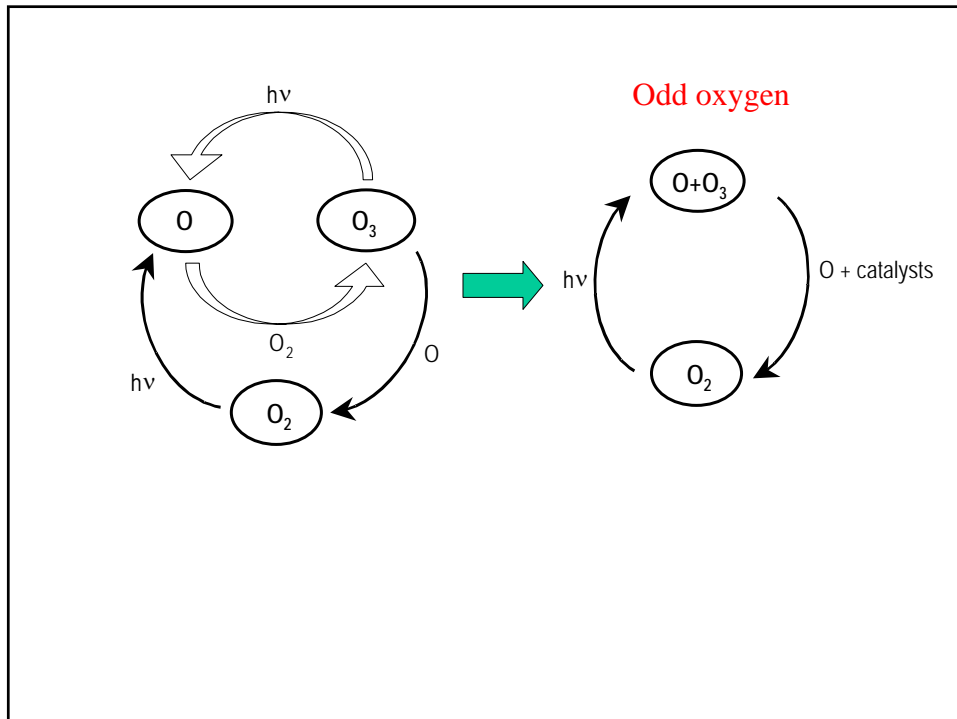
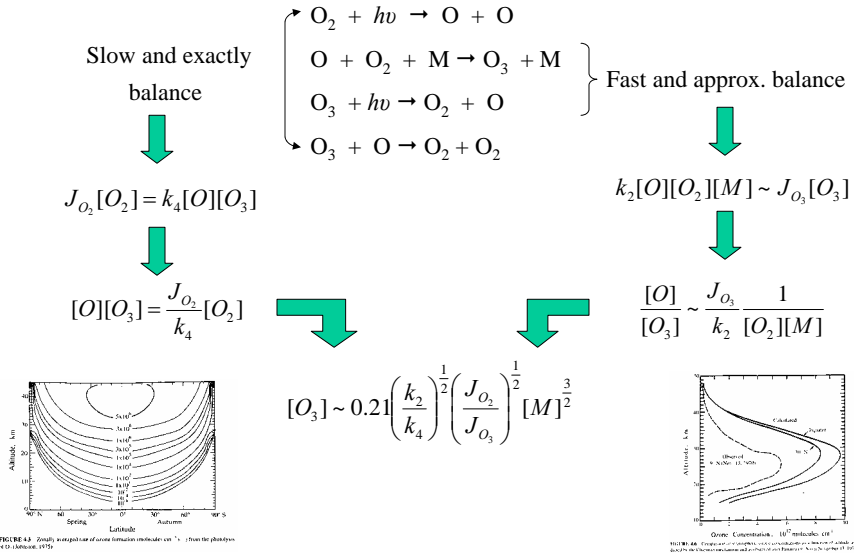


Stratospheric Chemistry – Part 2  
Darin Toohey – CU PAOS

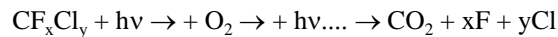
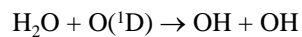
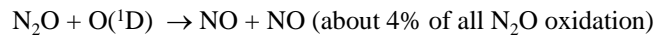
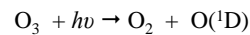
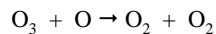
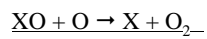
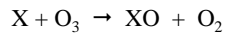
- Quick summary from last time
- The controversy
- The “Big Surprise of 1985”
- Heterogeneous chemistry
- Chlorine and  $\text{NO}_y$
- Why Antarctica and the Arctic?
- The story continues



## Chapman chemistry (in steady state)



## Catalysts



SSTs – H<sub>2</sub>O, NO<sub>x</sub>

Chlorine – volcanoes, space shuttle

N<sub>2</sub>O from fertilizing

H<sub>2</sub>O from CH<sub>4</sub> oxidation

CFCs – refrigerants, propellants, foam blowing, etc.

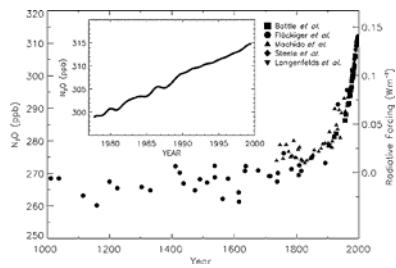
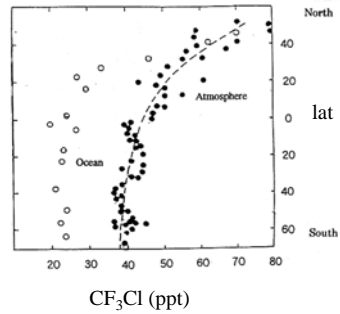
“...are unusually stable chemically and only slightly soluble in water and might therefore persist and accumulate in the atmosphere ... The presence of these compounds constitutes no conceivable hazard.”  
(Lovelock)

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

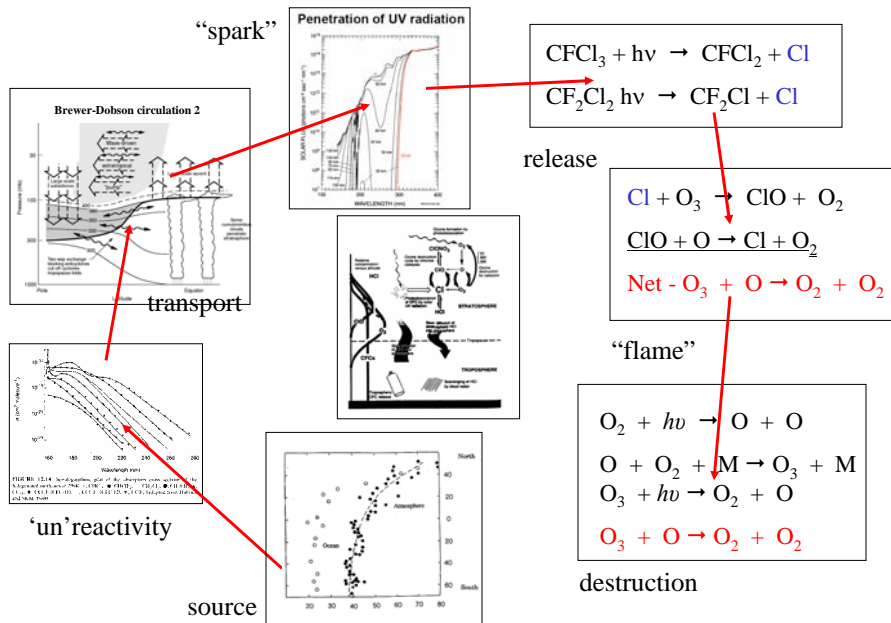
- Can't be too soluble in water (e.g. HCl, NaCl)
- Can't react rapidly with OH or O<sub>3</sub>
- Can't have large cross sections at visible λs

•Examples

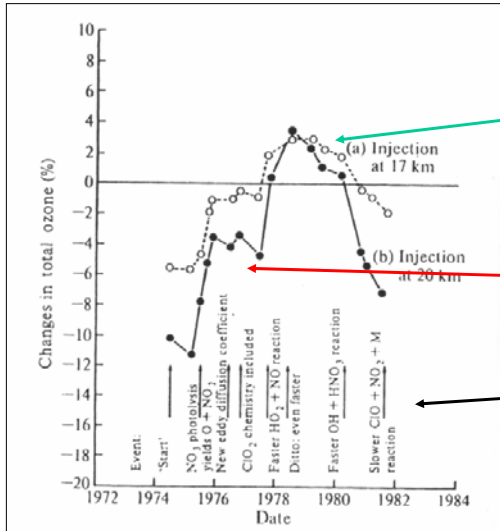
- N<sub>2</sub>O – hundreds of years
- F-11 (CFCl<sub>3</sub>) – 50 years
- F-12 (CF<sub>2</sub>Cl<sub>2</sub>) – 100 years
- HCFCs (CHFCl<sub>2</sub>) – year
- CH<sub>3</sub>Br – ~1-2 years



The pieces come together!



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!

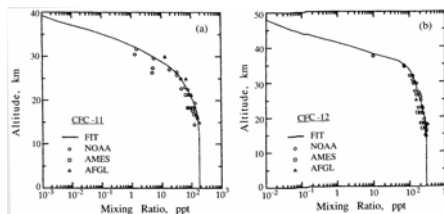
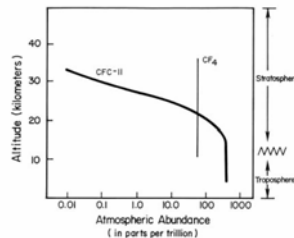
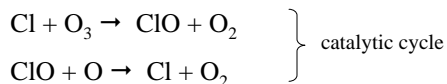
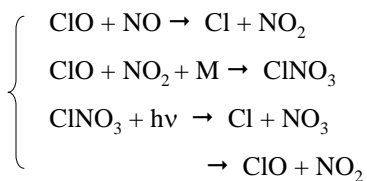


FIGURE 4.8 (a) Vertical profiles for CFC<sub>1</sub> (CFC-11) in the tropics circa 1980. Balloon-borne measurements at 9° N and 5° S (1980) and 9° N (1983) are denoted by circles and triangles, respectively; squares represent aircraft measurements between 16° S and 9° N. This compilation of data was presented by Minschwaner et al. (1993). The solid curve in the vertical profile used by the authors in calculating the lifetime of CFC<sub>1</sub>. (b) Vertical profiles of CFC<sub>2</sub> (CFC-12) in the tropics circa 1980. Same as part (a).

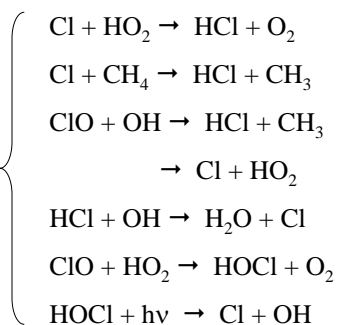
What really goes on?



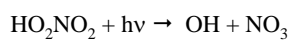
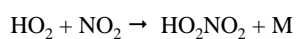
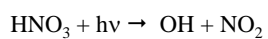
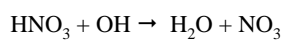
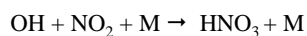
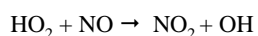
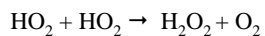
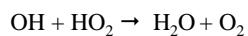
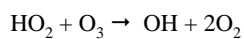
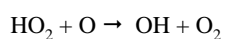
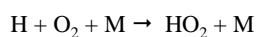
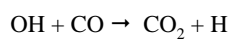
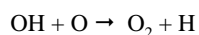
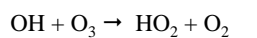
Couples  $\text{ClO}_x$  to  $\text{NO}_x$



Couples  $\text{ClO}_x$  to  $\text{HO}_x$



And  $\text{NO}_x$  is coupled to  $\text{HO}_x$ !



+ halogen reactions...

Couples  $\text{HO}_x$  to  $\text{NO}_x$

Which reactions determine the rate of ozone loss?

$$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$$

$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$$

$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$$

Net:  $\text{ClO} + \text{O}_2 \rightarrow \text{Cl} + \text{O}_3$

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

$$-\frac{d([\text{O}_3] + [\text{O}])}{dt} = (k_{\text{O}_3}[\text{Cl}][\text{O}_3] - k_{\text{NO}}[\text{ClO}][\text{NO}]) + k_{\text{O}}[\text{ClO}][\text{O}]$$

↓

Assume steady state  $-k_{\text{O}_3}[\text{Cl}][\text{O}_3] + k_{\text{O}}[\text{ClO}][\text{O}]$

$$\frac{d([\text{O}_3] + [\text{O}])}{dt} = 2k_{\text{O}}[\text{ClO}][\text{O}]$$

“twice the rate-determining step”

### Build a “model”

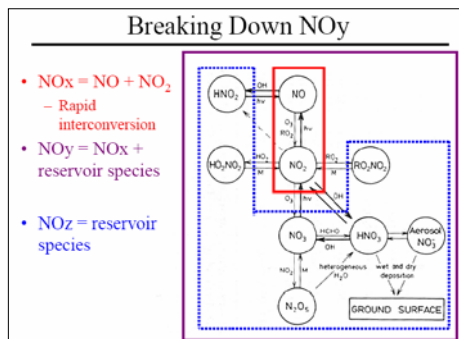
1. Source gas
2. Release of radical
3. Fast cycling/partitioning
4. Rate determining step
5. Short-lived reservoirs
6. Long-lived reservoirs
7. Removal

## 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'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!

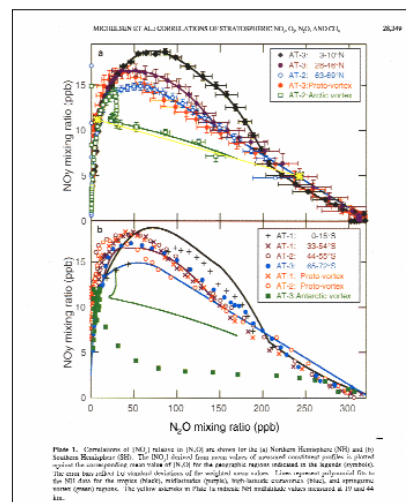
## How Much $NO_y$ is There?

$$NO_{y, \text{strat}} \sim HNO_3 + N_2O_5 + NO + NO_2 + NO_3 + ClONO_2 = 0-15 \text{ ppb}$$

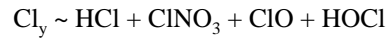
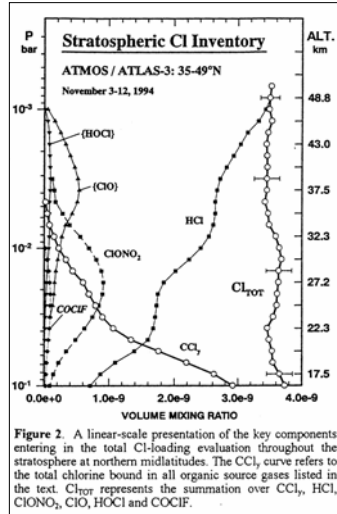


From Ed Dunlea's lecture

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



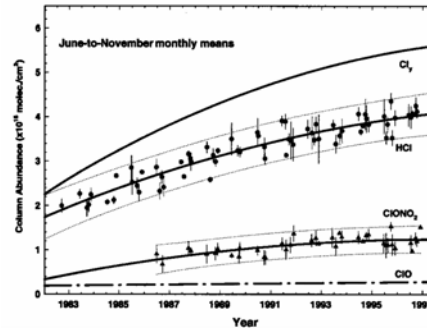
## Stratospheric chlorine burden



2-4 ppb

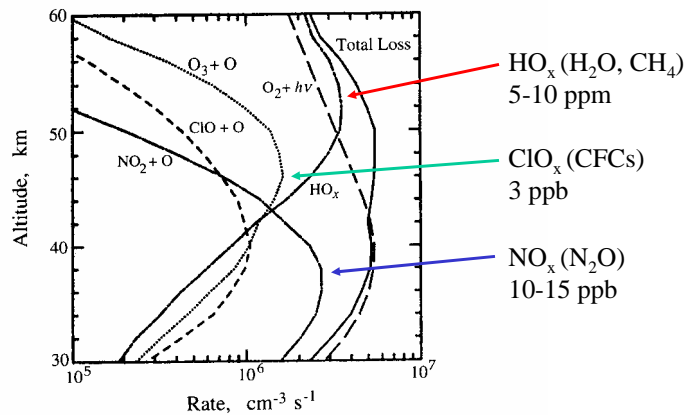
$O_3$  destruction

WMO, 1998



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

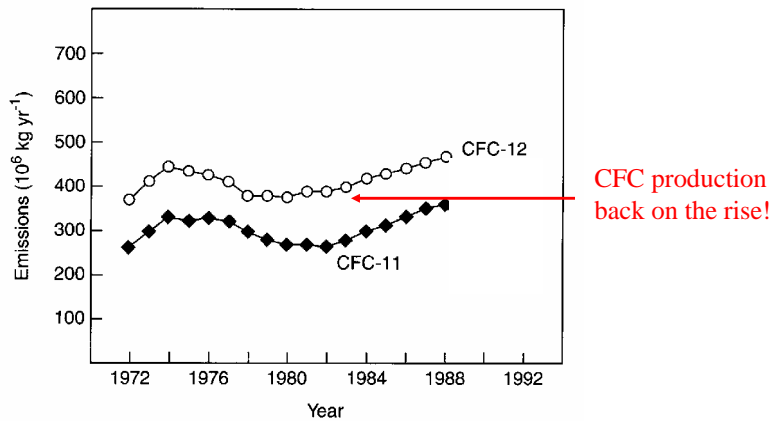
## How the radical families contribute to ozone loss



**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

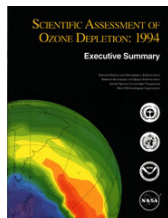


**FIGURE 12.12** Estimated global annual emissions of CFC-11 and CFC-12 (adapted from World Meteorological Organization, 1995).

## Atmospheric Ozone 1985 The First Big WMO Ozone Assessment

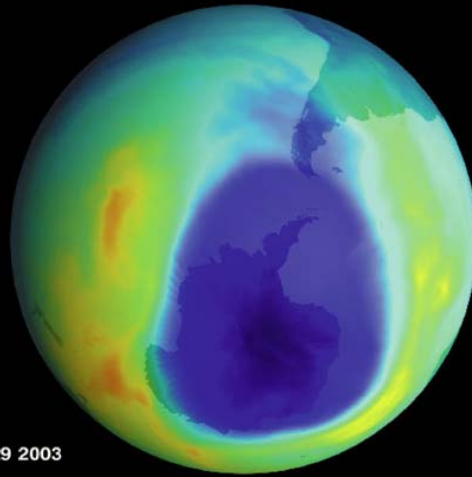
“The formation of  $\text{Cl}_2\text{O}_2$ ...may serve as a temporary  $\text{ClO}_x$  reservoir.... The subsequent chemistry of  $\text{Cl}_2\text{O}_2$ , however, is not well defined. Its likely fate is photolysis and reaction with  $\text{Cl}$ ,  $\text{O}$ , or  $\text{OH}$ . Mutual reactions between  $\text{ClO}$  are expected to become important at  $\text{ClO}_x$  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)

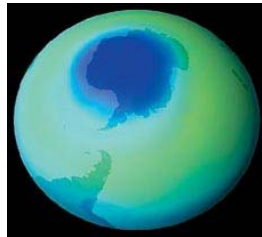
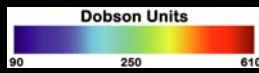


The 1994 Assessment

# The Big Surprise of 1985!



Sep 29 2003



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.

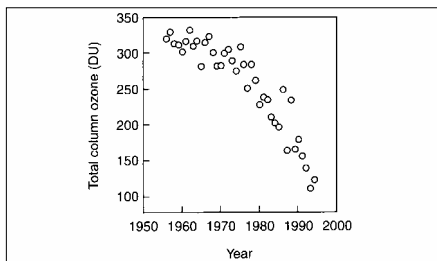
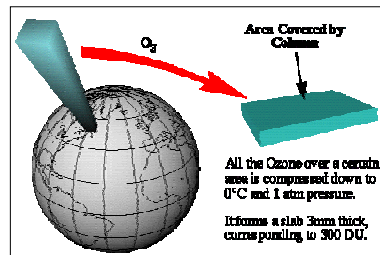


FIGURE 12.16 Average total column ozone measured in October at Halley Bay, Antarctica, from 1957 to 1994 [DU = Dobson units (see text)] (adapted from Jones and Shanklin, 1995).



### Three Theories

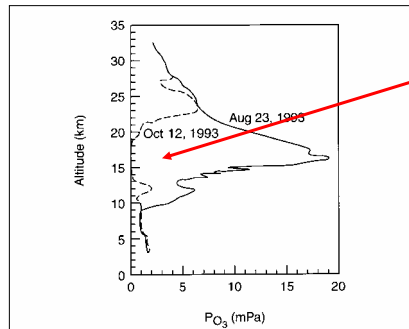


FIGURE 12.17 Vertical O<sub>3</sub> profile before (August 23) and after (October 12) development of the ozone hole at the U.S. Amundsen-Scott Station, South Pole, in 1993 (adapted from Hofmann *et al.*, 1994a).

~~Solar activity – increased NO<sub>x</sub> 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 ClNO<sub>3</sub> into sources of ClO, rapid catalysis by unknown mechanism

### NOZE (1986 National Ozone Experiment)

- Enhanced OCIO (indicator of bromine and chlorine chemistry)
- Low N<sub>2</sub>O (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

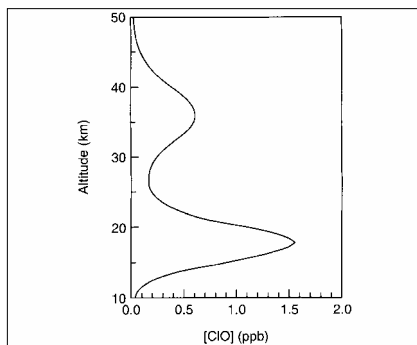


FIGURE 12.20 Vertical profile of ClO on September 19–20, 1992, at McMurdo Station, Antarctica (adapted from Emmons *et al.*, 1995).

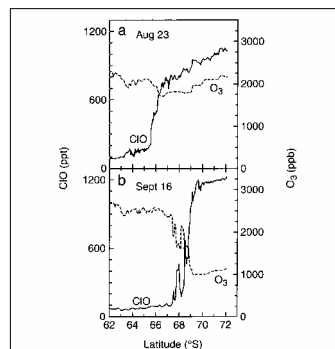
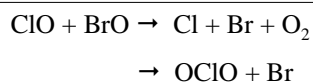


FIGURE 12.19 Aircraft measurements of ClO and O<sub>3</sub> on (a) August 23 and (b) September 16, 1987, as the aircraft flew south (adapted from Anderson *et al.*, 1991).

## But How?

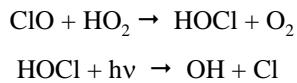
McElroy and Wofsy



problem

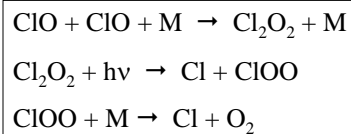
← Not much Br<sub>y</sub>

Solomon *et al.*



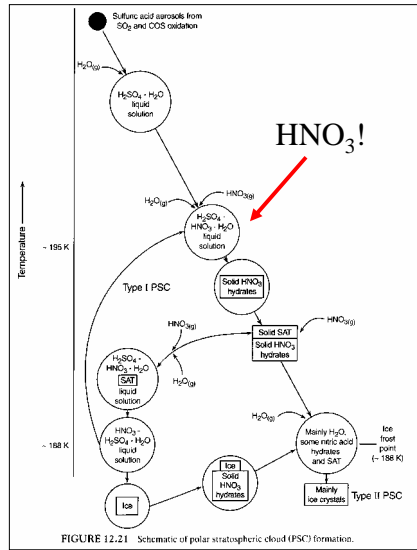
← Slow

Molina and Molina



← Cl<sub>2</sub>O<sub>2</sub> must be stable and photolyze into Cl atoms

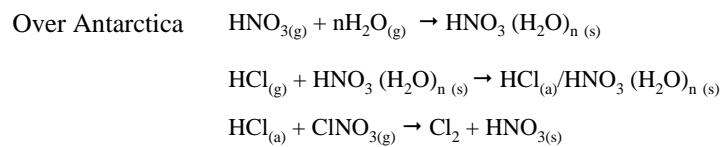
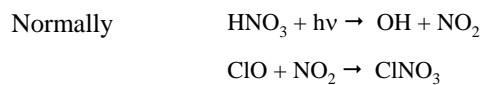
And of course, how to convert HCl and ClNO<sub>3</sub> into ClO?



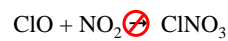
Clouds with large optical depths observed over Antarctica and the Arctic by satellites – appear at ~195-196 K, too warm to be ice at 5 ppm of H<sub>2</sub>O

Even thicker clouds appear at 188 K, consistent with ice

### The two faces of NO<sub>y</sub>



Sedimentation = irreversible removal of NO<sub>y</sub>



## Lots of reactions that activate chlorine and produce HNO<sub>3</sub>

**TABLE 12.5 Some Values of Reaction Probabilities ( $\gamma$ ) for the Heterogeneous Chlorine Activation Reactions under Typical Stratospheric Conditions<sup>a</sup>**

Reaction	Solid or solution <sup>b</sup>				
	Ice	NAT	SAT	Liquid H <sub>2</sub> SO <sub>4</sub> -H <sub>2</sub> O	Liquid H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> -H <sub>2</sub> O
ClONO <sub>2</sub> + HCl → Cl <sub>2</sub> + HNO <sub>3</sub>	0.2	0.1	~10 <sup>-3</sup> -10 <sup>-1</sup> <sup>c</sup>	0.01-0.5 <sup>d</sup>	0.02-0.2 <sup>d</sup>
N <sub>2</sub> O <sub>5</sub> + HCl → ClONO <sub>2</sub> + HNO <sub>3</sub>	0.03	3 × 10 <sup>-3</sup>		—	—
HOCl + HCl → Cl <sub>2</sub> + H <sub>2</sub> O	0.3	0.1		≥ 0.1 <sup>e</sup>	≥ 0.1 <sup>e</sup>
ClONO <sub>2</sub> + H <sub>2</sub> O → HOCl + HNO <sub>3</sub>	≥ 0.1	~10 <sup>-4</sup> -10 <sup>-2</sup> <sup>i</sup>	~10 <sup>-2</sup> -10 <sup>-3</sup> <sup>e</sup>	~1 × 10 <sup>-4</sup> -0.1 <sup>f</sup>	
N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O → HOCl + HNO <sub>3</sub>	0.02	3 × 10 <sup>-4</sup>	~10 <sup>-2</sup>	0.1 <sup>g</sup>	0.06-0.095 <sup>g</sup>
HO <sub>2</sub> NO <sub>2</sub> + HCl → HOCl + HNO <sub>3</sub>				< 1 × 10 <sup>-4</sup> <sup>h</sup>	

<sup>a</sup> From DeMore *et al.* (1997) and Ravishankara and Hanson (1996) and references therein.  
<sup>b</sup> NAT = nitric acid trihydrate (solid); SAT = sulfuric acid tetrahydrate (solid).  
<sup>c</sup> Hanson and Ravishankara, 1993b; Zhang *et al.* (1994a), see Fig. 12.25a.  
<sup>d</sup> Zhang *et al.* (1994b), Elrod *et al.* (1995) and Hanson (1998).  $\gamma$  increases as temperature falls primarily due to increased solubility of HCl.  $\gamma$  decreases as percentage of H<sub>2</sub>SO<sub>4</sub> increases, and Hanson (1998) reports that it also decreases with increased HNO<sub>3</sub>; see Fig. 12.25a.  
<sup>e</sup> Zhang *et al.* (1994b); bimolecular rate constant in the liquid phase is ~1.4 × 10<sup>6</sup> L mol<sup>-1</sup> s<sup>-1</sup> for 60 wt% H<sub>2</sub>SO<sub>4</sub> at 251 K (Hanson and Lovejoy, 1996).  
<sup>f</sup> Hanson (1998) and Ball *et al.* (1998) and references therein.  $\gamma$  decreases from ~0.1 at 35 wt% H<sub>2</sub>SO<sub>4</sub> to ~10<sup>-4</sup> at 75 wt% H<sub>2</sub>SO<sub>4</sub>. It also has a small temperature dependence, especially at 75 wt% H<sub>2</sub>SO<sub>4</sub>, where the reaction probability increases with temperature.  
<sup>g</sup> Hanson (1997); HNO<sub>3</sub> from 0.8 to 15%.  
<sup>h</sup> Zhang *et al.* (1997).  
<sup>i</sup> Depends on the amount of surface water; see Barone *et al.* (1997) and references therein.

## Why 195 K?

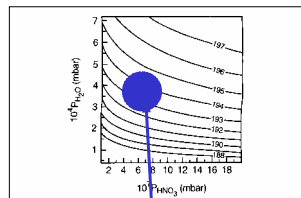


FIGURE 12.23 Temperatures (K) at which SAT deliquesces at different gas-phase pressures of H<sub>2</sub>O and HNO<sub>3</sub> typical of the stratosphere (from Koop and Carlav, 1996).

Typical 20 km values in polar regions

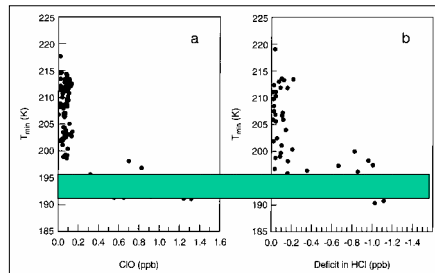


FIGURE 12.37 (a) ClO concentrations and (b) HCl deficit at various minimum temperatures experienced by the air masses in the Arctic stratosphere during October 1991–February 1992 (adapted from Tooley *et al.* (1993) and Webster *et al.* (1993a)).

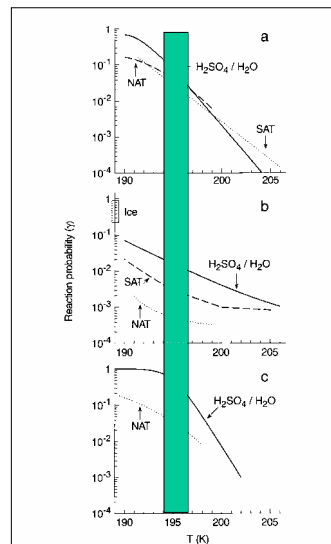


FIGURE 12.25 Typical measured reaction probabilities for (a) ClONO<sub>2</sub> + HCl, (b) ClONO<sub>2</sub> + H<sub>2</sub>O, and (c) HOCl + HCl for different surfaces that can be present and promote heterogeneous chemistry under typical stratospheric conditions (adapted from Ravishankara and Hanson, 1996, and references therein).

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

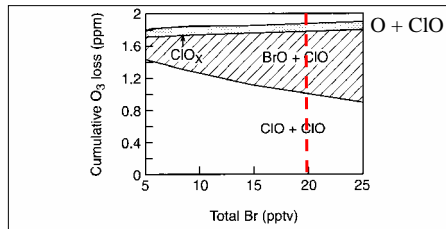
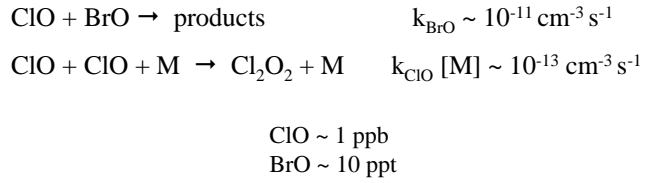
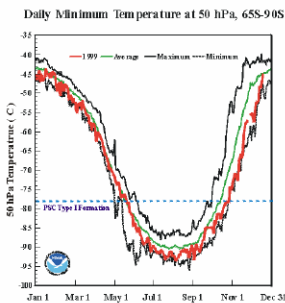
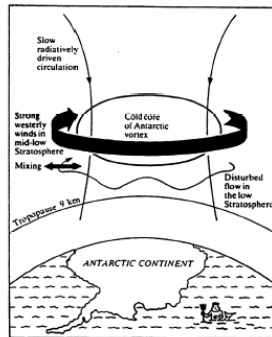


FIGURE 12.46 Model-calculated cumulative loss of ozone from August 1 to the day of maximum ozone depletion as a function of stratospheric bromine ( $[\text{Cl}_2] = 12.5 \text{ ppbv}$ ,  $[\text{NO}_y] = 2 \text{ ppb}$ ,  $70^\circ\text{S}$  at an altitude corresponding to 50 mbar total pressure in these calculations) (adapted from Danilin *et al.*, 1996).



Why the poles?

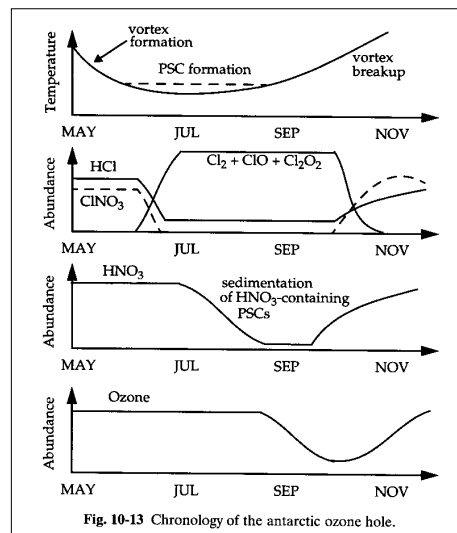


Fig. 10-13 Chronology of the antarctic ozone hole.

1974! **Stratospheric Chlorine: a Possible Sink for Ozone**

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This study proposes that the oxides of chlorine, ClO<sub>x</sub>, may constitute an important sink for stratospheric ozone. A photochemical scheme is devised which includes two catalytic cycles through which ClO<sub>x</sub> destroys odd oxygen. The individual ClO<sub>x</sub> constituents (HCl, Cl, ClO, and OClO) perform analogously to the respective constituents (HNO<sub>x</sub>, NO, NO<sub>2</sub>, and NO<sub>3</sub>) in the NO<sub>x</sub> catalytic cycles, but the ozone destruction efficiency is higher for ClO<sub>x</sub>. 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 ClO<sub>x</sub> 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<sub>x</sub> cycles with NO<sub>x</sub> and HO<sub>x</sub> 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...

