozone column is largely confined to altitudes from ~12 to 25 km, far below the altitudes where gas phase chlorine chemistry would predict major changes. Figure 5 also illustrates the shape of the unperturbed ozone "layer" observed in historical ozone data, as well as the near-total removal of ozone in the heart of the layer in a typical contemporary sounding for early October. Finally, Figure 5 shows the close correspondence between the region where most of the ozone is depleted and a vertical profile of a typical *polar stratospheric cloud (PSC)* observed at the South Pole [Collins *et al.*, 1993]; the critical role of these clouds in formation of the ozone hole is discussed in section 3.3.

3.2. Solar and Dynamical Theories of the Origin of the Ozone Hole

Observations not just of Antarctic ozone, but also of the factors that affect it, such as chemical species (e.g., NO₂ and ClO) and meteorological properties, were extremely limited at the time of the discovery of this dramatic and unanticipated ozone loss. As a result, a variety of different theories were advanced as plausible explanations. The conflicting theories were reviewed by

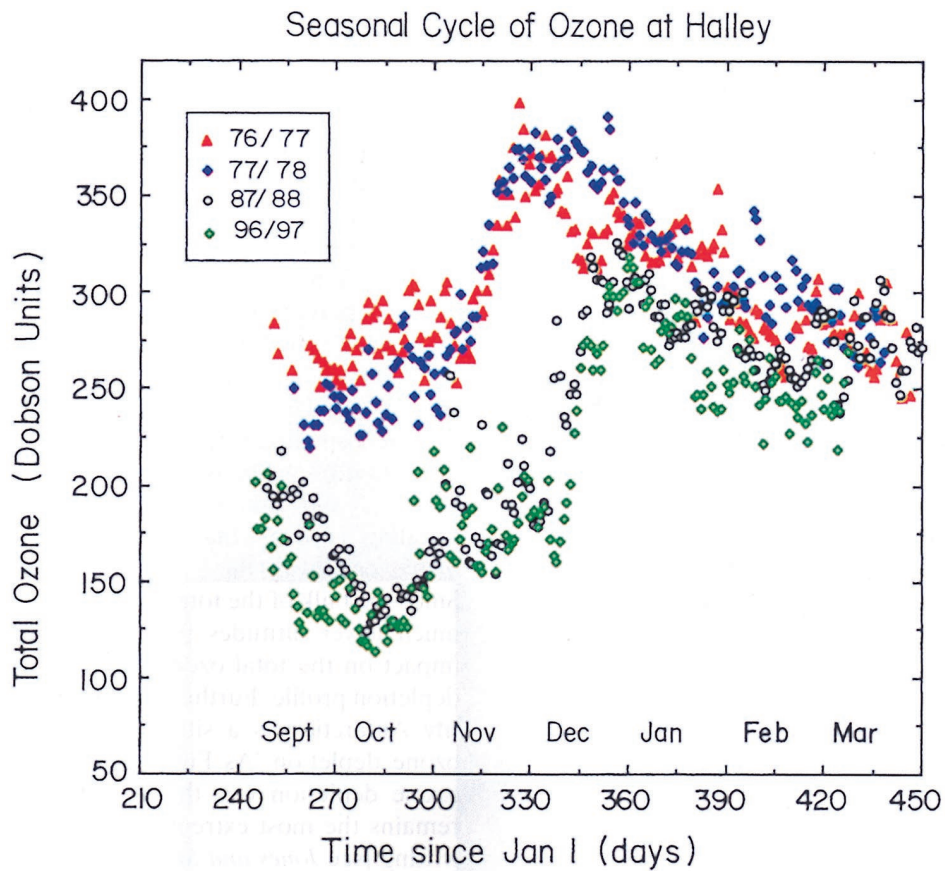


Plate 2. Observations of the full seasonal cycle of daily ozone at Halley, Antarctica, in the years before the ozone hole (1976–1977 and 1977–1978), and in 1987–1988 and 1996–1997, courtesy of J. Shanklin. Note the rapid September drop in total ozone in the ozone hole years.

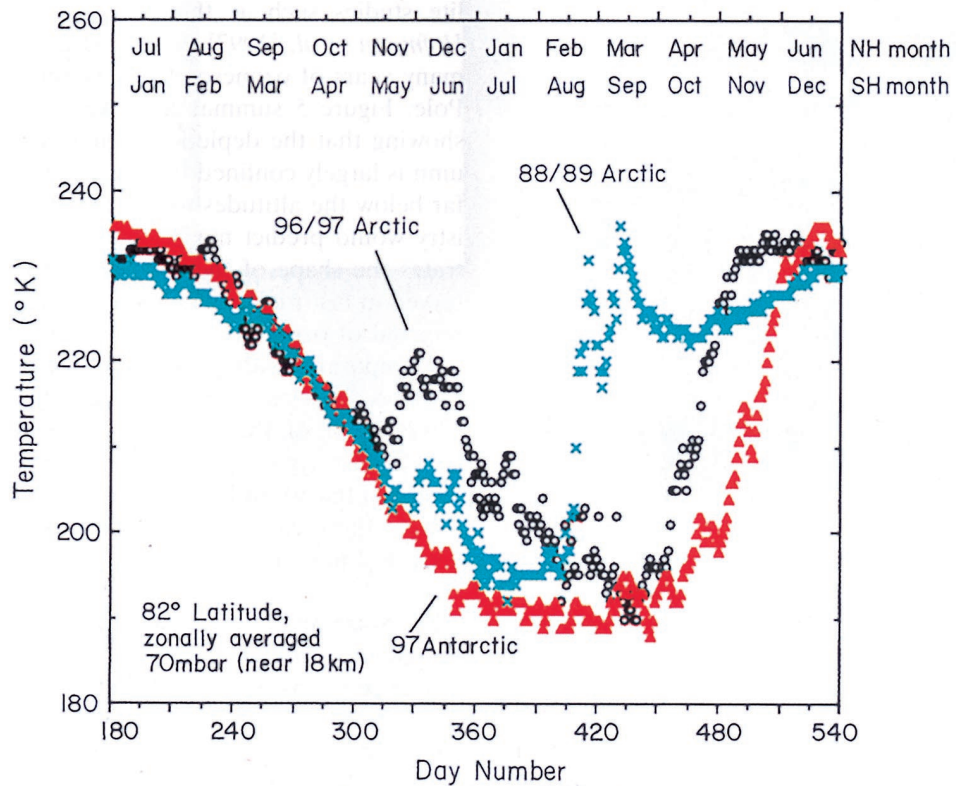


Plate 3. Observations of the zonally averaged temperatures in the Arctic for 82°N near 18 km, from the National Center for Environmental Prediction (NCEP) meteorological database for two illustrative recent years, together with Antarctic observations at 82°S in 1997 (shifted by 6 months for comparison).

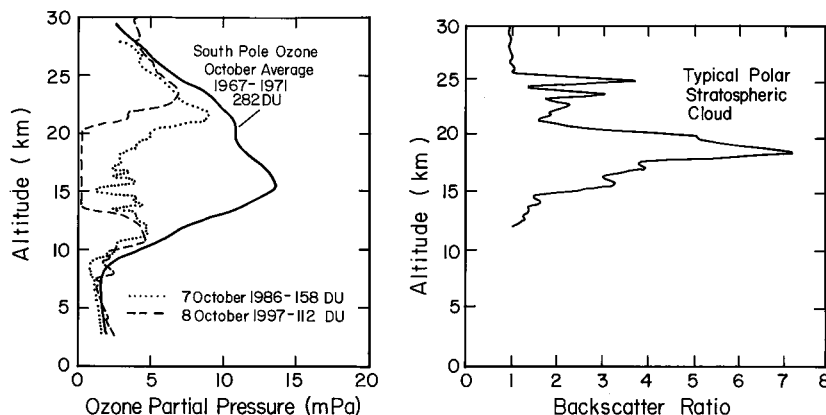


Figure 5. (left) Observations of the vertical profile of ozone observed at the South Pole during Octobers in the late 1960s and early 1970s, contrasted with those of 1986 and 1997. Total ozone (DU) is indicated for each profile, from Hofmann *et al.* [1997]. (right) Typical polar stratospheric cloud observed at the South Pole from the observations of Collins *et al.* [1993].

Solomon [1988]; the theories that were not supported by observations will be briefly discussed in this section.

The primary dynamical theory of ozone depletion rested upon the notion that illumination of the cold polar lower stratosphere at the end of winter could give rise to heating and net upward motion [Tung *et al.*, 1986; Mahlman and Fels, 1986]. As is illustrated in Figure 5, there is far less ozone in the troposphere than the stratosphere, so that upward transport of ozone-poor air from the troposphere to the stratosphere could locally decrease the Antarctic ozone column. However, observations of conservative tracers that serve to illustrate the direction of dynamical flow such as aerosols [Hofmann *et al.*, 1987], nitrous oxide [Parrish *et al.*, 1988; Loewenstein *et al.*, 1989], and other long-lived gases [Jaramillo *et al.*, 1989; Toon *et al.*, 1989] quickly demonstrated that the ozone hole was not caused by such upward motion. Indeed, much as Brewer [1949] deduced the nature of global transport from observations of water vapor as a tracer of atmospheric dynamics, so have observations of a wide variety of chemical tracers shown that transport is directed downward within the Antarctic stratosphere in spring rather than upward, although there is still debate about the strength of this fluid flow and the degree of exchange of air between lower latitudes and polar regions [e.g., Hartmann *et al.*, 1989; Tuck, 1989; Tuck *et al.*, 1997; Schoeberl *et al.*, 1990, 1992a, 1995; Manney *et al.*, 1995a, b].

Enhanced nitrogen oxides from high solar activity that occurred in the early 1980s were also proposed as a cause of the ozone hole [Callis and Natarajan, 1986], drawing upon the well-known catalytic chemistry of NO_x and its enhancement by processes such as solar proton events as discussed in section 1. While chemical in character, this theory is diametrically opposite to the chlorine theory, which requires that nitrogen oxide abundances be suppressed so that chlorine oxides are not tied up in the chlorine nitrate reservoir (see Figure 3 and section

3.3). The solar theory proved to be in conflict with observations. Measurements of the nitrogen dioxide column by Noxon [1978] and McKenzie and Johnston [1984] displayed reduced rather than enhanced nitrogen oxides over the south polar regions. After the discovery of the ozone hole, similar measurements confirmed those early data using both infrared and visible spectroscopy methods [Coffey *et al.*, 1989; Farmer *et al.*, 1987; Mount *et al.*, 1987]. Airborne measurements of the latitudinal gradient of nitric oxide at 20 km (in the heart of the south polar ozone destruction region as shown in Figure 5) by Fahey *et al.* [1989a] using a chemiluminescence method are compared with the data of Noxon [1978] in Figure 6. Both data sets show that the southern high-latitude winter–spring stratosphere contains a minimum in nitrogen oxides rather than a maximum as required by the solar theory of Antarctic ozone depletion. The differences in the location of the steep gradient between the two data sets likely reflect differences in season and local motion of the polar vortex. The observed shape of the profile of ozone depletion is also in conflict with the solar theory, which would predict greater ozone losses at higher altitudes rather than removal only in a narrow range of altitude from ~ 12 to 25 km as shown in Figure 5.

It is interesting to note that the observations of Noxon [1978, 1979] revealed strong evidence for a “cliff” in NO_2 in polar regions several years before the Antarctic ozone hole was discovered. The chemistry of this anomaly was not understood, and it was called out as one of the challenges to scientific understanding of stratospheric chemistry of the time [see, e.g., WMO, 1985]. We now know that the chemistry that produced Noxon’s cliff is tied to that of the ozone hole; the relationship between NO_2 and ClO will be discussed further below. Arguably, the ozone hole might have been predicted before it was observed had the Noxon cliff been better understood in the early 1980s.

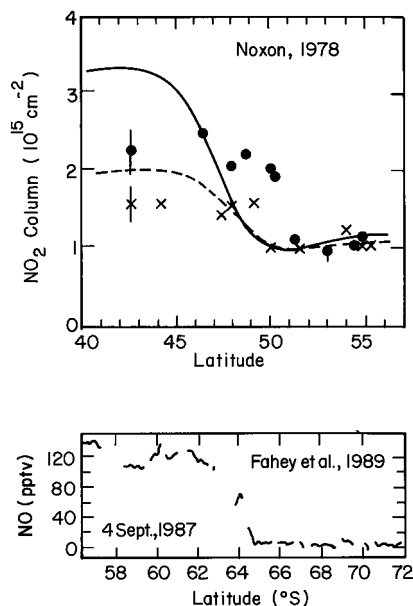


Figure 6. Observations of the “cliff” in NO₂ reported by Noxon [1978]. The solid and dashed lines represent Northern Hemisphere measurements, while the solid circles and crosses show Southern Hemisphere evening and morning twilight data, respectively. The NO measurements of Fahey et al. [1989a] are shown for comparison. The two molecules interchange rapidly with one another in the sunlit atmosphere and hence provide a measure of NO_x. Both data sets show very low NO_x in the high-latitude stratosphere.

3.3. Heterogeneous Chlorine Chemistry and Antarctic Ozone Depletion: Early Theoretical Studies

The light was especially good today; the sun was directly reflected by a single twisted iridescent cloud in the North, a brilliant and most beautiful object.

Robert Falcon Scott, diary entry for August 1, 1911
[Scott, 1996, p. 264]

This quotation from one of the first explorers to stand at the South Pole documents the fact that polar stratospheric clouds were present in the Antarctic long before the advent of the ozone hole. The term “polar stratospheric clouds” was coined by McCormick et al. [1982], who first presented satellite observations of high-altitude clouds in the Antarctic and Arctic stratospheres. The data showed that the Antarctic clouds were present from June to late September, that they were associated with cold temperatures below ~200 K, and that they occurred between ~12 and 25 km. Three quarters of a century after their observation during Scott’s expedition and several years after the first satellite observations, it became clear that PSCs are a critical factor in the ozone hole.

Solomon et al. [1986] suggested that HCl and ClONO₂ might react on the surfaces of PSCs, perturbing gas phase chlorine partitioning in a manner that could greatly accelerate ozone loss in the Antarctic lower stratosphere ($\text{HCl} + \text{ClONO}_2 \rightarrow \text{HNO}_3 + \text{Cl}_2$; see

(R28) in Table 1). The Cl₂ formed would photolyze rapidly in sunlit air and rapidly form ClO. They also pointed out that this and related heterogeneous reactions would suppress the concentration of NO₂ by forming HNO₃, so that the ClO thereby released could not readily reform the ClONO₂ reservoir. Thus it was recognized that rapid ozone loss via chlorine chemistry would require (1) the heterogeneous “activation” of chlorine from both the HCl and ClONO₂ reservoirs and (2) the suppression of NO₂, an essential element in keeping the chlorine active. The production of Cl₂ in this process implies that sunlight would be required to release Cl, so that the ozone depletion would occur when air was not only cold but also sunlit (i.e., largely in spring as observed, rather than in winter when the polar cap is continuously dark or summer when it is warm). Some ozone loss can take place even in polar winter, however, due to atmospheric waves that move polar air out to the sunlit atmosphere for brief periods [Tuck, 1989; Sanders et al., 1993; Roscoe et al., 1997].

Observations of PSCs, low NO₂ amounts in polar regions (Figure 6), enhanced polar HNO₃ [Murcray et al., 1975; Williams et al., 1982] and the vertical profile of the ozone depletion based upon the Japanese measurements [Chubachi, 1984] were cited in support of heterogeneous chemistry as the primary process initiating Antarctic ozone depletion. Such a mechanism would be most effective in the Antarctic because of colder temperatures and greater PSC frequencies there than in the corresponding seasons in the Arctic [McCormick et al., 1982], a point discussed further below.

As in the discussion of gas phase chemistry, a complete understanding of ozone depletion requires consideration not only of how much ClO is present (i.e., ClO/Cl_y) but also of the catalytic cycles in which ClO may engage. Solomon et al. [1986] emphasized the catalytic ozone destruction initiated by the reaction between HO₂ and ClO. However, this process cannot destroy enough ozone early enough in the spring season to be consistent with the detailed seasonality of the ozone loss process as shown above in Plate 2.

Molina and Molina [1987] showed that very rapid ozone depletion can occur through a previously unrecognized catalytic cycle involving formation and photolysis of a ClO dimer, Cl₂O₂. Following a period of some uncertainty regarding the kinetics and photochemistry of the dimer, laboratory studies confirmed its importance [e.g., Sander et al., 1989] (see Rodriguez et al. [1990] for model calculations and JPL [1997] for a detailed summary of laboratory data). This cycle is now well recognized as the primary catalytic process responsible for about 75% of the ozone removal in the ozone hole.

McElroy et al. [1986] and Tung et al. [1986] emphasized the role of bromine chemistry in ozone hole formation (in particular, its coupling to chlorine through the reaction between ClO and BrO); this cycle is now known to contribute about 20% to the annual formation of the Antarctic ozone hole [e.g., Anderson et al., 1989].

Both *McElroy et al.* [1986] and *Tung et al.* [1986] also emphasized the need for reduced NO_2 in order for ClO to remain active (noting the links to the Noxon cliff), and *McElroy et al.* [1986] also emphasized the Japanese ozonesonde observations, particularly the observation of ozone loss at low altitudes, where bromine can be very effective for ozone destruction.

Partly because of limited analysis of Antarctic stratospheric temperatures, early studies such as those described above were not specific about the type of particles of which the observed PSCs were composed. It was generally assumed that the particles were mainly water ice [*Steele et al.*, 1983]. Stratospheric ice clouds are frequently optically thick and brilliant in color, like those observed by Captain Scott. Such clouds form when temperatures drop below the *frost point* and are now referred to as *type 2* PSCs. However, more sensitive satellite measurements [*McCormick et al.*, 1982] suggested that optically thinner PSCs were also present at warmer temperatures.

Toon et al. [1986] and *Crutzen and Arnold* [1986] pointed out that the PSCs particles might be composed not only of water ice but also of solid nitric acid trihydrate (*NAT*). Both studies noted that such composition could affect the impact on ozone in two ways: (1) by reducing the amount of nitrogen oxide that could be present (i.e., not only by forming nitric acid but also by removing it from the gas phase) and (2) by raising the temperature at which clouds could form, since thermodynamic analyses suggested that *NAT* could condense at temperatures well above the frost point. These clouds came to be known as *type 1* PSCs. In addition, *Toon et al.* [1986] suggested that sedimentation of large particles could result in *denitrification* of the stratosphere. The removal of nitric acid not only from the gas phase but from the stratosphere altogether would have a potential to further reduce NO_2 concentrations and hence enhance $\text{ClO}/\text{ClONO}_2$ ratios and attendant chlorine-catalyzed ozone loss. *McElroy et al.* [1986] also considered the possibility of nitric acid–water particles, suggesting that nitric acid monohydrate (*NAM*) was likely to form.

Table 1 includes a list of the major heterogeneous processes of importance in the stratosphere. Through these heterogeneous reactions, the chemical partitioning of chlorine in the Antarctic lower stratosphere in spring can be greatly perturbed in comparison with gas phase chemistry, making chlorine (and its coupling with bromine) far more damaging to ozone than it would be in a gas phase framework. A broad range of models, including two-dimensional [e.g., *Isaksen and Stordal*, 1986; *Chipperfield and Pyle*, 1988; *Brasseur and Hitchman*, 1988; *Ko et al.*, 1989; *Rodriguez et al.*, 1989; *Tie et al.*, 1997], three-dimensional [e.g., *Cariolle et al.*, 1990; *Austin et al.*, 1992; *Brasseur et al.*, 1997; *Knight et al.*, 1998], and trajectory and Lagrangian studies [e.g., *Jones et al.*, 1989; *Schoeberl et al.*, 1996] have probed this basic framework and presented numerical analyses of calculated ozone trends. Several authors have emphasized the

importance of atmospheric waves in modulating the temperatures and sunlight that influence the ozone loss process [e.g., *Jones et al.*, 1989], while others have underscored the role of interannual variability in dynamical conditions in determining not only the temperature-dependent chemistry [*Tie et al.*, 1997] but also the re-supply of ozone into the depleted region, hence modulating the chemistry [*Knight et al.*, 1998]. *Schoeberl and Hartmann* [1991] and *Schoeberl et al.* [1996] have used dynamical tracers such as N_2O to carefully identify the edge of the vortex and show its links to both dynamics and chemistry. In particular, they have simulated chemical perturbations at the outer fringes of the Antarctic vortex, including high ClONO_2 abundances observed, for example, by *Toon et al.* [1989].

Since ozone provides the primary source of heat to the stratosphere through its absorption of UV radiation, *Shine* [1986] noted that the ozone hole should be expected to lead to a stratospheric cooling, which in turn could make heterogeneous chemistry even more effective. The seasonal increase in Antarctic ozone observed after October as shown in Plate 2 is associated with the seasonal warming and breakdown of the Antarctic vortex, which allows ozone-rich air to flow into the region. Its delay in recent years compared with historical data is evident in Plate 2 and suggests that such a positive feedback mechanism has indeed modified not only the October–November temperatures [*Newman and Randel*, 1988] but also the meteorological characteristics of the Antarctic stratosphere [see *Jones and Shanklin*, 1995] in a fashion that prolongs the ozone hole. It is important to note, however, that analyses of winter temperatures in the Antarctic stratosphere reveal little or no evidence for cooling before the ozone depletion occurs in September [*Newman and Randel*, 1988; *Trenberth and Olson*, 1989; *Jones and Shanklin*, 1995], confirming that the meteorological changes are primarily a consequence and not a cause of the ozone hole.

3.4. Heterogeneous Chlorine Chemistry and the Ozone Hole: Field and Laboratory Observations

Foremost among the data that established the cause of the ozone hole are observations of active chlorine species, particularly ClO . *De Zafra et al.* [1987, 1989] presented ground-based microwave emission measurements at McMurdo Station, Antarctica, showing evidence for greatly enhanced ClO in the lower stratosphere. Near 20 km the observations suggested mixing ratios of ~ 1 ppbv in September, about 100 times greater than the 10 *pptv* predicted by gas phase photochemical theory. *Anderson et al.* [1989] presented in situ airborne measurements of ClO using a resonance fluorescence method. The latitudinal coverage of the airborne data taken flying south from Chile near 20 km showed a very steep gradient in ClO as the airplane crossed into cold regions within the Antarctic vortex, increasing to about 1 ppbv in mid-September as shown in Figure 7. Hence within a few years after the discovery of the ozone hole,

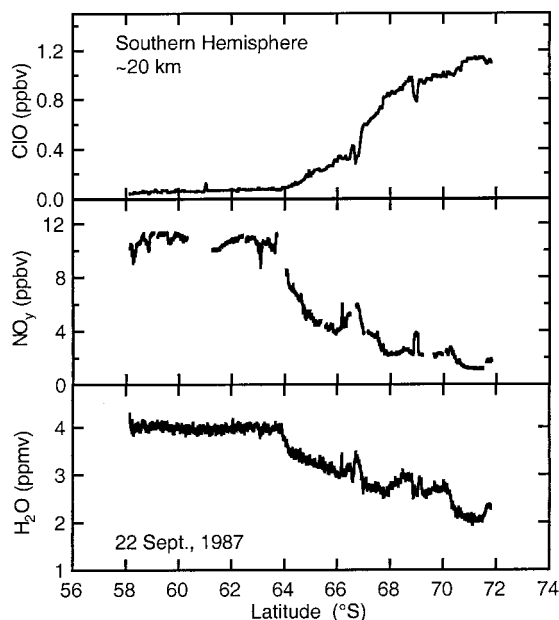


Figure 7. Observations of the latitude gradients in CIO, NO_y , and H_2O on a flight of the ER-2 aircraft in September 1987, showing evidence for extremely high CIO in the Antarctic together with substantial denitrification and dehydration (removal of NO_y and H_2O) associated with PSCs.

two independent methods confirmed remarkably elevated CIO abundances in the ozone hole region, which are possible only if chlorine is released from both of the reservoir gases, HCl and ClONO_2 .

Figure 8 shows both ground-based and airborne measurements of CIO in September over Antarctica from 1987, and compares them with gas phase and heterogeneous photochemical theory. More recently, satellite

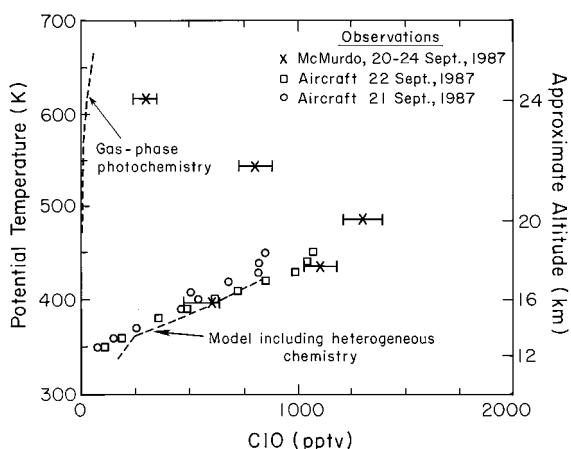


Figure 8. Observations of the vertical profiles of CIO in the Antarctic stratosphere in September 1987 from both ground-based microwave remote sensing [de Zafra *et al.*, 1989] and aircraft resonance fluorescence techniques [Anderson *et al.*, 1989]. These data are compared with a gas phase photochemistry model and with the heterogeneous chemistry model of Jones *et al.* [1989], which accounts for air parcel trajectories.

observations as depicted in Plate 1 have allowed study of the full global distribution of CIO [Waters *et al.*, 1993, 1999] using microwave emission methods that further tie the ozone destruction region with the spatial distribution of enhancements in CIO [Manney *et al.*, 1995b; MacKenzie *et al.*, 1996]. The front cover of this issue of *Reviews of Geophysics* presents satellite observations of lower stratospheric ozone and CIO on August 30, 1996, over Antarctica. The data show that the region of reduced ozone extends over an area larger than the continent beneath and illustrate the close spatial correspondence between the regions of depleted ozone and those of enhanced CIO as first emphasized by Anderson *et al.* [1989].

Observations of chlorine dioxide (OCIO) via visible spectroscopy was another independent method of probing the chlorine chemistry that also revealed hundred-fold enhancements of active chlorine in the Antarctic vortex [Solomon *et al.*, 1987; Wahner *et al.*, 1989; Kreher *et al.*, 1996]. This technique also allowed study of the seasonal changes in Antarctic chlorine activation and its links to PSC chemistry. These showed a seasonal decline of OCIO between late August and early October, associated with increasing temperatures and the cessation of heterogeneous chemistry [Solomon *et al.*, 1987].

Observations of the HCl column, and in particular its ratio to the HF column, strongly suggested that HCl had indeed been converted to active chlorine in the Antarctic spring [Farmer *et al.*, 1987; Toon *et al.*, 1989; Coffey *et al.*, 1989]. The recent global satellite data by Russell *et al.* [1993] further demonstrate this behavior on larger spatial scales. The first in situ measurements of HCl showing evidence for conversion to active chlorine were obtained in Arctic studies by Webster *et al.* [1993]; see section 6.1. Concurrent global HCl and ClONO_2 data from the UARS satellite illustrated the simultaneous chemical conversion of both species where polar stratospheric cloud surfaces were also present [Geller *et al.*, 1995; Yudin *et al.*, 1997]. A detailed view of the temperature dependence of chlorine activation is provided from Antarctic in situ observations of both CIO and HCl, which dramatically illustrate rapid activation at temperatures below about 195 K [Kawa *et al.*, 1997] (see earlier studies by Toohey *et al.* [1993] and Schoeberl *et al.* [1993a, b]) and provide a key demonstration of rapid heterogeneous chemistry under cold conditions.

The combination of simultaneous observations of CIO, HCl, OCIO, NO, NO_2 , and other gases by a variety of independent chemical methods demonstrates that the springtime Antarctic stratosphere is indeed heavily perturbed compared to expectations from gas phase chemistry, and in a manner consistent with heterogeneous reactions on PSC particles. Through the resulting dramatic enhancements in the CIO/ Cl_y ratio, chlorine's effectiveness for ozone destruction is greatly enhanced. For CIO abundances near 1–1.3 ppbv as observed since 1986–1987 (and BrO abundances near 7–10 pptv [see Brune *et al.*, 1989]), Antarctic ozone is destroyed near 20

km in September at a rate of about $0.06\text{--}0.1\text{ ppmv d}^{-1}$, so that within $\sim 40\text{--}60$ days virtually all of the ozone at this level can be depleted unless rapid dynamical resupply occurs, broadly consistent with Figure 5 [see *Anderson et al.*, 1989; *Murphy*, 1991; *MacKenzie et al.*, 1996]. The cold temperatures observed in the Antarctic during September in most years suggest that net downward motion (which would tend to warm the air through adiabatic compression) and horizontal mixing is relatively limited at that time. This general picture of relative dynamical isolation in the heart of the ozone depletion region is supported by a number of dynamical studies [e.g., *Hartmann et al.*, 1989; *Manney et al.*, 1994b, 1995a, b; *Schoeberl et al.*, 1995, 1996].

The observations offer several different spatial and temporal fingerprints that strongly support the identification of chlorine chemistry and its perturbations by heterogeneous processes as the principal cause of the ozone hole. The measurements shown in Figure 8 reveal that the enhanced ClO occurs over about the 12- to 25-km range, the region where PSCs are observed and where the ozone is depleted as shown in Figure 5. The airborne data of Anderson and colleagues, as depicted, for example, in Figure 7, demonstrate the steep latitudinal gradient in ClO, consistent with the connection of the ozone hole to cold Antarctic latitudes; a fully three-dimensional view of the same behavior based upon satellite data [*Waters et al.*, 1993, 1999] is illustrated in Plate 2 and the cover of this issue. Seasonal observations of OClO, ClO, HCl, NO_2 , and other gases have been used to show that the large temporal changes in the abundances of these chemical species are consistent with the time evolution of the ozone hole and with heterogeneous chemistry. In short, the vertical, latitudinal, and seasonal behavior observed in active chlorine and a host of related species all provide independent evidence confirming the basic processes that control the occurrence of the ozone hole.

Antarctic field measurements also allowed study of the formation, composition, and seasonal behavior of polar stratospheric clouds. *Fahey et al.* [1989b, 1990b], *Gandrud et al.* [1989], and *Pueschel et al.* [1989] carried out the first observations of the composition of polar stratospheric clouds and demonstrated that the particles do indeed contain nitric acid as had been predicted. Laboratory studies [*Hanson and Mauersberger*, 1988] confirmed the thermodynamic stability of NAT at temperatures well above the frost point. Observations demonstrated that gas phase reactive nitrogen or NO_y [*Fahey et al.*, 1989b] and water vapor [*Kelly et al.*, 1989] are strongly depleted in the Antarctic stratosphere, as was predicted by *Toon et al.* [1986] on the basis of sedimentation of large type 2 PSC particles. Figure 7 shows evidence for NO_y and H_2O removal in the same region displaying enhanced ClO in the Antarctic stratosphere (poleward of $\sim 64^\circ\text{S}$ in that particular transect) from airborne studies. Later measurements documenting the “denitrification” and “dehydration” of the Antarctic

lower stratosphere include those of *Santee et al.* [1998, 1999], *Voemel et al.* [1995] and *Pierce et al.* [1994].

Many laboratory studies have confirmed that rapid heterogeneous processes do indeed take place on the kind of surfaces present in polar regions. The fundamental principles of surface chemistry are outlined in the excellent book by *Somorjai* [1994], which illustrates many of the factors that allow surfaces to facilitate processes that do not happen, or happen only very slowly, in the gas phase. *Fairbrother et al.* [1997] review thermodynamic principles behind stratospheric heterogeneous chemistry. The first laboratory studies of stratospheric reactions on ice by *Molina et al.* [1987] and *Tolbert et al.* [1987] showed that the reaction of HCl with ClONO_2 indeed takes place readily on water ice films. *Hanson and Ravishankara* [1994] showed that a portion of the reaction is due to $\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$, following formation of HOCl through the surface reaction $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$. *Prather* [1992a] discussed the implications of a surface $\text{HOCl} + \text{HCl}$ reaction for ozone depletion. Numerous laboratory investigations have shown that HCl reacts with ClONO_2 on nitric acid trihydrate ice surfaces as well, although the rate depends on factors such as the HCl partial pressure and on the water content of the NAT surface [*Leu*, 1988; *Abbatt et al.*, 1992; *Hanson and Ravishankara*, 1993; *Peter*, 1997; *Carlsaw and Peter*, 1997]. Some authors have noted that heterogeneous reactions between bromine and chlorine can also contribute to chlorine activation, through, for example, reaction between HOBr and HCl [*Hanson and Ravishankara*, 1995; *Danilin and McConnell*, 1995]. For a review of recent laboratory studies of these and other heterogeneous processes, see *JPL* [1997].

Both the nature of stratospheric surfaces and the detailed reaction mechanisms that can occur within them have been the subjects of many studies. ClONO_2 hydrolysis on ice may proceed via nucleophilic attack at Cl by a lattice water molecule in concert with proton transfer [*Bianco and Hynes*, 1998]. It is possible that proton transfer from HCl to water forms Cl^- on ice surfaces, allowing reaction with ClONO_2 through an ion-assisted and hence efficient mechanism [*Van Doren et al.*, 1994]. Fundamental surface chemistry models suggest that HCl forms a bilayer on ice, allowing ionization and subsequent surface chemistry [*Gertner and Hynes*, 1996]. On the other hand, *Materer et al.* [1997] suggest that a quasi-liquid layer displaying less order than the bulk may be present at an ice surface under stratospheric conditions, so that uptake of HCl into stratospheric ice particles may occur through a process akin to solution at a quasi-liquid interface. In addition to these interesting questions regarding the fundamental physical chemistry of heterogeneous reactions in the stratosphere, the understanding of the composition of polar stratospheric clouds has also been a subject of intense study and is the subject of the next section.

4. FORMATION, COMPOSITION, AND CHEMICAL ROLE OF POLAR STRATOSPHERIC CLOUDS: RETHINKING PSCS

The foregoing discussion illustrates the rapid progress made toward understanding the key role of heterogeneous chlorine chemistry on polar stratospheric clouds in the formation of the Antarctic ozone hole in the last half of the decade of the 1980s. However, at present our conceptual picture of the composition and chemistry of PSCs has evolved considerably from the relatively simple one that prevailed a decade ago. Detailed recent reviews of the microphysics, thermodynamics, and heterogeneous chemistry of stratospheric particulates are provided by *Peter* [1997] and *Carlsaw et al.* [1997a], and excellent short summaries of laboratory work are given by *Tolbert* [1994, 1996]. Only the key points will be reviewed here. Both Arctic and Antarctic observations that jointly contribute to this understanding will be described in this section.

4.1. What Are PSCs Made of?

Toon et al. [1990] were the first to present evidence that PSCs may be composed of liquid as well as solid particles, drawing upon lidar measurements by *Browell et al.* [1990]. Briefly, the observations by *Browell et al.* [1990], and later work [e.g., *Beyerle et al.*, 1994; *Adriani et al.*, 1995; *Steffanutti et al.*, 1995; *Gobbi et al.*, 1998] showed evidence for high backscatter (hence the detection of clouds). However, while some data revealed high accompanying depolarization as expected for aspherical solid particles, other measurements showed very low depolarization of the backscatter signal, suggesting liquid rather than solid particles. The two distinct cloud types resulted in a further subdivision of PSCs into *type 1a* (depolarizing solid) and *type 1b* (nondepolarizing liquid).

In situ and satellite measurements also showed evidence for shortcomings in our understanding by demonstrating that while PSCs form at temperatures above the frost point and do contain nitric acid, the detailed relationships to temperature are often difficult to reconcile with NAT thermodynamics [*Kawa et al.*, 1990, 1992; *Rosen et al.*, 1989; *Arnold*, 1992; *Dye et al.*, 1996; *Del Negro et al.*, 1997; *Santee et al.*, 1998a]. *Toon and Tolbert* [1995] further showed that infrared spectra of type 1 PSCs observed over Antarctica were inconsistent with those expected for NAT.

Arnold [1992] showed evidence for uptake of HNO_3 into PSCs that could not be reconciled with NAT particles and suggested that ternary liquid $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ particles might be responsible for the observed anomalies. The introduction of H_2SO_4 in this discussion merits a brief description of its origins. It has been known since the pioneering work of *Junge et al.* [1961] that particles composed of sulfuric acid and water form throughout the stratosphere. The mechanism responsible for growth of PSCs was originally thought to involve

freezing of these “background” sulfate aerosol particles followed by uptake of nitric acid and water when the NAT condensation temperature was reached [*Dye et al.*, 1992; *Molina et al.*, 1993] (see *Peter* [1997] and references therein). Recent observations and theoretical studies raise many questions about this picture, as is discussed below.

Observations by *Dye et al.* [1992] and their analysis by *Carlsaw et al.* [1994], *Drdla et al.* [1994] and *Tabazadeh et al.* [1994] have demonstrated that some PSCs are probably composed of supercooled ternary liquid solutions of $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$. Briefly, the observations showed a smooth growth in particulate volume with decreasing temperature rather than a “step function” in growth at the stability point for NAT. The dependence of the growth of particulate volume with temperature closely followed model predictions based on the thermodynamics of ternary liquid solutions (see *Carlsaw et al.* [1997a] for an in-depth review). Laboratory studies support this picture by demonstrating that realistic solutions and particles containing sulfuric acid, water, and nitric acid remain liquid even at very cold temperatures, as low as 188 K [e.g., *Beyer et al.*, 1994; *Koop et al.*, 1995, 1997; *Anthony et al.*, 1997; *Clapp et al.*, 1997; *Bertram and Sloan*, 1998]. Indeed, the results of these recent laboratory studies show that it is extremely difficult to make such particles freeze at temperatures above the frost point, even when they are kept cold for many hours.

Thus recent field and laboratory observations, and related modeling studies, have substantially altered the conceptual understanding of PSCs. The data show that PSCs are liquid much of the time. While there is no difficulty understanding the formation of frozen type 2 water ice clouds that form below the frost point [see *Poole and McCormick*, 1988a, b; *MacKenzie et al.*, 1995; *Peter*, 1997], the mechanism whereby solid type 1 PSCs sometimes (but not always) are present at temperatures above the frost point [e.g., *Poole et al.*, 1988] is not clear. The studies by *Tabazadeh et al.* [1996], *Santee et al.* [1998a], and *Larsen et al.* [1997] suggest that temperature histories as well as local temperatures are likely to be important in determining when and if freezing occurs. Mesoscale temperature fluctuations (i.e., transient rapid cooling in atmospheric waves) could lead to nonequilibrium conditions under which NAT or the nitric acid dihydrate, NAD (emphasized by *Worsnop et al.* [1993]) could freeze [*Meilinger et al.*, 1995; *Tsias et al.*, 1997].

On the other hand, *Tabazadeh et al.* [1994] and *Tabazadeh and Toon* [1996] have emphasized amorphous solid solutions and water-rich hydrates as possible precursors to freezing, while *MacKenzie et al.* [1995] and *Drdla et al.* [1994] suggested that trace impurities in stratospheric particles (such as meteoritic material, organics, or soot; see observations by *Murphy et al.* [1998]) may play a key role in the freezing process. However, *Iraci et al.* [1998] recently showed that solid sulfuric acid tetrahydrate (SAT) particles may form in the laboratory under certain conditions, then (in a perhaps ironic twist)

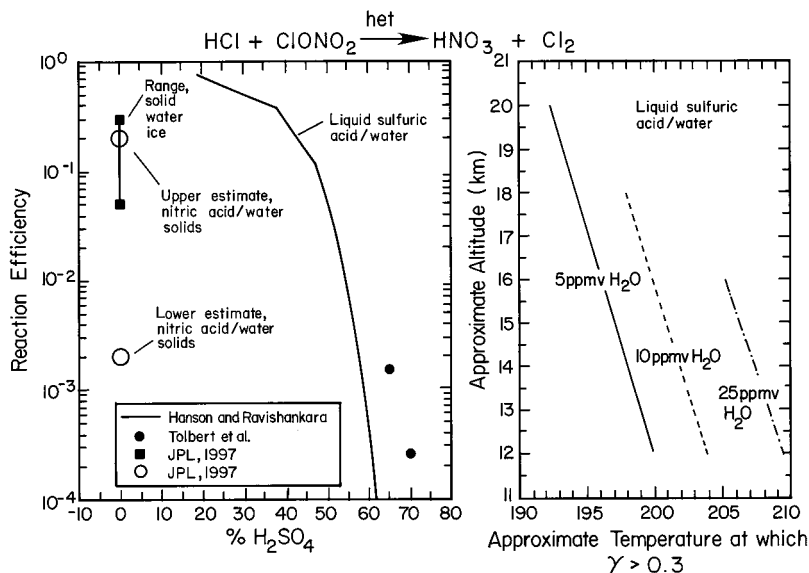


Figure 9. (left) Laboratory data on the efficiency of the reaction between HCl and ClONO₂ for ice, nitric acid–water solid surfaces, and liquid sulfuric acid–water solutions. (right) Altitude variation of the temperature at which the efficiency of this reaction on liquid sulfuric acid–water solutions becomes greater than 0.3 for water vapor mixing ratios typically observed in the lower stratosphere.

take up HNO₃ not in a cooling but in a melting phase, which could be followed not by complete melting of the particle but rather by crystallization of NAT. Thus the solid SAT could form a core that allows uptake of HNO₃ into a liquid melting surface, followed by freezing.

4.2. What is the Effect of Different Surfaces on Ozone Depletion Chemistry?

It is extremely important to consider whether the phase and microphysical mechanisms underlying PSC formation are important for ozone depletion. The uptake of condensable vapors enhances surface areas when PSCs are present. This increases the gas-particle collision frequency and hence can enhance the rates of heterogeneous reactions. Background stratospheric aerosols grow into type 1a and/or type 1b particles as they cool, then further grow into type 2 water ice PSCs if temperatures fall below the freezing point. The impact of enhanced surface areas for chemistry depends not only on the frequency with which gases strike these surfaces but also on the reactivity of the surfaces and the availability of those gases.

Let us first consider how reactive the different surfaces are and where they are to be found in the stratosphere. Laboratory studies have shown that water ice, NAT, and liquid ternary solutions are all effective for activating chlorine heterogeneously, but with differing efficiencies and with different dependencies on temperature, water vapor abundance, and pressure [e.g., Carlsaw *et al.*, 1997a; JPL, 1997, and references therein]. These dependencies are related to the thermodynamics of the different surfaces, which control not only their surface areas but also their composition (especially the uptake of HCl onto/into the particles).

Figure 9 summarizes a number of laboratory measurements of the efficiency of the key heterogeneous surface reaction $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$ (where

1 indicates reaction on every collision of ClONO₂ with a surface, 0.1 indicates 1 reaction in 10 collisions, etc.). Water ice is believed to be highly reactive wherever it can form, but the thermodynamics of ice condensation imply that rather cold temperatures are required to form it in the stratosphere (e.g., below ~188 K near 20 km). There is currently debate about the efficiency of NAT for this reaction [Carlsaw and Peter, 1997; JPL, 1997] as well as the conditions under which NAT can form, but from a thermodynamic viewpoint, NAT may form near 20 km when temperatures drop below ~195 K, thus allowing reaction on a solid surface at temperatures above the frost point. In the case of liquid solutions, the efficiency of reaction depends strongly on the fraction of water in the particle [e.g., Tolbert *et al.*, 1988; Hanson *et al.*, 1994]. The HCl + ClONO₂ reaction becomes more efficient for lower percentages of sulfuric acid (and higher water in the liquid particles, which greatly increases the solubility of HCl; see Robinson *et al.* [1998] for a detailed recent analysis). This reaction takes place in liquid solutions with an efficiency greater than 1 in 100 (0.01 as shown in Figure 9) for temperatures colder than ~197 K at 20 km, and an efficiency of 1 in 10 for temperatures below ~195 K. Ravishankara and Hanson [1996] have emphasized that liquid PSCs can be comparable to or more effective than solid PSCs for many surface reactions at temperatures below ~195 K at 20 km, a point also illustrated by Cox *et al.* [1994], Borrmann *et al.* [1997a] and Del Negro *et al.* [1997].

Because liquid aerosols are present throughout the global stratosphere and because the water vapor pressures available to condense into them increases with increasing total pressure, the temperatures at which effective reactions may occur in liquid particles are higher for lower altitudes [Hofmann and Oltman, 1992], as is also shown in Figure 9. This is a critical issue for both the polar and midlatitude lower stratospheres. Fig-

ure 9 suggests that both liquid and solid surfaces can activate chlorine efficiently near the tropopause [Borrmann *et al.*, 1996, 1997b; Bregman *et al.*, 1997; Solomon *et al.*, 1997]. Observations of enhanced ClO and reduced NO close to the tropopause for relatively wet (15 ppmv of H₂O) conditions provide evidence for such liquid surface chemistry [Keim *et al.*, 1996]. Note that Figure 9 is based upon the thermodynamic model of Carslaw *et al.* [1997a]; its extrapolation to very high water vapor pressures (e.g., >5 ppmv at 200 mbar) is uncertain at present and requires laboratory studies for those conditions [see Robinson *et al.*, 1998].

It is useful to note that the HCl + ClONO₂ reaction competes with H₂O + ClONO₂ for the available ClONO₂ on liquid aerosol surfaces. Thus if HCl has been depleted, the rate of the latter reaction increases, so that effective heterogeneous activation of chlorine is not dependent upon both HCl and ClONO₂ being present. Further, the reactions of HCl with HOCl and HOBr are also quite efficient on liquid aerosol under moderately cold and/or wet conditions [Ravishankara and Hanson, 1996; JPL, 1997], providing additional pathways for chlorine activation.

A key conclusion of Figure 9 is that while there are differences and uncertainties in the reactivity of various surfaces, rather effective chlorine activating reactions can occur irrespective of particle phase below ~198 K at 20 km and below 200–210 K near 12–14 km. As an air parcel cools and particle reactivities increase, liquid chemistry will occur first. This may be followed by reactions on NAT and ice, depending on factors including microphysics, the minimum temperature reached, and whether or not all of the chlorine activation has already occurred [Turco and Hamill, 1992]. This latter point is critical. For example, if effective chemical processing on liquid surfaces has depleted all of the available HCl and/or ClONO₂ within an air parcel, then further lowering of temperature and formation of, for example NAT, may have a limited effect on ozone depletion. Moreover, an increased rate of reaction and/or an increased surface area (through, for example, formation of NAT type 1 PSCs or type 2 PSCs) may not enhance ozone depletion in a time averaged sense. If, for example, reactions on sulfate aerosols are sufficient to activate all of the available chlorine within a day, ozone depletion will not be increased if instead reactions on ice activate all of the chlorine in an hour, since the ozone depletion is a process that occurs over a much longer period (weeks) following the activation. Hence the details of the reactivities and the microphysics that control particle surface areas, while playing a role to some degree, are not critical to formation of the ozone hole [e.g., Portmann *et al.*, 1996; Carslaw *et al.*, 1997b]. They are likely to be more important at the margins, particularly regions where temperatures are cold but not extremely cold.

Primary sources of sulfur to the stratosphere are carbonyl sulfide [Crutzen, 1976; Chin and Davis, 1995]

and explosive volcanic eruptions that inject SO₂ gas directly into the stratosphere [e.g., McCormick *et al.*, 1995] which subsequently forms liquid sulfate aerosols. Observations of PSC extinction show that the major eruptions of El Chichón in 1981 and Mount Pinatubo in 1991 led to large increases in particle surface areas in polar regions [e.g., McCormick *et al.*, 1995; Deshler *et al.*, 1992; Thomason *et al.*, 1997]. Hofmann *et al.* [1992, 1997] and Hofmann and Oltmans [1993] showed that enhanced aerosol surface areas due to Pinatubo expanded the altitude range of significant Antarctic ozone depletion into one of its margins, down to lower, warmer altitudes (i.e., 10–14 km) where solid PSCs do not form. Observations of OCIO in the Antarctic fall season (March–April) at temperatures above 200 K in the year immediately following Pinatubo also suggest significant activation of chlorine through sulfate aerosol processing [Solomon *et al.*, 1993]. Hence both ozone and trace gas observations from the Antarctic provide support for the role of temperature-dependent heterogeneous chemistry on liquid aerosols. Portmann *et al.* [1996] showed that volcanically enhanced PSC surface areas were likely responsible for the sharp onset of the ozone hole in the early 1980s following the El Chichón eruption, and for the very deep ozone holes observed in the early 1990s following the Pinatubo eruption.

It may be useful to pause for a brief summary of the conceptual picture for Antarctic ozone depletion that emerged in the late 1980s and describe how it has changed. Initial observations of Antarctic chemistry as discussed above showed evidence both for heterogeneous chlorine activation on PSCs and for denitrification. An understanding emerged that chlorine-activating reactions took place on solid PSCs in Antarctic winter, accompanied by denitrification that allowed the depletion to persist in spring, even in the absence of further PSC formation. This picture was simple and easy to explain in chemical terms. However, the current understanding suggests that denitrification can increase ozone destruction somewhat but is not required for polar ozone losses. This is because chlorine activation can continue to occur on liquid aerosols in spring, keeping the chlorine active in sunlit air whether denitrified or not [Portmann *et al.*, 1996; Chipperfield and Pyle, 1998]. Observations following the eruption of Mount Pinatubo support the view that liquid aerosol chemistry has been a key factor in determining the depth of the ozone hole after major eruptions. More generally, the expansion of heterogeneous chemistry from ice, to NAT, to liquid sulfate aerosols has lessened the expected dependence of the ozone loss on extreme cold to one of relative cold, thereby expanding the height, time, and latitude ranges where ozone depletion may be expected to be enhanced by heterogeneous processes that affect chlorine partitioning. The next two sections explore these issues by illustrating the important role of heterogeneous processes for both mid-latitude and Arctic ozone depletion.

5. MIDLATITUDE OZONE DEPLETION

The discovery of the Antarctic ozone hole naturally raised the question of whether other latitudes might also display greater ozone depletion than expected. Within a few years after the ozone hole was discovered, statistically significant trends in ozone were found at northern midlatitudes as well [*Ozone Trends Panel*, 1988, and references therein]. By the 1990s, significant trends had been established for both northern and southern midlatitudes, not only in winter and spring but also in summer [*WMO/UNEP*, 1991, 1994; *Stolarski et al.*, 1991; *McPeters et al.*, 1996a, b; *Harris et al.*, 1997; *Stahelin et al.*, submitted manuscript, 1998]. Midlatitude ozone column trends as of the 1990s are of the order of 5–10%, much smaller than those of the Antarctic (Figure 1) but far greater than gas phase model predictions. As in Antarctica, recent analyses have shown that the bulk of the northern midlatitude ozone decline is occurring in the lower stratosphere (near 12–20 km [see *McCormick et al.*, 1992; *Miller et al.*, 1995; *WMO/UNEP*, 1994; *Bojkov and Fioletov*, 1997; *Harris et al.*, 1998]).

5.1. Heterogeneous Chemistry and Midlatitude Ozone Depletion

One mechanism that could affect midlatitude ozone depletion is heterogeneous chemistry. It had long been suspected that some heterogeneous process involving N_2O_5 might be responsible for the Noxon ‘cliff’ and for anomalously high HNO_3 abundances in middle to high latitudes of the Northern Hemisphere [e.g., *Wofsy*, 1978; *Noxon*, 1979; *Austin et al.*, 1986] but it was not until the late 1980s that laboratory studies showed that N_2O_5 can hydrolyze rapidly (reaction efficiency of about 0.1) on sulfuric acid–water films [*Tolbert et al.*, 1988] and particles [*Mozurkiewicz and Calvert*, 1988]. Hence the possibility of heterogeneous chemistry on the liquid sulfate layer that is pervasive throughout the stratosphere began to be considered in earnest (but see also *Cadle et al.* [1975] for an early and interesting exploratory paper).

The hydrolysis of N_2O_5 reduces NO_x and its impact on ozone in the lower stratosphere, and indirectly enhances the effect of ClO through its control of the $\text{ClONO}_2/\text{ClO}$ ratio, as was discussed earlier. Recent studies have examined the dependence of the N_2O_5 hydrolysis reaction on temperature and pressure [*Robinson et al.*, 1997] and have probed reaction conditions in extensive detail [*JPL*, 1997]. This key reaction and the related hydrolysis of bromine nitrate [*Hanson et al.*, 1996] both take place rather rapidly at virtually all stratospheric conditions, making their influence extremely widespread (and, as is shown below, extremely important). In addition to these indirect effects, however, there is evidence for direct activation of chlorine on liquid sulfate aerosols as well. As noted above in connection with polar chemistry, *Tolbert et al.* [1988] suggested that ClONO_2 could react with water and with HCl on sulfuric acid–water surfaces, but with a strong

dependence on the particle composition, specifically, the water content of the particle (hence on the temperature and water vapor pressure).

The laboratory investigations of *Tolbert et al.* [1988] and *Mozurkiewicz and Calvert* [1988] prompted *Hofmann and Solomon* [1989] to study the role of N_2O_5 hydrolysis and chlorine activation on sulfuric acid aerosols at midlatitudes, particularly under volcanic conditions when such processes would be enhanced. They suggested that this chemistry could be significant for both background and volcanically perturbed conditions, and that the ozone reductions noted by several authors [e.g., *Adriani et al.*, 1987] following the eruption of El Chichón in 1981 might be linked to heterogeneous reactions similar to those occurring in Antarctica, albeit with reduced rates. Observations of marked reductions in NO_2 over New Zealand after the El Chichón eruption [*Johnston and McKenzie*, 1989] provided some of the first chemical evidence that such processes could be important at midlatitudes. Several modeling studies [e.g., *Rodriguez et al.*, 1991, 1994; *Brasseur and Granier*, 1992; *Prather*, 1992b; *McElroy et al.*, 1992; *Pitari and Rizi*, 1993; *Toumi et al.*, 1993] further probed the role of this chemistry in determining global ozone trends and related questions of chemical partitioning and odd oxygen destruction cycles. *Prather* [1992b] pointed out that the hydrolysis of N_2O_5 saturates beyond a certain aerosol load at which N_2O_5 is converted to HNO_3 as fast as it can be formed, so that further increases in aerosol do not affect NO_x abundances through this process.

Rodriguez et al. [1991] and *McElroy et al.* [1992] pointed out that hydrolysis of N_2O_5 would have the effect of dramatically altering the competition between the various catalytic cycles in the lower stratosphere, enhancing the roles of the odd hydrogen and odd chlorine/bromine destruction mechanisms, even for background aerosol conditions. Direct observations by *Wennberg et al.* [1994] later confirmed this view by providing simultaneous measurements of a suite of key radicals including OH, HO_2 , NO, and ClO near 20 km; these data can be related in hindsight to the anomalously low NO mixing ratios reported in the midlatitude lowermost stratosphere by *Ridley et al.* [1987]. *Cohen et al.* [1994] present a detailed chemical argument demonstrating the dominance of HO_x chemistry in the natural lower stratospheric ozone balance based on observations. Taken together, this improved understanding of the balance of terms among chemical cycles of ozone destruction is a key building block for attempts to evaluate ozone loss, which is tied to the competition of chlorine- and bromine-catalyzed destruction compared with other chemical processes and to transport. In short, slower rates of ozone loss through other processes (especially NO_x chemistry) result in a larger relative role for human-induced perturbations at midlatitude due to chlorine and/or bromine increases.

From about 1988 to the early 1990s the scientific understanding of midlatitude ozone depletion evolved

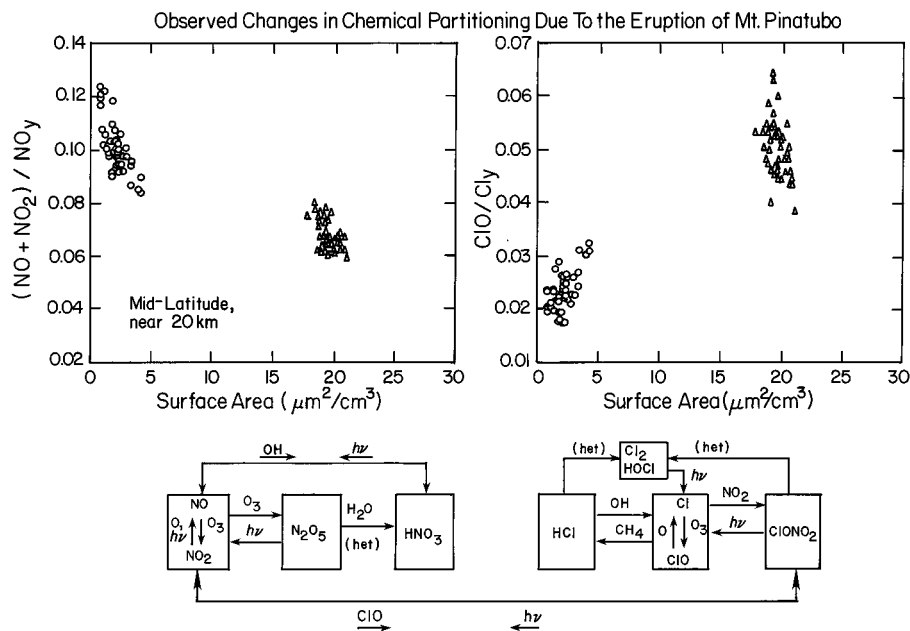


Figure 10. Observations of the changes in chemical partitioning as a function of aerosol load after the eruption of Mount Pinatubo at 20 km at midlatitudes [Fahey *et al.*, 1993]. The primary chemistry responsible for the observed behavior is depicted by the schematic diagram.

from a gas phase picture into the expectation of enhanced ozone depletion at least via the N_2O_5 hydrolysis process, not only for volcanically perturbed conditions but also for background aerosol loading. The eruption of Mount Pinatubo in June 1991 was the largest thus far in the twentieth century and occurred near the peak loading of atmospheric chlorine (see section 7). This geophysical event provided numerous lines of evidence suggesting that heterogeneous chemical reactions on sulfate aerosols play a key role in ozone chemistry and its depletion. Gleason *et al.* [1993] were the first to report record low northern midlatitude ozone abundances in the following year. Hofmann *et al.* [1994] and McGee *et al.* [1994] demonstrated that substantial ozone losses occurred in the lower stratosphere following the Pinatubo eruption, particularly in winter and spring, with peak local depletions near 20 km at 40° – 50°N as large as about 25%. Randel and Cobb [1994] showed that changes in temperatures relating to aerosol heating can provide an important means of distinguishing ozone losses due to volcanic eruptions from those relating to the quasi-biennial oscillation (QBO), El Niño, or other perturbations in statistical analyses of ozone data (see also Jäger and Wege [1990], Bojkov *et al.* [1993] and Zerefos *et al.* [1994]). The high aerosol load present just after the eruption in mid-1991 changed stratospheric heating and hence reduced tropical ozone through dynamical effects [Brasseur and Granier, 1992], but this lasted only a few months and was largely confined to the tropics [see Schoeberl *et al.*, 1992b; Tie *et al.*, 1994]. For reviews of the many studies establishing the large and persistent midlatitude ozone changes after Pinatubo, see

Toohey [1995] and WMO/UNEP [1994, 1998]. Because the stratospheric Brewer-Dobson circulation (as depicted in Figure 2) transports material upward and poleward, major volcanic eruptions that inject material into the tropical stratosphere can have the greatest and longest impacts on global ozone, while volcanic injections at higher latitudes are removed by downward motion. Both El Chichón and Pinatubo are tropical volcanoes.

Chemical measurements after Pinatubo have identified many signatures of heterogeneous reactions on sulfate aerosols at midlatitudes that are akin to those occurring in the ozone hole region. Observations from New Zealand showed both reduced NO_2 and enhanced HNO_3 column abundances [Johnston *et al.*, 1992; Koike *et al.*, 1994]. Aircraft, ground-based, and balloon- and shuttle-borne experiments revealed similar large changes in NO_x/NO_y partitioning associated with the roughly thirty-fold increases in aerosol surface observed [e.g., Rinsland *et al.*, 1994; Webster *et al.*, 1994; Fahey *et al.*, 1993; Mills *et al.*, 1993; Coffey and Mankin, 1993; Sen *et al.*, 1998]. Figure 10 shows direct observations of perturbations in NO_x/NO_y and ClO/Cl_y at 20 km from Fahey *et al.* [1993], associated with the buildup of Pinatubo aerosols at midlatitudes. NO_x/NO_y decreases follow the behavior broadly predicted by Prather [1992b] and expected from the dominance of N_2O_5 hydrolysis. Randeniya *et al.* [1997] and Slusser *et al.* [1997] used summer polar observations of NO_2 to show evidence for BrONO_2 hydrolysis on sulfate aerosols as well. Observations of enhanced OH at sunrise further suggest that the latter process is significant not only in reducing NO_x via heterogeneous chemistry but also as a source of OH

[Hanson and Ravishankara, 1995; Hanson *et al.*, 1996; Salawitch *et al.*, 1994; Lary *et al.*, 1996].

Turning to the key chlorine-related species, Avallone *et al.* [1993a, b] and Wilson *et al.* [1993] showed post-Pinatubo ClO observations suggesting heterogeneous perturbations in midlatitude air. HCl observations by Webster *et al.* [1998] provide evidence that ClO not only is enhanced by high volcanic loading at midlatitudes as an indirect effect through shifts in NO₂, but also is directly affected by chlorine activation (as reflected in reduced HCl). Debate on the magnitude of the latter effect in some regions has focused both on the rates of chlorine activation in liquid aerosols for midlatitude conditions and on mass balance among Cl_y species [see Dessler *et al.*, 1996, 1997, 1998; Stimpfle *et al.*, 1994]. While chlorine-activating reactions on liquid sulfate aerosols are thought to be relatively slow at 20 km for the average temperatures that prevail at midlatitudes, the strongly nonlinear dependence of these reactions on temperatures implies that the reaction rate averaged over the actual temperatures including cold fluctuations associated with wave motions will substantially exceed the rate computed for the average temperature [Murphy and Ravishankara, 1994]. In other words, brief exposure to cold temperatures may alter ClO/Cl_y partitioning and hence enhance ozone depletion at midlatitudes, especially under high aerosol loads [Webster *et al.*, 1998; Solomon *et al.*, 1998].

Figure 10 shows that even rather modest changes in aerosol abundances can substantially affect the ClO/Cl_y partitioning near 20 km. Indeed, Figure 10 suggests that aerosol surface area increases of a factor of only about 5 (as observed, for example, in some locations following the relatively minor Mount St. Helens eruption [see Thomason *et al.*, 1997] could increase ClO/Cl_y by 50%, thus greatly enhancing the chlorine-driven local ozone destruction reactions.

As has been emphasized throughout this paper, processes that enhance ClO relative to Cl_y are at the heart of ozone depletion. A point of useful comparison may be drawn by noting that if ClO/Cl_y had been constant from 1980 to 1990, then ClO would have been expected to increase by about 50% over this decade (owing to the roughly 50% increase in Cl_y from the gradual increase in chlorofluorocarbons during that period). However, Figure 10 demonstrates that much larger changes in ClO can be rapidly induced by volcanic aerosol increases through their effects on chemical partitioning. Solomon *et al.* [1996, 1998] showed that both the long-term ozone trend at northern midlatitudes and its year-to-year variations over the past 20 years are highly likely to be closely tied to volcanic-aerosol-driven changes in ClO/Cl_y partitioning (see Plate 6 below). Jackman *et al.* [1996] and Zerefos *et al.* [1997] reached similar conclusions with their models, and showed that solar cycle contributions to interannual ozone depletion are much smaller. Several authors have shown that the ozone response to volcanic aerosols before humans perturbed stratospheric

chlorine (e.g., in the nineteenth century after the eruption of Krakatoa) would likely be a slight column increase as a result of suppression of NO_x-catalyzed destruction as depicted in Figure 10 rather than the observed decreases obtained for current chlorine loads [Solomon *et al.*, 1996; Tie and Brasseur, 1995]. It is also useful to note that observations such as those at Arosa in Figure 1 show no noticeable depletion after a series of large eruptions in the 1960s, most notably the major tropical eruption of Agung in 1963. Observations from many other ground-based sites confirm that the enhancements in aerosol of the 1960s had little effect on ozone [e.g., Bojkov *et al.*, 1995]. Only since about 1980 have chlorine levels become sufficiently elevated that volcanic perturbations to ClO/Cl_y such as those shown in Figure 10 result in significant ozone loss. Hence the evidence suggests that volcanic particles at midlatitudes exacerbate halogen-induced ozone depletion in the contemporary stratosphere (much as PSCs do for polar regions, and with some similar chemistry) but cannot on their own significantly destroy stratospheric ozone.

Lary *et al.* [1997] were the first to suggest that soot may also affect Northern Hemisphere midlatitude ozone, mainly through possible reactions involving reactive nitrogen species [see Rogaski *et al.*, 1997]. A study by Bekki [1997] further probed this chemistry in some detail and argued for significant impacts on ozone trends in the vicinity of the tropopause. There is currently debate about the surface area of soot available at stratospheric altitudes, the extent to which it can remain active for chemistry or be quickly “poisoned,” and whether or not chemical data support such perturbations [Gao *et al.*, 1998].

The observation of large midlatitude ozone depletion following Pinatubo and El Chichón, substantial related changes in chemical species, and a wide range of modeling studies [e.g., Hofmann and Solomon, 1989; Brasseur and Granier, 1992; Michelangeli *et al.*, 1989; Pitari and Rizi, 1993; Bekki and Pyle, 1994; Tie *et al.*, 1997; Solomon *et al.*, 1996; Jackman *et al.*, 1996] provide strong evidence that heterogeneous sulfate aerosol chemistry plays a major role together with man-made chlorine in the processes controlling midlatitude ozone trends. The observed ClO/Cl_y and NO_x/NO_y dependencies upon volcanic aerosol amounts as shown, for example, in Figure 10 may be considered a chemical fingerprint underlying these effects, like the observations of greatly enhanced ClO in the ozone hole region. Another parallel with Antarctic ozone depletion is the observation of a close correspondence in altitude between the region of enhanced Pinatubo aerosol abundances and ozone depletion [e.g., McGee *et al.*, 1994; Hofmann *et al.*, 1994]. A third fingerprint is the onset and slow relaxation of the ozone depletion after Pinatubo observed at midlatitudes [see, e.g., Solomon *et al.*, 1996, 1998; Jackman *et al.*, 1996] over a period of a few years, mirroring in a slower manner the seasonal depletion of the ozone hole.

5.2. Dynamical Processes and Midlatitude Ozone Trends

Although the focus of this review is on ozone chemistry, other mechanisms that could contribute to midlatitude ozone depletion will be briefly summarized here. Several studies examined the extent to which dynamical processes might spread the influence of the ozone hole, either through a one-time “dilution” at the end of the winter when stratospheric warmings break up the polar vortex or through vortex “processing” whereby flow of air through the vortex (and hence chemical activation of chlorine) might be transported to lower latitudes [e.g., Tuck, 1989; Tuck *et al.*, 1992; Waugh *et al.*, 1994, 1997; Wauben *et al.*, 1997; Tuck and Proffitt, 1997].

The amount of ozone depletion observed at both northern and southern midlatitudes is considerably greater than that implied by a one-time end-of-winter dilution process [see, e.g., Sze *et al.*, 1989; Prather *et al.*, 1990; Pitari *et al.*, 1992]. For the Southern Hemisphere, such one-time dilution likely provides an average midlatitude column ozone depletion of $\sim 1\text{--}2\%$. Locally larger but transient dilution effects following the breakup of the Antarctic ozone hole in late spring have been documented in observations over New Zealand, Australia, Brazil, and Chile [Atkinson *et al.*, 1989; Lehmann *et al.*, 1992; Kirchhoff *et al.*, 1996, 1997a]. The city of Punta Arenas, Chile, at 53°S occasionally lies just beneath the tip of the Antarctic ozone hole itself for brief periods in October when wave disturbances push the vortex overhead [Kirchhoff *et al.*, 1997a, b]. Because of greater dynamical activity, the northern vortex is likely to be subject to a greater degree of processing, and many studies conclude that there is ample evidence for the spread of polar “filaments” to midlatitudes at times [Tuck *et al.*, 1992; Gerber and Kampfer, 1994; Pyle *et al.*, 1995; Lutman *et al.*, 1997]. However, dynamical analyses and tracer studies suggest that the transport from polar regions alone cannot account for the observed ozone losses in midlatitudes [e.g., Schoeberl *et al.*, 1992b; Waugh *et al.*, 1994; Manney *et al.*, 1994b; Jones and MacKenzie, 1995; Chipperfield *et al.*, 1996; Wauben *et al.*, 1997; Grewe *et al.*, 1998]. This subject will be discussed further below in the section relating to Arctic ozone depletion.

In addition to vortex processing as described above, the notion of PSC processing has also been suggested (wherein PSCs forming outside the vortex provide the sites for heterogeneous reactions), particularly in association with locally cold temperatures that may be related to mountain lee waves and hence of quite small spatial and temporal scale [e.g., Godin *et al.*, 1994; Carslaw *et al.*, 1998]. All of these processing mechanisms depend upon heterogeneous chlorine-related chemistry in some fashion and hence connect midlatitude ozone depletion to chlorine trends, but with important differences in the degree of nonlocal (i.e., transport-related) linkages.

A few authors have argued that changes in strato-

spheric dynamics themselves could have contributed to the observed midlatitude ozone trends. A recent review is provided by Ravishankara *et al.* [1999] (see references therein). In brief, some studies [e.g., Hood and Zaff, 1995; McCormack and Hood, 1997; Hood *et al.*, 1997; Fusco and Salby, 1999] have argued for a component of purely dynamical change in midlatitude ozone relating, for example, to changes in the transport of ozone. It is well known that dynamical processes strongly influence ozone from year to year, particularly in January in the Northern Hemisphere [Fusco and Salby, 1999]. However, evaluation of trends requires long records and analysis of low-frequency trends (i.e., timescales of the order of a decade) rather than higher-frequency variations. While some contribution to the observed trends from dynamical processes that could change over long time intervals (decadal) cannot be ruled out, the evidence cited above and in Plate 6 below demonstrates that chlorine chemistry has played an important and very likely dominant role in the observed trends in midlatitude ozone over the past 2 decades.

6. CHEMICAL/DYNAMICAL COUPLING: ARCTIC OZONE DEPLETION

Perhaps ironically in view of the extremely remote nature of the Antarctic, ozone depletion was more readily observed there than in the Arctic. This was due in part to the fact that no corresponding “hole” developed in the Arctic stratosphere in the early 1980s, but also to the paucity of ground-based long-term measurements in the high Arctic and to the greater local variability of Arctic ozone associated with atmospheric waves, as discussed above [see Reed, 1950]. As the mechanism for Antarctic ozone depletion began to be elucidated in the latter half of the 1980s, it was understood in general terms that Arctic ozone depletion would likely be smaller on account of warmer temperatures (hence fewer PSCs as documented by McCormick *et al.* [1982]) and the associated dynamical differences (i.e., a less isolated vortex). The top panel of Figure 11 illustrates the climatological differences in the seasonal cycles of temperature for 65°N and 65°S , the edge regions of the Arctic and Antarctic. Colder temperatures are typically found at higher latitudes, but this region is shown in order to illustrate accompanying satellite total ozone data (which are available only in the sunlit atmosphere). Perhaps most importantly, the typical springtime increase in stratospheric temperatures occurs in association with much earlier stratospheric warmings in the north than in the south [e.g., Andrews *et al.*, 1987], suggesting that the overlap between cold temperatures and sunlight would be limited and the Arctic ozone depletion hence less severe (see, e.g., the review by Pyle *et al.* [1992]). However, not all years are typical (a point discussed below).

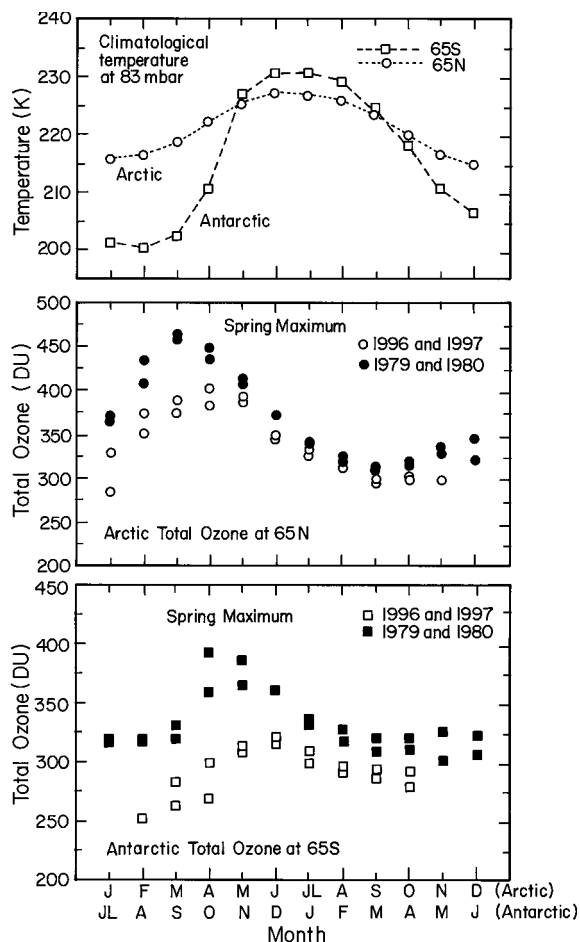


Figure 11. (top) Observations of the average temperatures at 65°S and 65°N from the Fleming *et al.* [1990] Cospas International Reference Atmosphere (CIRA) climatology, with satellite measurements of the annual cycles of total ozone at (middle) 65°N and (bottom) 65°S in the late 1970s and in 1996 and 1997 (from SBUV/SBUV2, courtesy of R. Nagatani).

6.1. Chemical Processes in the Arctic

As in the Antarctic, direct observations of a broad range of chemical species have shown that heterogeneous chemistry greatly perturbs the composition of the Arctic vortex. Evidence for effective winter activation of chlorine was provided by measurements of enhanced OCIO [Solomon *et al.*, 1988; Schiller *et al.*, 1990; Pommereau and Piquard, 1994a; Perner *et al.*, 1994; Pfeilsticker and Platt, 1994] and ClO [Brune *et al.*, 1990, 1991; Toohy *et al.*, 1993; Waters *et al.*, 1993; Crewell *et al.*, 1994; Bell *et al.*, 1994; de Zafra *et al.*, 1994; Shindell *et al.*, 1994; Donovan *et al.*, 1997]. Decreased NO and NO₂ were also observed with several independent methods [Fahey *et al.*, 1990a; Noxon, 1978; Toon *et al.*, 1994; Mankin *et al.*, 1990; Wahner *et al.*, 1990; Pommereau and Piquard, 1994b; Goutail *et al.*, 1994; Pfeilsticker and Platt, 1994; Van Roozendaal *et al.*, 1994]. The column abundances of HCl and HF supported the view that chlorine activation on PSCs must be effective in the Arctic [Toon *et al.*, 1994; Mankin *et al.*, 1990; Traub *et al.*, 1994]. In situ

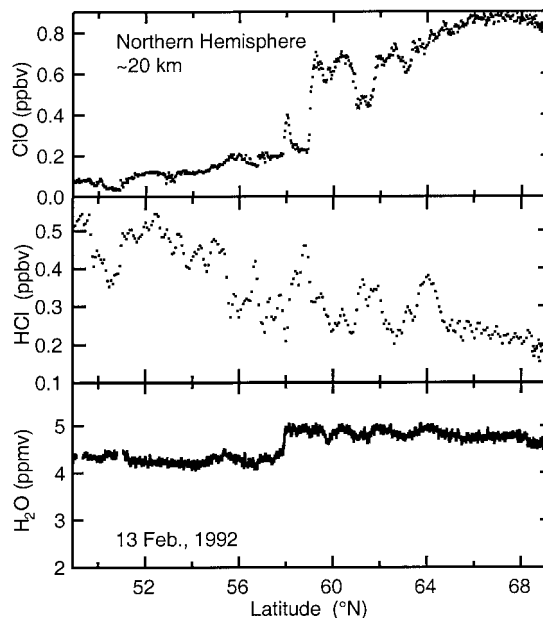


Figure 12. Observations of the chemical composition of the Arctic stratosphere from the ER-2 aircraft in February 1992. The data show high ClO abundances associated with reduced HCl abundances as would be expected from heterogeneous conversion. H₂O does not display evidence for dehydration on this Arctic transect.

measurements of HCl were particularly important in sharpening the link between enhanced ClO and conversion from HCl [Webster *et al.*, 1993; Michelsen *et al.*, 1999], as shown for example in Figure 12. Measurements of ClONO₂ also displayed evidence for heterogeneous processing on PSCs [e.g., von Clarmann *et al.*, 1993; Roche *et al.*, 1994; Oelhaf *et al.*, 1994; Adrian *et al.*, 1994; Geller *et al.*, 1995; Yudin *et al.*, 1997]. Concurrent in situ and space-based observations of ClO and PSCs together with trajectory studies further linked the activated chlorine to heterogeneous chemistry [Jones *et al.*, 1990b; Yudin *et al.*, 1997; Dessler *et al.*, 1998, and references therein]. Thus the same general fingerprints of heterogeneous chemistry that were first observed in the Antarctic were not only apparent in, but also further strengthened by Arctic data.

Observations of NO_y and water vapor displayed signs of sporadic and limited denitrification and dehydration (compare Figures 12 and 7), in marked contrast with the pervasive characteristics of these chemical conditions in the Antarctic [Kawa *et al.*, 1990; Fahey *et al.*, 1990b] (see later work by Kondo *et al.*, 1994; Oelhaf *et al.*, 1994; Khattatov *et al.*, 1994; Rinsland *et al.*, 1996; Santee *et al.*, 1998, 1999]. In some cases, denitrification was observed without accompanying dehydration, raising new challenges regarding the mechanism underlying the microphysics of the denitrification process that still are not completely resolved [see, e.g., Toon *et al.*, 1990; Gandrud *et al.*, 1990; Salawitch *et al.*, 1989; Koop *et al.*, 1995].

On the basis of ClO observations [Brune *et al.*, 1990]

and related model calculations, observed and calculated rates of ozone loss in February 1989 were shown to be of the order of 20 ppbv day⁻¹ near 20 km [Schoeberl *et al.*, 1990; Salawitch *et al.*, 1990; McKenna *et al.*, 1990]. Further, the BrO observations of Toohy *et al.* [1990] revealed that the ClO-BrO catalytic cycle was probably of particular importance for the Arctic, since ClO enhancements were smaller there than in the Antarctic and hence the efficiency of the ClO dimer cycle was reduced (note that the rate of the latter depends on the square of ClO density [e.g., Salawitch *et al.*, 1990, 1993]). However, the early warming observed in February 1989 as illustrated in Plate 3 prevented extensive total ozone loss in that year. Several studies suggested that the less extensive denitrification of the Arctic would limit ozone losses there [Brune *et al.*, 1991; Salawitch *et al.*, 1993] through less effective NO_x reduction in sunlit air and hence an early cutoff of the depletion process in spring; the preceding section illustrates that new understanding of liquid aerosol chemistry has affected this picture. Thermal decomposition of the Cl₂O₂ dimer (which cuts off the ClO dimer ozone loss cycle) also affects the degree of ozone loss as air warms in spring even if denitrified [McKenna *et al.*, 1990; MacKenzie *et al.*, 1996]. As will be discussed further below, recent observations of large Arctic ozone depletions (see Figure 1) have not been associated with extensive denitrification.

6.2. Quantifying Arctic Ozone Depletion

The more complex dynamics of the Arctic vortex as compared with the Antarctic demands the application of sophisticated tools for analysis of ozone destruction. The greater wave activity of the Northern Hemisphere can enhance ozone losses even in winter by increasing the exposure of polar air to sunlight in the distortions caused by atmospheric waves, as compared with the Southern Hemisphere [see, e.g., Jones *et al.*, 1990a]. However, the same wave activity can warm the air and perhaps even distort it sufficiently to mix with its surroundings, thus reducing ozone depletion. Detailed methods have been developed [Schoeberl *et al.*, 1990; Manney *et al.*, 1994b, 1995a, b, 1996] to evaluate the air parcel trajectories along which ozone and other trace gases are transported. These help to quantify the amount of ozone chemically destroyed by revealing that while the time evolution of inert tracers such as N₂O can be well simulated in the Arctic using such approaches, the evolution of ozone shows large departures from conservation that likely reflect chemical loss [Manney *et al.*, 1994a, 1995a, b, c, 1996, 1997]. Further, the regions of apparent ozone depletion identified in this manner occur in regions of enhanced ClO revealed by concurrent satellite observations [e.g., Waters *et al.*, 1993; Manney *et al.*, 1994a, 1995c; Lutman *et al.*, 1994a, b; MacKenzie *et al.*, 1996].

Tracer-ozone correlations are another method used to provide insights into polar ozone loss. Briefly, changes

in the amount of ozone observed for a given amount of conserved tracer such as N₂O or CH₄ [Proffitt *et al.*, 1993; Müller *et al.*, 1996, 1997a, b] provide a useful (albeit imperfect) diagnostic for ozone loss based upon understanding of ozone-inert tracer relationships [Plumb and Ko, 1992] and their spatial distributions. Using satellite data for CH₄, O₃, and HCl, for example, Müller *et al.* [1996] suggest that 60 DU of total Arctic ozone was depleted on constant CH₄ surfaces in a manner inconsistent with transport from any other region of the stratosphere in the Arctic winter of 1991–1992. The reduced ozone was associated with pronounced HCl depletion observed in the same air, as was expected on the basis of heterogeneous chemistry on PSCs.

Another method of quantifying ozone destruction involves the use of trajectory analyses of airflow together with multiple ozonesondes to find “matches” wherein the air observed at one site is observed again some days later. Changes in the observed ozone then provide a measure of ozone loss [Von der Gaathen *et al.*, 1995]. This approach has provided strong evidence for extensive Arctic ozone depletion that is closely tied to cold temperatures near 195 K [Rex *et al.*, 1997, 1998]. Understanding can be further tested by comparing the observed depletion derived from such “matches” with chemistry calculations along the same trajectories. These studies have shown good agreement in February and March, but some evidence for midwinter ozone loss that exceeds photochemical theory has recently been suggested [Rex *et al.*, 1998; Becker *et al.*, 1998].

Fully three-dimensional models driven in some cases by the meteorological data for specific years have also been used to probe the Arctic ozone losses and test photochemical understanding. These models have succeeded in explaining much of the observed ozone depletion, documenting its connections to chemical processes, and even reproducing much of the observed variability seen from one year to another as depicted, for example, in Figure 1 [see, e.g., Chipperfield *et al.*, 1994, 1996; Deniel *et al.*, 1998; Douglass *et al.*, 1995].

Taken together, these combined approaches to transport analyses using tracers, matches, chemical transport models, or Lagrangian calculations together with ozone and trace constituent observations provide strong evidence for a chemically driven Arctic ozone loss (order of 60–120 DU) in several recent years. Each approach is subject to different sources of quantitative error and uncertainty, such as inaccuracies in temperature data used as input in observationally-based transport studies, incomplete understanding of the factors influencing tracer-tracer correlations, and small scale dynamical processes that are not well represented in modelling studies (e.g., mountain waves). In spite of these shortcomings and in contrast with the Antarctic, there is substantial evidence for a dynamical contribution to recent trends as well. These are discussed in section 6.3.

6.3. Variability of Arctic Temperatures

Since Antarctic ozone depletion occurs mainly in September under cold conditions, it is natural to consider whether comparable conditions are ever attained in the Arctic in the analogous month of March. *Nagatani et al.* [1990] pointed out that while such conditions appear to be quite rare based on the available record (which extends back to about the 1950s), they are not unknown. For example, during the Arctic winter of 1975–1976, March temperatures were close to those typically seen in the Antarctic in September, but chlorine loading was small in 1975, and no discernible Antarctic ozone hole was observed at that point (see Figure 1). *Nagatani et al.* [1990] noted that extensive Arctic ozone loss might be expected if such meteorological conditions were to be realized in an atmosphere with current chlorine loadings.

There have been several unusually cold Arctic winters since 1990, with correspondingly large Arctic ozone losses [see *Newman et al.*, 1997; *Coy et al.*, 1997] illustrated in Figure 1. Not all the years since 1990 have been cold, as is reflected for example in the high spring ozone observed in 1998 for example. Enhanced volcanic aerosol from the Mount Pinatubo eruption probably contributed to the very low ozone observed in 1992 and 1993, but the continuing depletions in, for example, 1996 and 1997 suggest a strong effect of temperature. Plate 3 illustrates the full seasonal behavior of temperatures observed in some recent cold years, and contrasts their behavior with the Antarctic. As has already been emphasized, the warmer temperatures generally observed in the winter Arctic stratosphere as compared with the Antarctic reflect adiabatic heating associated with faster downward motion, which also leads to a rapid wintertime increase in Arctic total ozone (from values of ~300 DU in September to as much as 450 DU at the spring maximum in March in 1979 and 1980, for example, as shown in Figure 11). In the much colder Antarctic, pre-ozone hole total ozone did not show such a winter increase (remaining instead near 250–300 DU from March through September; see Plate 2 and Figure 11), suggestive of an isolated and less dynamic vortex. In today's Antarctic atmosphere, an abrupt drop in ozone occurs in September deep in the vortex as shown in Plate 2 and even earlier on the edge of the vortex as shown in Figure 11, reflecting rapid chemical removal in sunlit air with limited dynamical resupply as discussed earlier. In the relatively stagnant Antarctic vortex the total ozone actually decreases in spring to form a "hole" compared with the surrounding midlatitude air. In the more dynamic Arctic, transport replaces a substantial portion of the ozone lost, even in recent cold years [see, e.g., *Manney et al.*, 1997]. Indeed, Figure 11 shows that even in the very cold years 1996 and 1997, Arctic ozone continued to increase at 65°N during spring; it simply did not do so as rapidly as it had in 1979 or 1980. Hence large chemical ozone losses of the order of 60–120 DU occurred, but no Arctic hole formed (see the detailed

analyses by *Manney et al.* [1997] and *Müller et al.* [1997a, b]). The formation of an Arctic ozone hole may require not only cold March temperatures but also cold temperatures throughout the winter, both in order to cause activation of chlorine in sunlit air and to inhibit the buildup of ozone through downward transport. Such conditions were not satisfied even in the very cold Arctic winter/spring seasons of recent years [see *Coy et al.*, 1997; *Zurek et al.*, 1996].

It is important to note that denitrification was observed but was rather limited in degree in the Arctic springs of 1993, 1996, and 1997 [*Santee et al.*, 1995, 1996, 1997, 1999], so that the observations of the order of 60–120 DU of ozone depletion in each of these years are not associated with denitrification. Rather, as in the Antarctic and consistent with current understanding of liquid aerosol chemistry, the evidence suggests that heterogeneous reactions in the sunlit atmosphere are mainly responsible for maintaining the high ClO [*Santee et al.*, 1997] that depleted the Arctic ozone in those years [*Manney et al.*, 1997].

Plate 4 shows observed changes in the vertical profile of Arctic ozone at Sodankylä, Finland (67°N), in 1996 that illustrate this general picture. Plate 4 is intended for the purpose of illustration. A detailed analysis would be needed to quantify dynamical and chemical contributions to ozone losses as in the studies of *Rex et al.* [1998] and *Manney et al.* [1997]; the points sketched here are consistent with those papers. The ozone observed in late March 1996 lies well below the climatology for this location, much as the South Pole ozone in September 1986 lay below its climatology (Figure 5); other dates in March display similar behavior. The ozone at ~15–20 km at South Pole was depleted in 1986, similar to the layer of reduced ozone observed over Finland at nearly the same altitudes in March 1996 (and at those altitudes where PSCs are frequently observed). However, at the South Pole, the historical and current ozone profiles display nearly the same values above the depleted region, showing little evidence for large changes in the amount of ozone brought down from above. The data from Finland present an interesting contrast, with reduced ozone above 20 km not only in March but also in February, likely reflecting reduced dynamical transport from above. This is not surprising, since the cold temperatures observed in that year must reflect reduced downward motion. Hence particularly cold Arctic winters must be associated with less downward motion and a component of dynamic impact on total ozone. The shape of the profile is suggestive of chemical removal in the broad layer near 15–20 km.

In summary, there is abundant evidence for some chemical perturbations and ozone destruction in the Arctic even in relatively warm years, but the degree of ozone depletion depends upon cold temperatures in sunlit conditions, just as in the Antarctic. An unprecedented number of cold years have occurred in the Arctic since 1990. Each of these is reflected in low ozone in the

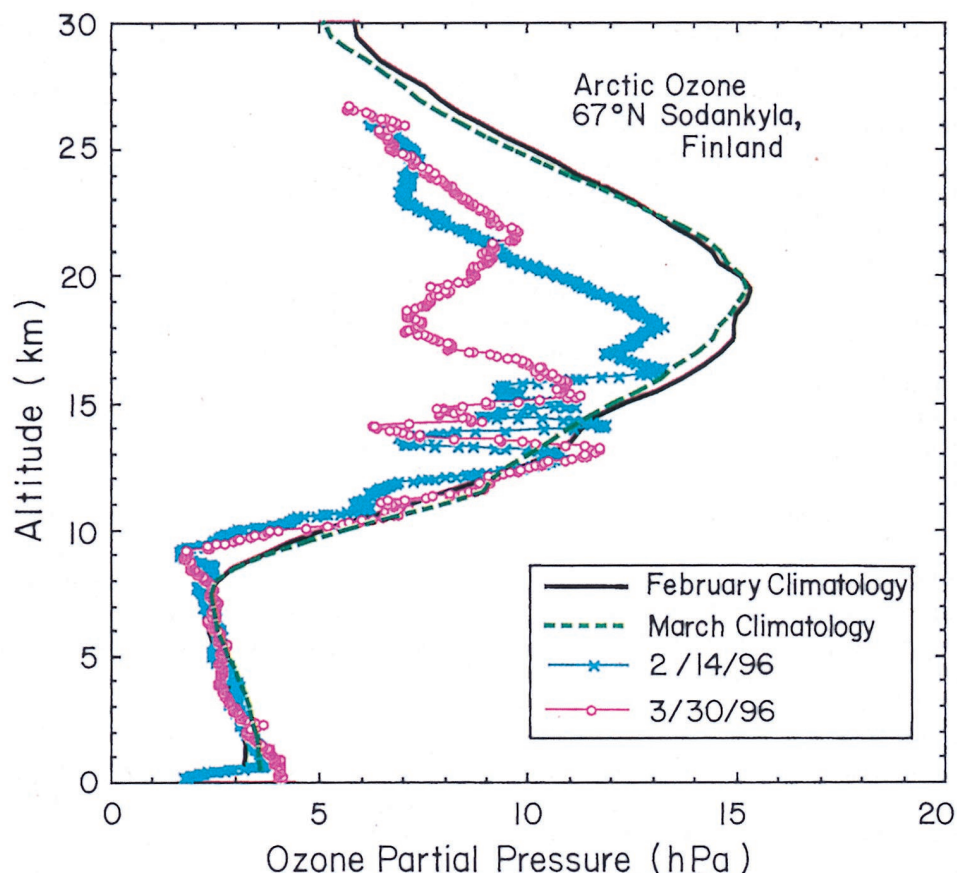


Plate 4. Arctic ozonesonde data from Sodankylä, Finland. The climatologies for February and March represent the averages of all data for 1988–1997. Sample profiles observed in February and March 1996 are shown for comparison.

Arctic record as shown in Figure 1. Five of the years from 1991 to 1998 have been significantly colder than average [Coy *et al.*, 1998; Zurek *et al.*, 1996]. This series of unusually cold years raises the key question of cause. Randel and Wu [1999] argue that the cooling observed in both the Arctic and the Antarctic is due to the ozone depletion itself; hence they propose a feedback mechanism, following Shine [1986], wherein ozone losses lead to colder temperatures and hence even greater depletion. The study by Thompson and Wallace [1998] suggests that changes in the dynamics of the north polar vortex are linked to the underlying tropospheric wave field, particularly the North Atlantic Oscillation (NAO). These authors thus suggest a wave-driven systematic linkage between tropospheric waves and stratospheric temperature, which could reflect ozone changes. Hartley *et al.* [1998] argue for a similar linkage involving the modification of stratospheric dynamics due to the ozone changes, with tropospheric propagation as a key element.

It has long been known that the “greenhouse effect” due to increases in CO₂ and other gases warm the planet surface but cool the stratosphere [e.g., Fels *et al.*, 1980], with attendant effects on temperature-dependent ozone chemistry [Haigh and Pyle, 1979]. While this effect is predicted to be small (only a few tenths of a degree in today’s atmosphere, far less than the recent coolings

observed in the Arctic), dynamical amplification of such changes is also possible, as was noted above. A number of studies have suggested that increased CO₂ and other greenhouse gases could substantially affect Arctic ozone [e.g., Austin *et al.*, 1992; Shindell *et al.*, 1998]. The work of Shindell *et al.* argues for a key role for such a feedback both in the 1990s and perhaps in future years, with the peak Arctic ozone losses being predicted to occur near 2010, well after the expected peak of chlorine loading (see also Dameris *et al.* [1998]). However, at present the possibility that the recent colder Arctic temperatures are part of a natural low-frequency cycle that could, for example, induce a series of colder years every 50 years or so cannot be ruled out given the short record of existing global stratospheric temperature data. Hence while it is clear that there has been significant chemical ozone depletion associated with the cold Arctic winter–spring seasons of recent years, the fundamental reason for those cold temperatures remains a topic of research.

7. SUMMARY OF THE PAST AND A LOOK TO THE FUTURE

This paper has outlined the history and conceptual understanding of the processes responsible for ozone

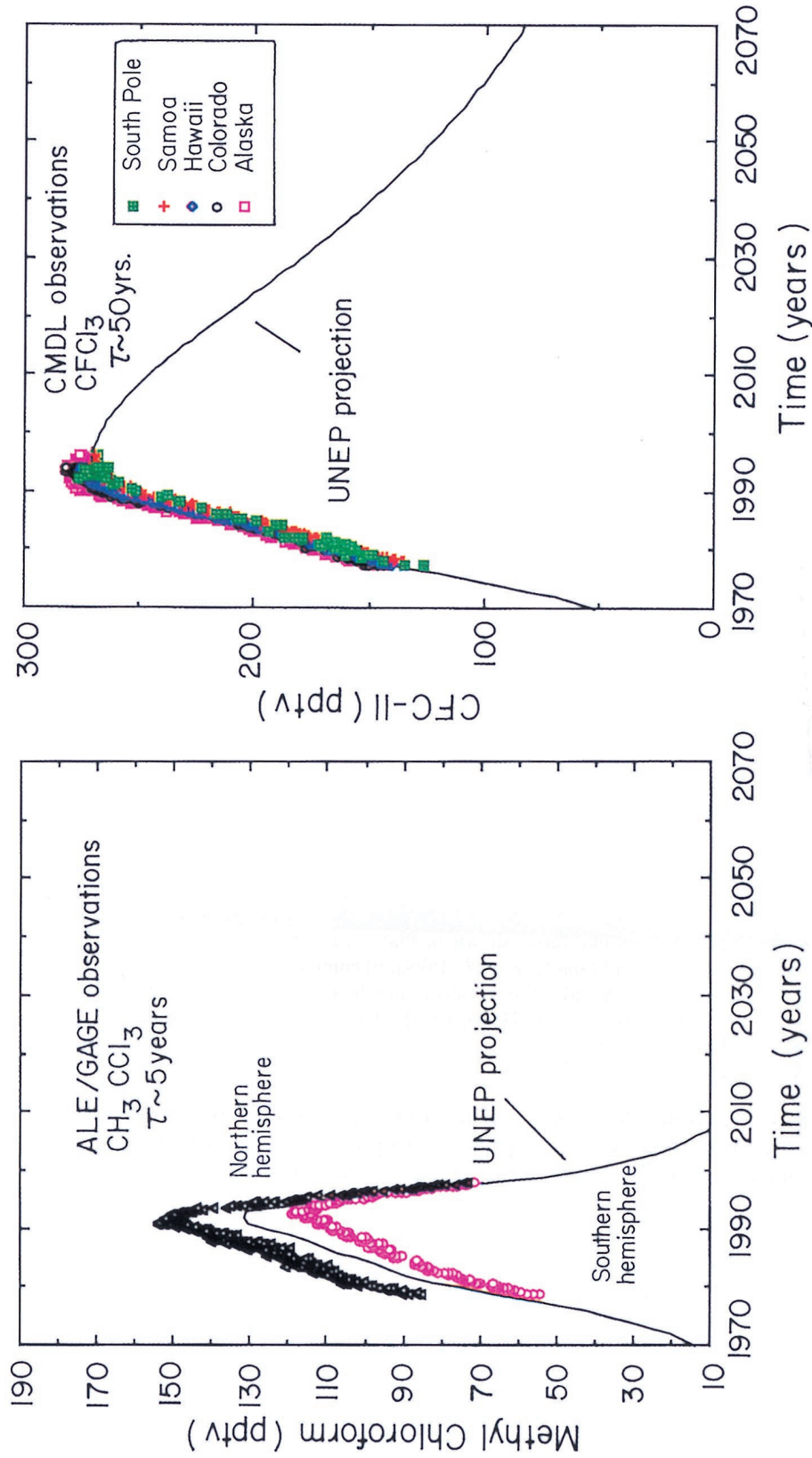


Plate 5. Observations of methyl chloroform ($CH_3 CCl_3$) and CFC-11 from the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) and Climate Monitoring and Diagnostics Laboratory (CMDL) databases, respectively. The projections from the baseline emission scenario of *WMO/UNEP* [1999] are shown for comparison. The scenario includes estimated industrial production and emission for each year (including the effects of delayed release in some applications such as refrigeration [see *WMO/UNEP*, 1999]. The methyl chloroform data show a rapid decline observed in recent years due to reduced emissions and the 5-year lifetime of this gas [Prinn *et al.*, 1995; *WMO/UNEP*, 1999], while the CFC-11 abundances have just passed their peak [Elkins *et al.*, 1993; Montzka *et al.*, 1996] (updated courtesy of J. Elkins and S. Montzka) and are projected to decline slowly in the future owing to the 50-year lifetime of this gas.

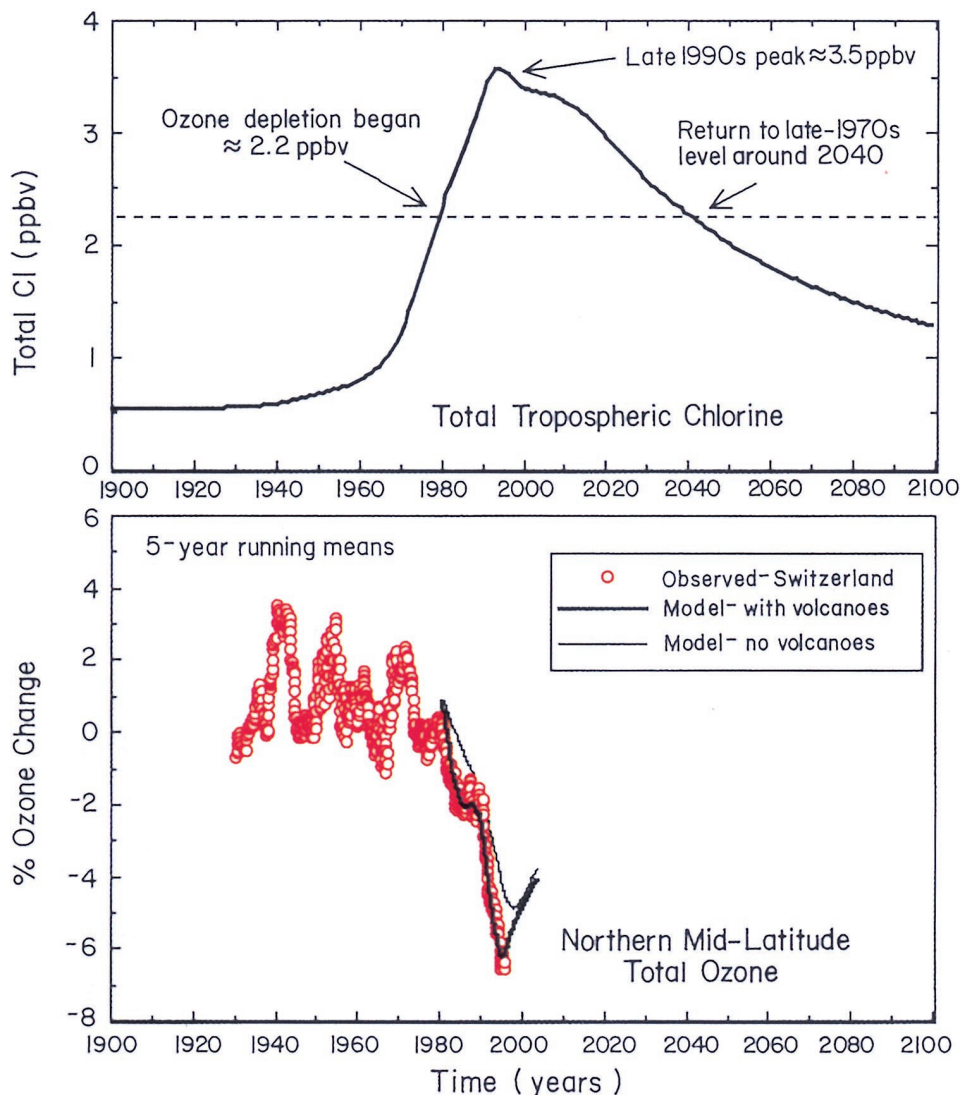


Plate 6. (top) Total tropospheric chlorine content estimated from the baseline scenario of *WMO/UNEP* [1999]; this is based on a gas-by-gas analysis like those shown in Plate 5. (bottom) Changes in the 5-year running mean ozone observed over Switzerland [Stahelin *et al.*, 1998a, b] compared with a model calculation for 45°N applying the same time averaging, with and without considering the effects of volcanic enhancements in aerosol chemistry (from the model of Solomon *et al.* [1996, 1998]). The major eruptions since 1980 were those of El Chichón in 1982 and Pinatubo in 1991.

depletion by chlorofluorocarbons in the stratosphere. In brief, the long lifetimes of chlorofluorocarbons are reflected in their observed worldwide accumulation in the atmosphere. Their role in stratospheric ozone depletion depends critically on partitioning processes that follow release of halogen atoms; indeed, the marked contrasts between fluorine (which does not deplete stratospheric ozone), chlorine, and bromine illustrate the central role of partitioning chemistry. Table 2 summarizes a series of spatial and temporal fingerprints that connect chlorine chemistry to ozone depletion. Observational evidence for gas phase chlorine chemistry impacts on ozone is provided, for example, by observations of the ClO/Cl_y and ozone trend profiles above about 25 km at midlatitudes and by the similarities in their observed latitudinal distributions.

The cold conditions of the Antarctic winter and spring stratosphere lead to formation of polar stratospheric clouds. Heterogeneous chemistry involving man-made chlorine takes place on these surfaces and results in the dramatic and unanticipated Antarctic ozone hole. The heterogeneous activation of chlorine from both its HCl and ClONO₂ reservoirs and the suppression of the NO₂ (that would otherwise reform ClONO₂) alters chlorine partitioning and allows effective ozone loss in cold sunlit air. The close correspondence between observed enhancements in ClO and depleted Antarctic ozone through independent observational methods as functions of altitude, latitude, and longitude illustrates the key role of these chemical partitioning processes in producing the ozone hole. A broad range of chemical observations of HCl, HNO₃, NO₂, OClO, and other

TABLE 2. Summary of Key Fingerprints of Ozone Depletion

<i>Observation</i>	<i>Method</i>	<i>Latitude</i>	<i>Altitude</i>	<i>Primary Chemistry Linkage</i>
Profile shapes of upper stratospheric ozone depletion and ClO/Cl _y	satellite and ground-based	Northern Hemisphere midlatitude	30–50 km	Gas phase chlorine chemistry, particularly partitioning processes
Latitudinal structure of upper stratospheric ozone depletion and ClO	satellite	Polar, midlatitude, and tropical	30–50 km	Gas phase chlorine chemistry, particularly HCl/ClO
Latitudinal structure of ClO, HCl, NO, NO ₂ , and ozone loss in polar regions	airborne and satellite	50°–85°S, 50–85°N	20 km	Heterogeneous chlorine activation and NO ₂ suppression
Vertical structure of seasonal ozone loss and PSCs in polar regions	balloon-borne, lidar, and satellite	90°S, 50°–85°S, 50–85°N	12–24 km	Heterogeneous chlorine activation
Seasonal changes in PSCs, ozone depletion, OCIO, ClO, HCl, and ClONO ₂	balloon-borne, lidar, ground-based, and satellite	50°–90°S in both polar regions	~12–24 km and column	Heterogeneous chemistry
Post-Pinatubo (~1992–1995) ozone depletion and recovery; contrast with post-Agung (~1964–1968)	ground-based and some satellite	midlatitudes and polar regions	near 20 km and column	Heterogeneous liquid surface chemistry relating to chlorine
Post-Pinatubo changes in stratospheric chemical state and aerosol content (NO _x , ClO, HNO ₃ , OCIO)	airborne, ground-based, balloon-borne, and satellite	midlatitudes and some polar	near 20 km, near tropopause, and column	Heterogeneous chemistry, particularly N ₂ O ₅ hydrolysis and some chlorine activation

species support and extend this picture. Quantitative numerical modeling studies that include detailed analyses of transport and chemistry further connect the enhanced ClO produced by heterogeneous chemistry to the formation of the Antarctic ozone hole.

Scientific understanding of PSCs and heterogeneous chemistry has evolved considerably in recent years. The detailed microphysical mechanisms responsible for freezing of PSC particles and for denitrification are subject to debate at present, but these processes appear to be less critical to ozone depletion than was once thought. There is evidence from field, laboratory, and modeling studies that PSCs can be composed not only of solid water ice and nitric acid hydrates but also of liquid solutions of water, sulfuric acid, and nitric acid. The chemistry associated with these varying surfaces displays important differences in detail but has the common feature that all can suppress NO₂ and activate chlorine from the reservoir species, making the ozone depletion process more continuous in temperature and less dependent upon the abrupt temperature thresholds that are associated with formation of solids than was previously thought.

Observations of enhanced Antarctic and midlatitude ozone depletion following the eruption of Pinatubo con-

firm the impact of liquid aerosol surfaces on chlorine and nitrogen partitioning chemistry. Observations and laboratory studies have demonstrated the efficacy of heterogeneous processes on such surfaces (both at 20 km and at lower altitudes, where high water vapor pressures enhance chlorine activation chemistry). As in the Antarctic, concurrent observations of a broad range of chemical species show evidence for surface reactions associated with particles, which work to enhance ClO/Cl_y partitioning at midlatitudes. Dilution and processing of the polar ozone losses also contribute to midlatitude ozone depletion. While some studies suggest a role for a purely dynamical trend in midlatitude ozone depletion, these have not yet succeeded in quantifying a significant contribution.

There is abundant evidence for heterogeneous perturbations to Arctic chemistry through observations of ClO, OCIO, HCl, and many other key gases. Arctic ozone has reached record low values in many years in the 1990s, linked not only with heterogeneous chemistry on Pinatubo aerosols but also with unusually cold spring temperatures. A chemical contribution to these low values has been documented with a variety of methods including trajectory “matches,” chemistry transport modeling, and tracer correlation studies. The funda-

mental question of the cause or causes of record low temperatures in many of the Arctic winter–spring seasons of the 1990s remains a topic of debate and a key issue.

In closing, Plates 5 and 6 are presented to show the impact of changes in global emissions of chlorofluorocarbons and the likely future of the ozone layer based on the conceptual picture developed in this review. Plate 5 displays surface observations of CFC-11 and methyl chloroform (CH_3CCl_3). The latter gas is the only short-lived industrial chlorofluorocarbon produced in large amounts in the 1970s and 1980s. Because of its 5-year lifetime, the abundances of methyl chloroform have already begun to decline, as a result of reduced global emissions. Those of CFC-11 are just passing their peak and are projected to decline slowly in coming decades, reflecting its 50-year lifetime.

Plate 6 (top) shows the past and future projections of the total tropospheric chlorine content (which leads the stratosphere by 3–5 years). It is anticipated that the combined effect of all CFCs will lead to a peak stratospheric chlorine loading in the late 1990s. By about 2040, the chlorine will return to levels close to those of the late 1970s, when ozone depletion was first apparent. All other things being equal, the Antarctic ozone hole and midlatitude ozone depletion will likely disappear around this time. However, the key role of temperature and aerosols in modulating ozone depletion must also be considered. The unusually cold Arctic winter–spring seasons of recent years stand at the time of this writing as a critical challenge to our understanding that could affect the future of polar ozone depletion in both hemispheres. For example, if the majority of future Arctic winters were to be colder than average, then the Arctic ozone depletion would likely be prolonged. The bottom panel of Plate 6 shows the long-running Arosa, Switzerland, ozone record illustrating the onset of midlatitude ozone depletion, its links to heterogeneous chemistry, and its simulation with a current stratospheric chemistry model including the processes described in this review. The changes in ozone observed over Arosa are in good agreement with the zonally averaged global satellite data discussed earlier, and the time-averaged trends obtained there are representative of northern midlatitudes. Plate 6 illustrates that the future of midlatitude ozone depletion is likely to be linked not only to chlorine but also in part to volcanoes for at least several decades. If there were to be an extremely large volcanic eruption such as that of Tambora (whose 1815 eruption is estimated at about 3 times the stratospheric impact of Pinatubo) in coming decades, it is likely that midlatitude ozone depletion would be increased even though the chlorine content of the stratosphere is expected to be lower than it is today. This illustrates the connection between the accumulation of chlorine in today's atmosphere due to human activities of the industrial era and the unpredictable timescales of geologic phenomena that couple into this altered chemical state.

This review has emphasized many spatial and temporal “fingerprints” that illustrate the role of chlorine in depleting ozone in the contemporary stratosphere (Table 2). Indeed, it is the structure of the ozone loss in space (e.g., in the 40-km region) and time (e.g., in the Antarctic spring and in midlatitudes in the years following Pinatubo) that tests and confirms scientific understanding, illustrating how gas phase and heterogeneous modulation of ClO/Cl_y partitioning affects ozone depletion. Through the impacts of this chemistry, the stratospheric ozone layer in the twenty-first century will continue to reflect the impact of the changes in chlorine enacted in the twentieth.

GLOSSARY

Active chlorine: chlorine compounds that destroy ozone and interchange rapidly with one another in the sunlit atmosphere (mainly Cl , ClO , Cl_2O_2 , OClO , and HOCl); chlorine that is not tied up in the reservoir gases (HCl and ClONO_2).

Chlorine loading: Abundance of total chlorine in all forms (including CFCs) at a given location.

Chlorofluorocarbons (CFCs): Chemicals, used in a variety of industrial applications, that are the dominant source of chlorine to the present-day stratosphere.

Cl_y : The sum of all chlorine gases liberated by decomposition of CFCs, including Cl , ClO , HCl , ClONO_2 , HOCl , Cl_2O_2 , and other trace species.

ClO dimer: Cl_2O_2 , a key intermediate in the formation of the Antarctic ozone hole. See the catalytic cycle involving this gas illustrated in Table 1.

Denitrification: Removal of reactive nitrogen (NO_y) from the stratosphere through sedimentation of large particles containing nitric acid.

Dehydration: Removal of water vapor from the stratosphere through sedimentation of large particles containing water.

Dobson Unit (DU): Unit of measurement of total ozone column abundance, named for G. M. B. Dobson, a pioneer in measurement of ozone. One Dobson unit corresponds to 2.6×10^{16} molecules cm^{-2} of total overhead column ozone.

Frost point: The temperature at which water condenses to form solid ice.

NAT: Nitric acid trihydrate, or $\text{HNO}_3 \cdot (\text{H}_2\text{O})_3$. Some polar stratospheric clouds are probably composed of solid NAT particles.

NO_x : $\text{NO} + \text{NO}_2$, two reactive forms of nitrogen that interchange very rapidly with each other in the sunlit atmosphere. The amount of NO_x is linked to NO_2 and hence to formation of the ClONO_2 reservoir.

NO_y : The sum of the relatively reactive total nitrogen gases, including N , NO , NO_2 , ClONO_2 , NO_3 , N_2O_5 , BrONO_2 , HNO_3 , and other trace species.

Ozone hole: Widespread removal of total ozone in Antarctic spring. The hole is reflected in both the steep

latitudinal gradients in the observed ozone depletion and in its temporal evolution since the mid-1970s.

Partitioning: Distribution of chlorine between active compounds that destroy ozone and reservoirs that are inert toward ozone.

ppbv, pptv: Parts per billion by volume or parts per trillion by volume, indicating relative abundance of a given gas (i.e., 1 ppbv = 1 molecule per billion total air molecules).

Processing: General term describing conversion of chlorine to active forms. Chemical processing refers to in situ chemistry. Vortex processing refers to flow of air to midlatitudes from the vortex, while PSC processing refers to flow of air through PSCs associated with locally cold temperatures.

Polar stratospheric clouds (PSCs): Clouds that are observed to form at cold temperatures (below ~ 200 K) in the polar stratospheres of both hemispheres.

Reservoir: Long-lived compound capable of storing NO_x or active chlorine in a relatively inert form (mainly HNO_3 , HCl , and ClONO_2).

Stratosphere: The region of the atmosphere between ~ 12 and 50 km (a few kilometers lower in polar regions and higher in the tropics) in which heating by ozone leads to increasing temperatures with increasing altitude.

Sulfuric acid tetrahydrate (SAT): A solid form of sulfuric acid and water that can form under certain thermodynamic conditions.

Tracer: Long-lived chemical compound that can be used to trace the atmospheric airflow.

Tropopause: The transition region, in which temperatures reach a minimum, between the troposphere and stratosphere.

Troposphere: The region of the atmosphere between the surface and the stratosphere, in which temperatures decrease with increasing altitude.

Type 1: Polar stratospheric clouds that form at temperatures above the frost point.

Type 1a (1b): Solid (liquid) polar stratospheric clouds at temperatures above the frost point.

Type 2: Solid water ice polar stratospheric clouds that form when temperatures drop below the frost point.

Vortex: Dynamical structure of the stratosphere in polar winter caused by the absence of solar illumination, which leads to a cooling over the poles and a large temperature gradient relative to midlatitudes. This temperature gradient implies rapid zonal (east-west) flow characterizing the “jet” at the edge of the vortex, while the air within the vortex is relatively isolated in comparison with surrounding regions.

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