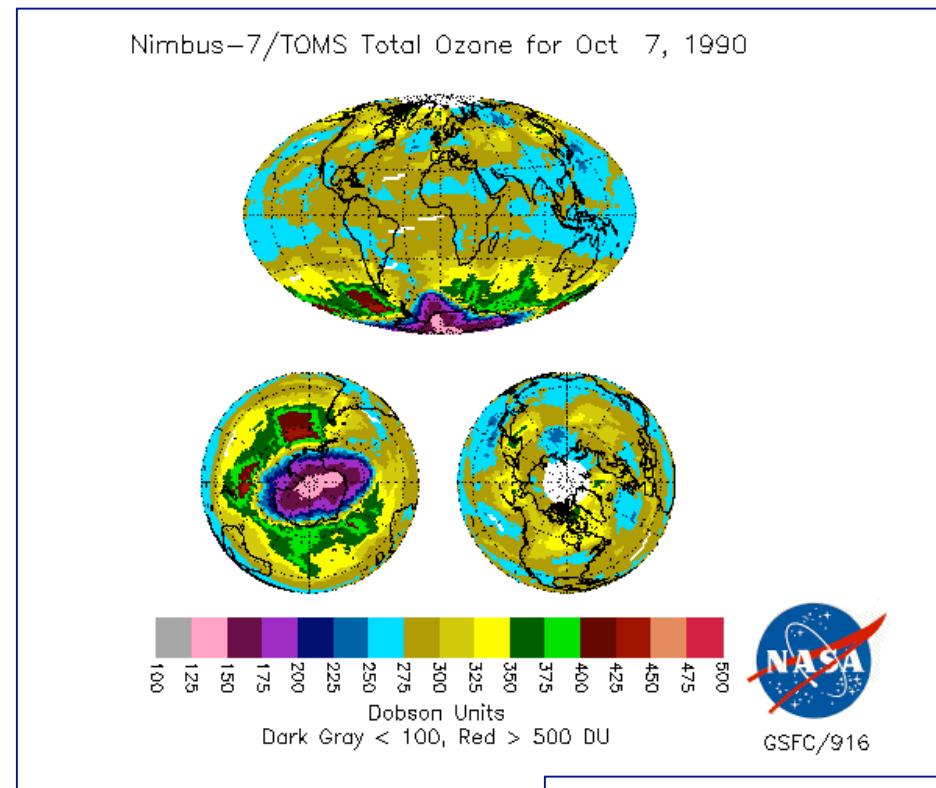


Alaska Satellite Facility Seminar
University of Alaska Fairbanks
November 1, 2005

Ozone Depletion 20 Years On

R. L. Collins



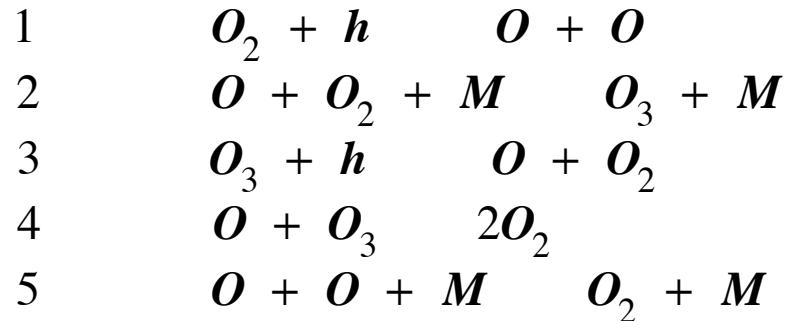
Column Ozone measurements from Total Ozone
Mapping Spectrometer aboard the Nimbus-7 satellite.
<http://toms.gsfc.nasa.gov/>

OZONE

1. Ozone absorbs virtually all solar radiation between wavelengths of 240 and 290 nm which would otherwise be transmitted to the surface. This radiation is lethal to simple single-cell organisms. At $\lambda = 250$ nm less than one part in 10^{30} of the incident radiation penetrates the ozone layer.
2. The meteorology of the upper atmosphere is greatly influenced by the heating that follows absorption of UV and visible light by ozone. Stratospheric air is statically stable because of the increase in temperature with altitude that results from this heating.

Ozone has been studied since the 1840's when Schönben noted an atmospheric constituent having a peculiar smell. Ozein is the Greek for "to smell". Ozone was detected in the troposphere by chemical means in 1858. By 1881, spectroscopic studies in the UV and visible showed that ozone mixing ratios are higher in the upper atmosphere than the lower stratosphere. In the early 20th century, Dobson and Fabry established the existence of the ozone layer.

Chapman proposed the first “all-oxygen” scheme for the ozone layer.



The reactions yield the following rate equations,

$$1 \quad \frac{d O_2}{dt} = J_1 O_2 = \frac{1}{2} \frac{d O}{dt}$$

$$2 \quad \frac{d O_2}{dt} = -\frac{d O}{dt} = k_2 O O_2 M = \frac{d O_3}{dt}$$

$$3 \quad \frac{d O_3}{dt} = J_3 O_3 = \frac{d O}{dt} = \frac{d O_2}{dt}$$

$$4 \quad \frac{d O_3}{dt} = \frac{d O}{dt} = k_4 O O_3 = \frac{1}{2} \frac{d O_2}{dt}$$

where J_i are photolysis rates (s^{-1}) and k_i are reaction rates (cm^3/s^{-1} or cm^6/s^{-1}).

Reaction 5 is now known to be too slow to play any significant role in stratospheric chemistry.

After dark reactions 1 and 3 are cut off, while reactions 2 and 4 continue. Thus concentrations of atomic oxygen fall at lower altitudes (< 40 km). With the decline of atomic oxygen, ozone is no longer destroyed in reaction 4. Thus after dark, little ozone is created or destroyed and the concentration stays relatively constant.

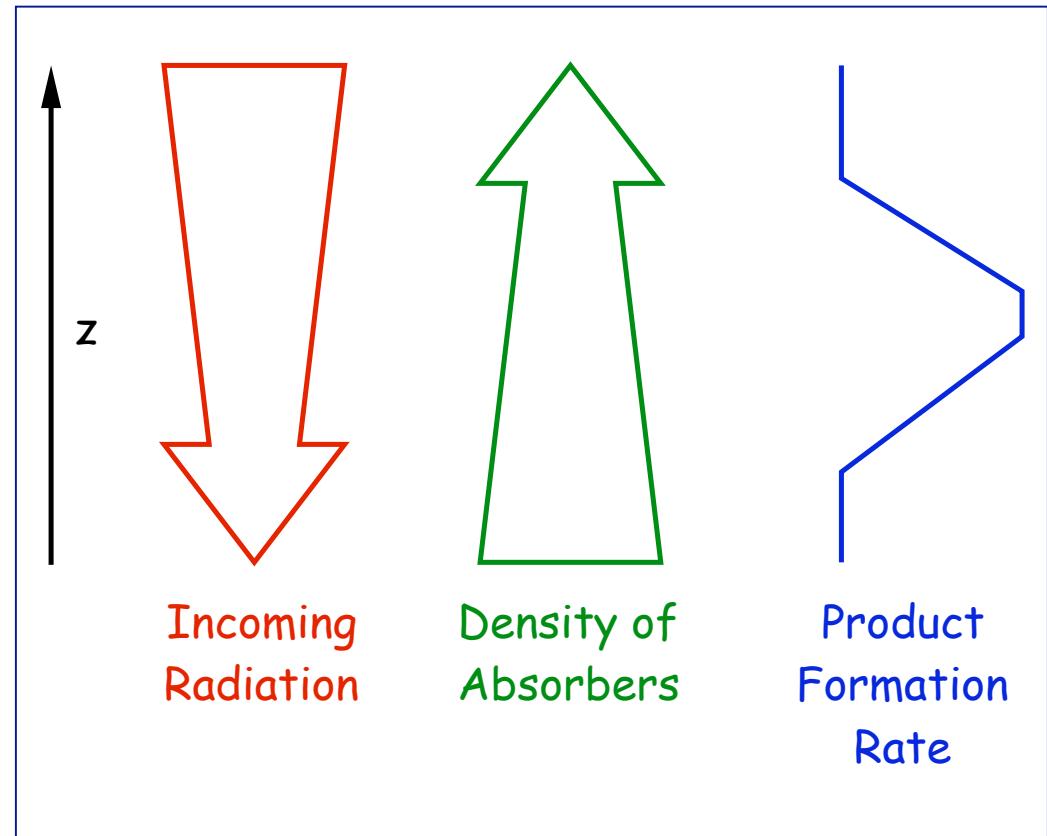
The diurnal variations in stratospheric ozone are expected - and found - to be small.

At higher altitudes (> 55 km) diurnal changes in ozone concentration are more pronounced, as daytime photolysis of ozone (reaction 3) becomes faster, and conversion of O back to O₃ (reaction 2) becomes slower.

CHAPMAN LAYERS

At the upper altitudes the solar intensity is high, but the molecular oxygen concentration is low, and so there is little formation of odd oxygen. At the lower altitudes the solar intensity is low, but the molecular oxygen concentration is high, and so again there is little formation of odd oxygen. At intermediate altitudes there is a compromise that maximizes the rate of odd oxygen formation.

Chapman first discussed the formation of layers in this way and the mathematical function that describes the shape of such a layer is called a Chapman function.



Consider radiation entering an isothermal atmosphere at some zenith angle the atmospheric number density of absorbing molecules (i.e. O_2) is given by,

$$n(z) = n_0 e^{-z/H} \quad H \triangleq RT/g$$

For $n_0 = 5.7 \cdot 10^{18} \text{ cm}^{-3}$, $a = 1.2 \cdot 10^{-23} \text{ cm}^2$, and $H = 6 \cdot 10^5 \text{ cm}$, $\sigma_0 = 41$.

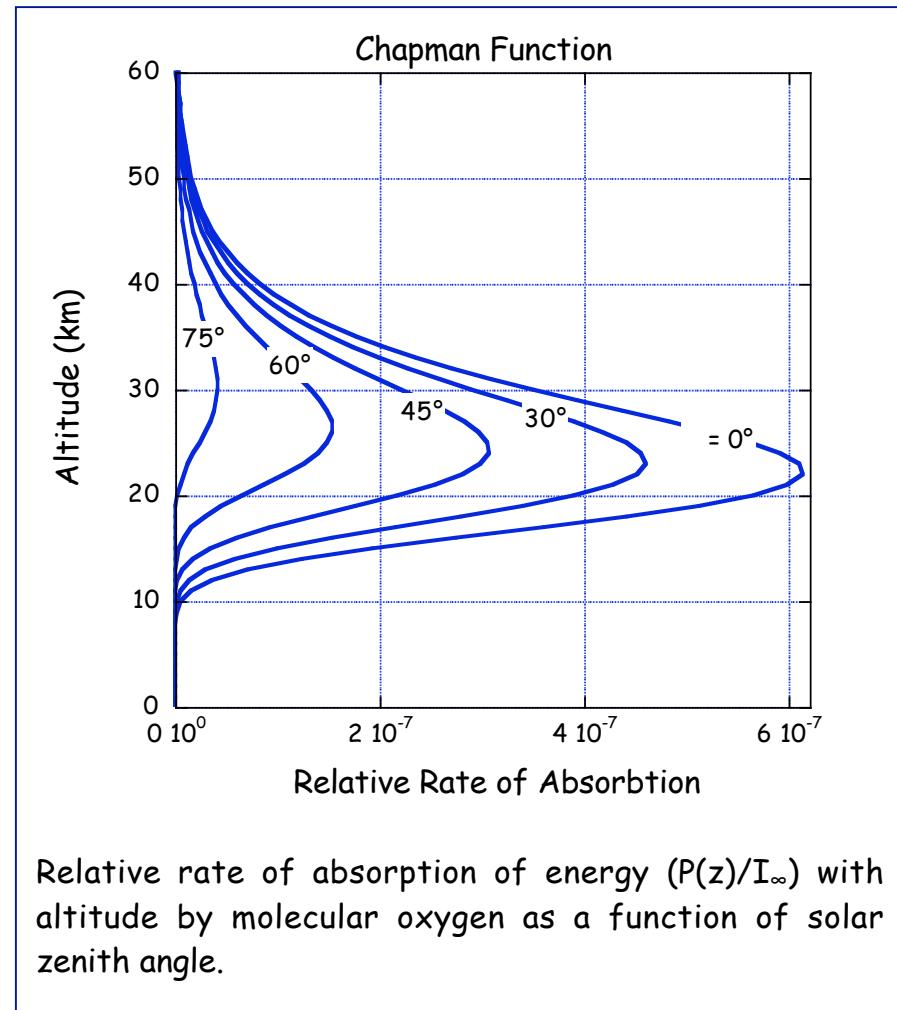
From the Chapman Scheme we have that

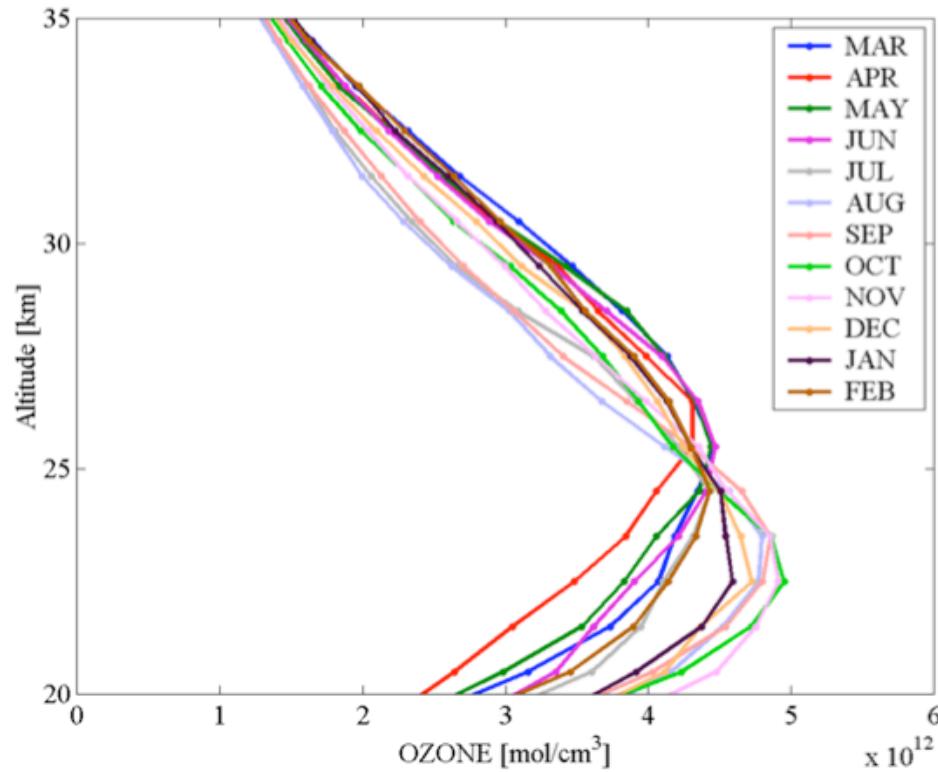
$$P(z) = J_1[O_2]$$

In steady state it can be shown that,

$$O_x = \sqrt{P}$$

where $[O_x]$ ($= [O] + [O_3]$) is the odd-oxygen concentration. Thus in the stratosphere (at $z < 50 \text{ km}$) where $[O_3] \gg [O]$ the ozone profile is proportional to the square root of the oxygen photolysis rate.





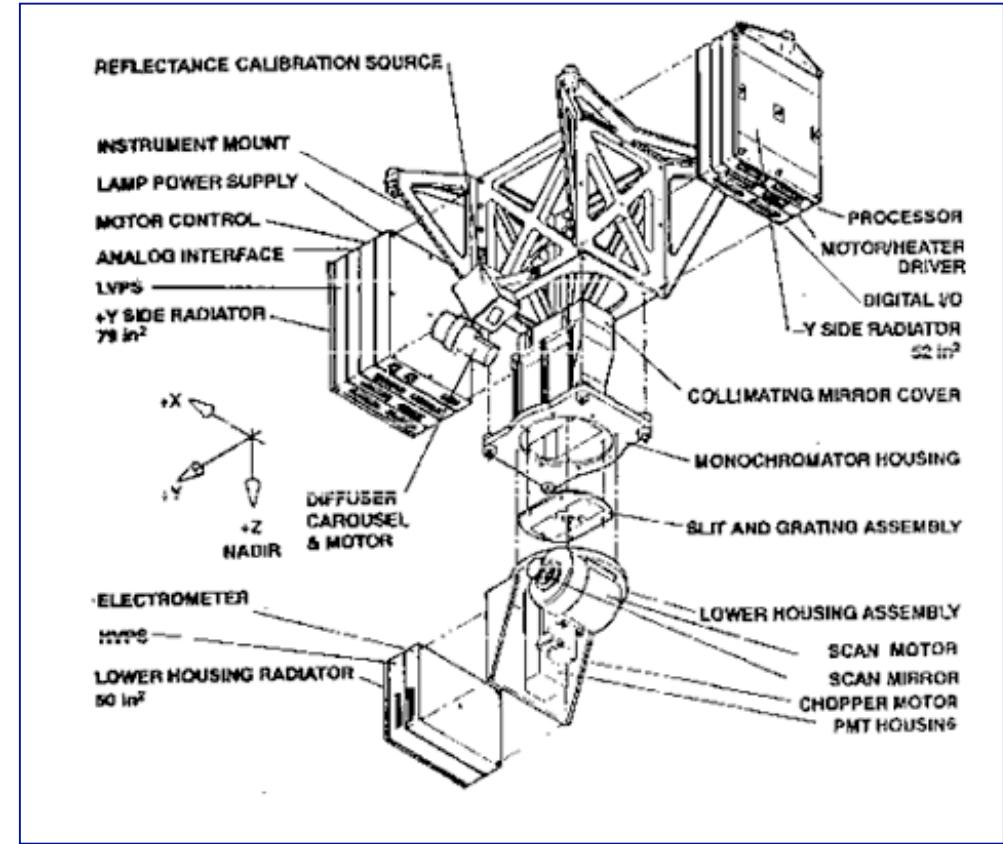
Ground-based measurements of the ozone layer over Buenos Aires (35°S, 53°E). The ozone layer is lower and thicker in summer than winter, showing general consistency with the Chapman layer model.

THE TOTAL OZONE MAPPING SPECTROMETER (TOMS)

http://science.hq.nasa.gov/missions/satellite_27.htm

The Total Ozone Mapping Spectrometer, launched in July 1996 onboard an Earth Probe Satellite (TOMS/EP), continues NASA's long-term daily mapping of the global distribution of the Earth's atmospheric ozone.

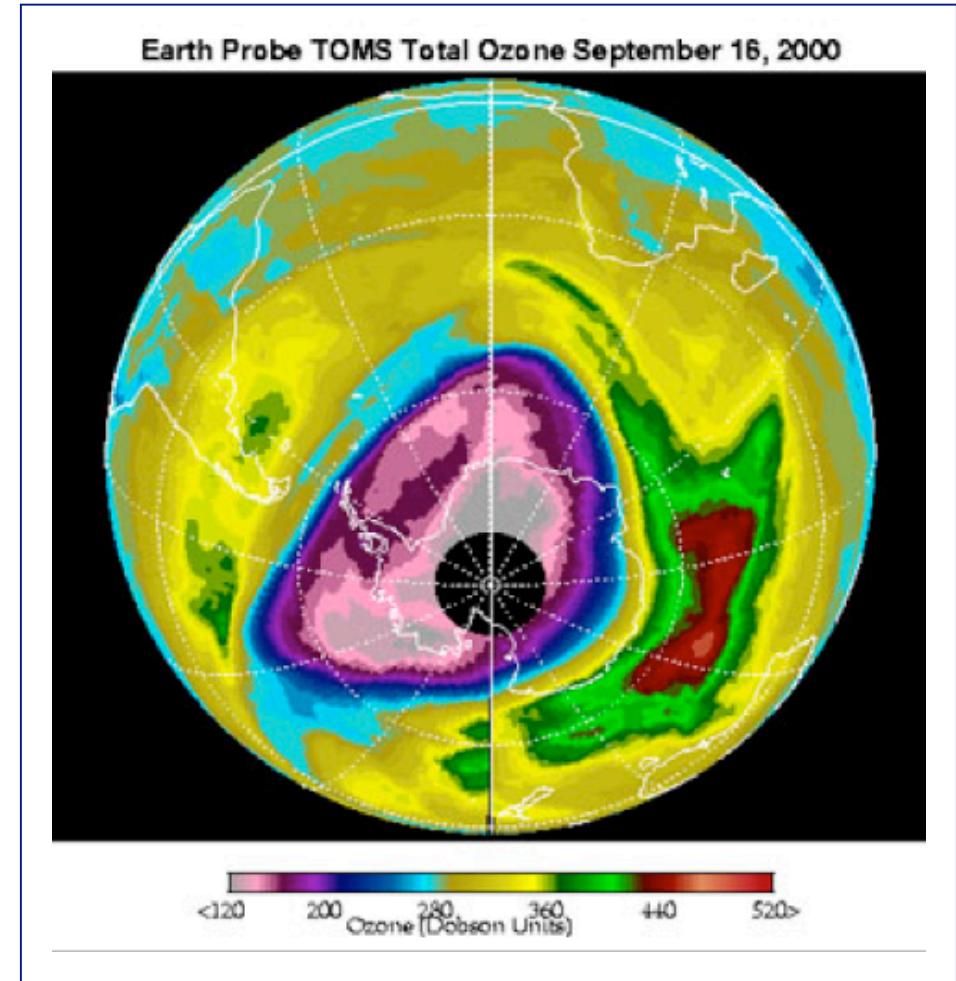
TOMS/EP will continue measurements of the total column amount of ozone from space that began with NASA's Nimbus-7 satellite in 1978 and continued with the TOMS aboard a Russian Meteor-3 satellite until the instrument stopped working in December 1994.



This NASA-developed instrument, measures ozone indirectly by mapping ultraviolet light emitted by the Sun to that scattered from the Earth's atmosphere back to the satellite. The TOMS instrument has mapped in detail the global ozone distribution as well as the Antarctic "ozone hole," which forms September through November of each year.

TOMS/EP measures total ozone by observing both incoming solar energy and backscattered ultraviolet (UV) radiation at six wavelengths. "Backscattered" radiation is solar radiation that has penetrated to the Earth's lower atmosphere and is then scattered by air molecules and clouds back through the stratosphere to the satellite sensors. Along that path, a fraction of the UV is absorbed by ozone. By comparing the amount of backscattered radiation to observations of incoming solar energy at identical wavelengths, scientists can calculate the Earth's albedo, the ratio of light reflected by Earth compared to that it receives. Changes in albedo at the selected wavelengths can be used to derive the amount of ozone above the surface.

TOMS makes 35 measurements every 8 seconds, each covering 30 to 125 miles (50 to 200 kilometers) wide on the ground, strung along a line perpendicular to the motion of the satellite.



Almost 200,000 daily measurements cover every single spot on the Earth except areas near one of the poles, where the Sun remains close to or below the horizon during the entire 24-hour period.

THE DOBSON SPECTROMETER

<http://OZONE.GI.ALASKA.EDU/dobson.htm>

The Dobson spectrophotometer is a ground-based instrument that measures the amount of ozone present in the atmosphere. The Dobson spectrophotometer was designed by Gordon M. B. Dobson in the 1930's. The Dobson spectrophotometer measures ultraviolet light from the Sun at 2 to 6 different wavelengths from 305 to 345 nm

By measuring UV light at two different wavelengths, the amount of ozone can be calculated. One of the wavelengths used to measure ozone is absorbed strongly by ozone (305 nm), whereas the other wavelength is not absorbed by ozone (325 nm). Therefore the ratio between the two light intensities is a measure of the amount of ozone in the light path from the sun to the observing spectrophotometer.



Dobson spectrometer being operated at Amundsen Scott South Pole Station. NOAA Corps Collection.
Lieutenant Mark Boland, NOAA Corps

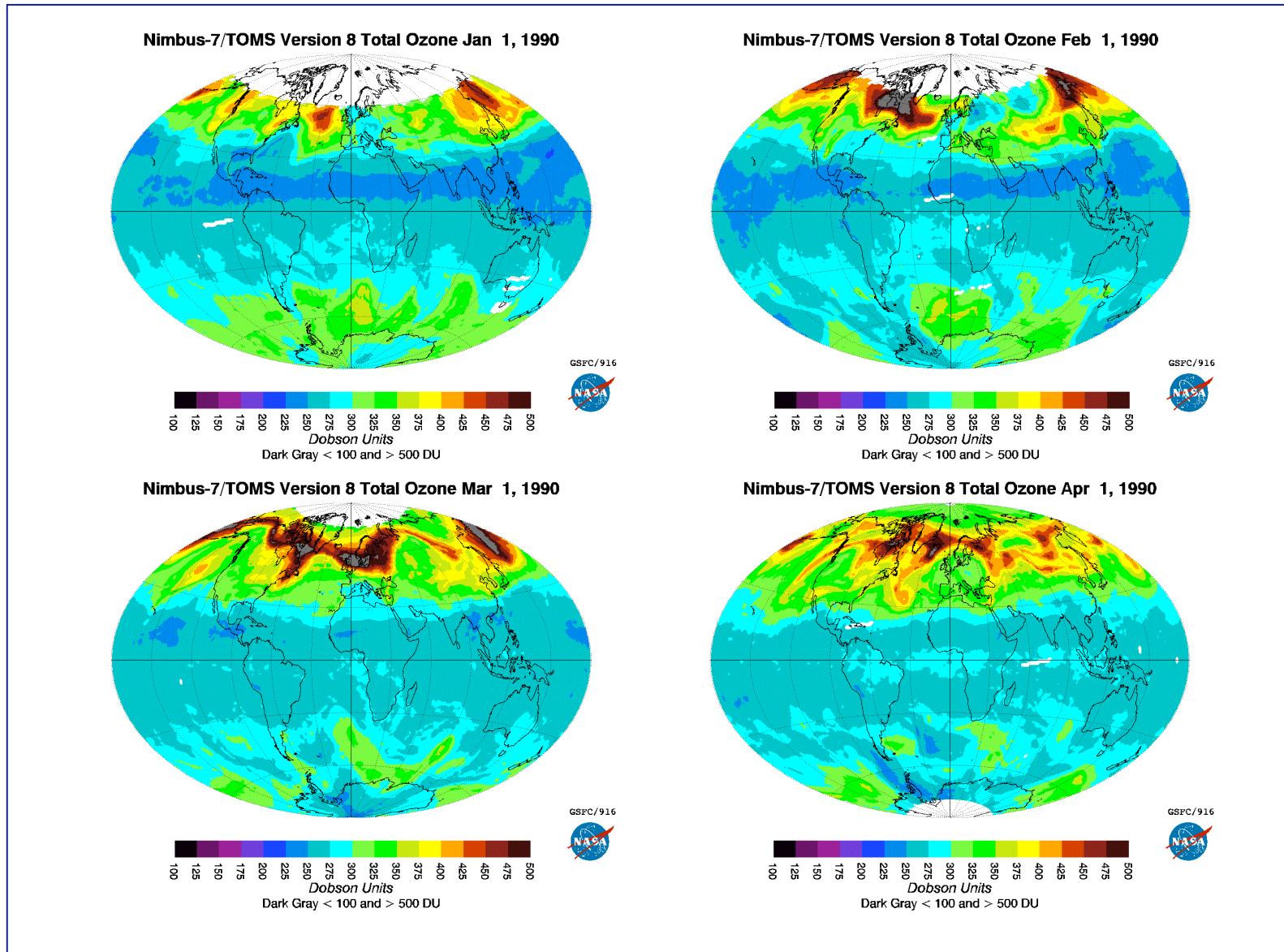
<http://www.photolib.noaa.gov/corps/>

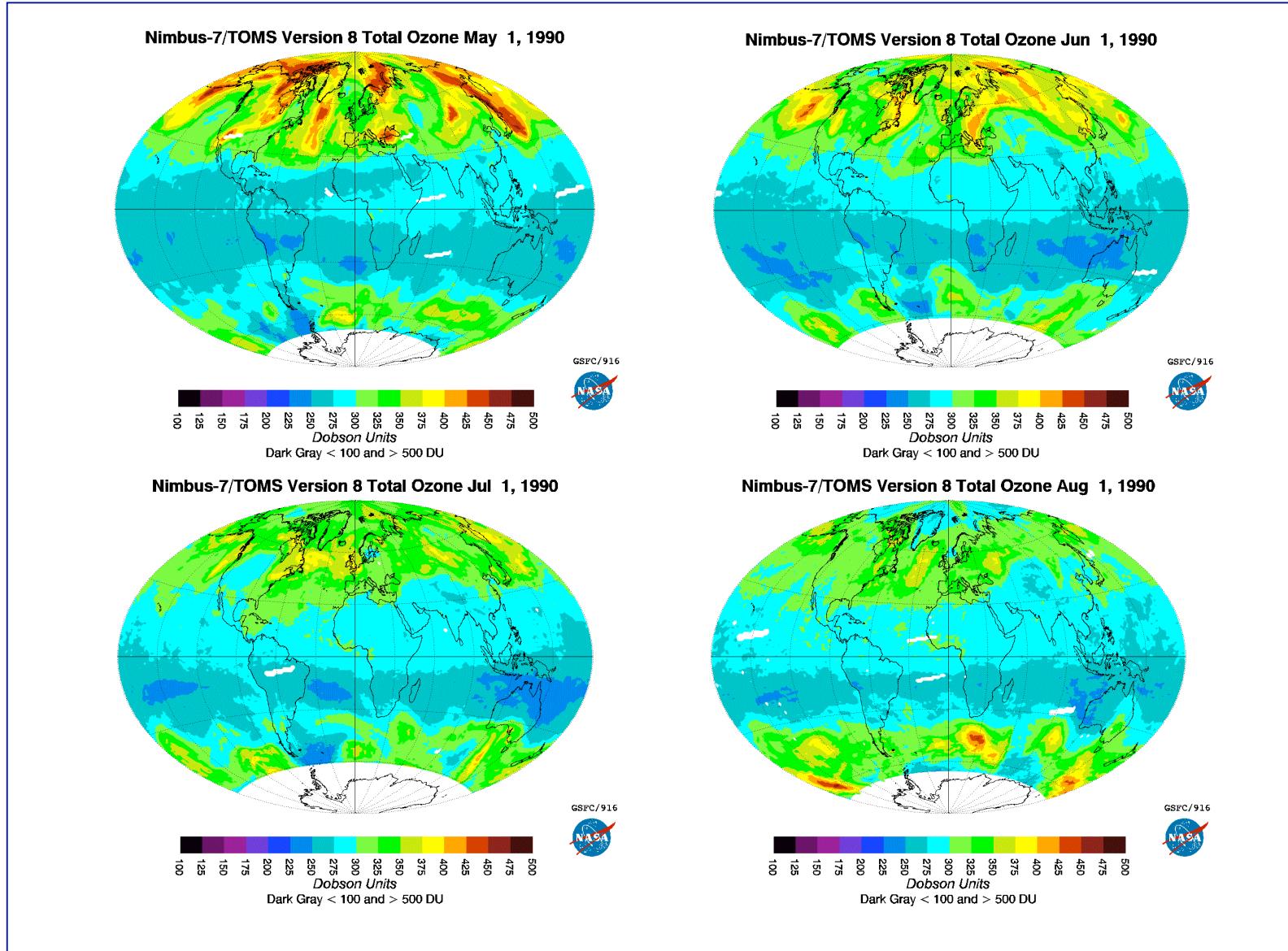
DOBSON AND THE DOBSON UNIT

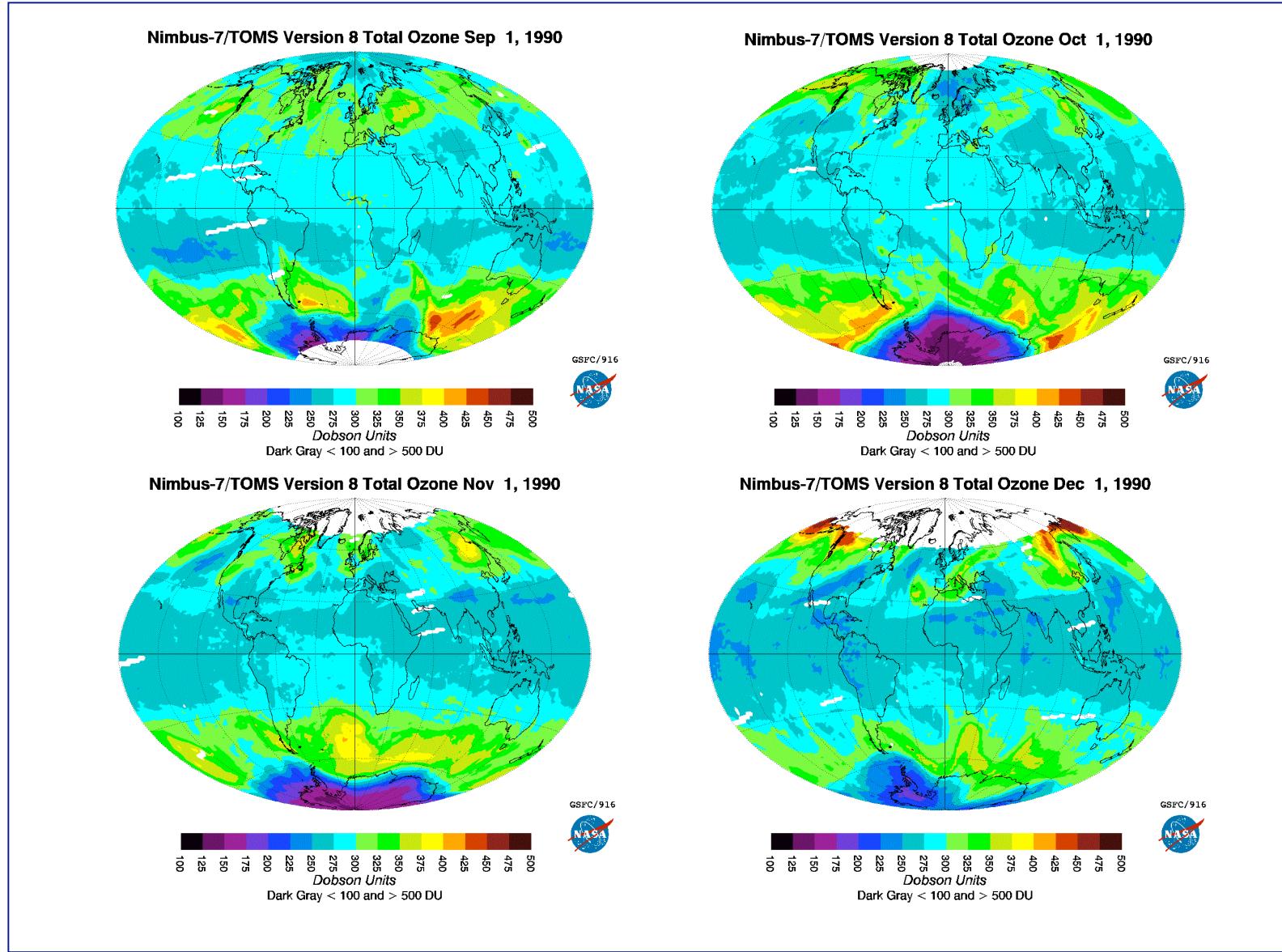
Gordon M. B. Dobson (1889-1976) came to the Clarendon Laboratory at Oxford University as Lecturer in Meteorology (Reader 1927, Professor 1945) in 1920 and began studies of the upper atmosphere. He deduced from meteor trails that the temperature of the upper atmosphere begins to rise above a height of 50 km, in contrast with the steady fall then expected. Realising that the source of energy for the warm layer is absorption of ultraviolet solar radiation by ozone, Dobson embarked on the study of atmospheric ozone that he was to pursue "with unrelenting vigour for the rest of his life". Extensive observations in 1925 established the seasonal variation of ozone (maximum in spring, minimum in autumn), and the close correlation with meteorological conditions in the upper troposphere and low stratosphere. Later, Dobson designed a sensitive, direct-reading photo-electric instrument, the prototype of the modern ozone spectrophotometer. Since the International Geophysical Year, 1956, for which 44 Dobson spectrometers were calibrated in Oxford, the ozone network has been a world-wide organisation.

The Dobson Unit is the thickness in hundredths of a millimeter that the ozone column would occupy at Standard temperature and pressure (273 K and one atmosphere (101325 Pa). The ozone column compressed in this way would typically be 3 mm thick and thus the atmospheric abundance is 300 DU. 1 DU equals 2.69×10^{16} molecule/cm², 446.2 mol/m², or 21.4 mg/m².

THE OBSERVED OZONE DISTRIBUTION

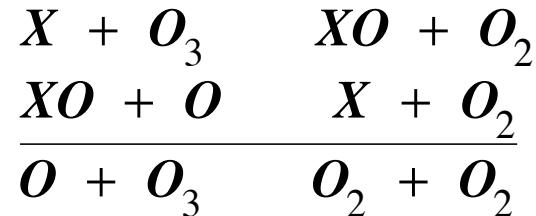






CHEMICAL CYCLES

Catalytic cycles were proposed to increase the loss of ozone,



The most important catalytic cycles are those where,

$X = OH$	Solomon Cycles 1
$X = NO$	Solomon Cycle 3
$X = Cl$	Solomon Cycle 6
$X = Br$	Solomon Cycle 6

At a stratospheric temperature of 220 K, the catalytic cycles,

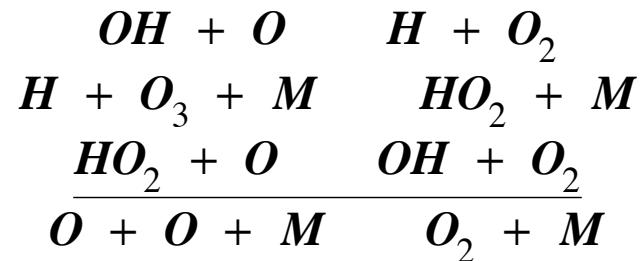


have rate constants that are orders of magnitude faster than the direct reaction,

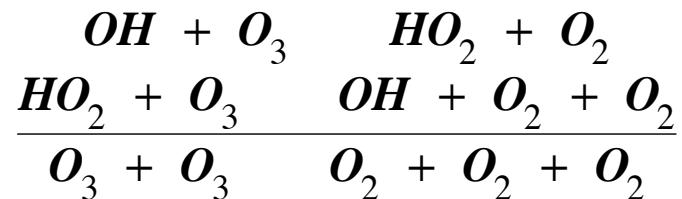


Whether the reactions are faster depends on the concentrations of XO and O_3 .

The chemistry of the stratosphere is understood in terms of cycles. The following cycles destroy odd oxygen, above 40 km the following cycle is important

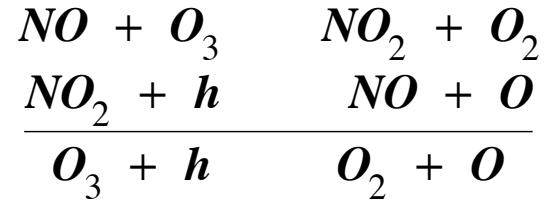


while below 30 km the following cycle, which does not require O, is important,

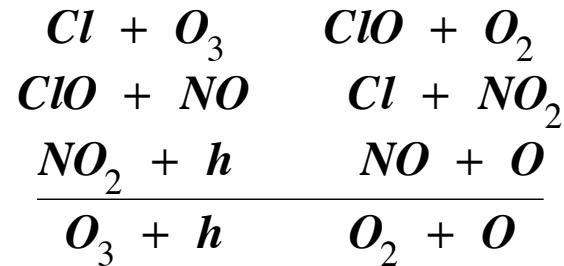
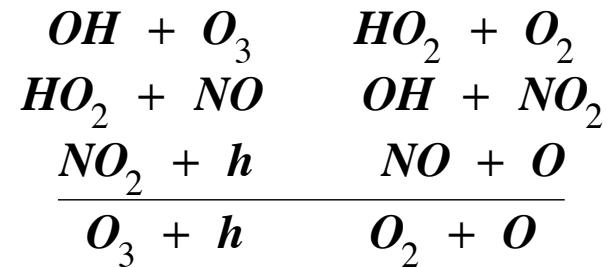


The precise destruction of odd oxygen depends on the partitioning of odd hydrogen (H, OH, HO₂).

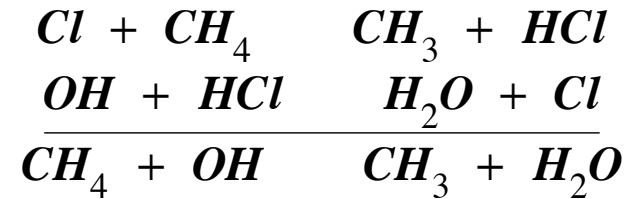
Null cycles where there is no net change in odd oxygen also operate in the stratosphere. The NO_x involved in this cycle is ineffective as a catalyst and so during the day NO_x is less effective than effective.



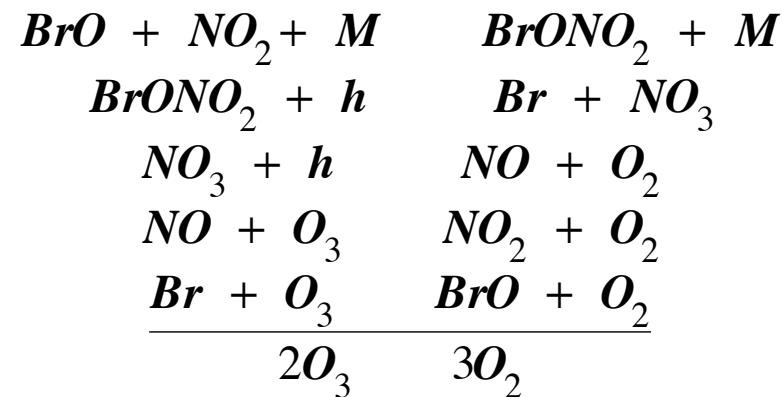
Reactions with NO allow the formation of null cycles for HO_x and ClO_x families,



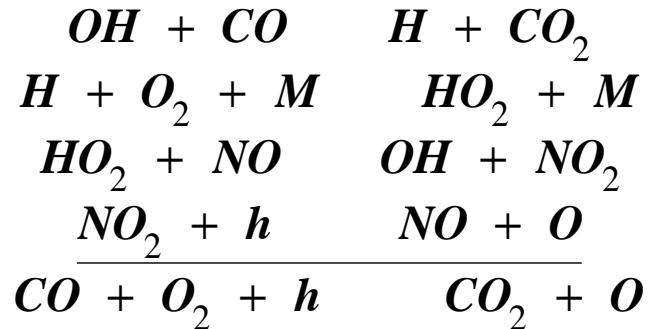
Cl participates in holding cycles with HCl as a reservoir,



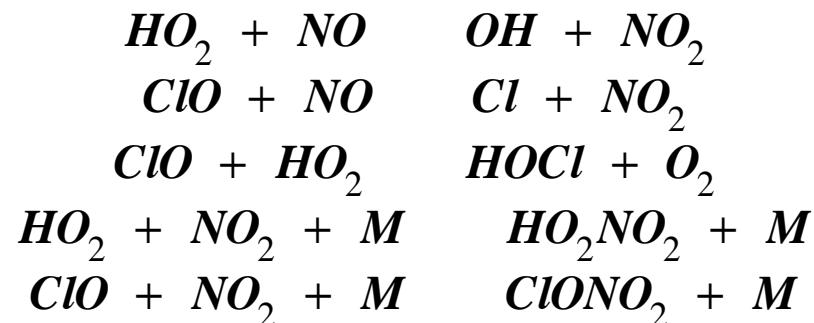
Analysis of Bromine reservoirs suggests that unlike Chlorine the reservoirs do not accumulate, however they may participate in cycles that are efficient.



Unusual cycles exist where odd oxygen is formed rather than destroyed.

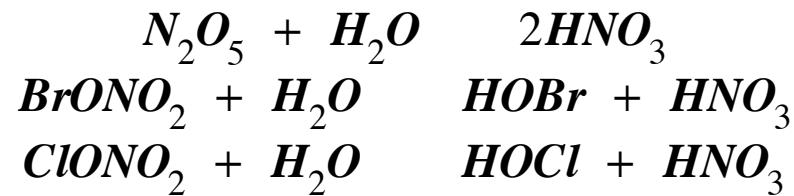


While identification of cycles gives insights into how complex families of reactions impact the chemistry of the stratosphere. The effects of various catalytic families is not additive. Members of different families of chemicals interact with members of another. Changes in reaction rates for these coupling reactions have necessitated drastic revision of stratospheric models. Important reactions are,



HETEROGENEOUS CHEMISTRY

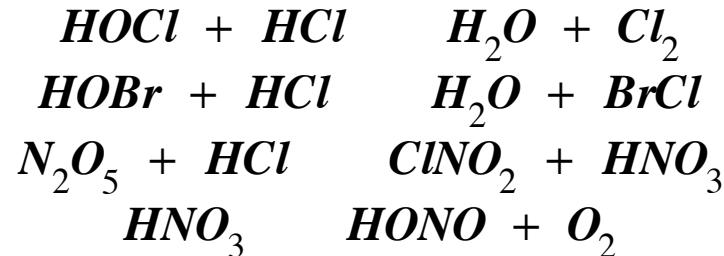
Heterogeneous processing is particularly significant in relation to the reservoir compounds and interactions between them. The surface reactions include hydrolysis reactions,



as well as critical conversion between $ClONO_2$ and HCl ,



Other proposed reactions include,

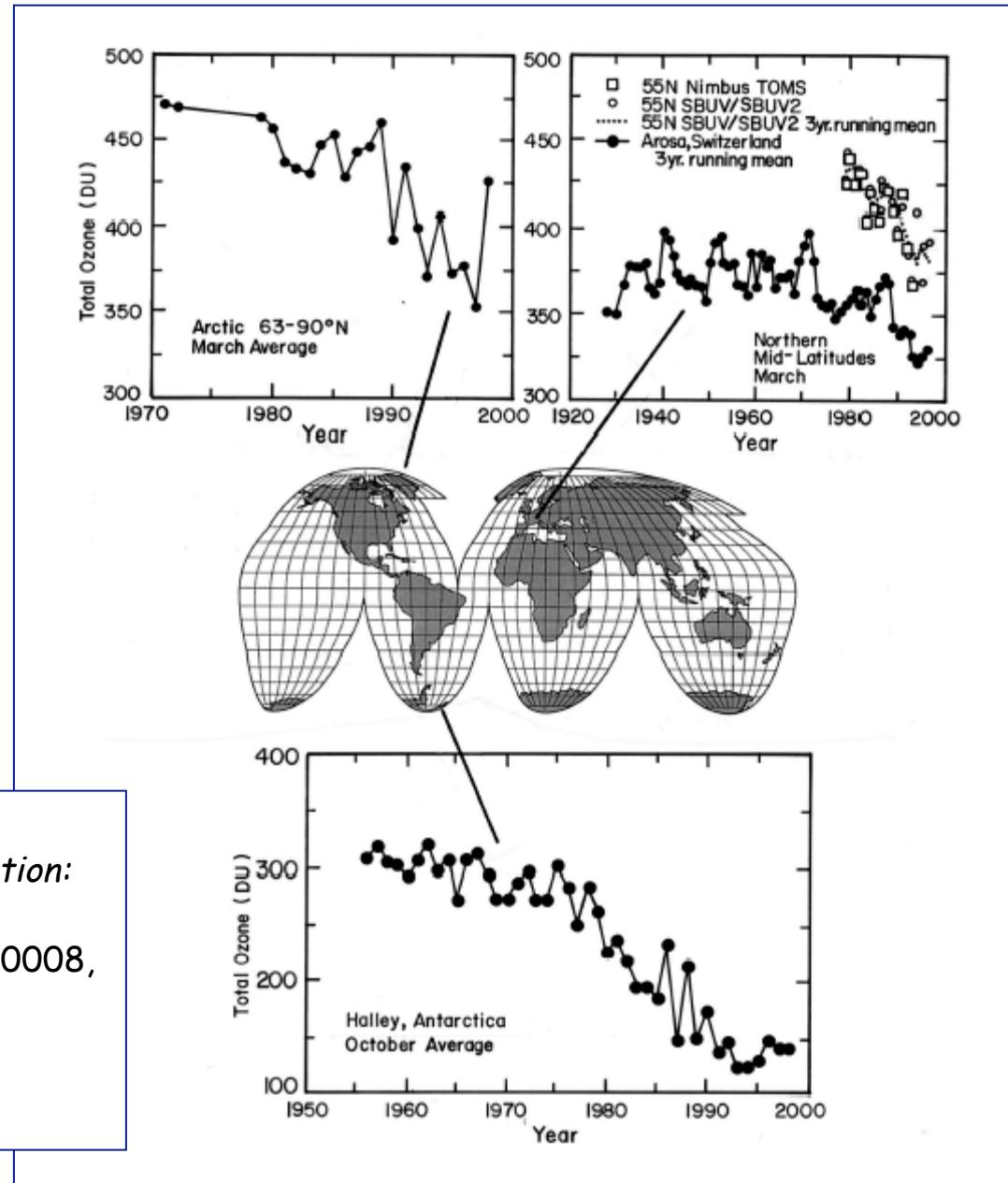


OZONE DEPLETION IS REAL

The trends are obvious, no subtle trend analysis is required to see that since the early 1980's ozone levels have been decreasing.

Recent trends observed are outside historic variability. The trends are observed around the globe, not just in Antarctica.

S. Solomon, *Stratospheric Ozone Depletion: A Review of Concepts and History*, Rev. Geophys. 37 (3), doi:10.1029/1999RG900008, 1999. Copyright 1999 by the American Geophysical Union.



OZONE CHEMISTRY

TABLE 1. Key Chemical Processes and Catalytic Cycles

<i>Chemical Process</i>	<i>Reaction Number</i>
	<i>Chapman Chemistry^a</i>
$\text{O}_2 + h\nu \rightarrow 2\text{O}$	R1
$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	R2
$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^{(1D)}$	R3
$\text{O}^{(1D)} + \text{M} \rightarrow \text{O} + \text{M}$	R4
$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$	R5
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	R6
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	R7
	<i>Illustrative Odd Hydrogen Catalytic Cycles^b</i>
$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$	R8
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	R9
$\text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH}$	R10
Net Cycle 1: $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	R6
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	R11
$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	R12
Net Cycle 2: $2\text{O}_3 \rightarrow 3\text{O}_2$	R13
	<i>Illustrative Odd Nitrogen Catalytic Cycle^c</i>
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	R14
$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	R15
Net Cycle 3: $\text{O} + \text{O}_3 \rightarrow \text{O}_2$	R7
...	

OZONE CHEMISTRY

Illustrative Odd Chlorine Catalytic Cycles^d

$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	R16
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	R17
Net Cycle 4: $\text{O} + \text{O}_3 \rightarrow \text{O}_2$	R7
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	R16
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	R16
$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$	R18
$\text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{Cl} + \text{ClO}_2$	R19
$\text{ClO}_2 + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$	R20
Net Cycle 5: $2 \text{O}_3 \rightarrow 3\text{O}_2$	R13

Illustrative Cl-Br Catalytic Cycle^e

$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	R16
$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	R21
$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{ClO}_2$	R22
$\text{ClO}_2 + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$	R20
Net Cycle 6: $2 \text{O}_3 \rightarrow 3\text{O}_2$	R13

Some Important Coupling and Reservoir Reactions

$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	R23
$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$	R24
$\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2$	R25
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	R26
$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	R27

Key Heterogeneous Reactions

$\text{HCl} + \text{ClONO}_2 \rightarrow \text{HNO}_3 + \text{Cl}_2$	R28
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	R29
$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}$	R30
$\text{HCl} + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{Cl}_2$	R31
$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOBr}$	R32
$\text{HCl} + \text{BrONO}_2 \rightarrow \text{HNO}_3 + \text{BrCl}$	R33
$\text{HCl} + \text{HOBr} \rightarrow \text{H}_2\text{O} + \text{BrCl}$	R34

^aChapman [1930].

^bBates and Nicolet [1950]; Hampson [1964].

^cCrutzen [1970]; Johnston [1971].

^dStolarski and Cicerone [1974]; Molina and Molina [1987].

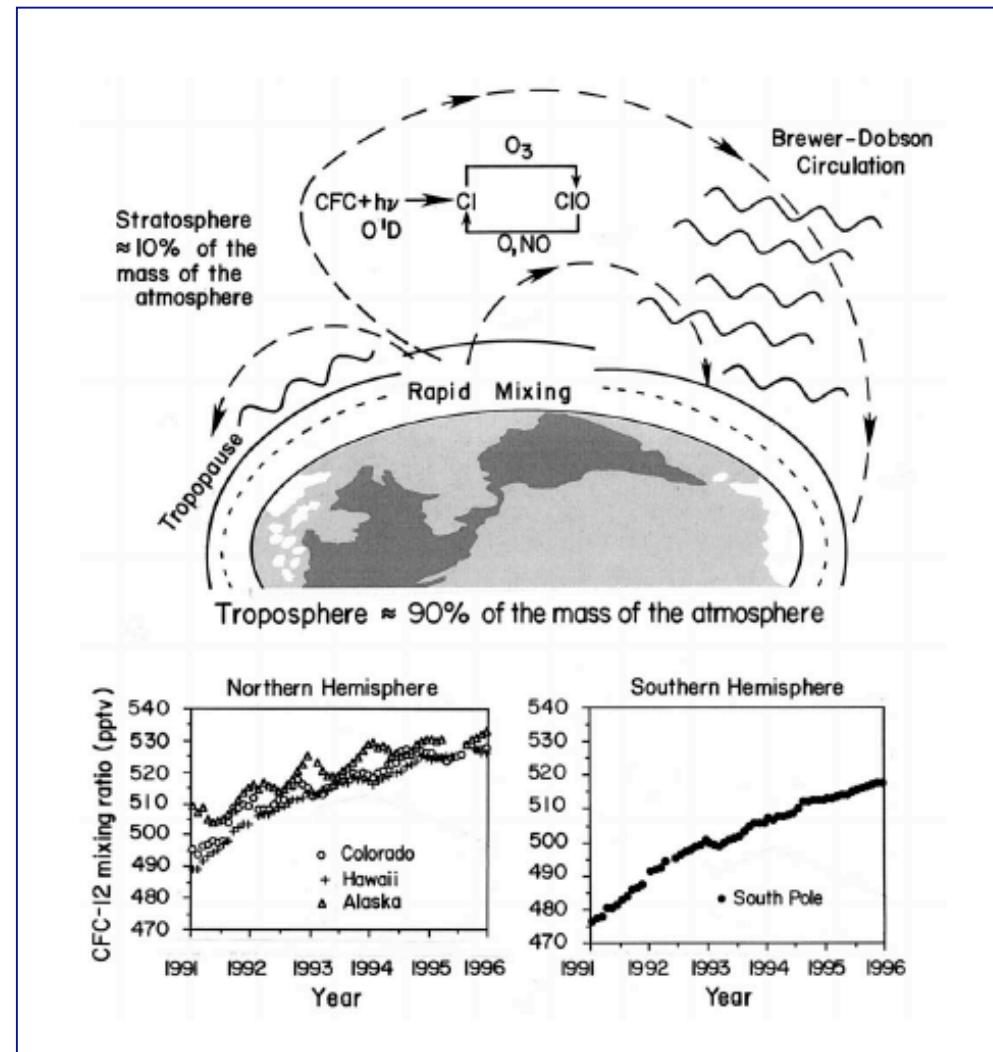
^eMcElroy et al. [1986]; Tung et al. [1986].

CHLOROCARBON LIFETIMES

Chlorofluorocarbons (CFCs) have very long residence lifetimes. They are inert in the troposphere and are globally mixed in the troposphere.

CFCs are destroyed by ultraviolet light in the stratosphere. On destruction free chlorine is released that can destroy ozone in a catalytic cycle.

The Brewer-Dobson circulation has an overturning timescale of ~ 5 years. With the mass of the stratosphere being $\sim 10\%$ of mass of troposphere it takes ~ 50 yrs to process the CFCs. The CFC chlorine returns to the troposphere as HCl where it is rained out and removed from the atmosphere.



GEOENGINEERING FIXES

Can we make more stratospheric ozone?

The energy required to break the O₂ bond is 5.1 eV. Thus the power required to produce the ozone layer is $\sim 10^{13}$ W.

This power is provided daily by the Sun but is ~ 3 times the artificial power produced in 1970.

"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".

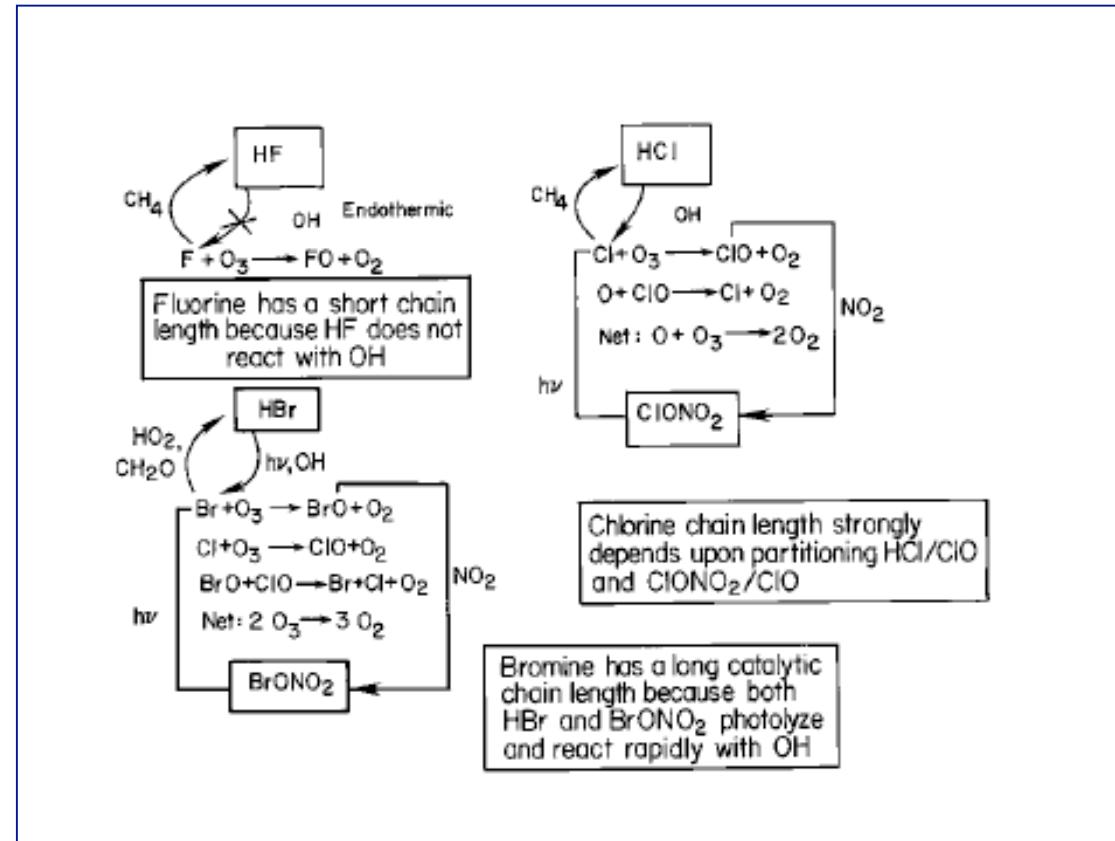


ALL HALOGENS ARE NOT EQUAL

Fluorine gets tied up in a HF reservoir and is "neutralized".

Chlorine is less tightly tied up in HCl and ClONO₂ reservoirs. There is significant formation of Cl and ClO from these reservoir species.

Bromine is even less tightly tied up in HBr and BrONO₂ reservoirs. Bromine is very effective at destroying ozone. However, Bromine abundances are about 200 times smaller than those of Chlorine.

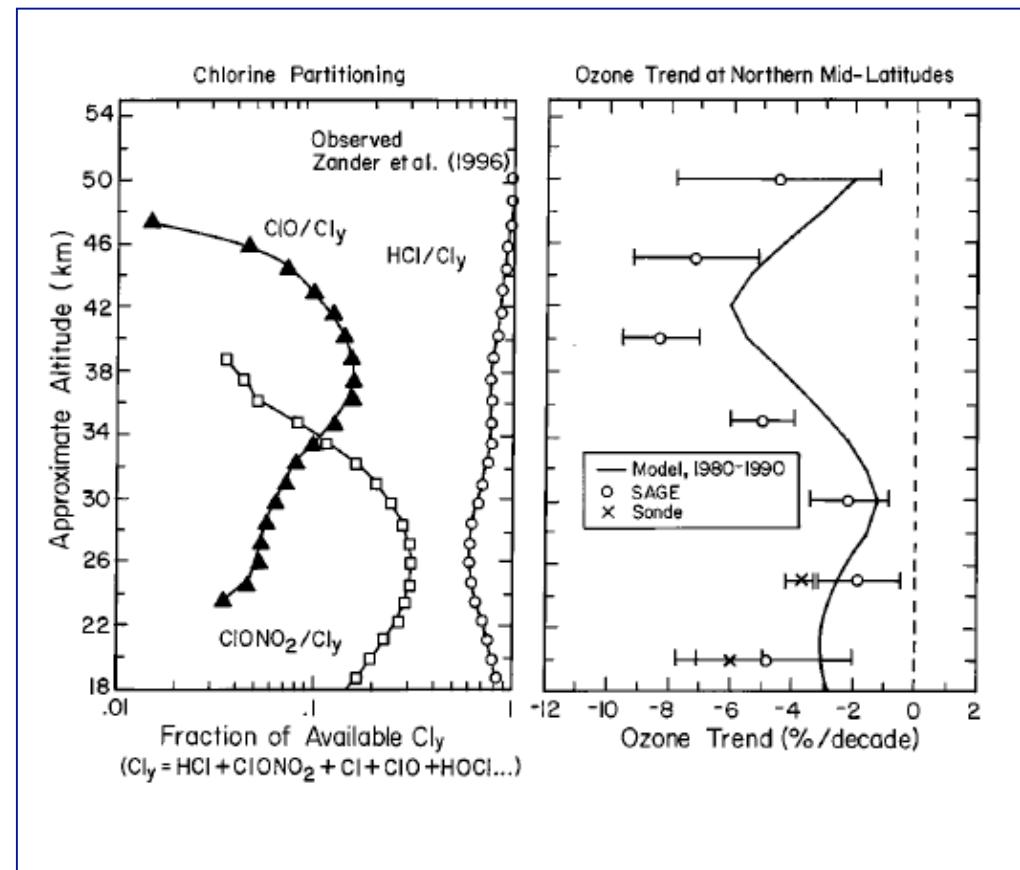


IS IT REALLY CFCs ?

Airborne measurements at base of stratosphere show the following chlorine sources;

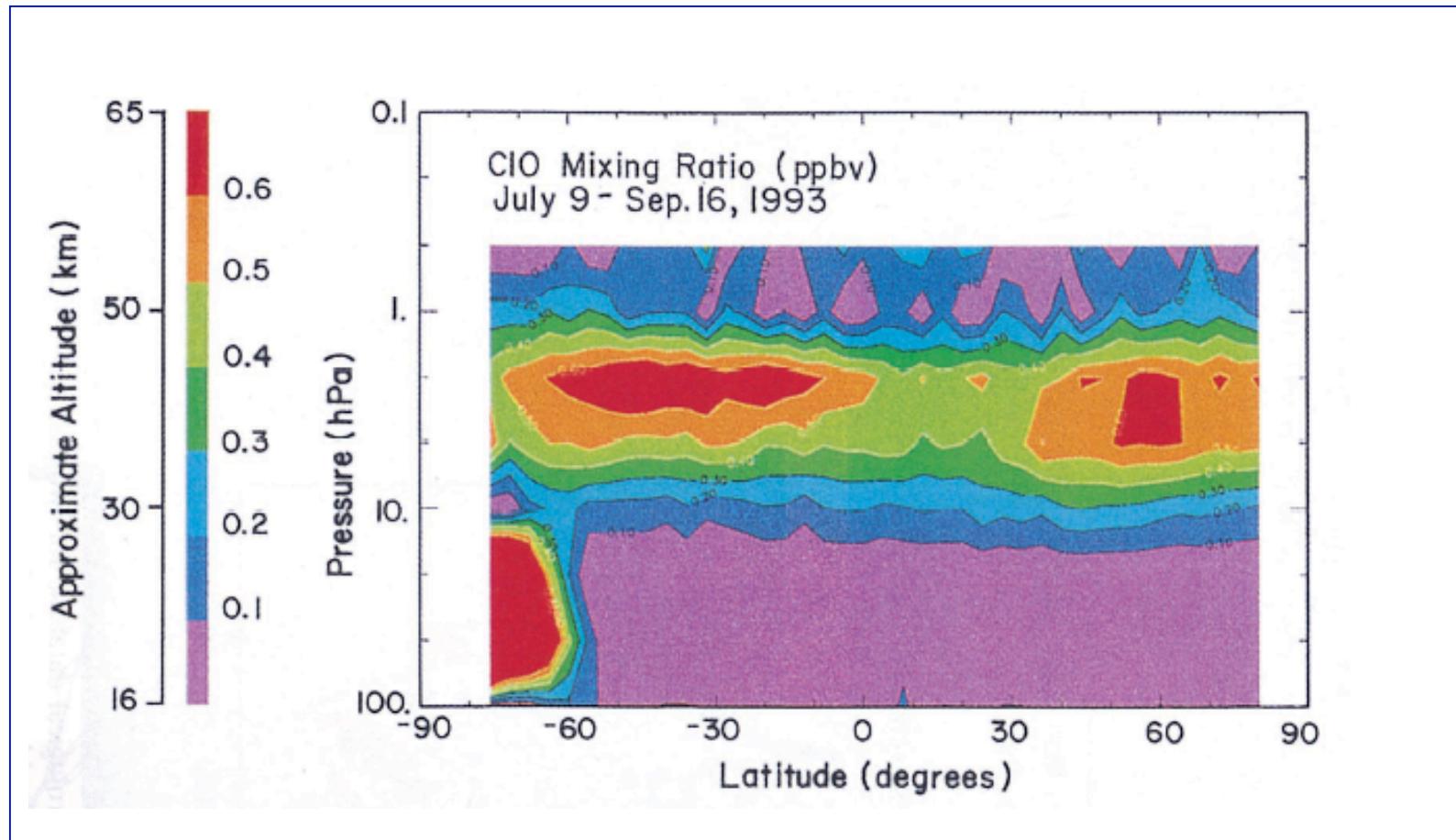
- ~ 3.0 ppbv CFCs
- ~ 0.1 - 0.2 ppbv HCl
- ~ 0.5 - 0.6 ppbv CH_3Cl

At about 45 km we expect all CFC chlorine to be bound in HCl. Abundances and trends in HCl and HF in the upper are consistent with models that have a CFC source,
~ 85% Stratospheric Chlorine was CFC-generated in 1992.



Furthermore the maximum in ClO corresponds to the maximum in ozone depletion. The partitioning of Chlorine in different compounds is critical.

EVIDENCE FOR CHLORINE ?



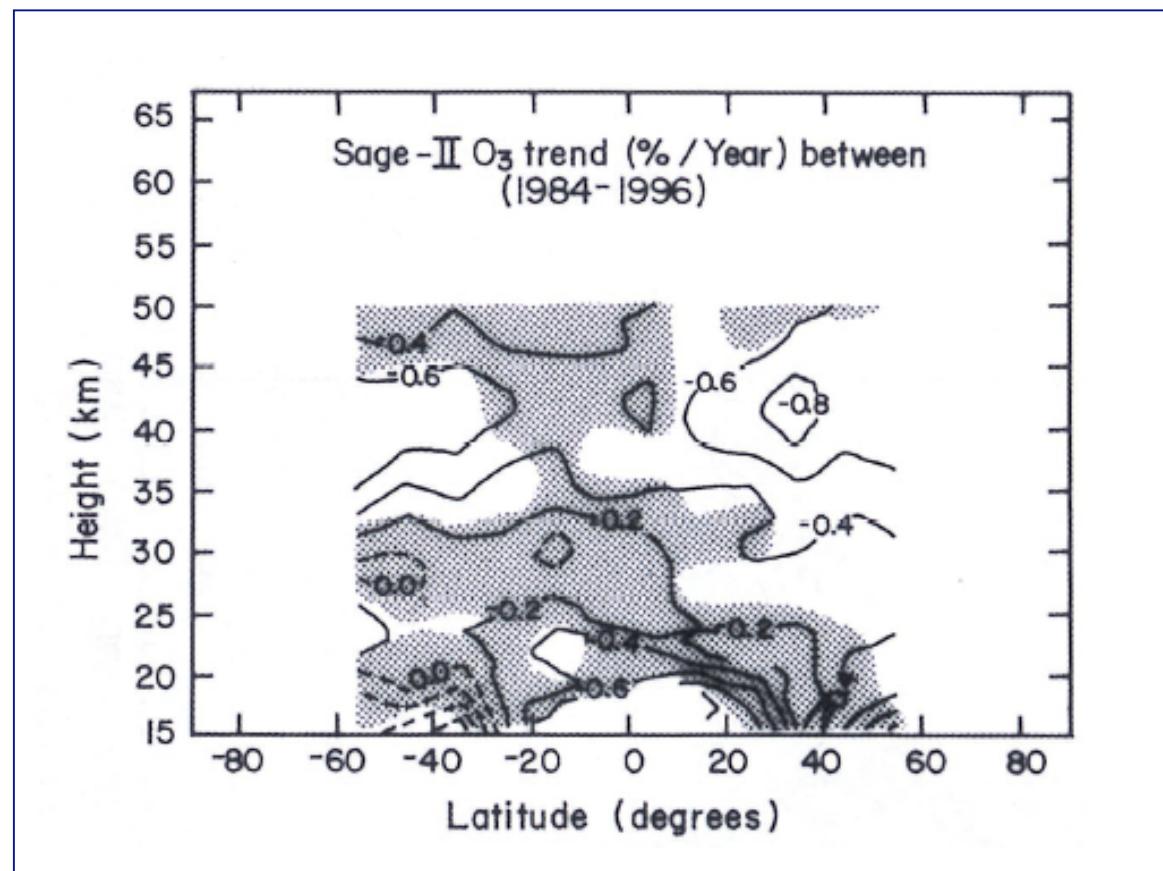
Global satellite observations of ClO shows a strong latitudinal gradient with a pronounced minimum in the tropics.

EVIDENCE FOR CHLORINE ?

Ozone trends in the upper stratosphere show the same patterns as ClO.

This observed correlation indicates that gas phase chlorine chemistry is responsible for the depletion of ozone.

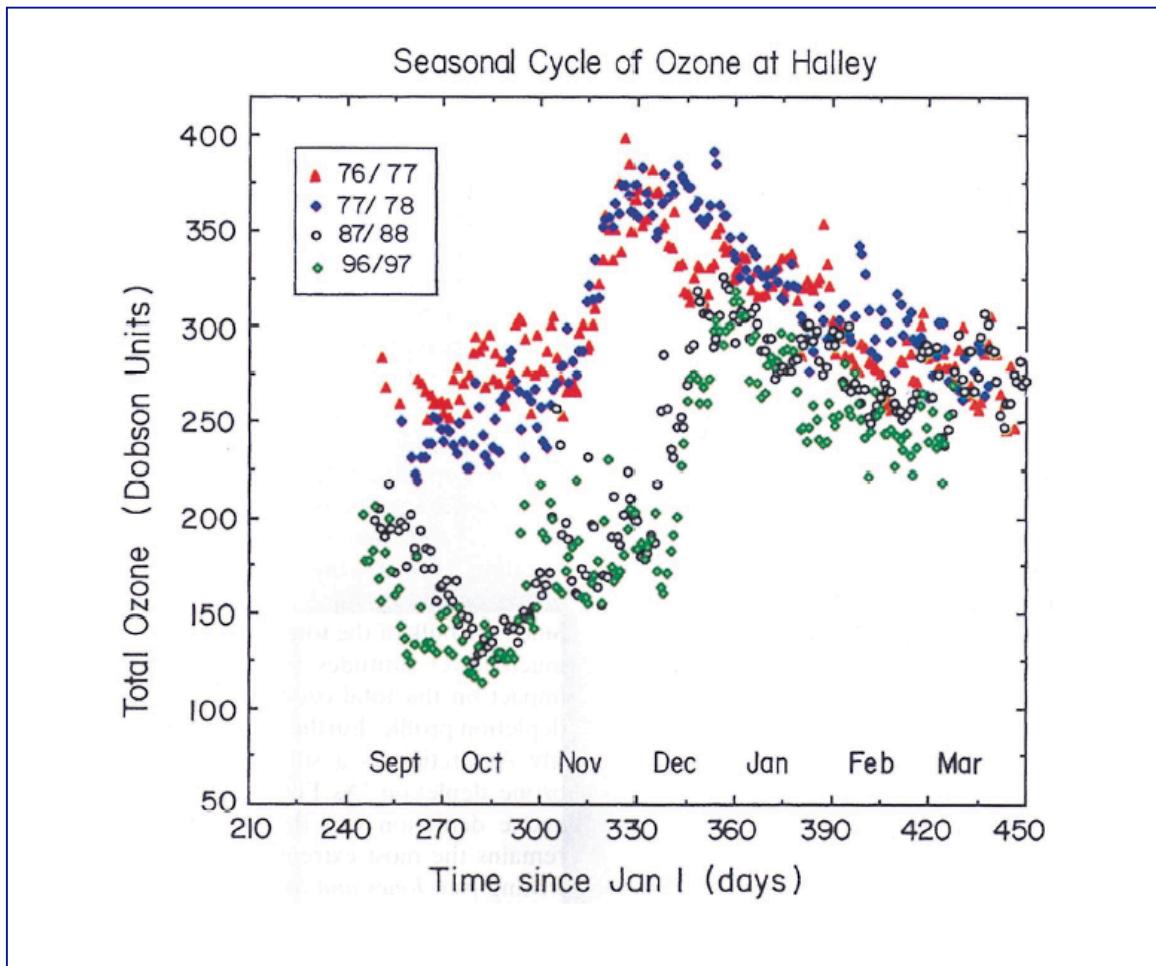
Furthermore, these observations indicate the importance of partitioning processes in modulating ozone depletion.



THE ANTARCTIC OZONE HOLE

The "ozone hole" was first reported from Antarctica by Farman and colleagues in 1985. These researchers used Dobson spectrometers to measure the column ozone over the research station at Halley. These findings were quickly confirmed by other researchers.

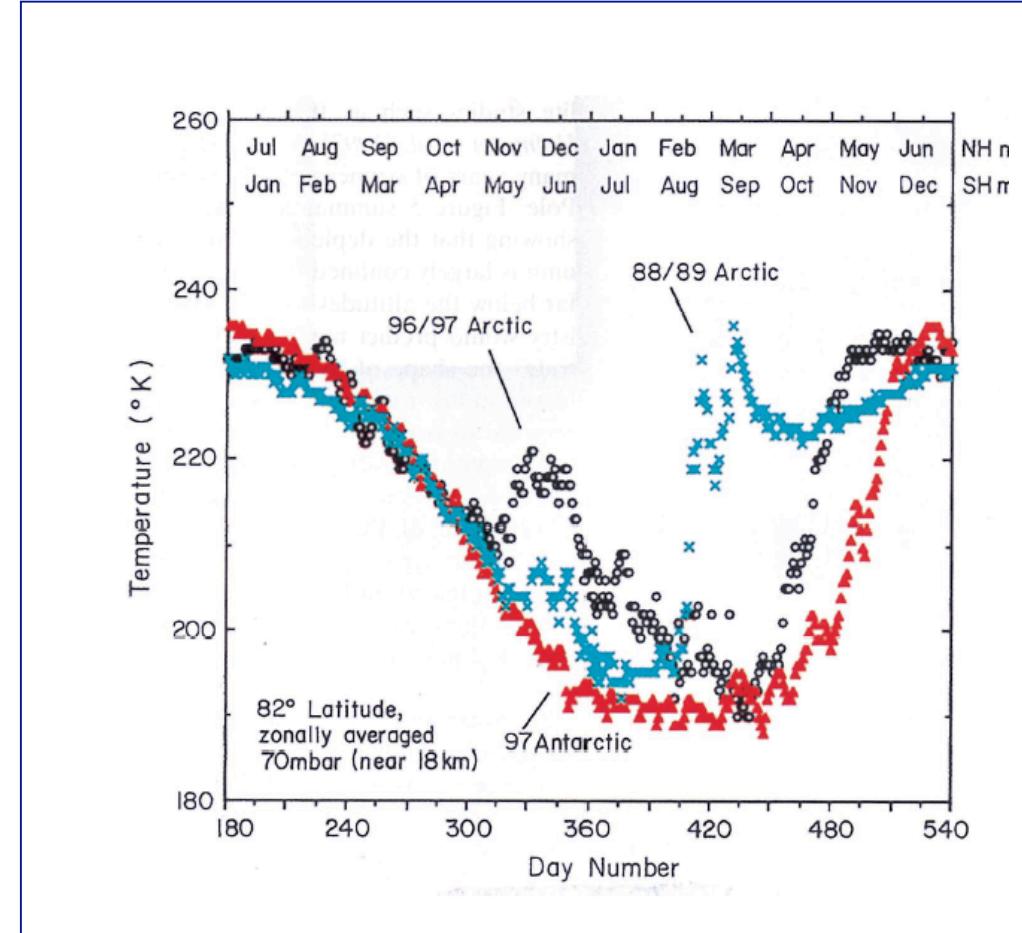
Traditionally the Arctic and Antarctic were expected to have differing amounts ozone due to differences in the general circulation. However, the extreme differences associated with the ozone hole were larger than expected.



THE ARCTIC AND THE ANTARCTIC

The large temperature gradient in the winter southern hemisphere produces a stable east-west Antarctic jet that effectively isolates the Antarctic stratosphere from lower latitudes in a vortex.

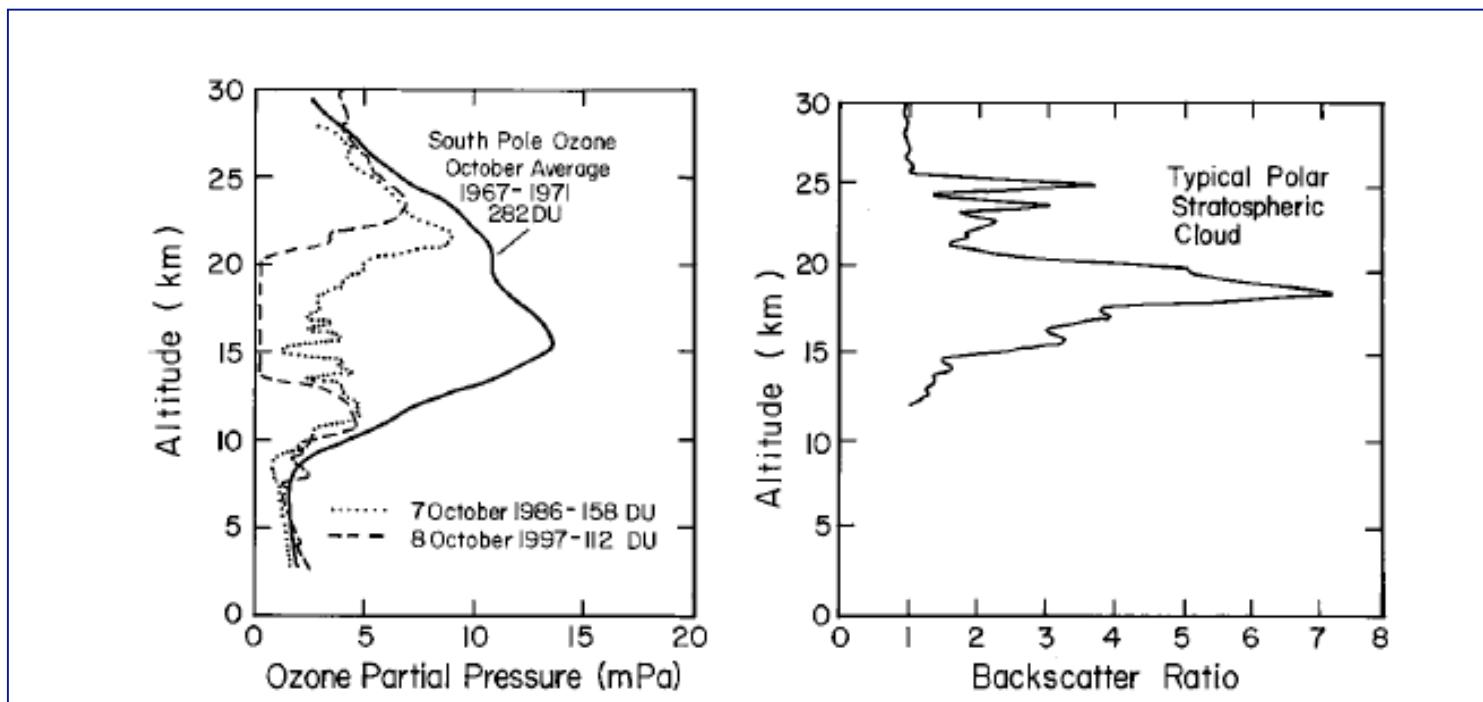
The geography of the northern hemisphere results in a well-mixed stratosphere with periodic warming due to intrusion of planetary waves that cause mixing of cold high-latitude and warm mid-latitude air. These waves do not penetrate into the southern hemisphere stratosphere.



Temperatures in the Antarctic vortex are colder and less variable than those in the Arctic.

MEASUREMENTS OF THE VERTICAL PROFILE OF OZONE

A key finding was that the ozone depletion was limited to the ~12-15 km altitude region.



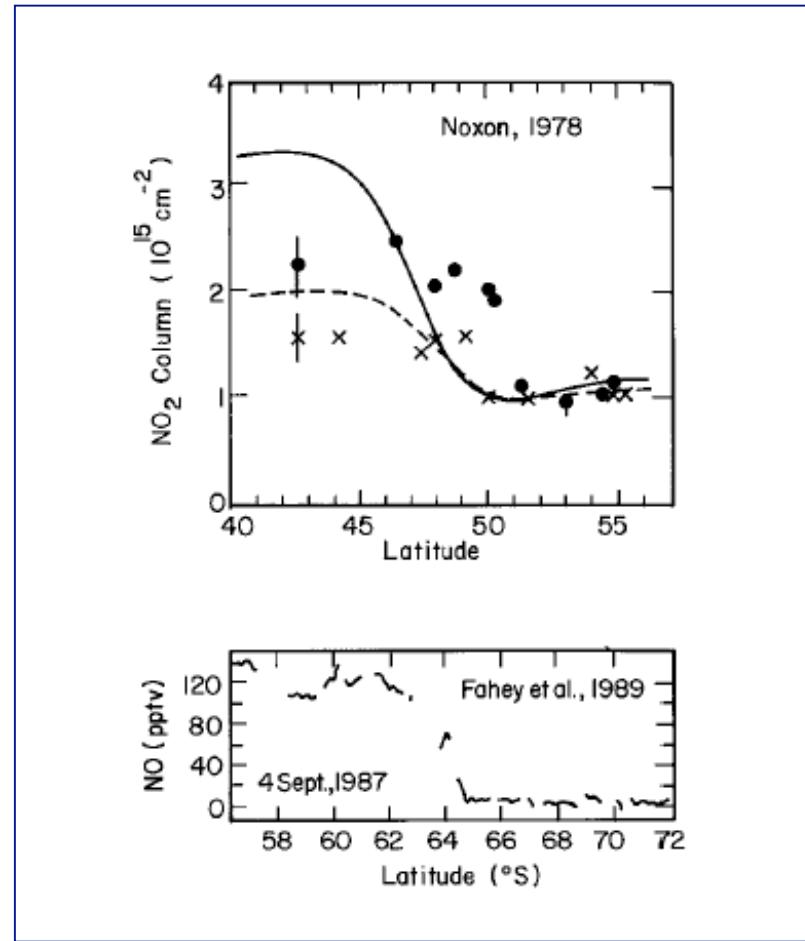
Traditional gas phase chemistry would suggest depletion in the upper stratosphere. The altitude of the depletion suspiciously corresponds to the altitude of polar stratospheric clouds (PSCs).

A PLETHORA OF THEORIES

A variety of theories were initially suggested to explain the loss of ozone. These included increases in solar activity that would perturb the nitrogen chemistry of the stratosphere (increased nitrogen oxides) and upward transport of ozone-poor tropospheric air.

Observations in and studies of the Antarctic stratosphere showed depressed levels of nitric oxide and a downward transport as part of a global circulation.

The depression of nitric oxide levels in the Antarctic stratosphere had been reported in the late 1970's but remained unexplained until the late 1980's.



HETEROGENEOUS CHEMISTRY AND PSCS

The basic schemes proposed to explain the Antarctic ozone hole was that HCl and ClONO₂ react on PSC surfaces to form HNO₃ and Cl₂,



The Cl₂ so formed photolyses in sunlight to form ClO. The ClO so formed does not reform ClONO₂ as the NO₂ concentrations have been depressed by formation of HNO₃ in this and companion heterogeneous reactions. The critical features of this scheme are;

- Heterogeneous activation of chlorine from both HCl and ClONO₂
- Suppression of NO₂.

An intense period of filed observations and laboratory experiments ensued that resulted in discovery new catalytic cycles (involving ClO dimers, Cl₂O₂) and further understanding of ozone chemistry.

Can the nitric acid be sequestered in Antarctica, in a way that is unique to that geographical region ?

METEOROLOGICAL FEEDBACKS

Ozone provides the primary source of heat to the stratosphere through absorption of ultraviolet radiation. Ozone depletion should lead to stratospheric cooling which would make heterogeneous chemistry more effective.

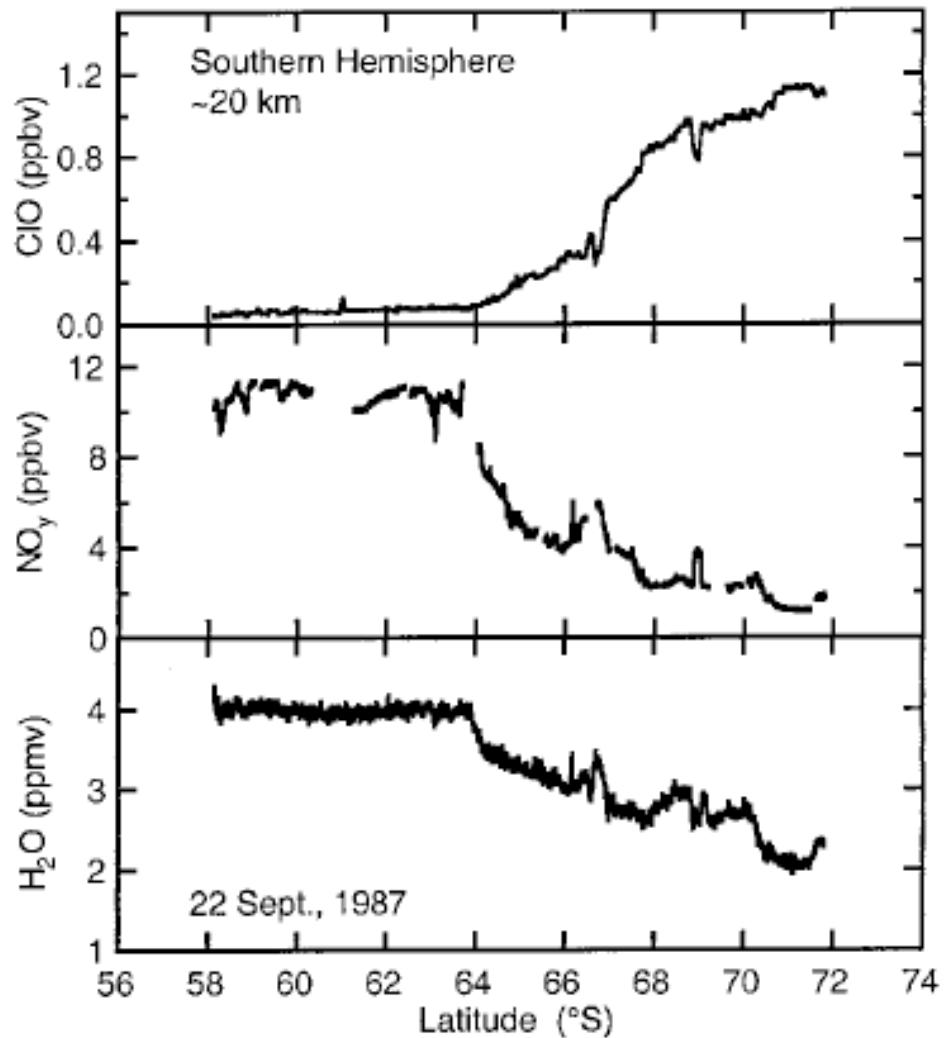
The delay in the seasonal breakdown of the Antarctic vortex in recent years suggests such a positive feedback has occurred.

Analysis of wintertime stratospheric temperatures reveals little if no cooling of the stratosphere before the ozone depletion in September. This confirms that the meteorological changes are a consequence of and not a cause of the ozone hole.

FIELD AND LABORATORY OBSERVATIONS

Observations of active chlorine species (e.g. ClO, OCIO) are foremost amongst the data that established the cause of the ozone hole. Ground based measurements at McMurdo and airborne measurements from Puenta Arenas, Chile were critical.

Steep latitudinal gradients in ClO are co-located with the sudden drop in temperature as the aircraft entered the Antarctic vortex.

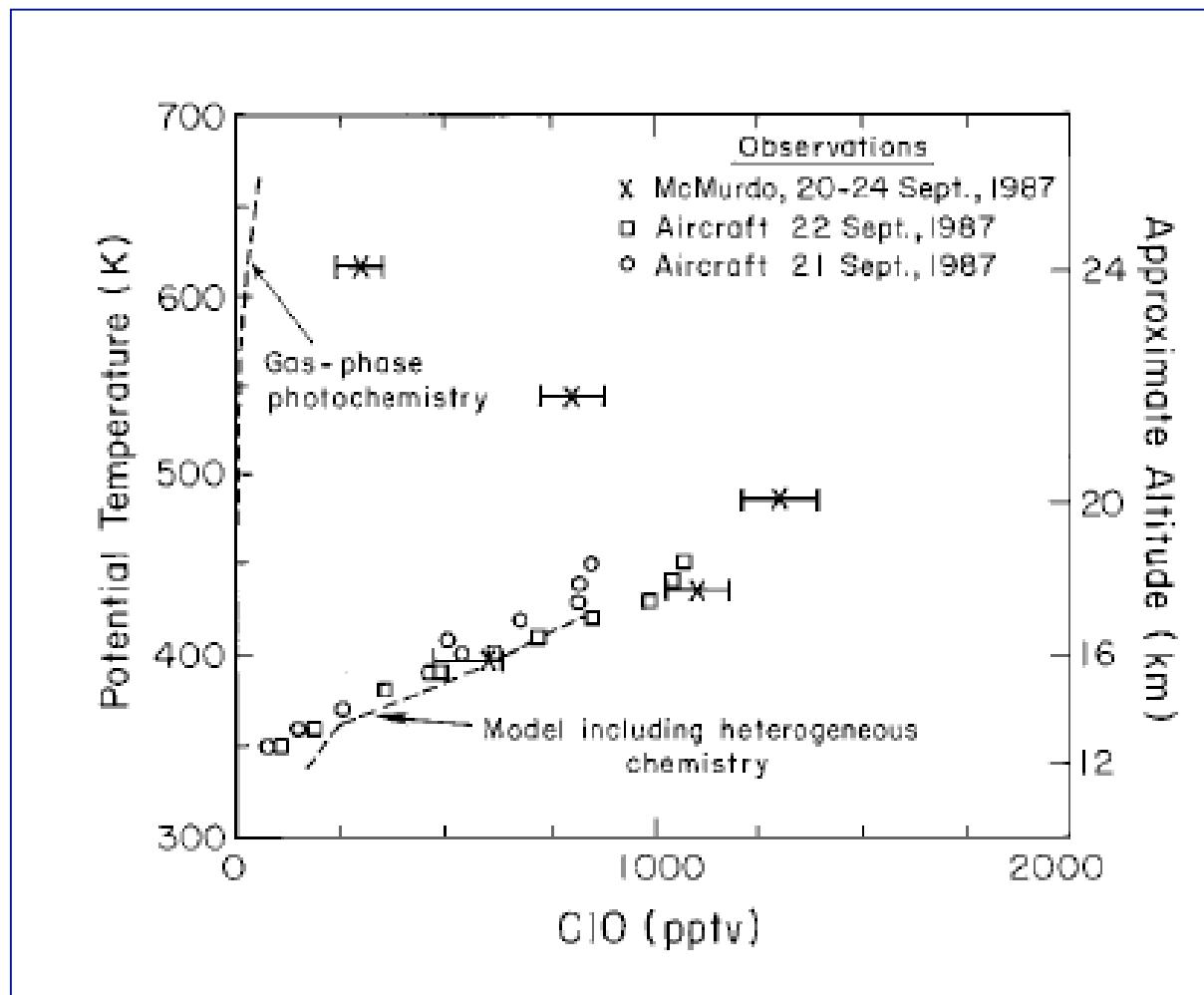


FIELD AND LABORATORY OBSERVATIONS

These observations indicated hundred-fold increases in active chlorine in the Antarctic vortex.

The HF/HCl ratio indicated conversion of HCl to active Cl. Activation of Cl was found to correlate with cold temperatures (< 195 K) and with presence of Polar Stratospheric Clouds.

Vertical profiles of ClO show a transition from heterogeneous chemistry to gas phase chemistry with altitude.



FIELD AND LABORATORY OBSERVATIONS

For ClO abundances $\sim 1.0\text{-}1.3$ ppbv ($\text{BrO} \sim 7\text{-}10$ pptv) O_3 is destroyed near 20 km at a rate of $\sim 0.06\text{-}0.1$ ppmv/day. Within $\sim 40\text{-}60$ days all the ozone at this level is depleted, unless rapid dynamical mixing occurs.

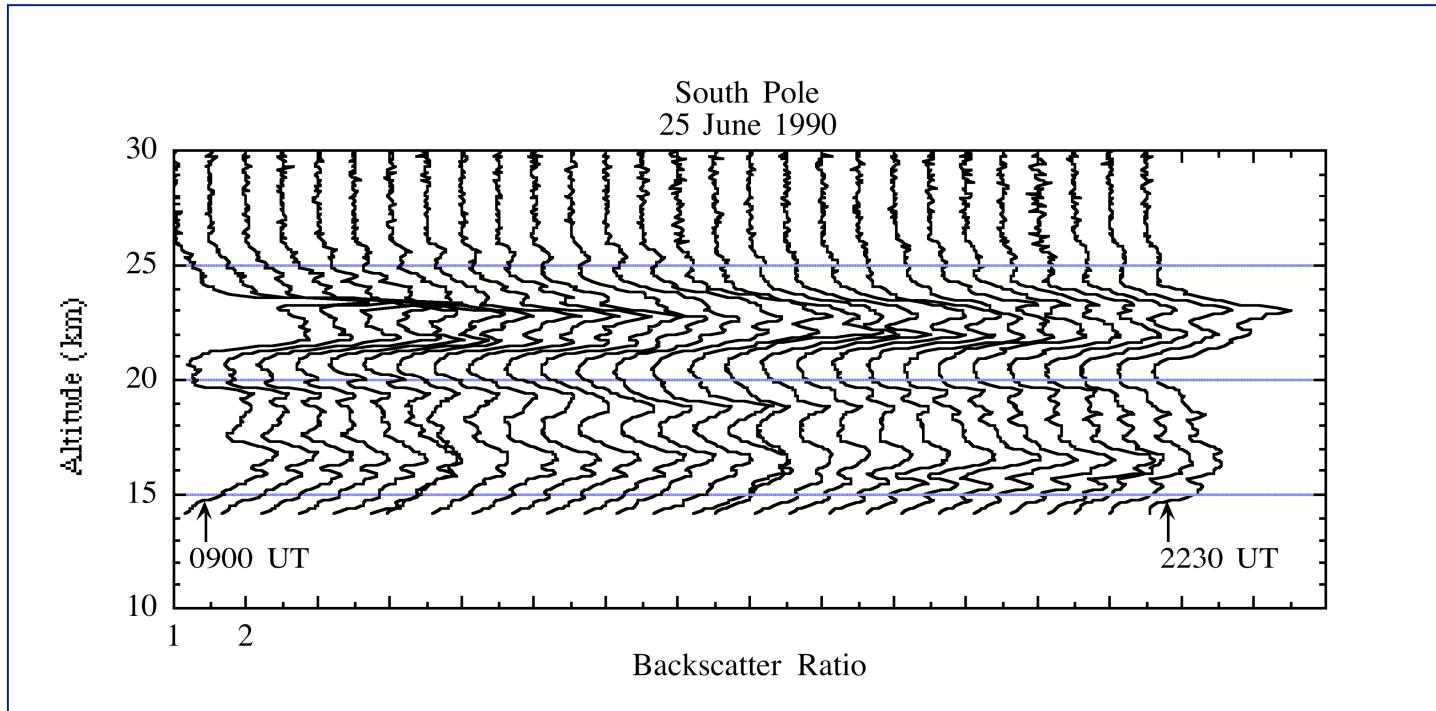
During this period net downward motion and horizontal mixing are limited and the Antarctic stratosphere is relatively isolated. A variety of dynamical studies support this view.

The ClO enhancement is in the same latitude range as PSCs ($\sim 12\text{-}25$ km).

"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".

POLAR STRATOSPHERIC CLOUDS (PSCs)

Studies showed dehydration and de-nitrification of the Antarctic stratosphere.

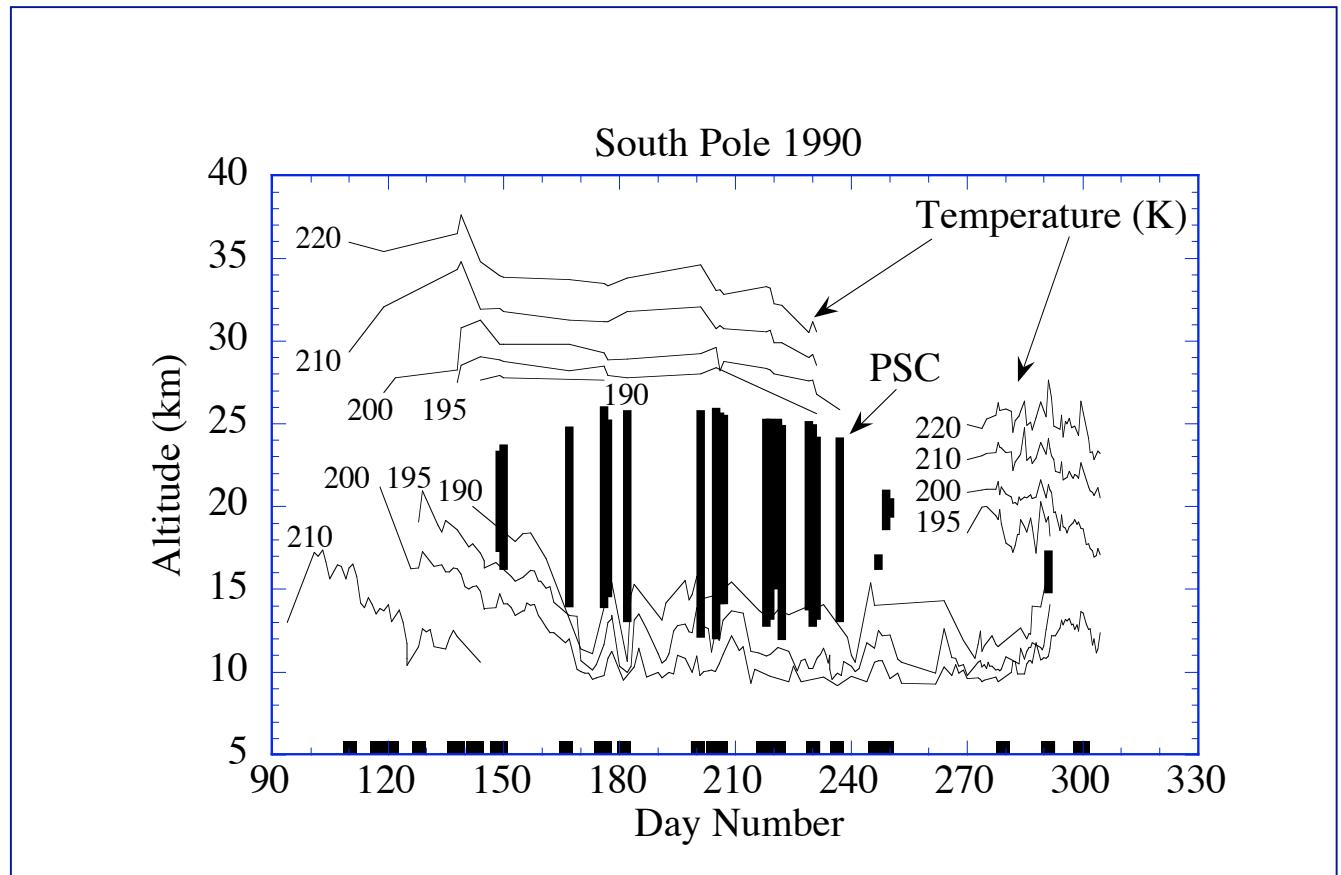


Early studies concluded that PSCs were initially formed from frozen nitric acid trihydrate (NAT) (Type I PSCs) and then as the seasonal temperatures fell further they were composed of water ice (Type II PSCs).

POLAR STRATOSPHERIC CLOUDS

Laboratory studies confirmed that rapid heterogeneous reactions could take place on these kinds of surfaces.

Early lidar studies indicated that Type I clouds had two types of particles present: depolarizing solid particles (Type Ia) and non-depolarizing liquid (Type Ib).



Further laboratory studies suggested that the thermodynamics of NAT were inconsistent with the detailed relationships between cloud formation and temperature.

POLAR STRATOSPHERIC CLOUDS

Researchers suggested that super-cooled ternary liquid solutions of $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ would play a significant role in the formation of PSCs. These solutions remain liquid down to temperatures of 188 K.

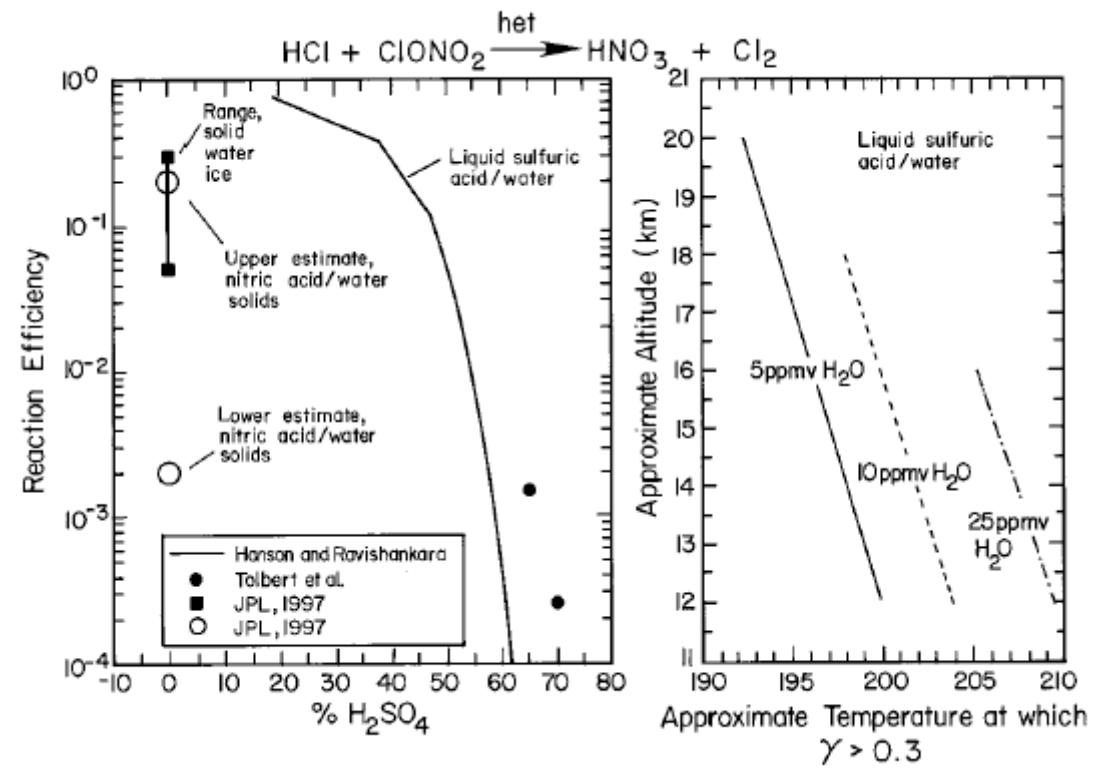
Laboratory studies have shown that it is extremely difficult to get these solutions to freeze at temperatures above the frost point, even if kept cold for many hours.

Thus we now believe that PSCs are liquid for much of the time. While Type II PSCs that form below the frost point are well understood, the formation of solid Type I PSCs at temperatures above the frost point is not.

SURFACE CHEMISTRY

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.

This may be followed by reactions on NAT and ice as the temperature falls further.

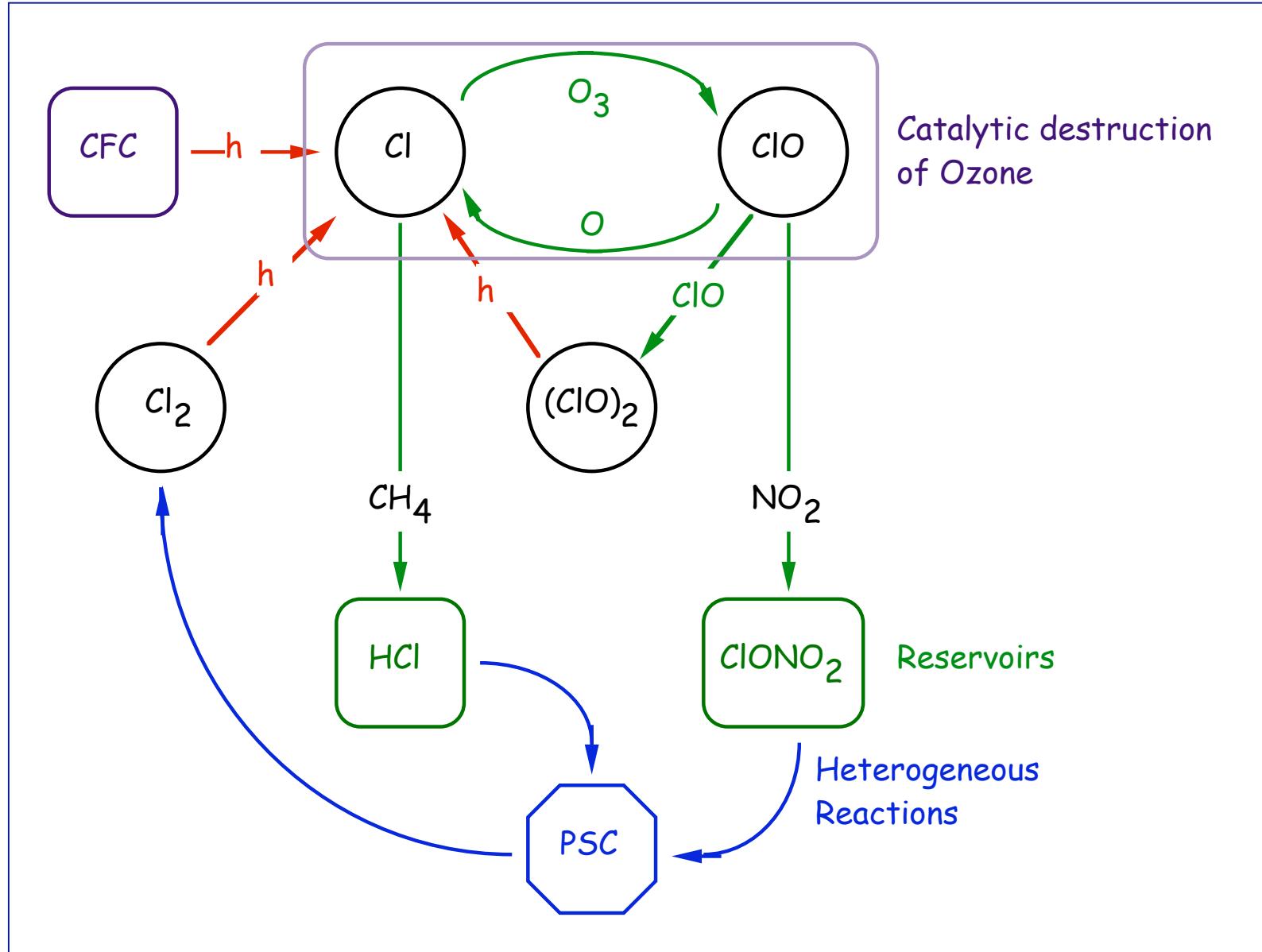


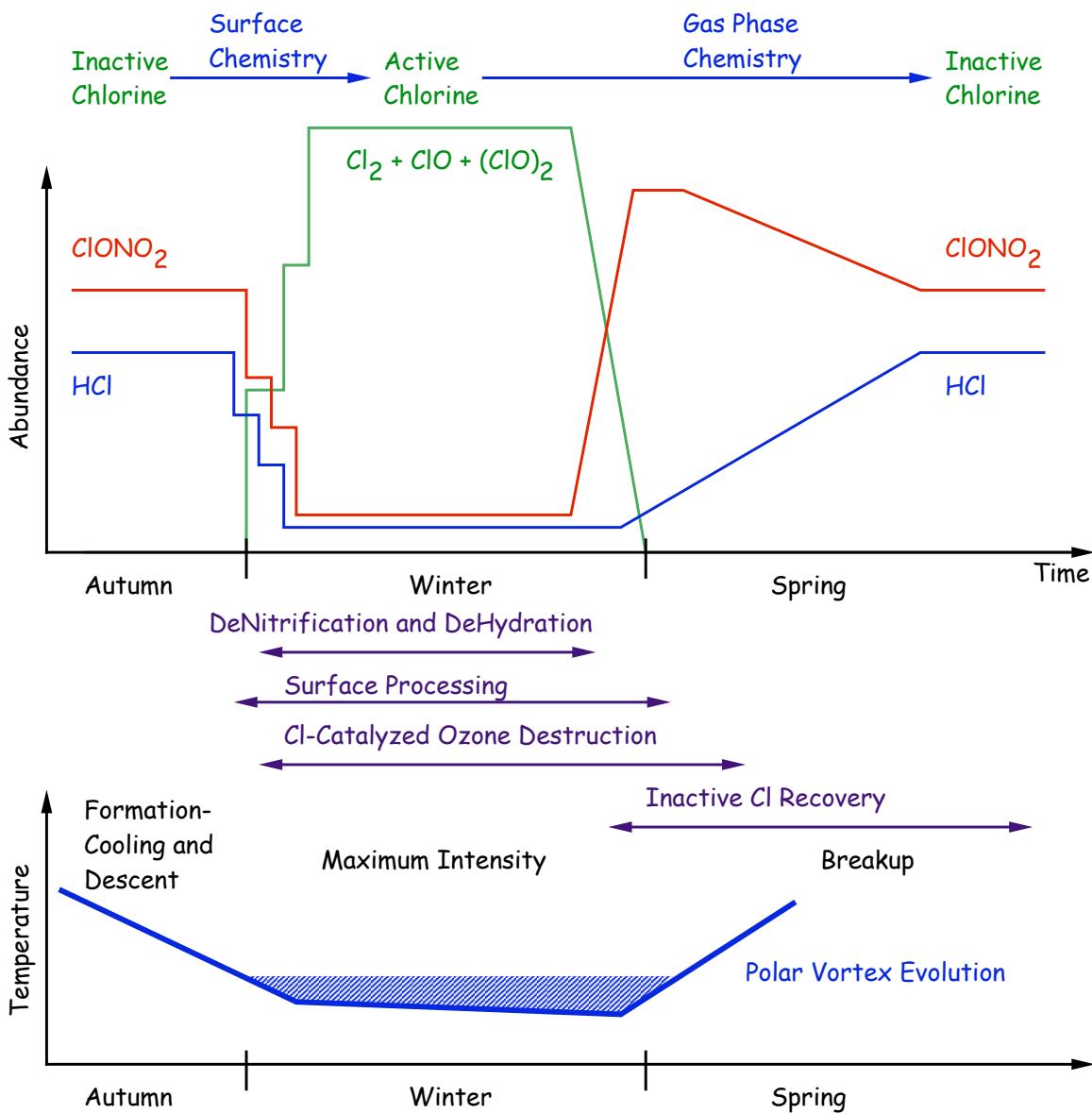
SURFACE CHEMISTRY

However, if effective chemical processing on liquid surfaces has depleted all the available HCl and/or ClONO₂ within an air parcel, then further lowering of temperature and formation of NAT will have a limited effect on ozone depletion.

Hence, the details of the reactivities and microphysics that control particle surface areas, while playing a role to some degree, are not critical to the formation of the ozone hole.

This view is important for understanding ozone depletion at the margins of the Antarctic vortex (or in the Arctic) where temperatures are cold but not extremely cold.



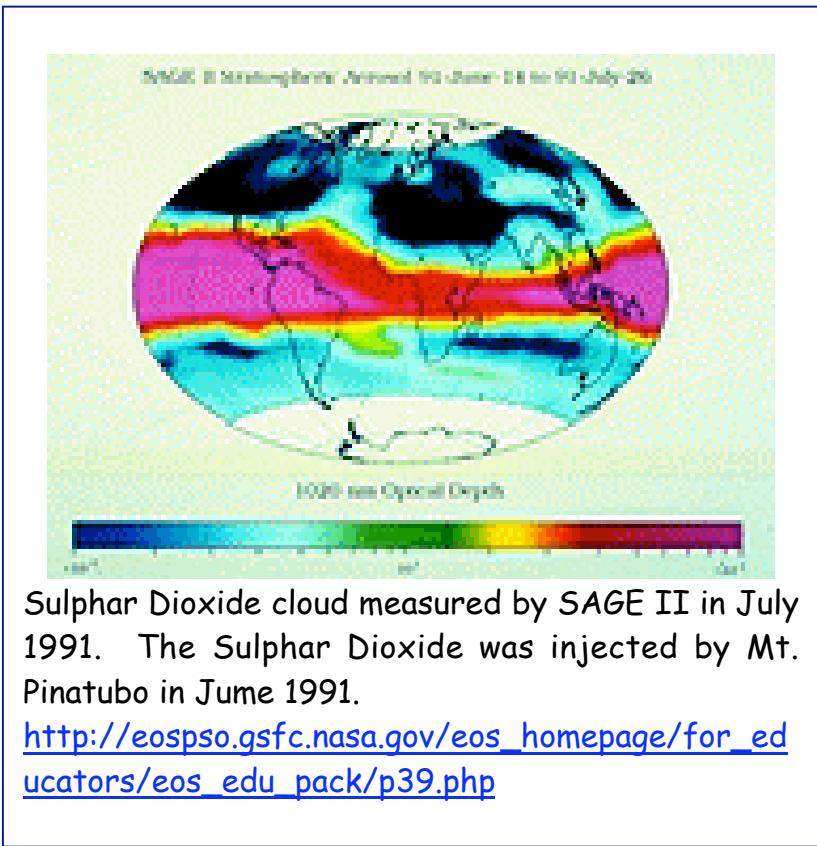


VOLCANOES

Observations of PSCs after the eruptions of El Chicon and Mount Pinatubo revealed large increases in particle surface areas in polar regions.

Enhanced aerosol surface areas extended the altitude range of ozone depletion into lower and warmer altitudes (~10-14 km).

The early onset of the ozone hole in the 1980s, following the El Chicon eruption, and the deep ozone holes in the early 1990's, following the Mount Pinatubo eruption, indicate that volcanic enhancements to PSC surfaces impact the formation of the ozone hole.



KEY FINGER PRINTS OF OZONE DEPLETION

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 _x	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

FURTHER QUESTIONS

Mid-latitude Ozone Depletion

Enhanced depletion after the Mount Pinatubo eruption.

Impact of liquid aerosol surfaces on chlorine and nitrogen partitioning chemistry.

Arctic Ozone Depletion

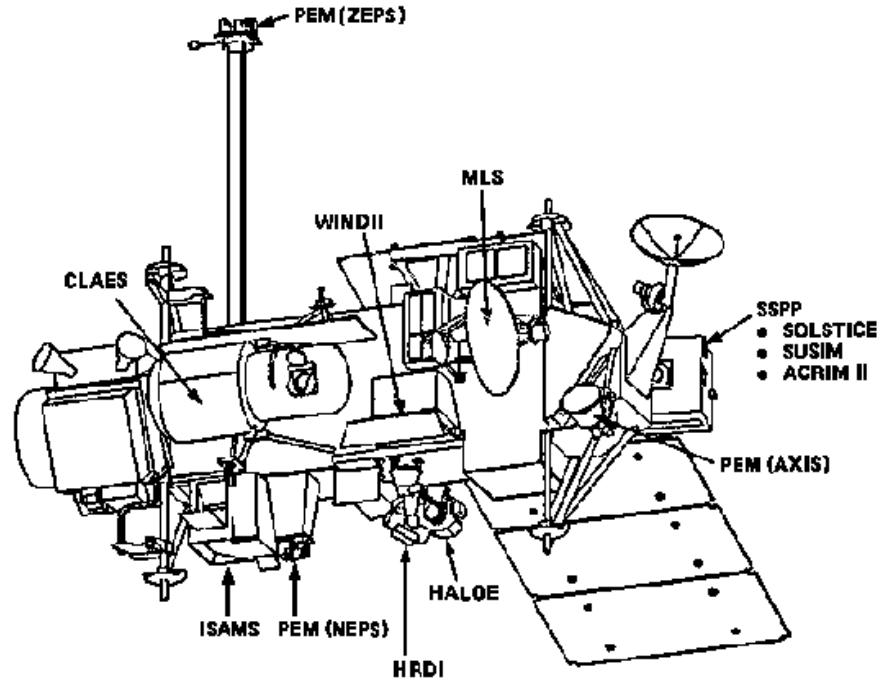
Record cold temperatures have yielded record depletion in 1990's.

Climate Significance

Statistically significant cooling in stratosphere consistent with ozone loss since early 1980's. Does a colder stratosphere, yield more PSCs, yield more ozone depletion, yield a colder stratosphere ?

THE UPPER ATMOSPHERE RESEARCH SATELLITE





- UARS lies in a near circular orbit at 585 km inclined 57° to the equator.
- The limb-scanning sensors mounted at 90° to the velocity vector see to 80° in one hemisphere and to 23° in the other.
- The orbital precession rate over all local times is 36 days.
- The spacecraft is oriented "forward" or "backward" and is rotated 180° every 36 days.
- The satellite orbit is "lifted" every 72 days to compensate for atmospheric drag.

UARS AND CHLORINE CHEMISTRY

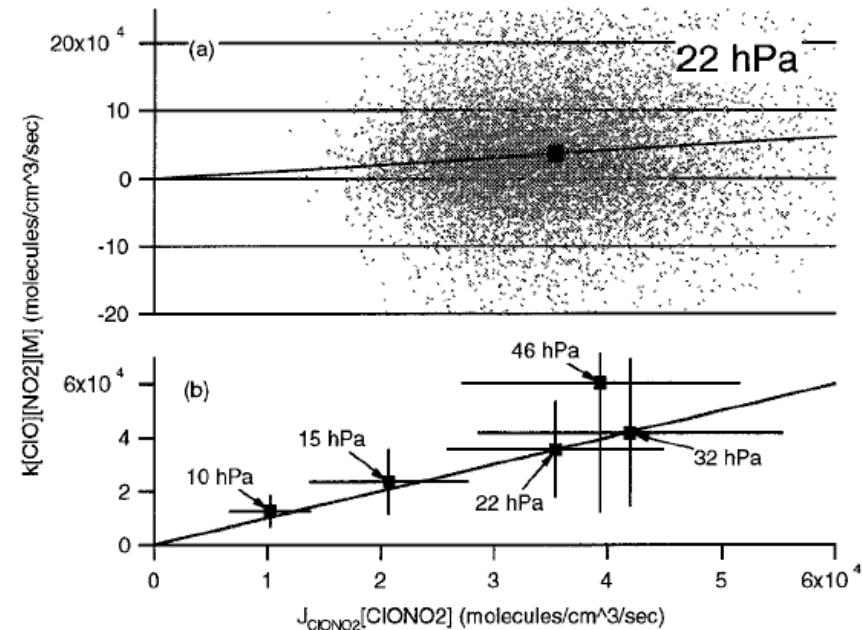


Figure 3. (a) Instantaneous production of ClONO_2 ($k[\text{ClO}][\text{NO}_2][\text{M}]$) versus loss of ClONO_2 ($J_{\text{ClONO}_2}[\text{ClONO}_2]$) on the 22-hPa pressure surface. Each dot represents a simultaneous measurement of ClO , NO_2 , and ClONO_2 and a calculation of J_{ClONO_2} and k . The square is the average production and loss rate. The line is the one-to-one line. (b) Average production and loss rates on the 10-, 15-, 22-, 32-, and 46-hPa surfaces. Error bars represent accuracy estimates; precision uncertainty is negligible and is not considered. Note the agreement between average production and loss. The data were obtained between January 1 and April 15, 1993, and between 20° and 60° latitude in both hemispheres. Adapted from Dessler *et al.* [1996b].

Confirm that,

$$k_{\text{ClO} + \text{NO}_2} \text{ClO} \text{NO}_2 = J_{\text{ClONO}_2} \text{ClONO}_2$$

using MLS measurements of ClO , CLAES measurements of NO_2 (adjusted with HALOE NO and N O_2) and CLAES measurements of ClONO_2 and temperature.

UARS AND ARCTIC OZONE DEPLETION

In the Arctic

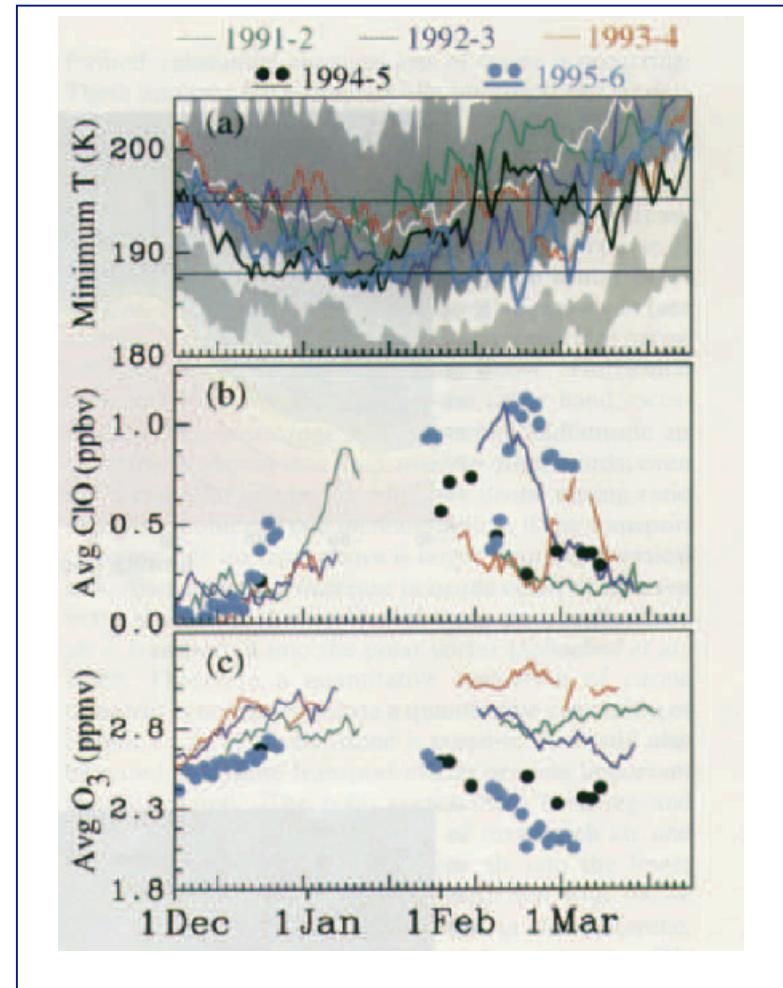
temperatures drop to 195 K every year ad support PSC formation and processing yielding significant abundances of ClO

sunlight is present to drive the ozone-destroying catalytic cycles

the region is isolated (though less than the Antarctic).

Transport as well as chemical loss must be quantified.

UARS-MLS measurements of ClO and O_3 have been combined with reverse trajectory studies to determine the true magnitude of the ozone loss due to chemistry.



LOOKING TO THE FUTURE

All other things being equal, the Antarctic ozone hole and mid-latitude ozone depletion will likely disappear around 2040.

The unusually cold Arctic winter-spring seasons of recent years stand as a critical challenge to our understanding that could affect these projections.

Eruptions in the current altered chemical state also are a source of great uncertainty.

