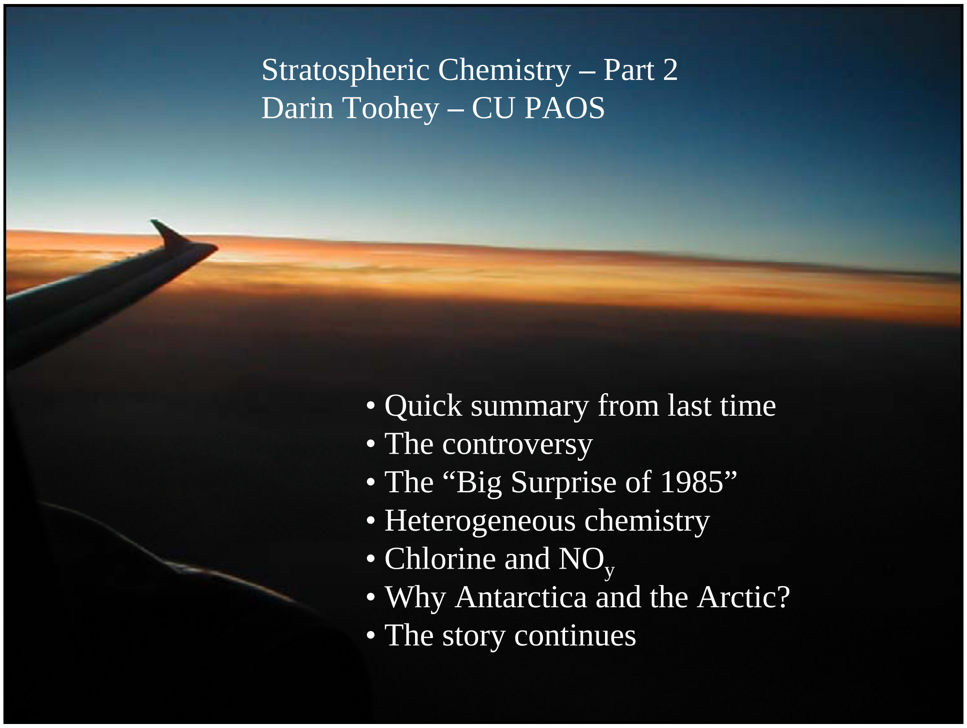
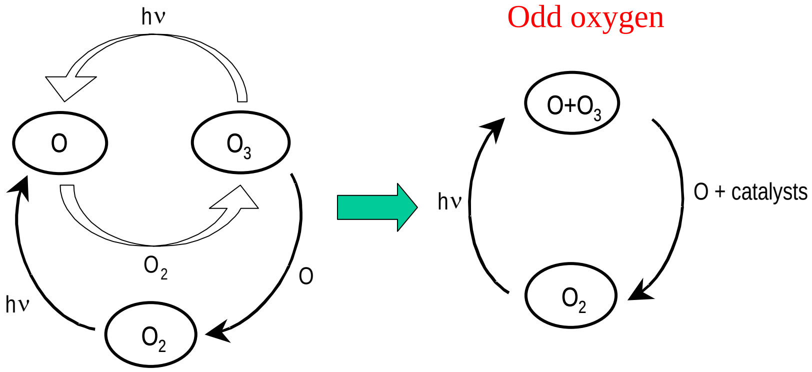


Stratospheric Chemistry – Part 2
Darin Toohey – CU PAOS

- Quick summary from last time
- The controversy
- The “Big Surprise of 1985”
- Heterogeneous chemistry
- Chlorine and NO_y
- Why Antarctica and the Arctic?
- The story continues

Odd oxygen



Chapman chemistry (in steady state)

$O_2 + h\upsilon \rightarrow O + O$

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\upsilon \rightarrow O_2 + O$

$O_3 + O \rightarrow O_2 + O_2$

Slow and exactly balance

$$J_{O_2}[O_2] = k_4[O][O_3]$$

$$[O][O_3] = \frac{J_{O_2}}{k_4}[O_2]$$

Fast and approx. balance

$$k_2[O][O_2][M] \sim J_{O_3}[O_3]$$

$$\frac{[O]}{[O_3]} \sim \frac{J_{O_3}}{k_2}\frac{1}{[O_2][M]}$$

$$[O_3] \sim 0.21\left(\frac{k_2}{k_4}\right)^{\frac{1}{2}}\left(\frac{J_{O_2}}{J_{O_3}}\right)^{\frac{1}{2}}[M]^{\frac{3}{2}}$$

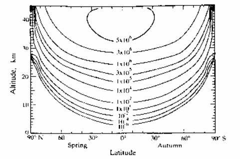


FIGURE 4.3 Zonally averaged rate of ozone formation (molecules cm^{-3} s^{-1}) from the photolysis of O_2 (Johnston, 1975)

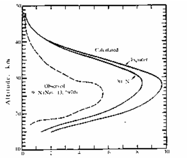


FIGURE 4.6 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9° N) on November 13, 1970

Catalysts

$X + O_3 \rightarrow XO + O_2$

$\underline{XO + O \rightarrow X + O_2}$

$O_3 + O \rightarrow O_2 + O_2$

$O_3 + h\upsilon \rightarrow O_2 + O(^1D)$

$N_2O + O(^1D) \rightarrow NO + NO$ (about 4% of all N_2O oxidation)

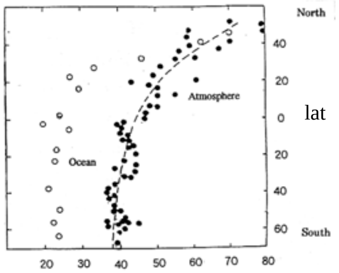
$H_2O + O(^1D) \rightarrow OH + OH$

$CF_xCl_y + h\nu \rightarrow + O_2 \rightarrow + h\nu .... \rightarrow CO_2 + xF + yCl$

SSTs – H_2O, NO_x
Chlorine – volcanoes, space shuttle
N_2O from fertilizing
H_2O from CH_4 oxidation
CFCs – refrigerants, propellants, foam blowing, etc.

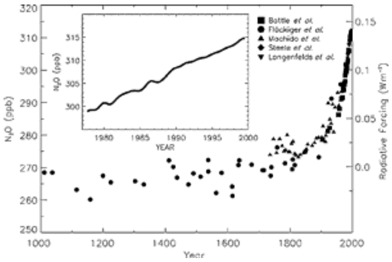
"…are unusually stable chemically and only slightly soluble in water and might therefore
persist and accumulate in the atmosphere … The presence of these compounds constitutes no conceivable hazard." (Lovelock)

Must have reasonably long lifetimes in troposphere (~years or more)



CF$_3$Cl (ppt)

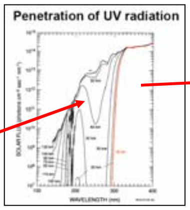
- Can't be too soluble in water (e.g. HCl, NaCl)
- Can't react rapidly with OH or O_3
- Can't have large cross sections at visible λs



- Examples
  - N_2O – hundreds of years
  - F-11 ($CFCl_3$) – 50 years
  - F-12 (CF_2Cl_2) – 100 years
  - HCFCs ($CHFCl_2$) – year
  - CH_3Br - ~1-2 years

The pieces come together!

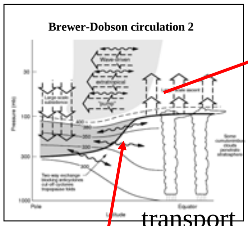
"spark"



$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$

$CF_2Cl_2\ h\nu \rightarrow CF_2Cl + Cl$

release



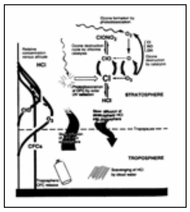
transport

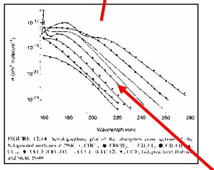
$Cl + O_3 \rightarrow ClO + O_2$

$\underline{ClO + O \rightarrow Cl + O_2}$

Net - $O_3 + O \rightarrow O_2 + O_2$

"flame"





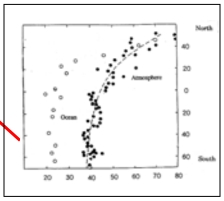
'un'reactivity

$O_2 + h\upsilon \rightarrow O + O$

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + h\upsilon \rightarrow O_2 + O$

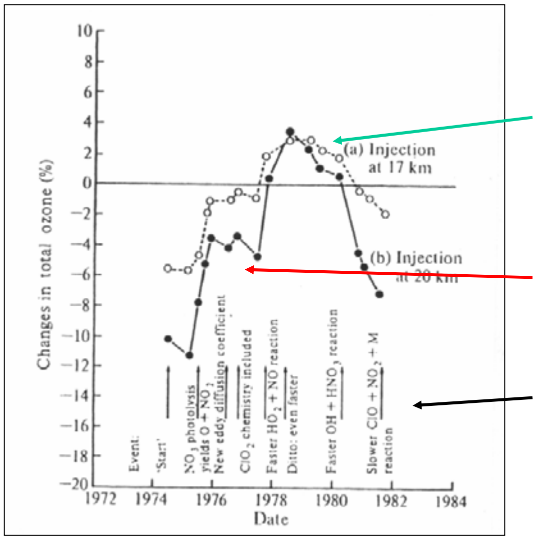
$O_3 + O \rightarrow O_2 + O_2$



source

destruction

Which one is it?
The SST story evolves…



SSTs make ozone
(smog chemistry)

SSTs destroy ozone

Those darned lab chemists

Meanwhile, scientists refine their understanding

But Industry is ready, and they come our firing!

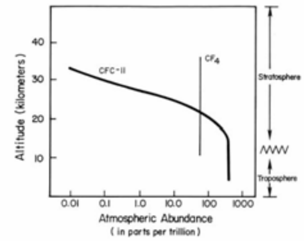
CFCs are heavier than air, and don't rise to the stratosphere – they sink!

There is more chlorine in sea spray than from CFCs!

Chlorine may get to the stratosphere, but it doesn't form ClO!

The natural variability of ozone is greater than any change expected due to man-made chemicals!

Even if there is ozone loss, there is no proof that more ultraviolet light will reach the surface!



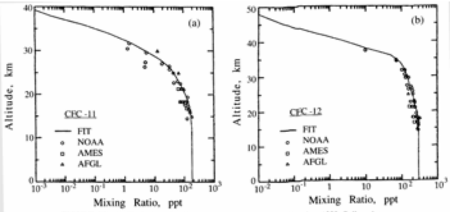


FIGURE 4.8 (a) Vertical profiles for $CFCl_3$ (CFC-11) in the tropics circa 1980. Balloon-borne measurements at 9° N and 5° S (1980) and 9° N (1983) are denoted by circles and triangles, respectively; squares represent aircraft measurements between 1.6° S and 9.9° N. This compilation of data was presented by Minschwaner et al. (1993). The solid curve is the vertical profile used by the authors in calculating the lifetime of $CFCl_3$ (b) Vertical profiles of CF_2Cl_2 (CFC-12) in the tropics circa 1980. Same as part (a).

What really goes on?

catalytic cycle

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Couples ClO_x to NO_x

$ClO + NO \rightarrow Cl + NO_2$

$ClO + NO_2 + M \rightarrow ClNO_3$

$ClNO_3 + h\nu \rightarrow Cl + NO_3$

$\rightarrow ClO + NO_2$

Couples ClO_x to HO_x

$Cl + HO_2 \rightarrow HCl + O_2$

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + OH \rightarrow HCl + CH_3$

$\rightarrow Cl + HO_2$

$HCl + OH \rightarrow H_2O + Cl$

$ClO + HO_2 \rightarrow HOCl + O_2$

$HOCl + h\nu \rightarrow Cl + OH$

And NO_x is coupled to HO_x!

$OH + O_3 \rightarrow HO_2 + O_2$

$OH + O \rightarrow O_2 + H$

$OH + CO \rightarrow CO_2 + H$

$H + O_2 + M \rightarrow HO_2 + M$

$HO_2 + O \rightarrow OH + O_2$

$HO_2 + O_3 \rightarrow OH + 2O_2$

$OH + HO_2 \rightarrow H_2O + O_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Couples HO_x to NO_x

$HO_2 + NO \rightarrow NO_2 + OH$

$OH + NO_2 + M \rightarrow HNO_3 + M$

$HNO_3 + OH \rightarrow H_2O + NO_3$

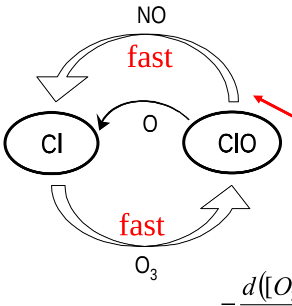
$HNO_3 + h\nu \rightarrow OH + NO_2$

$HO_2 + NO_2 \rightarrow HO_2NO_2 + M$

$HO_2NO_2 + h\nu \rightarrow OH + NO_3$

+ halogen reactions…

Which reactions determine the rate of ozone loss?



$ClO + NO \rightarrow Cl + NO_2$

$NO_2 + h\nu \rightarrow NO + O$

$\underline{O + O_2 + M \rightarrow O_3 + M}$

Net: $ClO + O_2 \rightarrow Cl + O_3$

this step reforms ozone nearly as fast as it is destroyed by chlorine atoms!

$$-\frac{d([O_3]+[O])}{dt} = \left(k_{O_3}[Cl][O_3] - k_{NO}[ClO][NO]\right) + k_O[ClO][O]$$

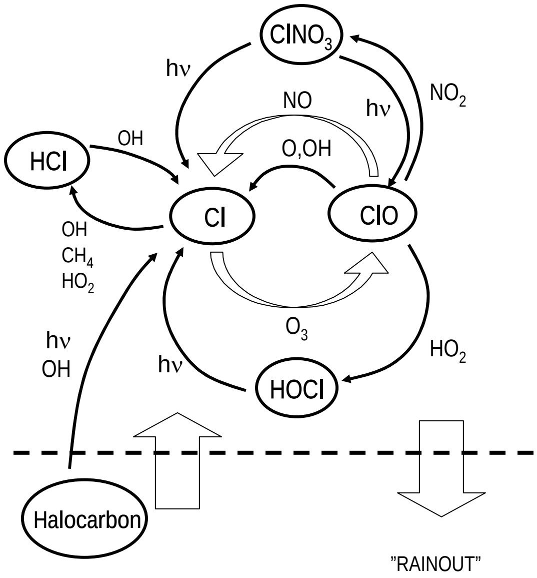
$$\Downarrow$$

Assume steady state

$$-k_{O_3}[Cl][O_3] + k_O[ClO][O]$$

$$\boxed{-\frac{d([O_3]+[O])}{dt} = 2k_O[ClO][O]}$$

"twice the rate-determining step"



Build a "model"

1. Source gas
2. Release of radical
3. Fast cycling/partitioning
4. Rate determining step
5. Short-lived reservoirs
6. Long-lived reservoirs
7. Removal

Summary of important points

- Stratospheric ozone is produced by photolysis of O_2, a process that is governed by abundances of O_2 and UV output of the sun. Mankind can’t easily tamper with these parameters

- Sir Sydney Chapman (who spent a lot of time in Boulder) nearly got it right. He was able to account for ozone in the stratosphere to within about a factor of two with just four simple reactions. You might as well memorize these… they will reappear on comps and cumulative exams (and it beats what you need to know to get the other factor of two!

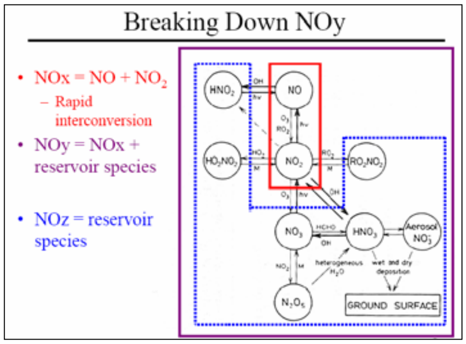
- Gases that are long-lived in the troposphere will eventually reach the stratosphere, where they nearly all break down (‘oxidize’) to produce highly reactive radicals that catalytically destroy ozone. It doesn’t matter where these gases originate from – the troposphere is the great homogenizer. The 1995 Nobel Prizes in Chemistry were awarded to Paul Crutzen, Mario Molina, and Sherry Rowland for recognizing the importance of this concept.

- The radical ‘families’ are highly coupled – changes in abundances of one family will result in changes in the others. Thus, the system is non-linear (although reasonably well behaved). However, it means that you can can’t just scale ozone losses with emissions. A ‘simple’ stratospheric model has dozens of chemical species and hundreds of chemical reactions. It will run on a PC (I have one written by Michael Prather on the computer that I am using for this lecture).

- Having a good idea isn’t good enough. It takes a lot of measurements to prove your point – or a global crisis… stay tuned for Part 2!

How Much NO_y is There?

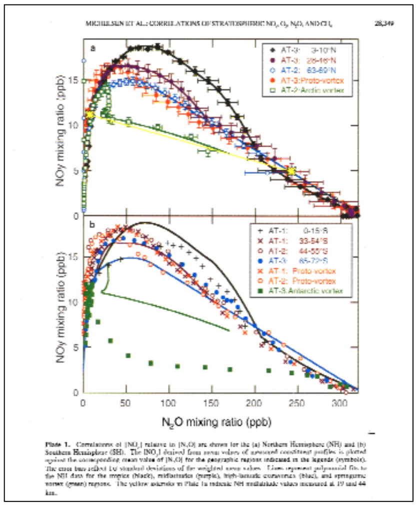
$$NO_y^{strat} \sim HNO_3 + N_2O_5 + NO + NO_2 + NO_3 + ClNO_3 = 0\text{-}15 \text{ ppb}$$



Breaking Down NOy

- NOx = NO + NO_2
  - Rapid interconversion
- NOy = NOx + reservoir species
- NOz = reservoir species

From Ed Dunlea’s lecture



MICHELSEN ET AL.: CORRELATIONS OF STRATOSPHERIC NOy, O3, N2O, AND CH4 28,349

Plate 1. Correlations of $[NO_y]$ relative to $[N_2O]$ are shown for the (a) Northern Hemisphere (NH) and (b) Southern Hemisphere (SH). The $[NO_y]$ derived from mean values of measured constituent profiles is plotted against the corresponding mean value of $[N_2O]$ for the geographic regions indicated in the legends (symbols). The error bars reflect 1σ standard deviations of the weighted mean values. Lines represent polynomial fits to the NH data for the tropics (black), midlatitudes (purple), high-latitude extravortex (blue), and springtime vortex (green) regions. The yellow asterisks in Plate 1a indicate NH midlatitude values measured at 19 and 44 km.

From Michelsen et al., JGR 103, 28347-28359, 1998

Stratospheric chlorine burden

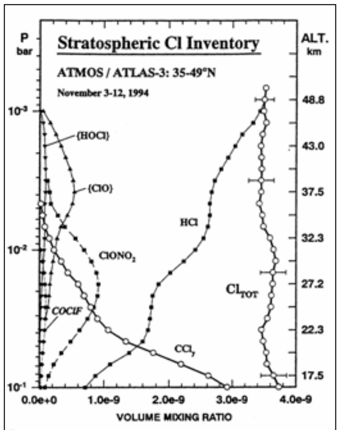


Figure 2. A linear-scale presentation of the key components entering in the total Cl-loading evaluation throughout the stratosphere at northern midlatitudes. The CCl_y curve refers to the total chlorine bound in all organic source gases listed in the text. Cl_{TOT} represents the summation over CCl_y, HCl, $ClONO_2$, ClO, HOCl and COClF.

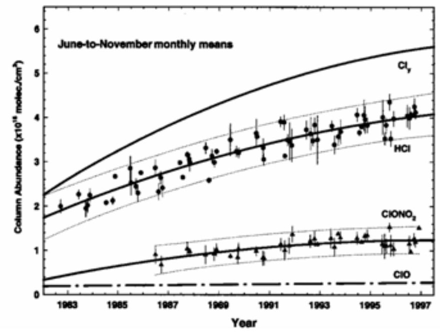
Zander et al., GRL, 23, 2357-2360, 1996

$Cl_y \sim HCl + ClNO_3 + ClO + HOCl$

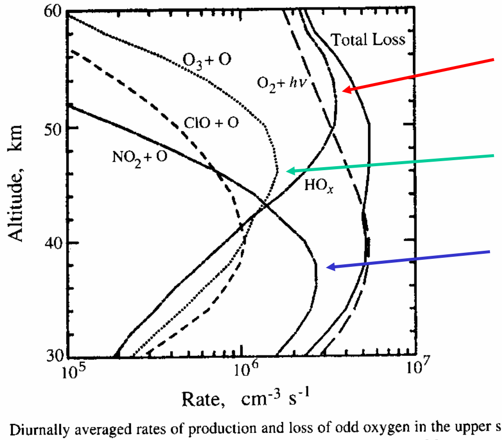
2-4 ppb

O_3 destruction

WMO, 1998



How the radical families contribute to ozone loss



HO_x (H_2O, CH_4)
5-10 ppm

ClO_x (CFCs)
3 ppb

NO_x (N_2O)
10-15 ppb

FIGURE 4.12 Diurnally averaged rates of production and loss of odd oxygen in the upper stratosphere (>30 km) calculated with a photochemical model for conditions of the ATMOS measurements at 30° N, May 1 (Minschwaner et al., 1993). Model calculations were constrained by measured profiles for O_3, H_2O, and CH_4. Photolysis of O_2 is the only source of odd oxygen. The total predicted removal rate of odd oxygen is given by the solid curve; removal rates for specific catalytic cycles are also shown.

The World Breathes a Sign of Relief…
In the form of CFCs

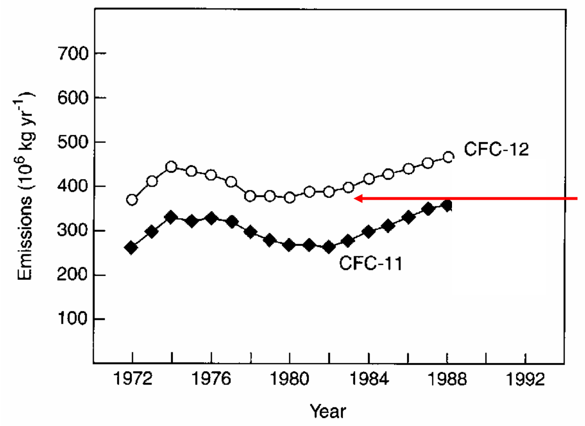


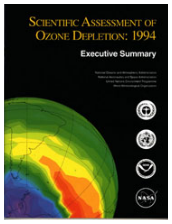
FIGURE 12.12 Estimated global annual emissions of CFC-11 and CFC-12 (adapted from World Meteorological Organization, 1995).

CFC production back on the rise!

Atmospheric Ozone 1985
The First Big WMO Ozone Assessment

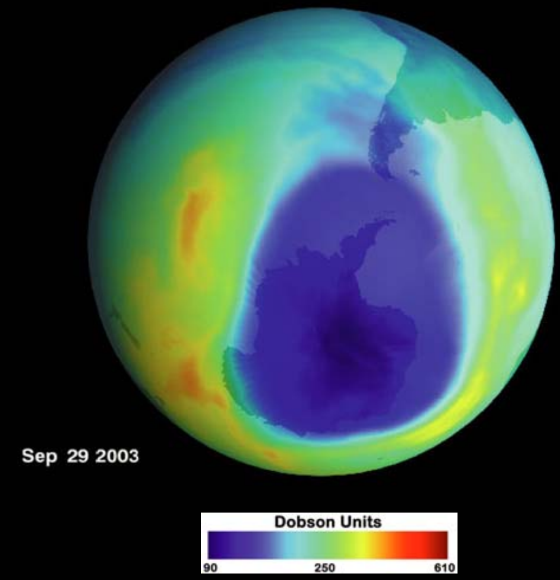
“The formation of Cl_2O_2…may serve as a temporary ClO_x reservoir…. The subsequent chemistry of Cl_2O_2, however, is not well defined. Its likely fate is photolysis and reaction with Cl, O, or OH. Mutual reactions between ClO are expected to become important at ClO_x levels exceeding 10 ppb.” (Vol 3, page 38)

“In assessing the current evidence relating to the question whether or not aerosols perturb the homogeneous chemistry related to stratospheric ozone, it can be concluded that the effects are minor and are unlikely to change our overall picture of the chemistry of the stratosphere.” (Vol 3, page 48)

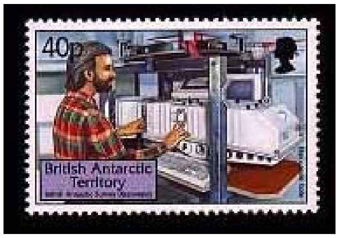


The 1994 Assessement

The Big Surprise of 1985!



1985 Joseph Farman, head of Geophysical Unit of the British Antarctic Survey reports on seasonal ozone depletion over Antarctica, describing a 30 to 40% annual ozone loss. Farman reports that a rise in CFCs over the Antarctica corresponds to the loss of ozone.



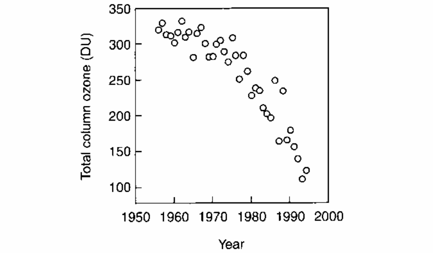
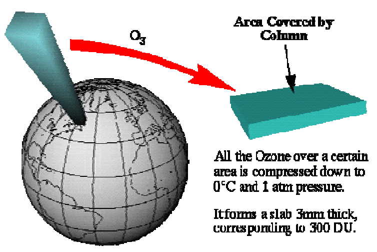


FIGURE 12.16 Average total column ozone measured in October at Halley Bay, Antarctica, from 1957 to 1994 [DU = Dobson units (see text)] (adapted from Jones and Shanklin, 1995).



All the Ozone over a certain area is compressed down to 0°C and 1 atm pressure.

It forms a slab 3mm thick, corresponding to 300 DU.

Three Theories

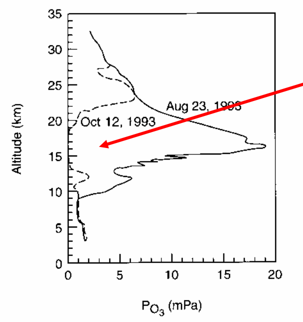


FIGURE 12.17 Vertical O_3 profile before (August 23) and after (October 12) development of the ozone hole at the U.S. Amundsen–Scott Station, South Pole, in 1993 (adapted from Hofmann *et al.*, 1994a).

Solar activity – increased NO_x at high altitudes would catalyze ozone loss

Dynamical – enhanced vertical lofting of air over Antarctica in springtime, troposphere low in ozone (mixing ratio)

Chlorine – heterogeneous reactions on polar stratospheric clouds convert HCl and ClNO3 into sources of ClO, rapid catalysis by unknown mechanism

---

NOZE (1986 National Ozone Experiment)

- Enhanced OClO (indicator of bromine and chlorine chemistry)
- Low N_2O (not vertical lifting of low-ozone air)

Susan Solomon, Ryan Sanders, Phil Solomon, Robert deZafra, Barney Farmer, Geoff Toon, Dave Hofmann, Jerald Harder

The Smoking Gun!

Ozone and ClO are anticorrelated

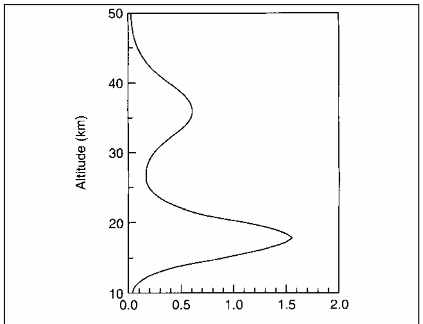


FIGURE 12.20 Vertical profile of ClO on September 19–20, 1992, at McMurdo Station, Antarctica (adapted from Emmons *et al.*, 1995).

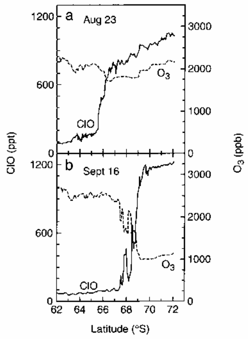


FIGURE 12.19 Aircraft measurements of ClO and O$_3$ on (a) August 23 and (b) September 16, 1987, as the aircraft flew south (adapted from Anderson *et al.*, 1991).

But How?

problem

McElroy and Wofsy

$ClO + BrO \rightarrow Cl + Br + O_2$

$\rightarrow OClO + Br$

← Not much Br_y

Solomon et al.

$ClO + HO_2 \rightarrow HOCl + O_2$

$HOCl + h\nu \rightarrow OH + Cl$

← Slow

Molina and Molina

$ClO + ClO + M \rightarrow Cl_2O_2 + M$

$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$

$ClOO + M \rightarrow Cl + O_2$

← Cl_2O_2 must be stable and photolyze into Cl atoms

And of course, how to convert HCl and $ClNO_3$ into ClO?

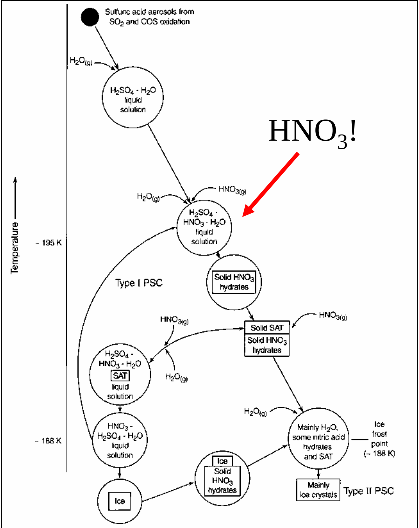


FIGURE 12.21 Schematic of polar stratospheric cloud (PSC) formation.

Clouds with large optical depths observed over Antarctica and the Arctic by satellites – appear at ~195-196 K, too warm to be ice at 5 ppm of H_2O

Even thicker clouds appear at 188 K, consistent with ice

The two faces of NO_y

Normally

$HNO_3 + h\nu \rightarrow OH + NO_2$

$ClO + NO_2 \rightarrow ClNO_3$

Over Antarctica

$HNO_{3(g)} + nH_2O_{(g)} \rightarrow HNO_3\,(H_2O)_{n\ (s)}$

$HCl_{(g)} + HNO_3\,(H_2O)_{n\ (s)} \rightarrow HCl_{(a)}/HNO_3\,(H_2O)_{n\ (s)}$

$HCl_{(a)} + ClNO_{3(g)} \rightarrow Cl_2 + HNO_{3(s)}$

$\Downarrow$

Sedimentation = irreversible removal of NO_y

$ClO + NO_2 \not\rightarrow ClNO_3$

Lots of reactions that activate chlorine and produce HNO_3

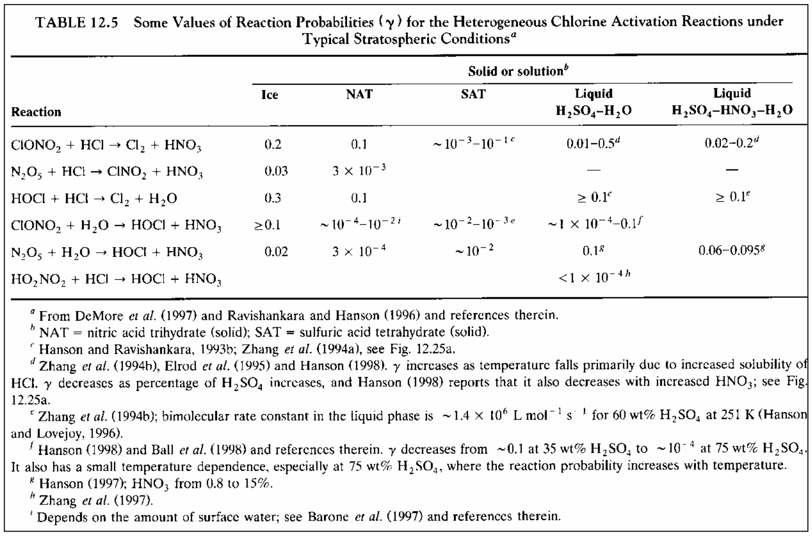


TABLE 12.5 Some Values of Reaction Probabilities (γ) for the Heterogeneous Chlorine Activation Reactions under Typical Stratospheric Conditions[a]

	Solid or solution[b]				
Reaction	Ice	NAT	SAT	Liquid H_2SO_4–H_2O	Liquid H_2SO_4–HNO_3–H_2O
$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	0.2	0.1	$\sim 10^{-3}$–10^{-1}[c]	0.01–0.5[d]	0.02–0.2[d]
$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$	0.03	3×10^{-3}		—	—
$HOCl + HCl \rightarrow Cl_2 + H_2O$	0.3	0.1		≥ 0.1[e]	≥ 0.1[e]
$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	≥ 0.1	$\sim 10^{-4}$–10^{-2}[i]	$\sim 10^{-2}$–10^{-3}[e]	$\sim 1 \times 10^{-4}$–0.1[f]	
$N_2O_5 + H_2O \rightarrow HOCl + HNO_3$	0.02	3×10^{-4}	$\sim 10^{-2}$	0.1[g]	0.06–0.095[g]
$HO_2NO_2 + HCl \rightarrow HOCl + HNO_3$				$< 1 \times 10^{-4}$[h]	

[a] From DeMore *et al.* (1997) and Ravishankara and Hanson (1996) and references therein.

[b] NAT = nitric acid trihydrate (solid); SAT = sulfuric acid tetrahydrate (solid).

[c] Hanson and Ravishankara, 1993b; Zhang *et al.* (1994a), see Fig. 12.25a.

[d] Zhang *et al.* (1994b), Elrod *et al.* (1995) and Hanson (1998). γ increases as temperature falls primarily due to increased solubility of HCl. γ decreases as percentage of H_2SO_4 increases, and Hanson (1998) reports that it also decreases with increased HNO_3; see Fig. 12.25a.

[e] Zhang *et al.* (1994b); bimolecular rate constant in the liquid phase is $\sim 1.4 \times 10^6$ L mol^{-1} s^{-1} for 60 wt% H_2SO_4 at 251 K (Hanson and Lovejoy, 1996).

[f] Hanson (1998) and Ball *et al.* (1998) and references therein. γ decreases from ~ 0.1 at 35 wt% H_2SO_4 to $\sim 10^{-4}$ at 75 wt% H_2SO_4. It also has a small temperature dependence, especially at 75 wt% H_2SO_4, where the reaction probability increases with temperature.

[g] Hanson (1997); HNO_3 from 0.8 to 15%.

[h] Zhang *et al.* (1997).

[i] Depends on the amount of surface water; see Barone *et al.* (1997) and references therein.

Why 195 K?

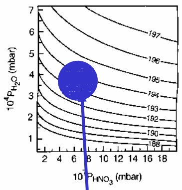


FIGURE 12.23 Temperatures (K) at which SAT deliquesces at different gas-phase pressures of H_2O and HNO_3 typical of the stratosphere (from Koop and Carslaw, 1996).

Typical 20 km values in polar regions

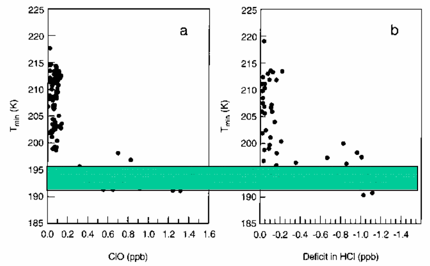


FIGURE 12.37 (a) ClO concentrations and (b) HCl deficit at various minimum temperatures experienced by the air masses in the Arctic stratosphere during October 1991–February 1992 (adapted from Toohey *et al.* (1993) and Webster *et al.* (1993a)).

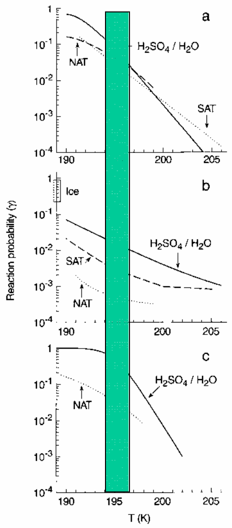


FIGURE 12.25 Typical measured reaction probabilities for (a) $ClONO_2$ + HCl, (b) $ClONO_2$ + H_2O, and (c) HOCl + HCl for different surfaces that can be present and promote heterogeneous chemistry under typical stratospheric conditions (adapted from Ravishankara and Hanson, 1996, and references therein).

It’s both chlorine AND bromine (about 50/50)

$ClO + BrO \rightarrow$ products $\quad k_{BrO} \sim 10^{-11}\ cm^{-3}\ s^{-1}$

$ClO + ClO + M \rightarrow Cl_2O_2 + M \quad k_{ClO}\ [M] \sim 10^{-13}\ cm^{-3}\ s^{-1}$

ClO ~ 1 ppb
BrO ~ 10 ppt

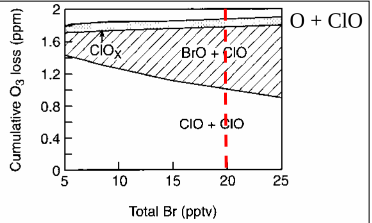
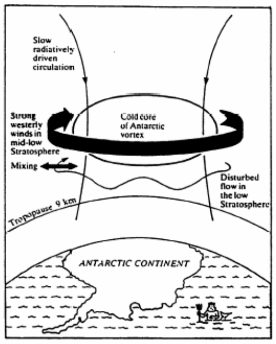
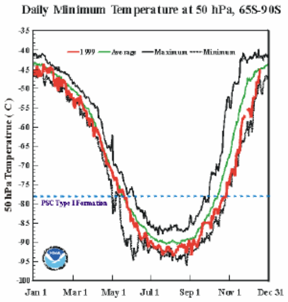


FIGURE 12.46 Model-calculated cumulative loss of ozone from August 1 to the day of maximum ozone depletion as a function of stratospheric bromine ($[Cl_y]$ = 12.5 ppbv, $[NO_y]$ = 2 ppb, 70°S at an altitude corresponding to 50 mbar total pressure in these calculations) (adapted from Danilin *et al.*, 1996).

Why the poles?




Daily Minimum Temperature at 50 hPa, 65S-90S

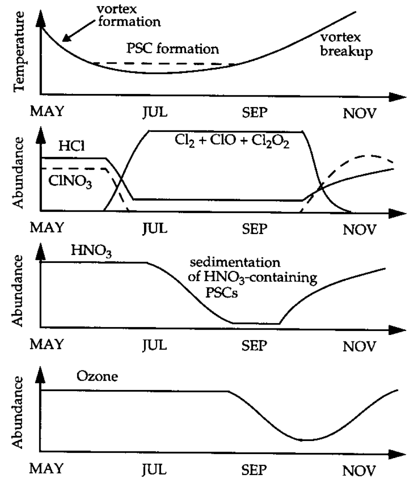
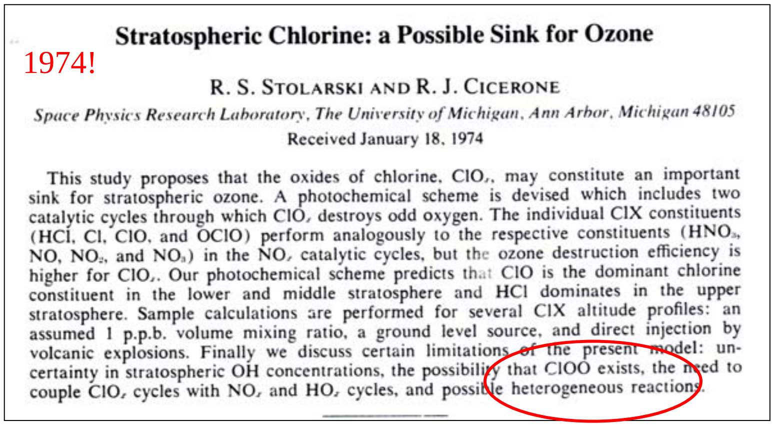


Fig. 10-13 Chronology of the antarctic ozone hole.



1974!

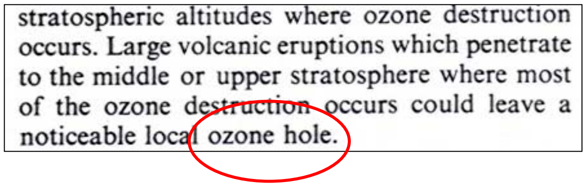
Stratospheric Chlorine: a Possible Sink for Ozone

R. S. STOLARSKI AND R. J. CICERONE

Space Physics Research Laboratory, The University of Michigan, Ann Arbor, Michigan 48105

Received January 18, 1974

This study proposes that the oxides of chlorine, ClO_x, may constitute an important sink for stratospheric ozone. A photochemical scheme is devised which includes two catalytic cycles through which ClO_x destroys odd oxygen. The individual ClX constituents (HCl, Cl, ClO, and OClO) perform analogously to the respective constituents (HNO_3, NO, NO_2, and NO_3) in the NO_x catalytic cycles, but the ozone destruction efficiency is higher for ClO_x. Our photochemical scheme predicts that ClO is the dominant chlorine constituent in the lower and middle stratosphere and HCl dominates in the upper stratosphere. Sample calculations are performed for several ClX altitude profiles: an assumed 1 p.p.b. volume mixing ratio, a ground level source, and direct injection by volcanic explosions. Finally we discuss certain limitations of the present model: uncertainty in stratospheric OH concentrations, the possibility that ClOO exists, the need to couple ClO_x cycles with NO_x and HO_x cycles, and possible heterogeneous reactions.



stratospheric altitudes where ozone destruction occurs. Large volcanic eruptions which penetrate to the middle or upper stratosphere where most of the ozone destruction occurs could leave a noticeable local ozone hole.

Scientists go back and reexamine other latitudes based on a new understanding of heterogeneous chemistry and aerosols in the lower stratosphere.

The story continues…