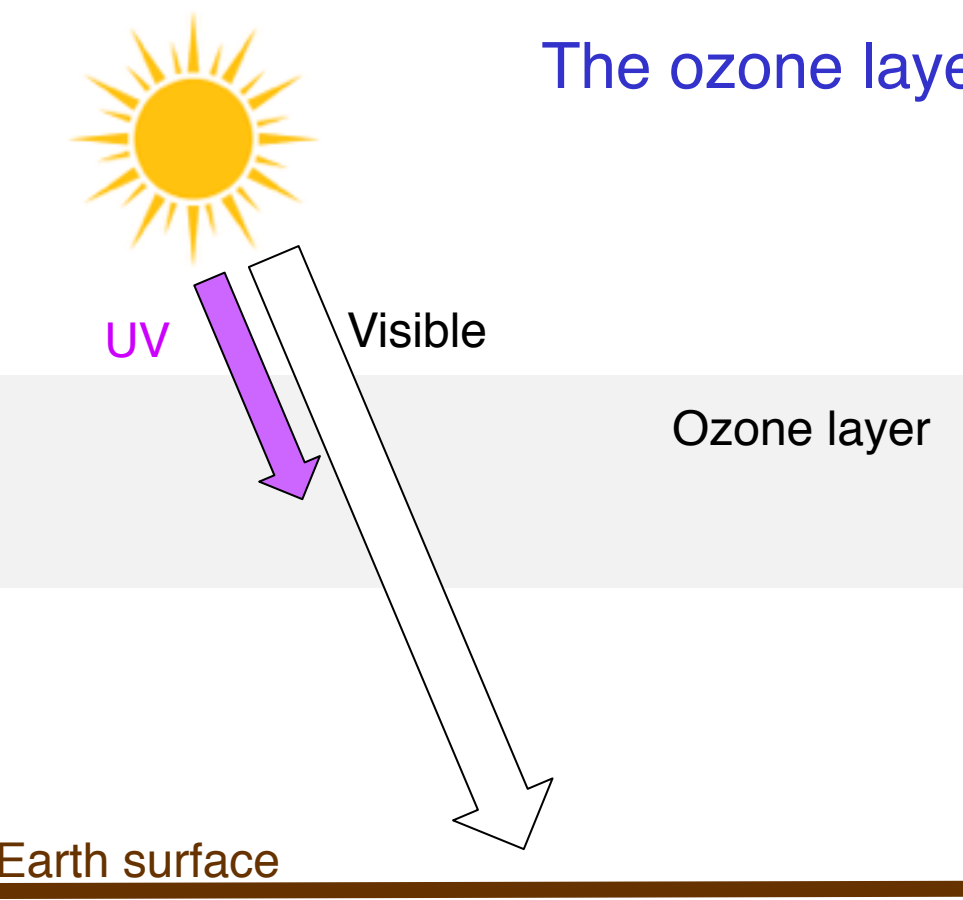
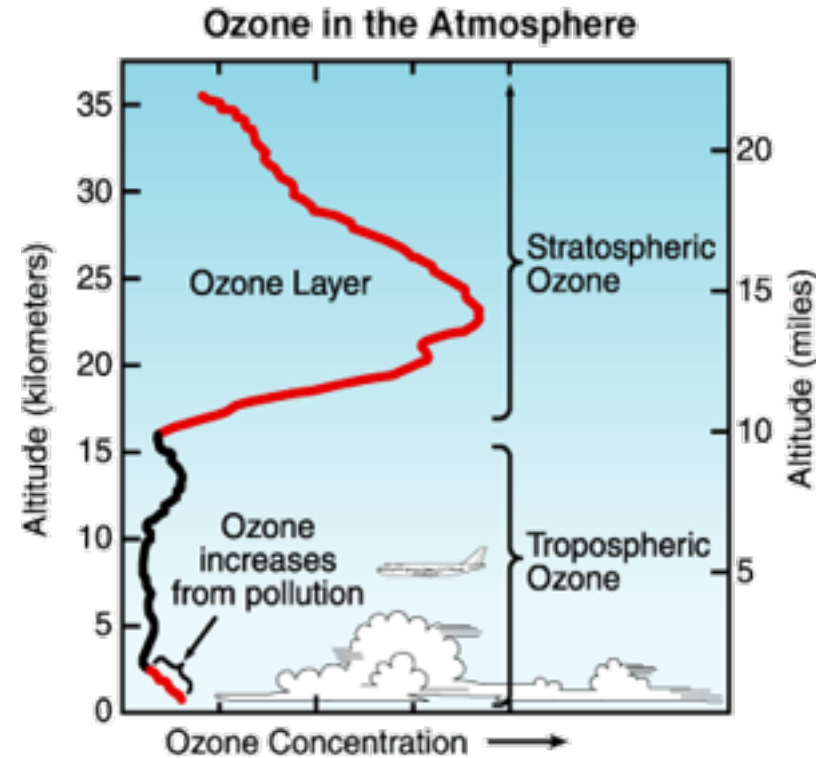


## **10. Stratospheric ozone**

# The ozone layer protects us from UV radiation



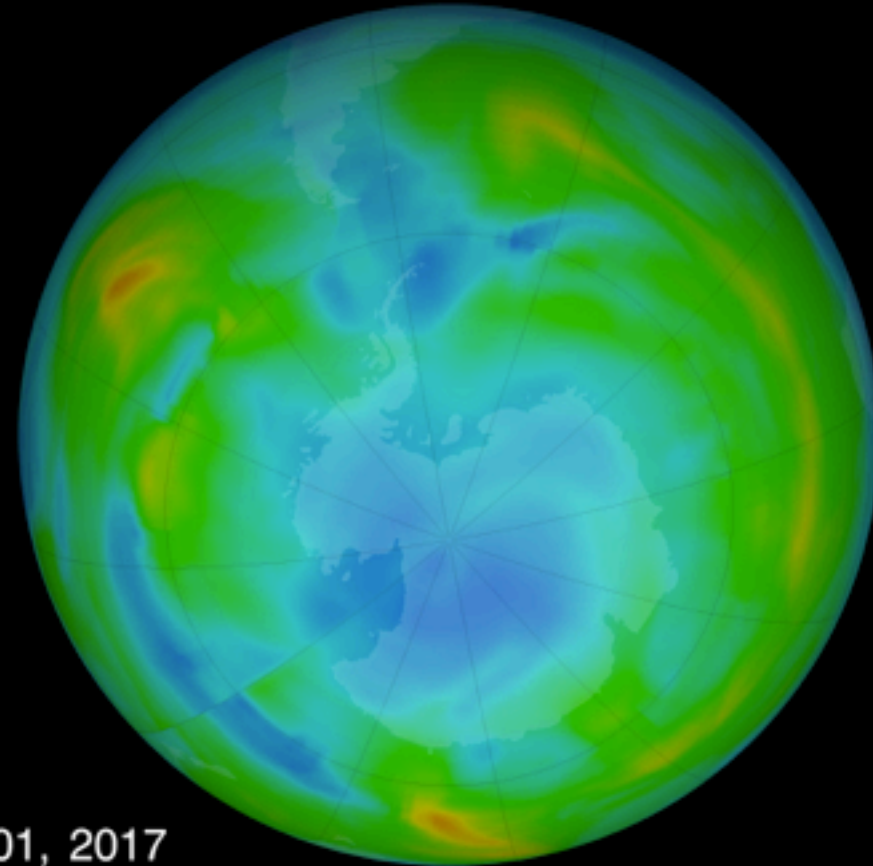
Ozone absorbs UV radiation while letting visible radiation through



Ozone ( $O_3$ ) is produced naturally in the stratosphere from molecular oxygen ( $O_2$ )



# Ozone hole develops over Antarctica every austral spring

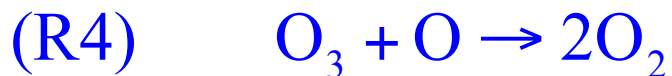
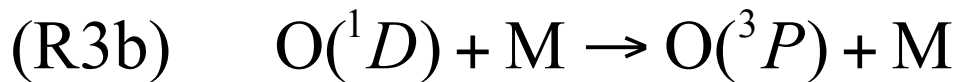
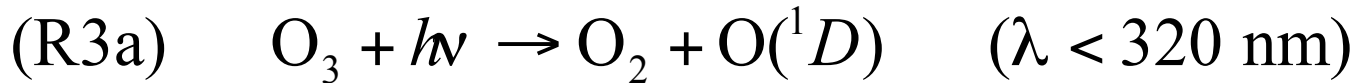


Jul 01, 2017

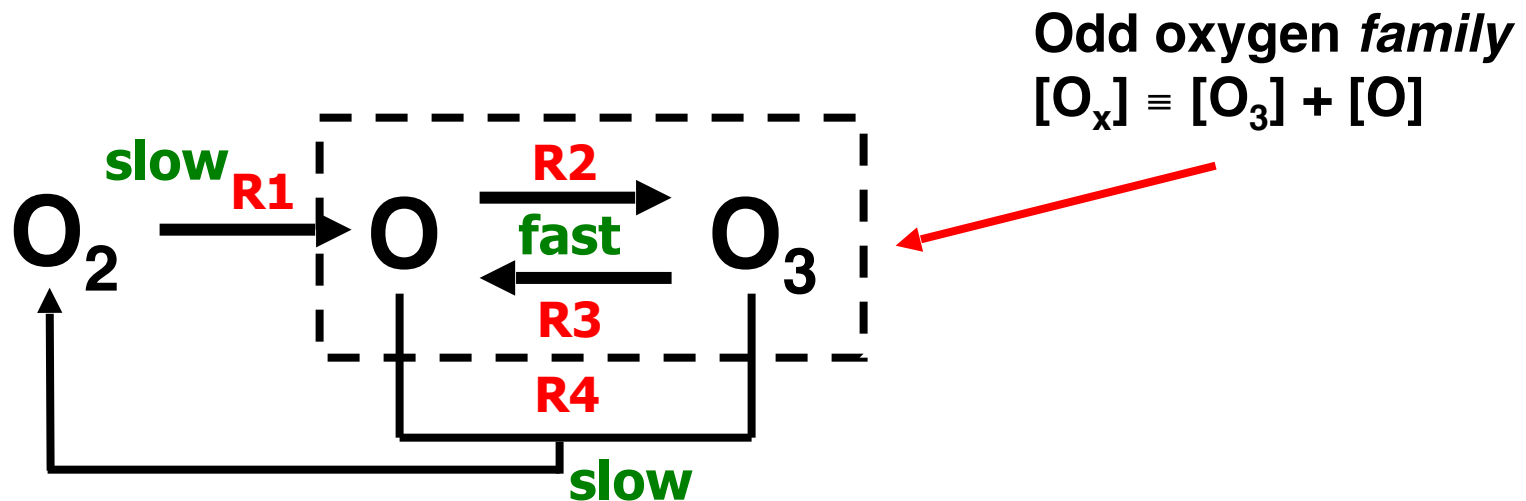
Jul 01

Dec 31

# Chapman mechanism for stratospheric ozone (1930)



$O(^1D)$ : excited state  
 $O(^3P) \equiv O$ : ground state



# Calculation of photolysis rates



$k$  is the photolysis rate constant (also called photolysis frequency)

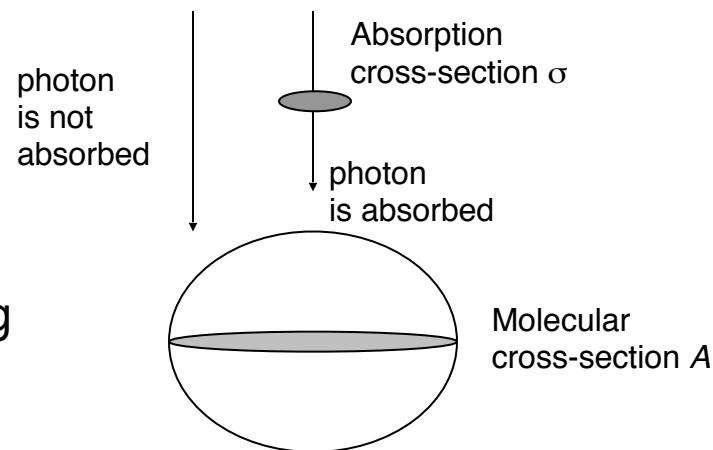
$$k = \int_0^{\infty} q_X(\lambda) \sigma_X(\lambda) \varphi_\lambda d\lambda$$

radiation flux [photons cm<sup>-2</sup> s<sup>-1</sup>]

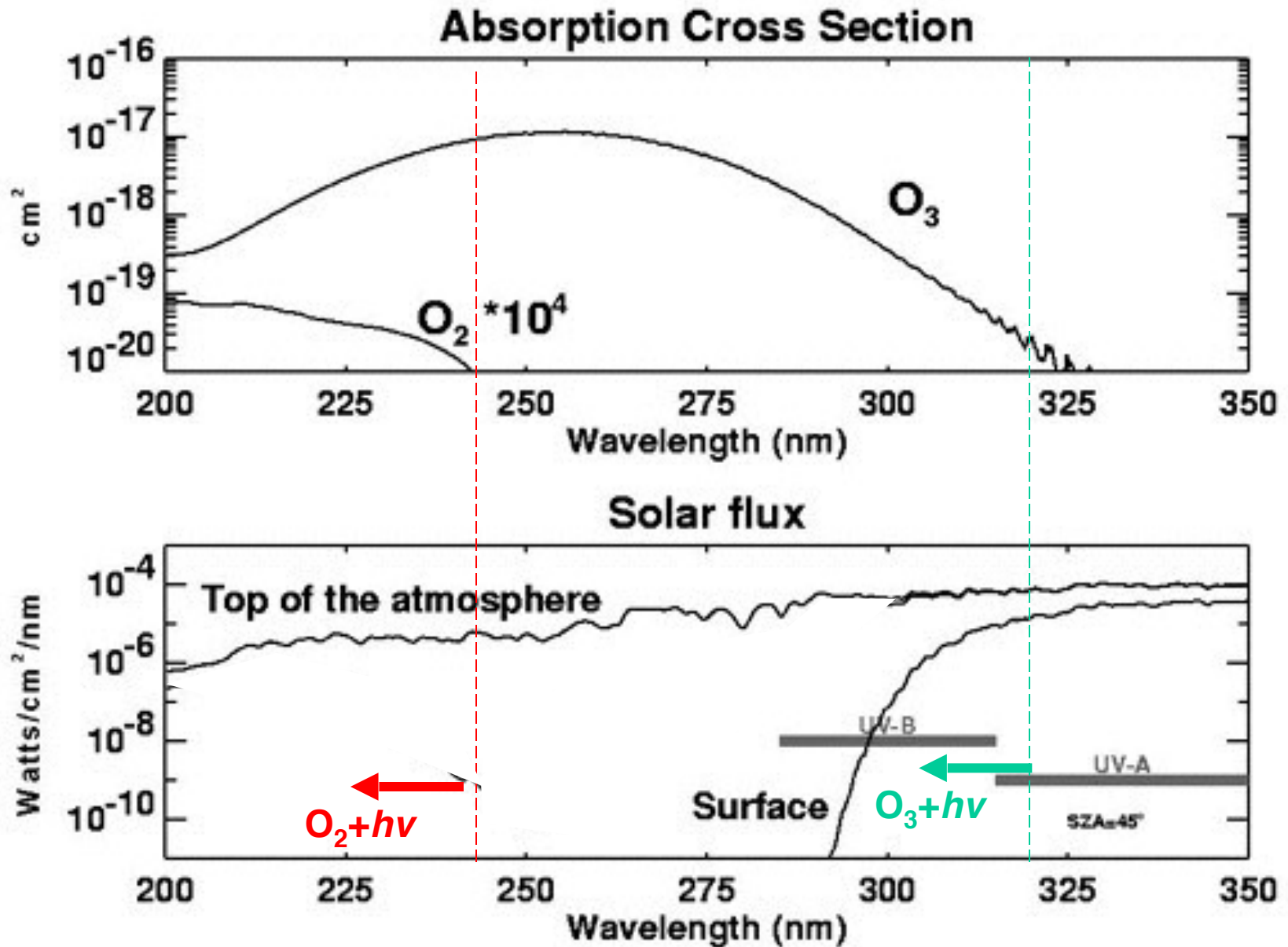
quantum yield:  
probability that photon absorption  
causes photolysis

absorption  
cross-section [cm<sup>2</sup> molecule<sup>-1</sup>]

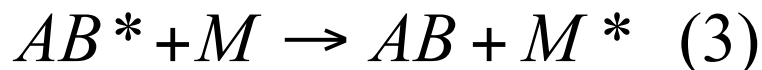
Probability of absorption for incoming  
photons =  $\sigma/A$



# Solar spectrum and absorption cross-sections



## Calculation of 3-body reaction rates



A and B are reactants;  
AB\* is the activated product;  
AB is the stable product;  
M is the "third body" (N<sub>2</sub>, O<sub>2</sub>)



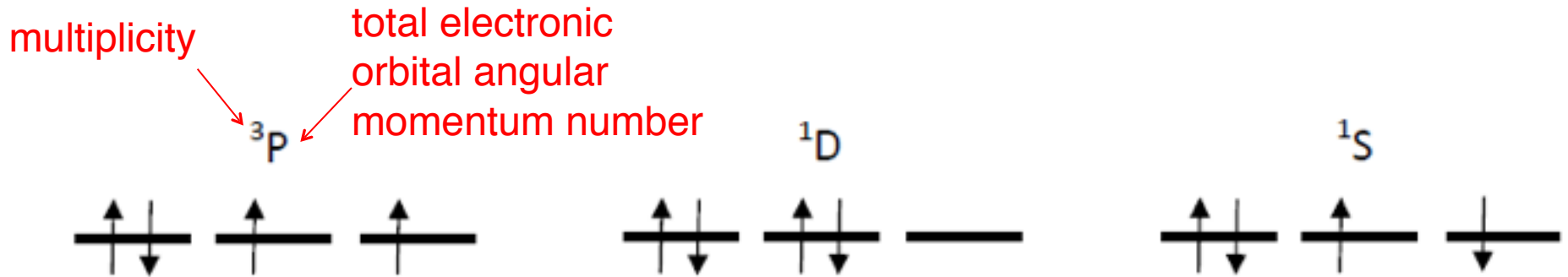
General solution: 
$$\frac{d[AB]}{dt} = \frac{k_1 k_3 [A][B][M]}{k_2 + k_3 [M]}$$

Low-pressure limit (Rate(2) >> Rate (3)): 
$$\frac{d[AB]}{dt} = \frac{k_1 k_3}{k_2} [A][B][M]$$

High-pressure limit (Rate(2) << Rate (3)): 
$$\frac{d[AB]}{dt} = k_1 [A][B]$$

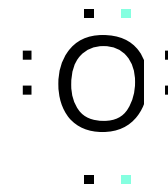
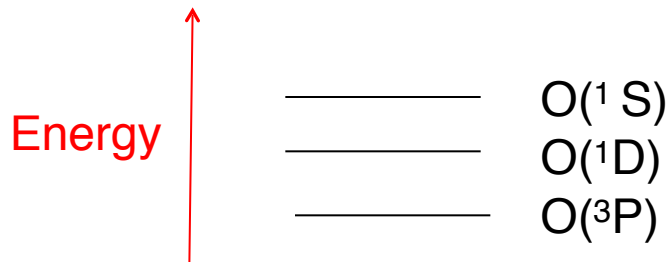
# Energy states of the O atom ( $1s^2 2s^2 2p^4$ )

determined by the arrangement of the four electrons in the 2p orbitals



Multiplicity =  $2S+1$ , where  $S$  is the spin. The spin of an electron is  $\pm 1/2$ .

Hund's Rule: lowest-lying energy state is the one of maximum multiplicity



$\text{O}(^3P)$  is a diradical



# Questions

1. Based on the Chapman mechanism, how would you expect O concentrations to vary between day and night? How would you expect O<sub>3</sub> concentrations to vary between day and night?
2. The original Chapman mechanism contained a fifth reaction:



What would be the effect of this reaction on ozone?

# Steady-state analysis of Chapman mechanism

Steady state for O atoms:

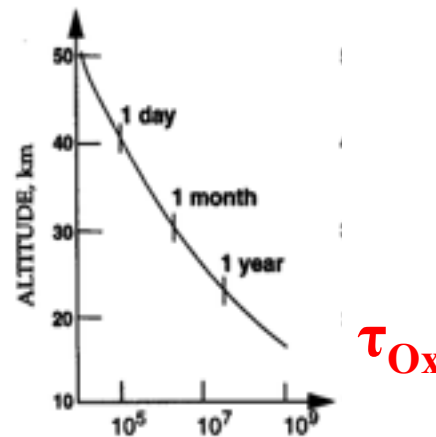
$$\text{Rate}(2) = \text{Rate}(3) \Rightarrow k_2[\text{O}][\text{O}_2][\text{M}] = k_3[\text{O}_3] \Rightarrow \frac{[\text{O}]}{[\text{O}_3]} = \frac{k_3}{k_2 C_{\text{O}_2} n_a^2} \ll 1$$

$$\Rightarrow [\text{O}_x] \approx [\text{O}_3]$$

...so the budget of  $\text{O}_3$  is controlled by the budget of  $\text{O}_x$ .

Lifetime of  $\text{O}_x$ :

$$\tau_{\text{O}_x} = \frac{[\text{O}_x]}{2k_4[\text{O}_3][\text{O}]} \approx \frac{1}{2k_4[\text{O}]}$$



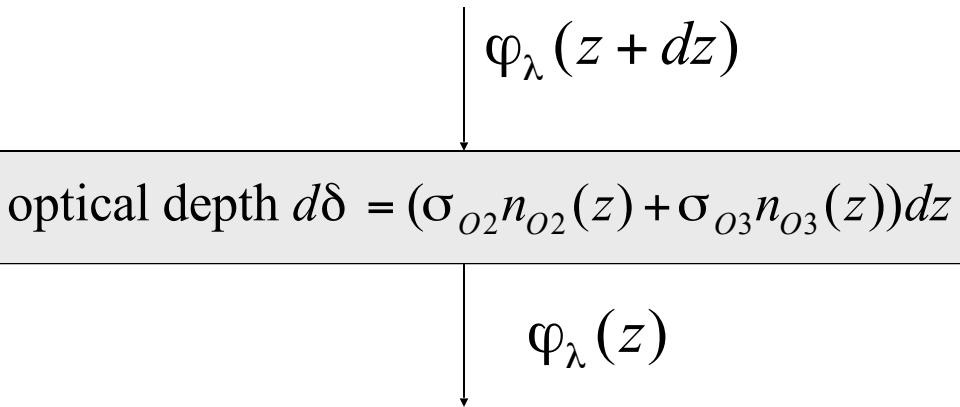
Steady state for  $\text{O}_x$ :

$$2R1 = 2R4 \Rightarrow k_1[\text{O}_2] = k_4[\text{O}_3][\text{O}] \Rightarrow [\text{O}_3] = \left[ \frac{k_1 k_2}{k_3 k_4} \right]^{\frac{1}{2}} C_{\text{O}_2} n_a^{\frac{3}{2}}$$

# Photolysis rate constants: dependence on altitude

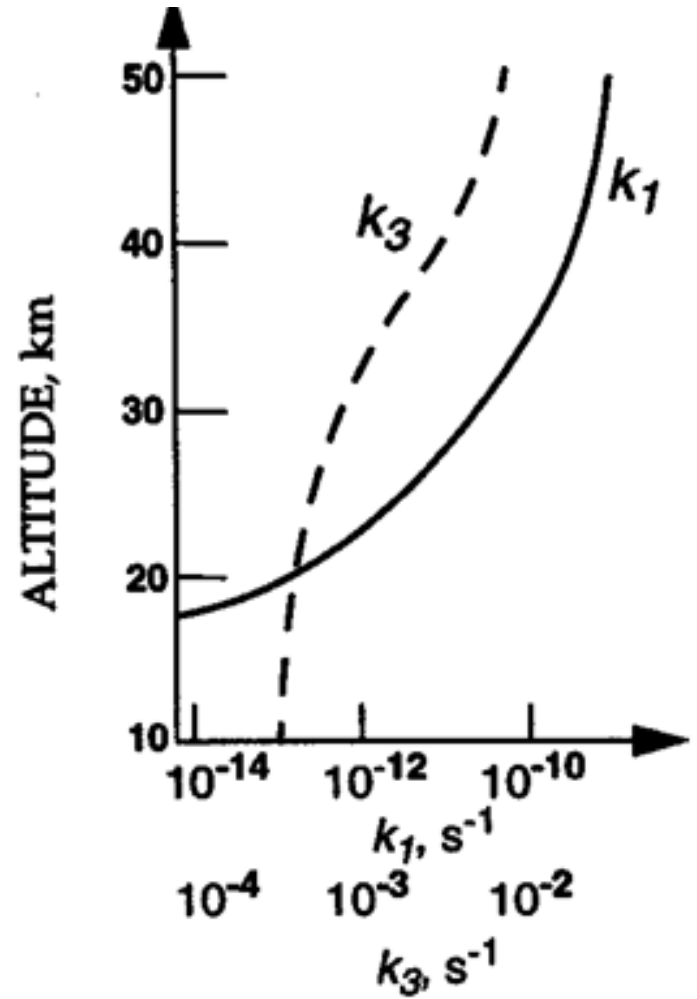
$$X + h\nu \rightarrow \dots \quad k = \int_0^\infty q_X(\lambda) \sigma_X(\lambda) \varphi_\lambda d\lambda$$

quantum yield      absorption x-section      photon flux

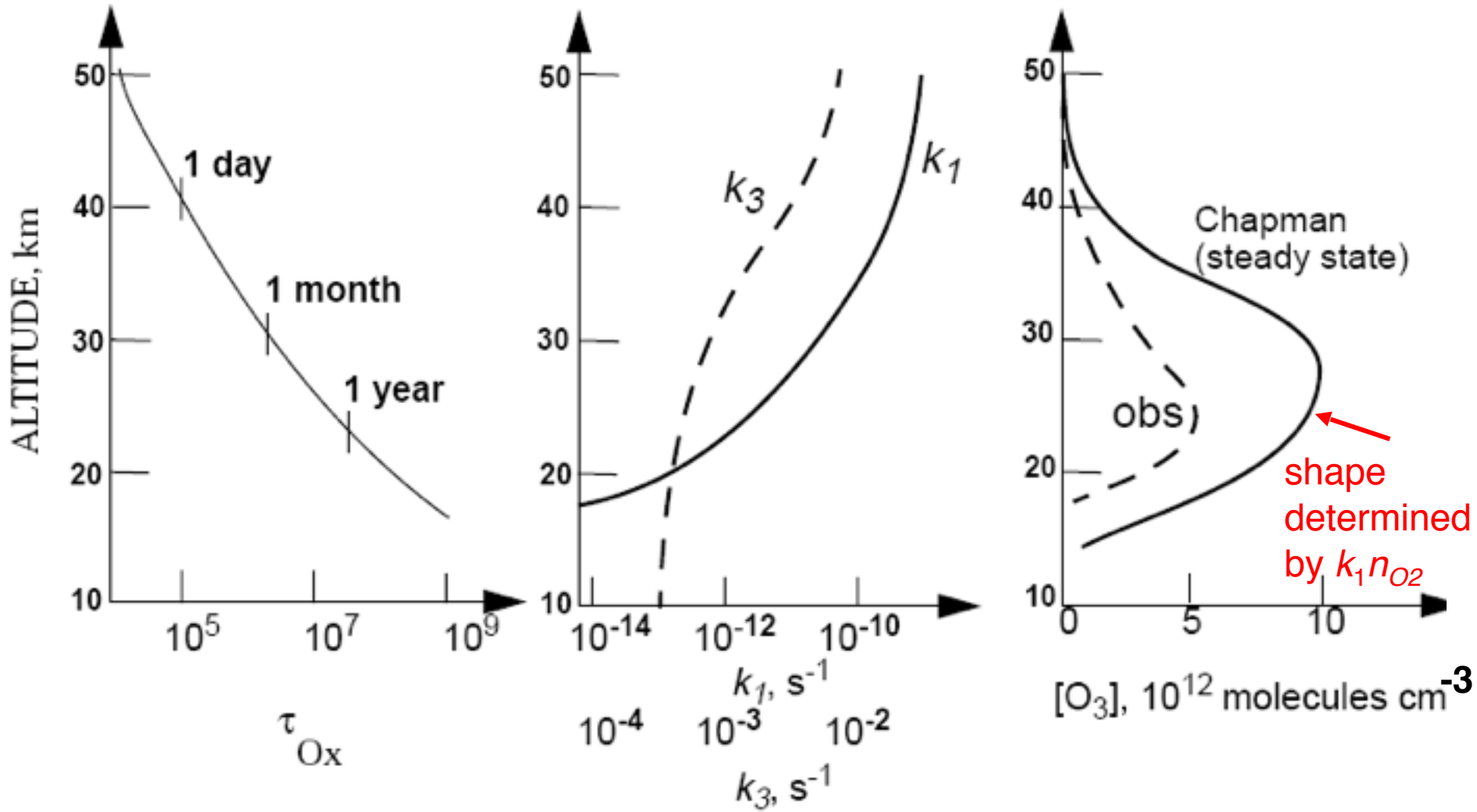


$$\varphi(z) = \varphi(\infty) e^{-\delta}$$

$$\delta = \int_z^\infty (\sigma_{O_2} n_{O_2}(z') + \sigma_{O_3} n_{O_3}(z')) dz'$$



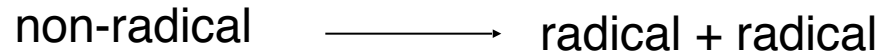
# Chapman mechanism vs. observations



Chapman mechanism reproduces shape, but is too high by factor 2-3  $\Rightarrow$  missing sink!

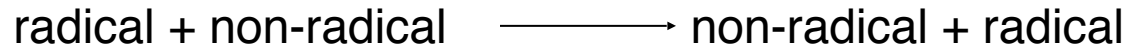
# General schematic of radical-assisted reaction chains

## Initiation:



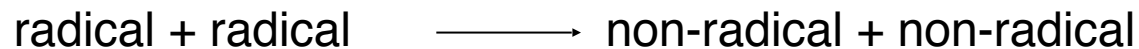
photolysis  
thermolysis  
oxidation by  $O(^1D)$

## Propagation:

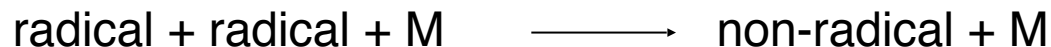


bimolecular  
redox reaction

## Termination:



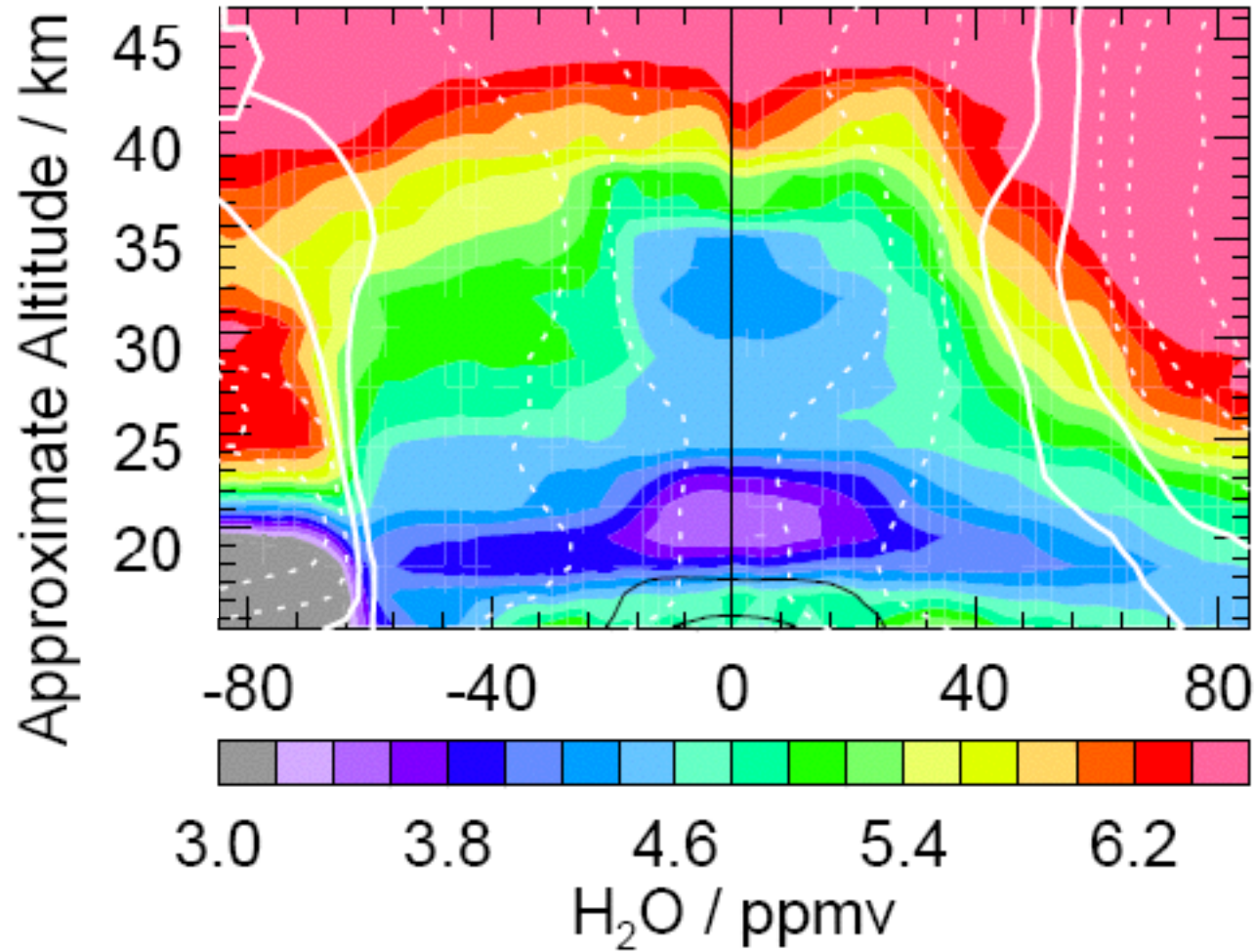
bimolecular  
redox reaction



3-body reaction

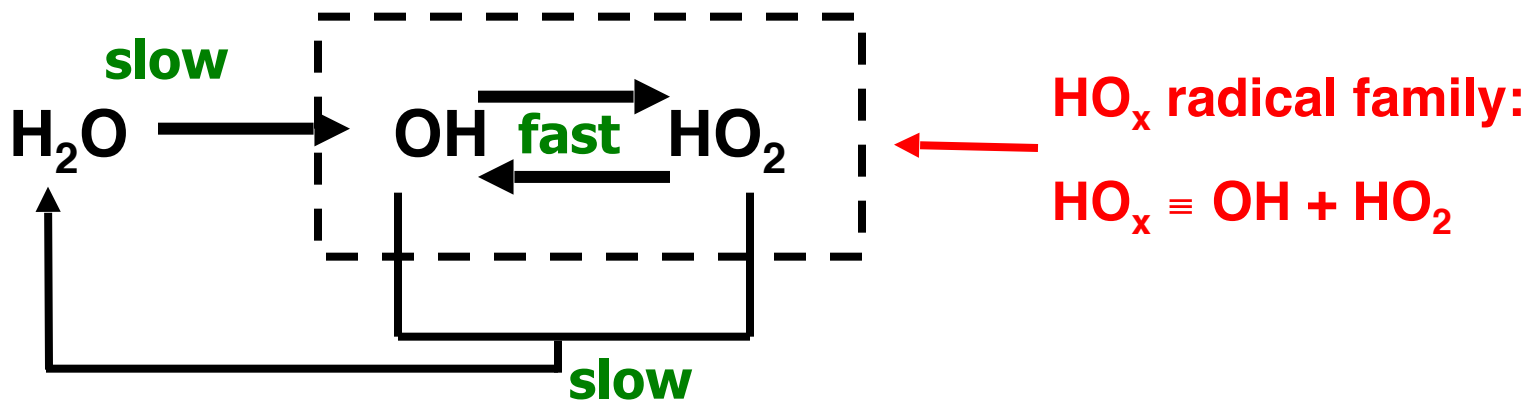
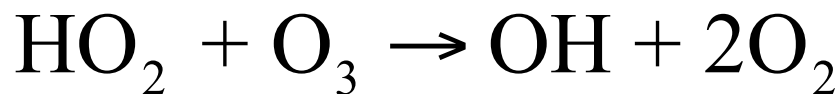
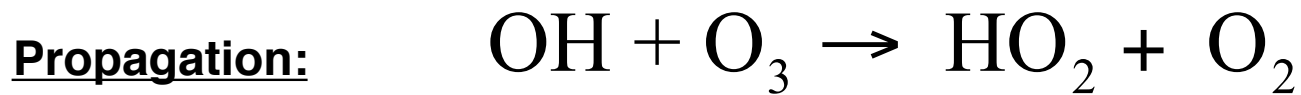
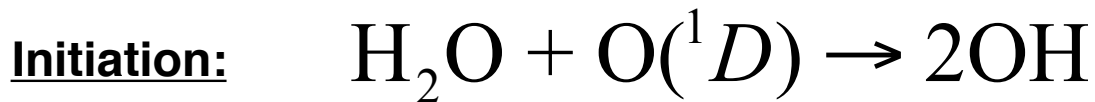
# Water vapor in stratosphere

Aura MLS Equivalent Latitude/ $\theta$  Global Section -- 6 Nov 2008 (2008d311)



Source: transport from troposphere, oxidation of methane (CH<sub>4</sub>)

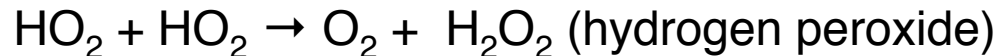
# Ozone loss catalyzed by hydrogen oxide radicals (HO<sub>x</sub>)



# Questions

1. Consider harmful UV radiation for which the ozone layer has an optical depth of 10. The ozone layer has thinned by 6% since 1970, causing a corresponding 6% decrease in optical depth. What is the resulting percent increase in the flux of this UV radiation at the surface of the Earth?

2. A termination step for the HO<sub>x</sub> radical chain is



Hydrogen peroxide can go on to either photolyze or react with OH:



Whether H<sub>2</sub>O<sub>2</sub> photolyzes or reacts with OH has a large effect on HO<sub>x</sub>-catalyzed ozone loss, explain why.

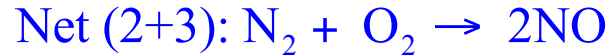
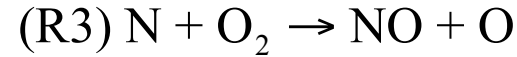
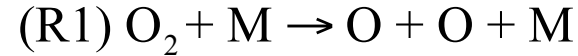


## Supersonic aircraft (Concorde) cruising at 60,000'

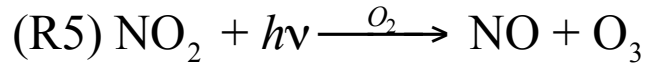
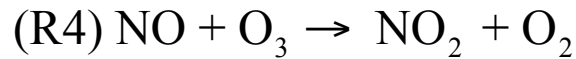
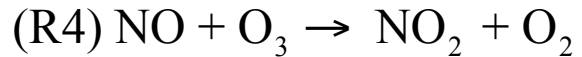


# Ozone loss catalyzed by nitrogen oxide radicals (NO<sub>x</sub>)

**Initiation:** conversion of air to NO radicals in combustion engine



**Propagation:** cycling of NO<sub>x</sub> radicals (NO<sub>x</sub> ≡ NO + NO<sub>2</sub>)

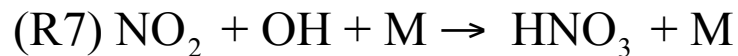


Net: null cycle



R6 is rate-limiting step for catalytic ozone loss:  
 $-d[O_3]/dt = 2k_6[NO_2][O]$

**Termination:** oxidation of NO<sub>x</sub> to HNO<sub>3</sub>



OH is a very strong oxidant (we will encounter it often)

**Recycling:** conversion of HNO<sub>3</sub> back to NO<sub>x</sub>



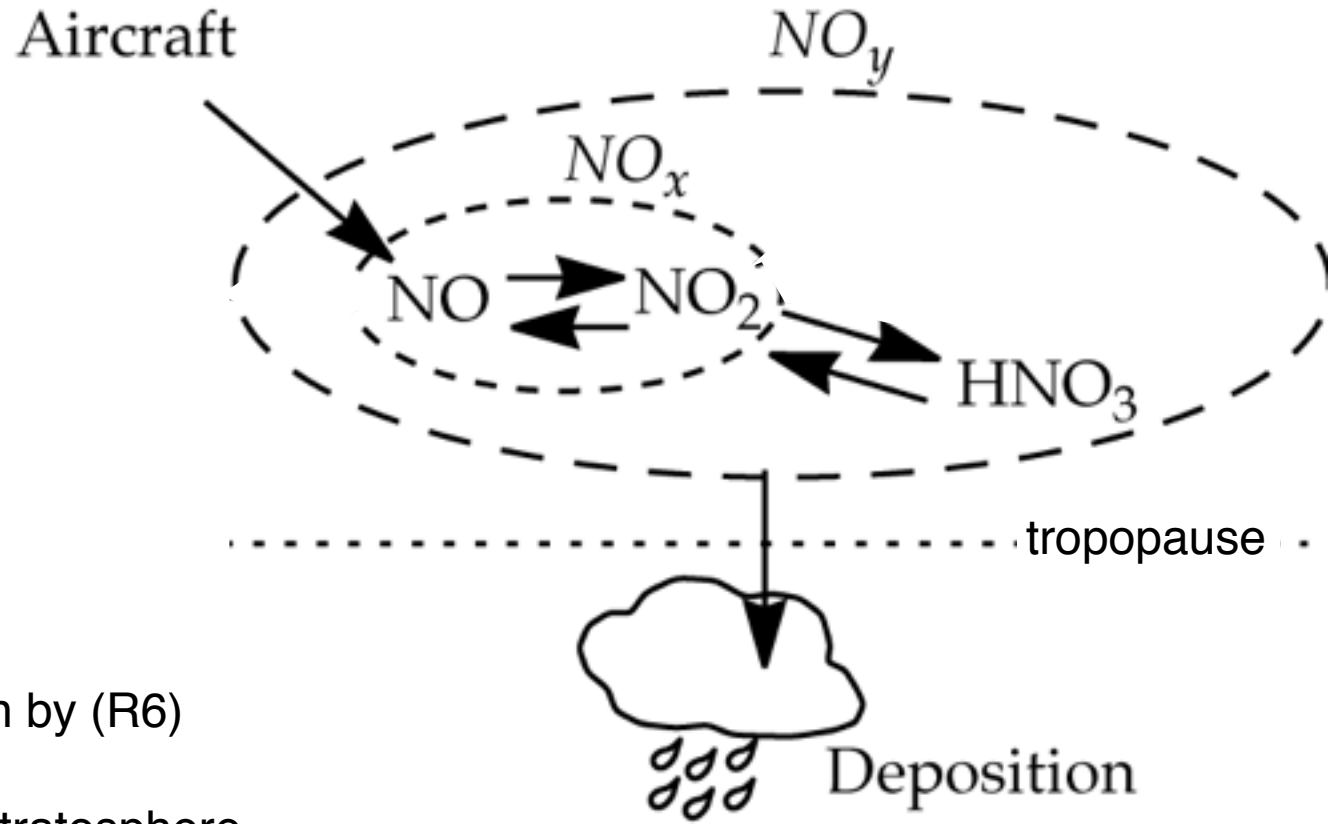
HNO<sub>3</sub> is called a 'reservoir' for NO<sub>x</sub>

## WHAT IS A RATE-LIMITING STEP?

- From IUPAC: “A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite reaction sequence is an *elementary reaction* the rate constant for which exerts a strong effect — stronger than that of any other rate constant — on the overall rate.”

It is not necessarily the slowest reaction in the sequence!

# Computing the NO<sub>x</sub>-catalyzed ozone loss rate



**Loss rate depends on:**

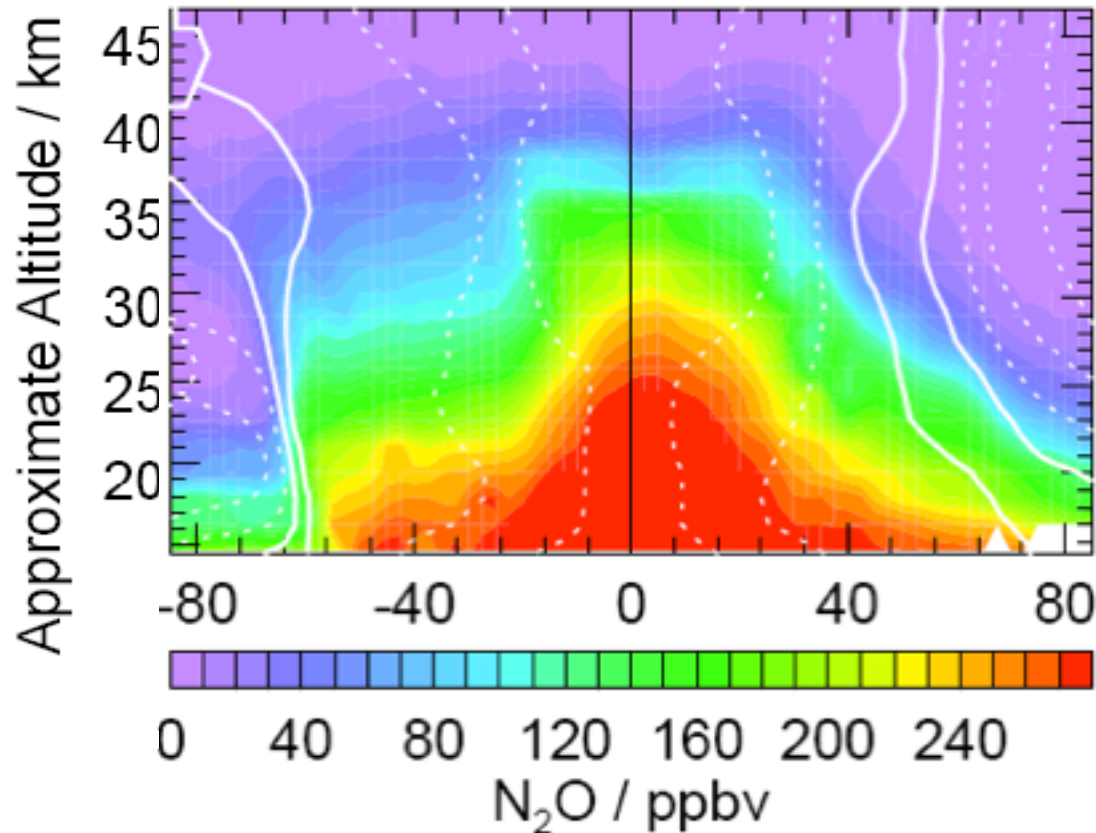
1. NO<sub>x</sub> emission rate  $E$
2.  $[\text{NO}_x]/[\text{NO}_y]$  ratio
3. Ozone loss rate given by (R6)
4. Residence time  $\tau$  in stratosphere

$$[\text{NO}_y] = E\tau \quad [\text{NO}_2] = \frac{[\text{NO}_2][\text{NO}_x]}{[\text{NO}_x][\text{NO}_y]} \quad -\frac{d[\text{O}_3]}{dt} = k_6[\text{NO}_2][\text{O}]$$

Typically  $[\text{NO}_x]/[\text{NO}_y] < 0.1$ ; importance of reservoirs!

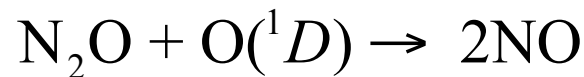
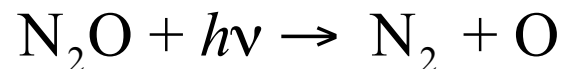
# Nitrous oxide: natural source of NO<sub>x</sub> in stratosphere

Aura MLS Equivalent Latitude/ $\theta$  Global Section -- 6 Nov 2008 (2008d311)

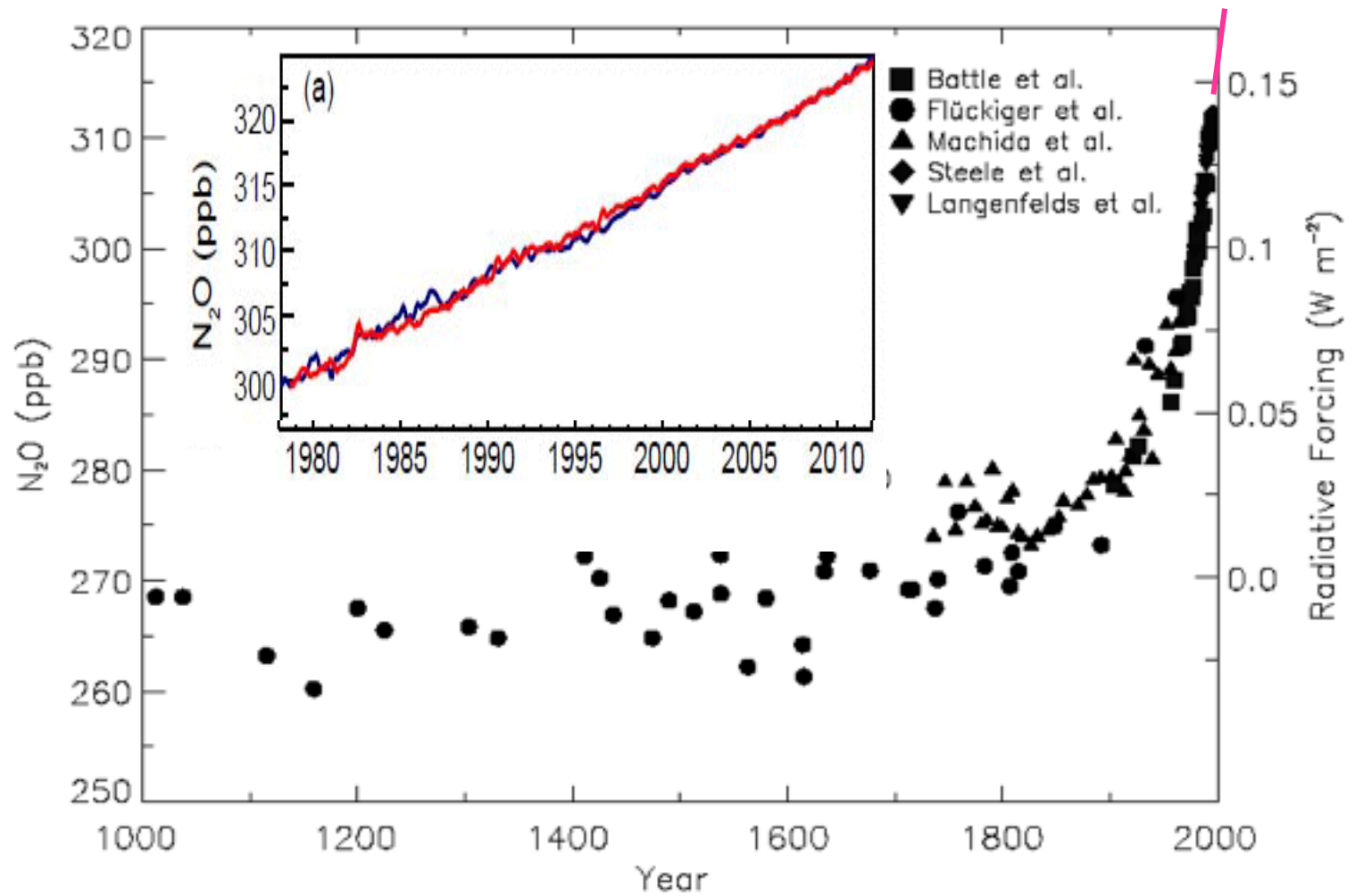


Source: nitrogen cycling in biosphere, N<sub>2</sub>O is emitted as a byproduct

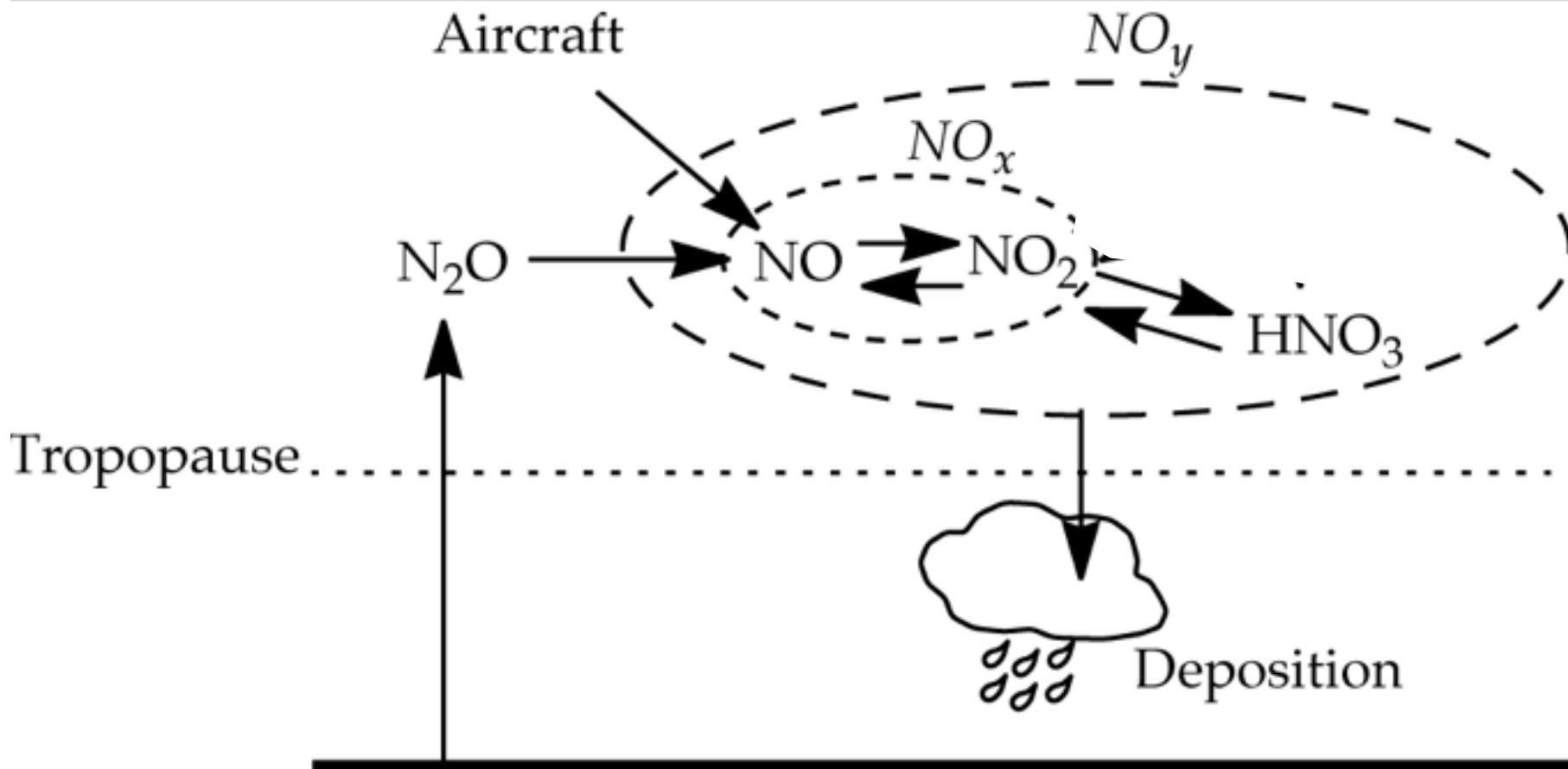
Sinks: photolysis, oxidation by O(<sup>1</sup>D)  $\tau_{\text{N}_2\text{O}} = 120$  years



# Rising concentration of N<sub>2</sub>O due to agriculture

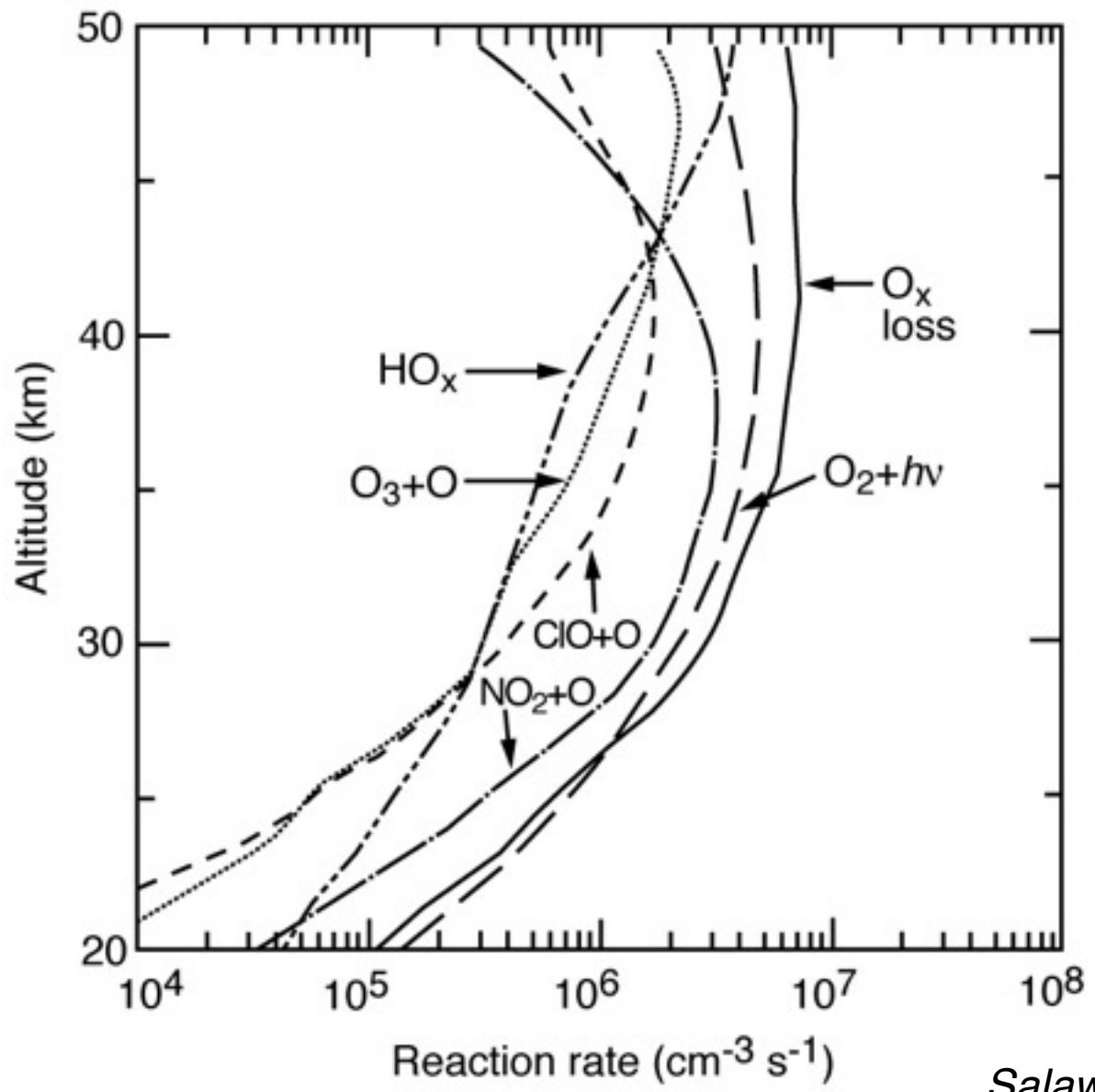


# Computing the $\text{NO}_x$ -catalyzed ozone loss rate



Same as before but with  $\text{NO}_x$  source from  $\text{N}_2\text{O}$  oxidation

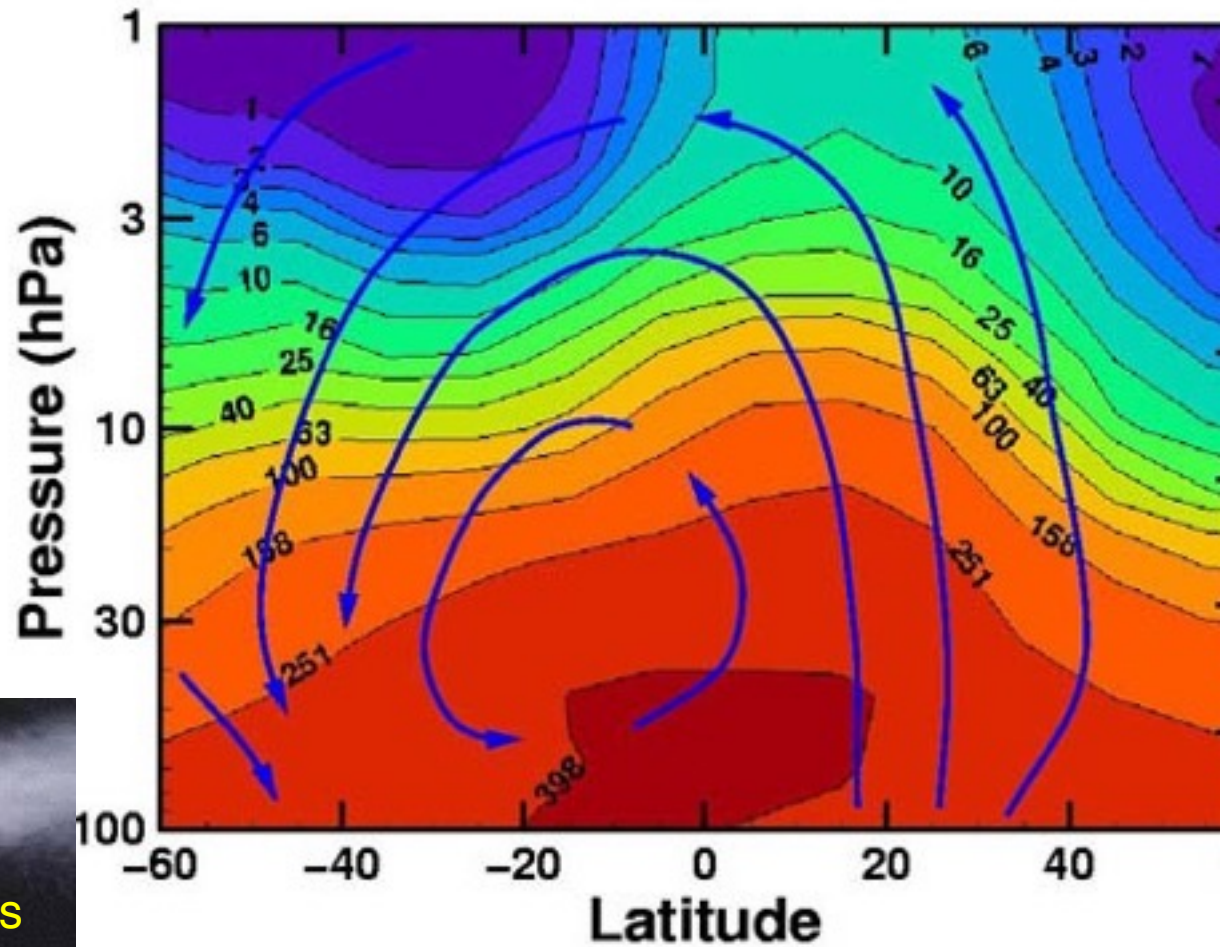
# STRATOSPHERIC OZONE BUDGET FOR MIDLATITUDES INFERRED FROM 1980s SPACE SHUTTLE OBSERVATIONS





# Chlorofluorocarbons (CFCs) in the atmosphere

CFC-12 (ppb)



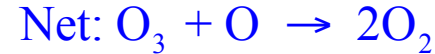
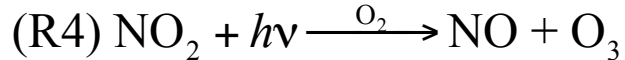
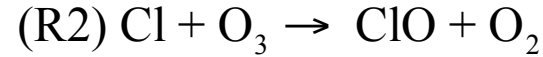
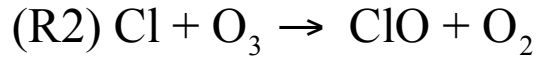
S-CLAES, June-July 1992



# Ozone loss catalyzed by chlorine radicals (ClO<sub>x</sub>)

**Initiation:** photolysis of CFCs      (R1)  $\text{CF}_2\text{Cl}_2 + h\nu \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$

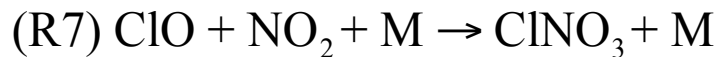
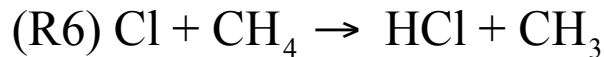
**Propagation:** cycling of ClO<sub>x</sub> radicals (ClO<sub>x</sub> ≡ Cl + ClO)



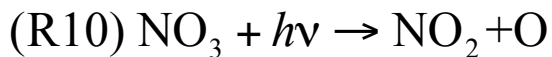
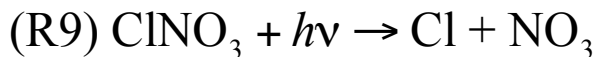
Net: null cycle

R5 is rate-limiting step  
for catalytic ozone loss

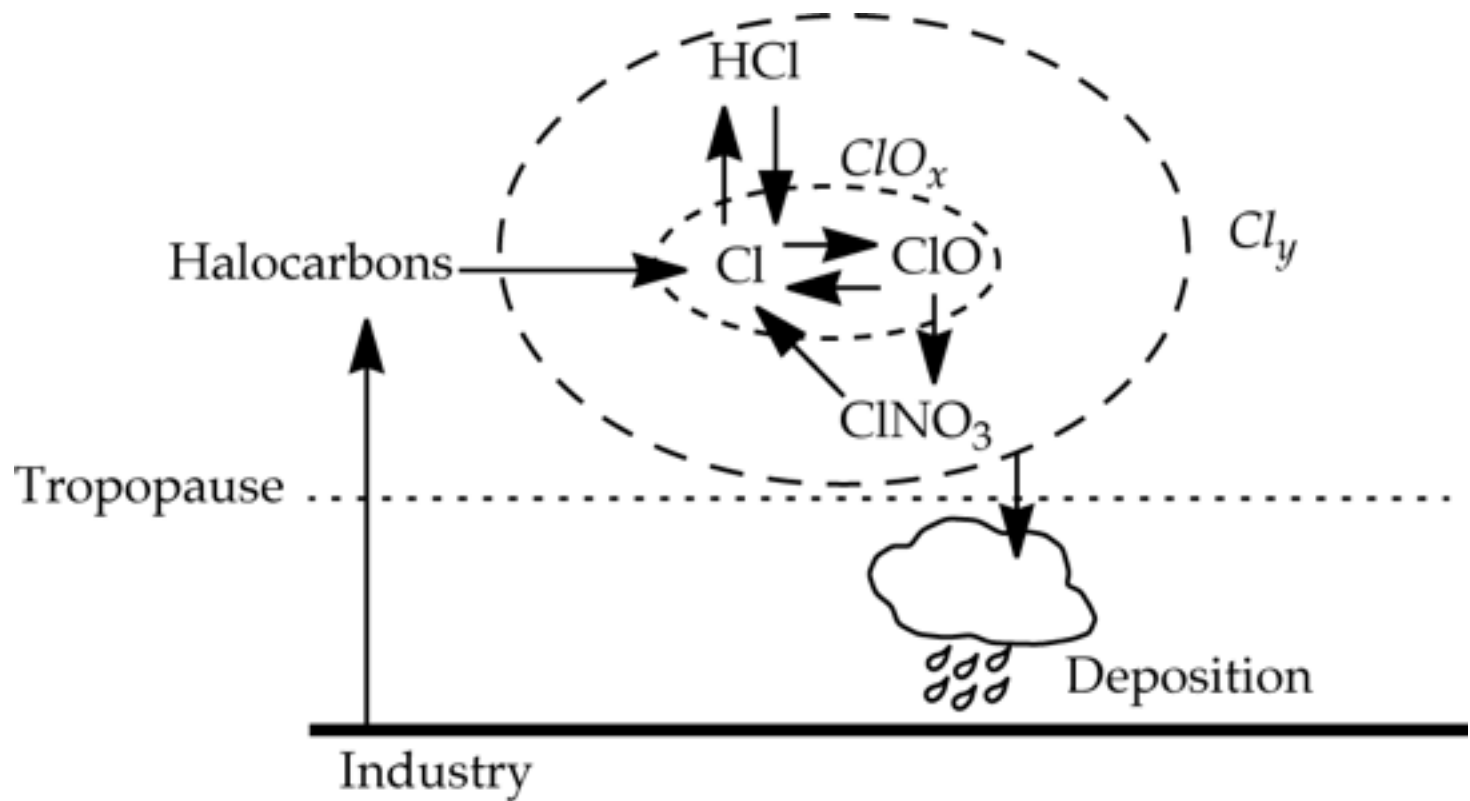
**Termination:** conversion of ClO<sub>x</sub> to HCl and ClNO<sub>3</sub> reservoirs



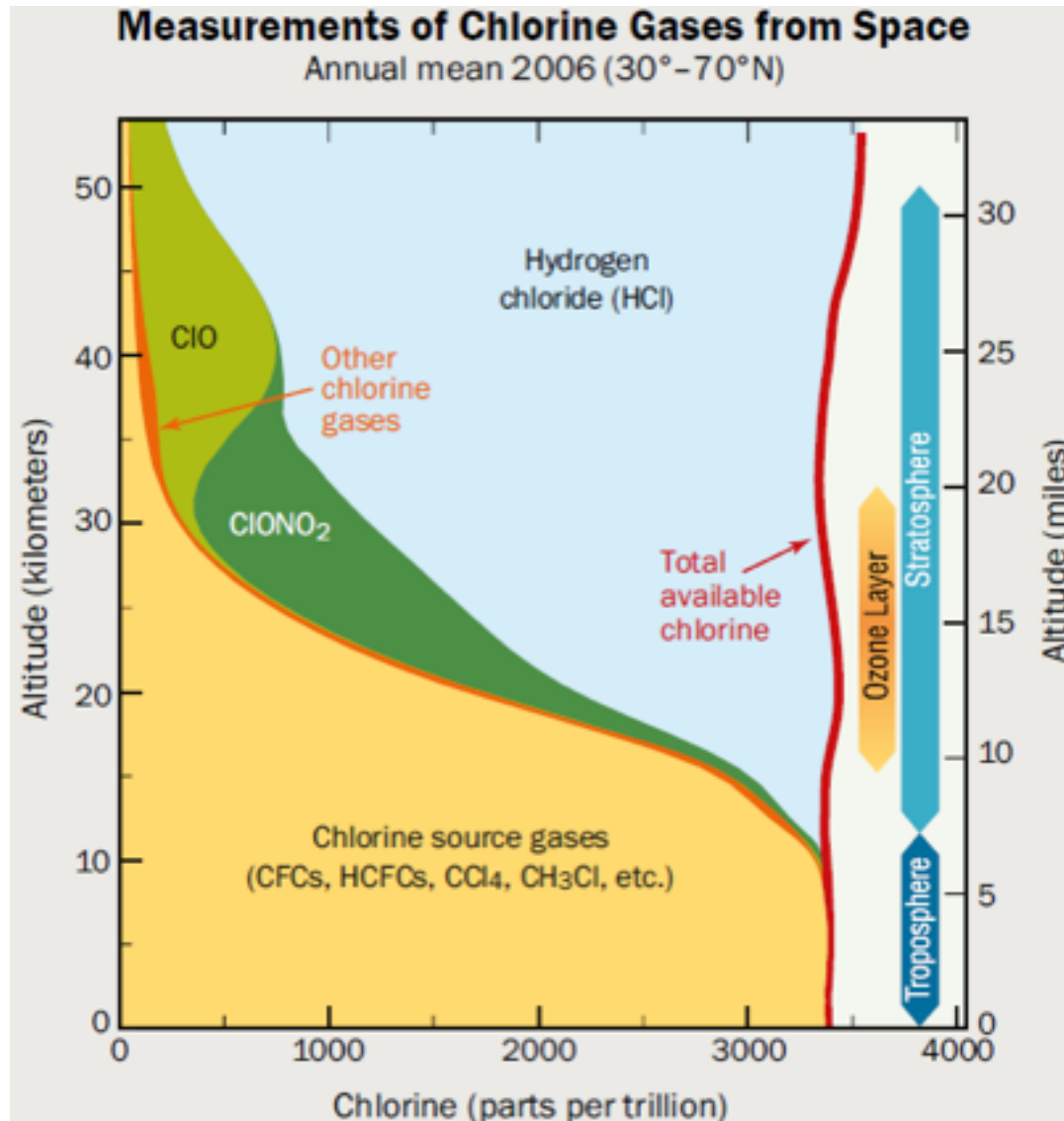
**Recycling:** conversion of HCl and ClNO<sub>3</sub> back to NO<sub>x</sub>



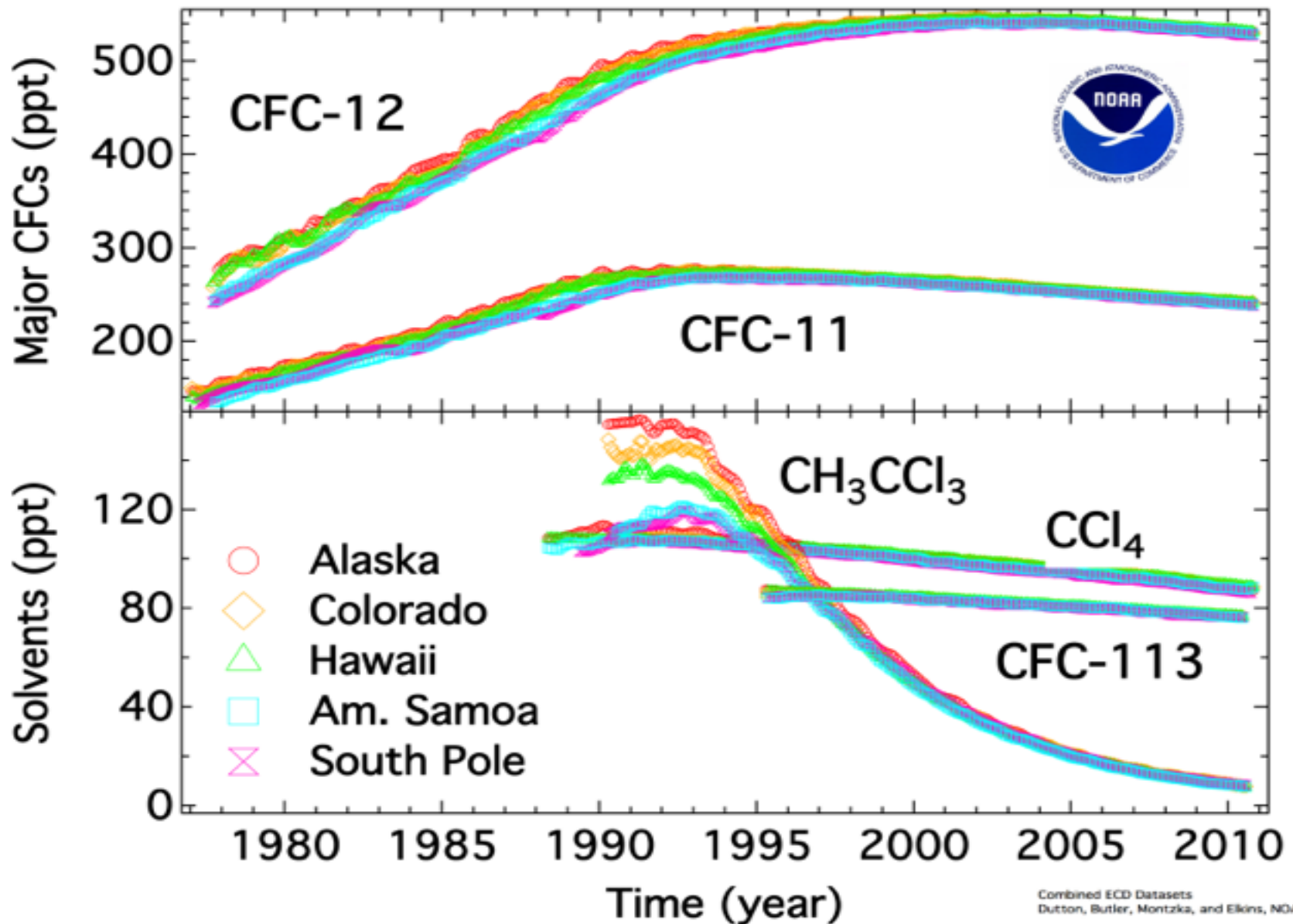
# Computing the $\text{ClO}_x$ -catalyzed ozone loss rate



# Chlorine partitioning in stratosphere



# CFC trends



## Questions

1. Peroxynitric acid ( $\text{HNO}_4$ ) is produced and removed in the stratosphere by

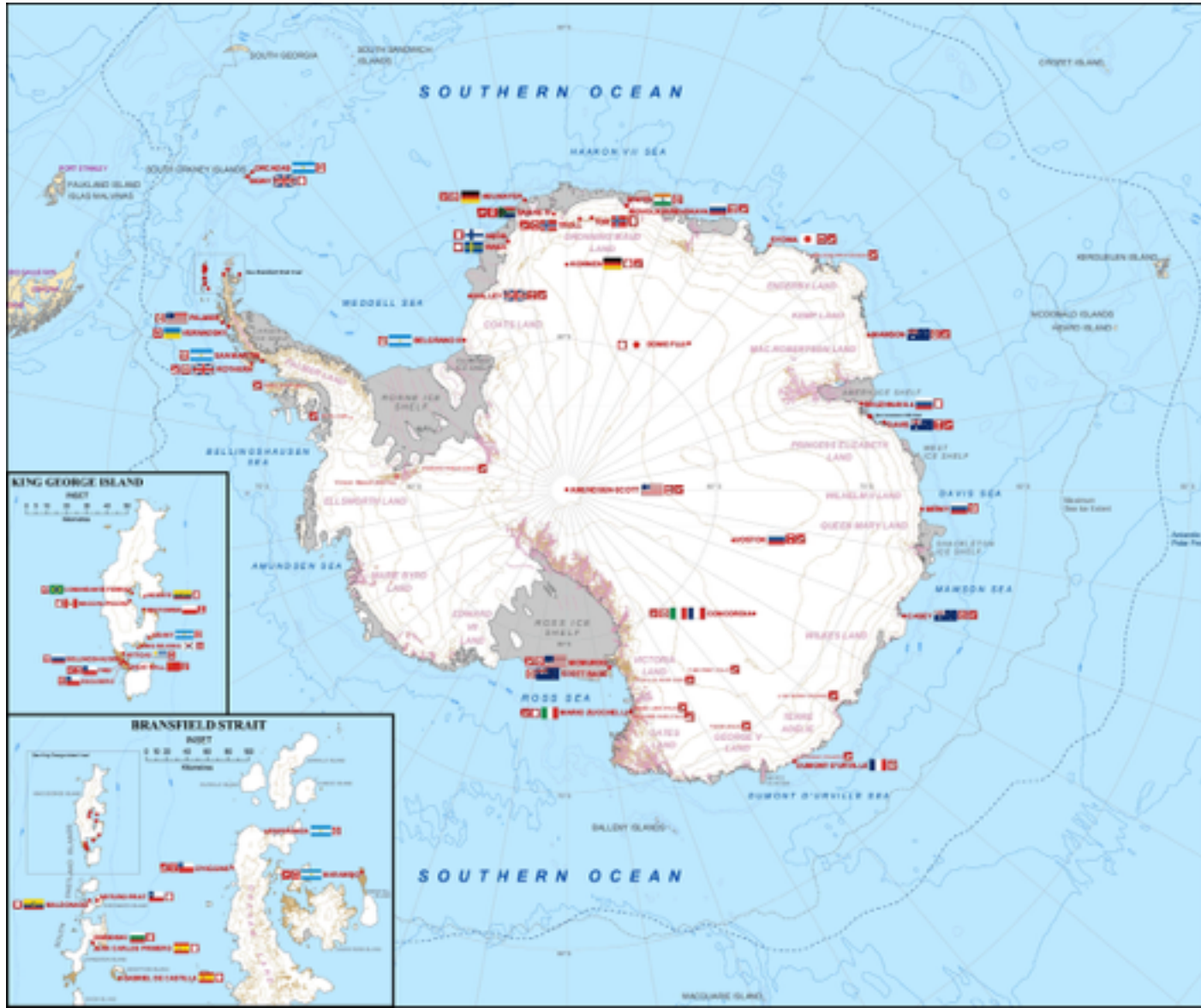


What is the effect on stratospheric ozone? Think of the effects on both the  $\text{NO}_x$  and  $\text{HO}_x$  budgets.

2. The stability of hydrogen halides decreases as  $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$ . What does that mean for the efficiency of different halogens in destroying ozone?

# Antarctica: the “scientific continent”

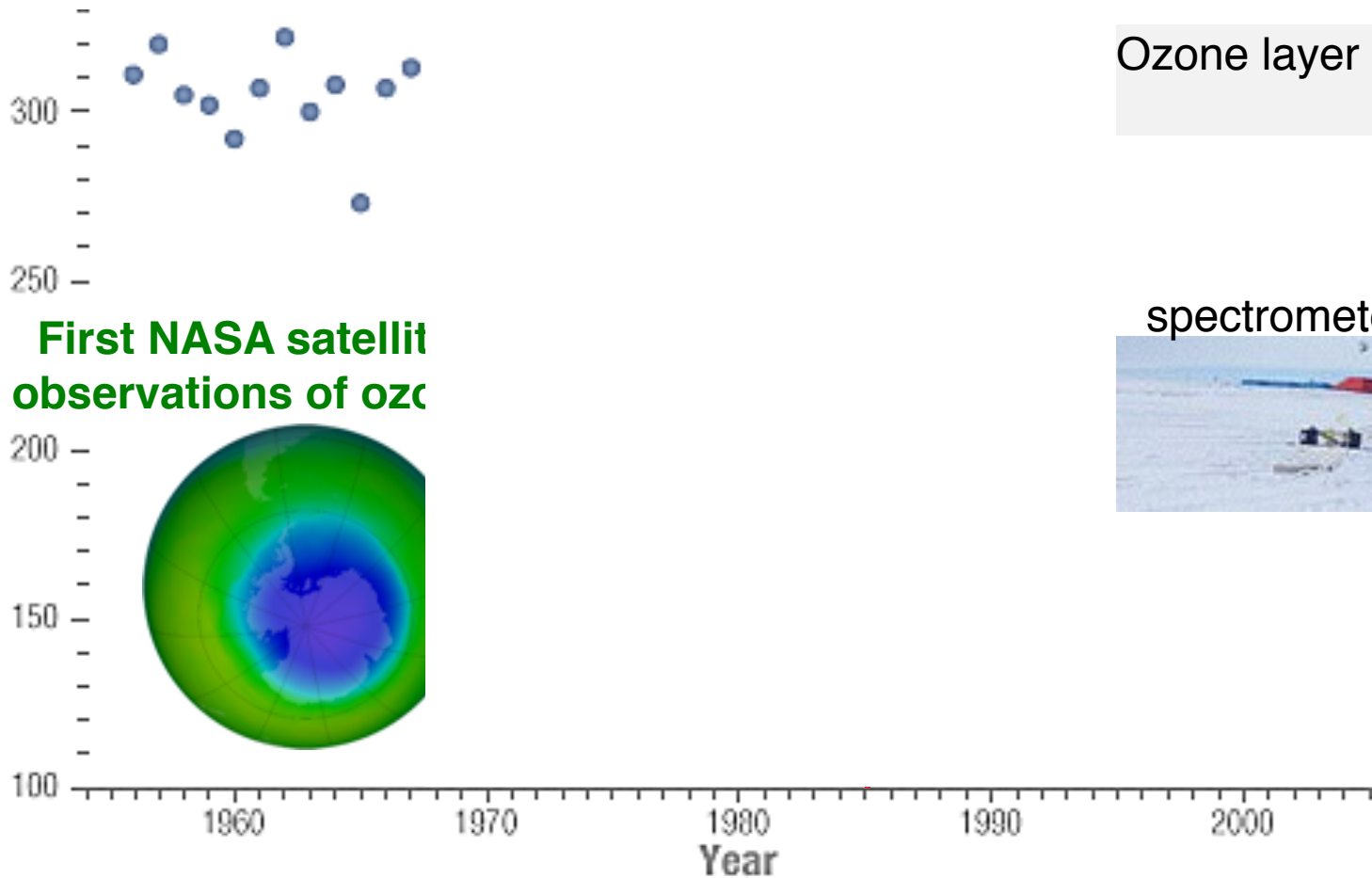
40 countries operate bases dedicated to scientific research



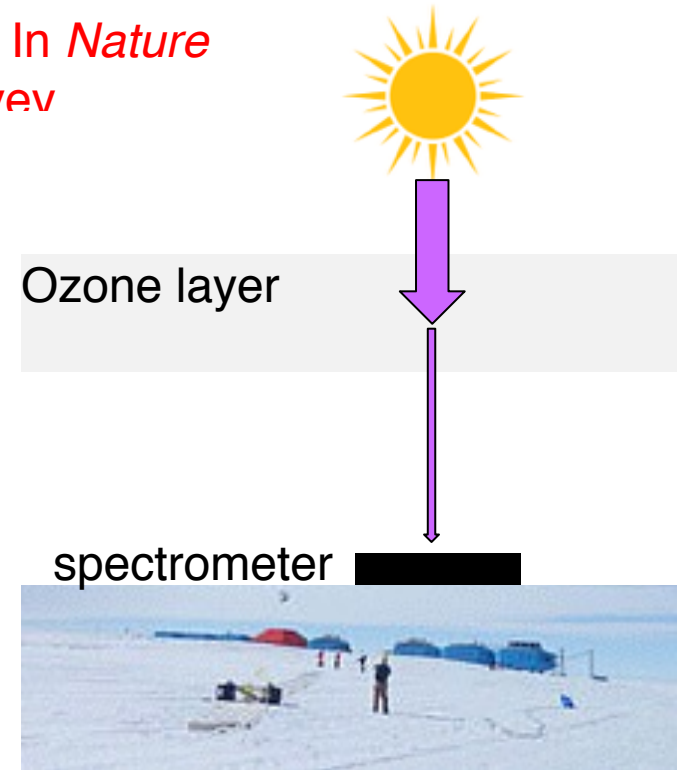
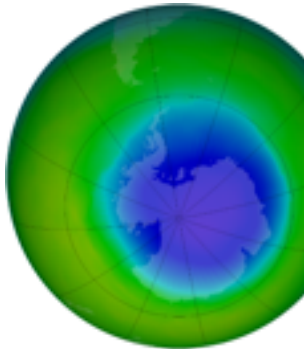
# Discovery of Antarctic ozone depletion at Halley Bay, Antarctica

1985: ozone hole first reported in *Nature*  
by British Antarctic Survey

Ozone layer thickness  
(October)



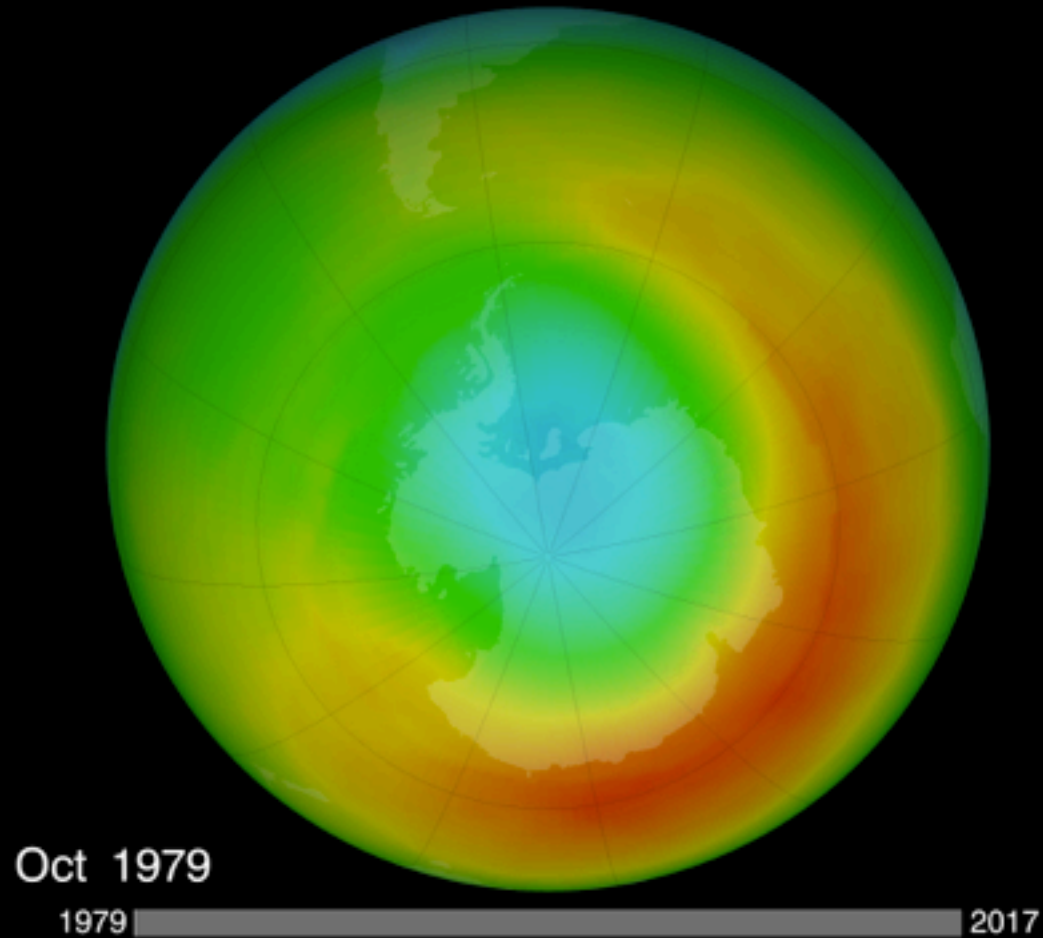
First NASA satellite observations of ozone



1 Dobson Unit (DU) = 0.01 mm pure ozone =  $2.69 \times 10^{16}$  molecules  $\text{cm}^{-2}$

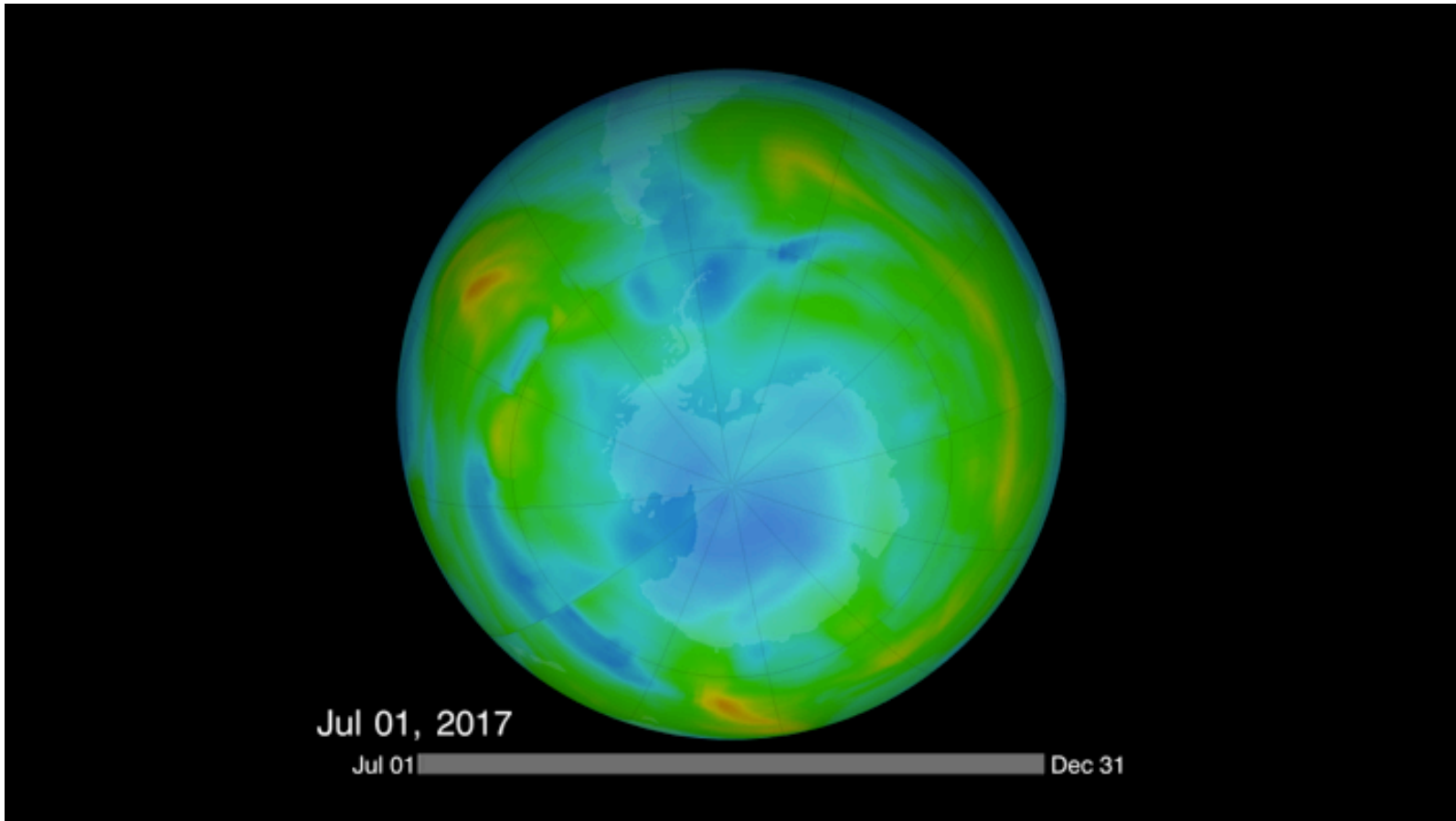


# Satellite data show recurrence of ozone hole every austral spring



# Ozone hole is a seasonal phenomenon

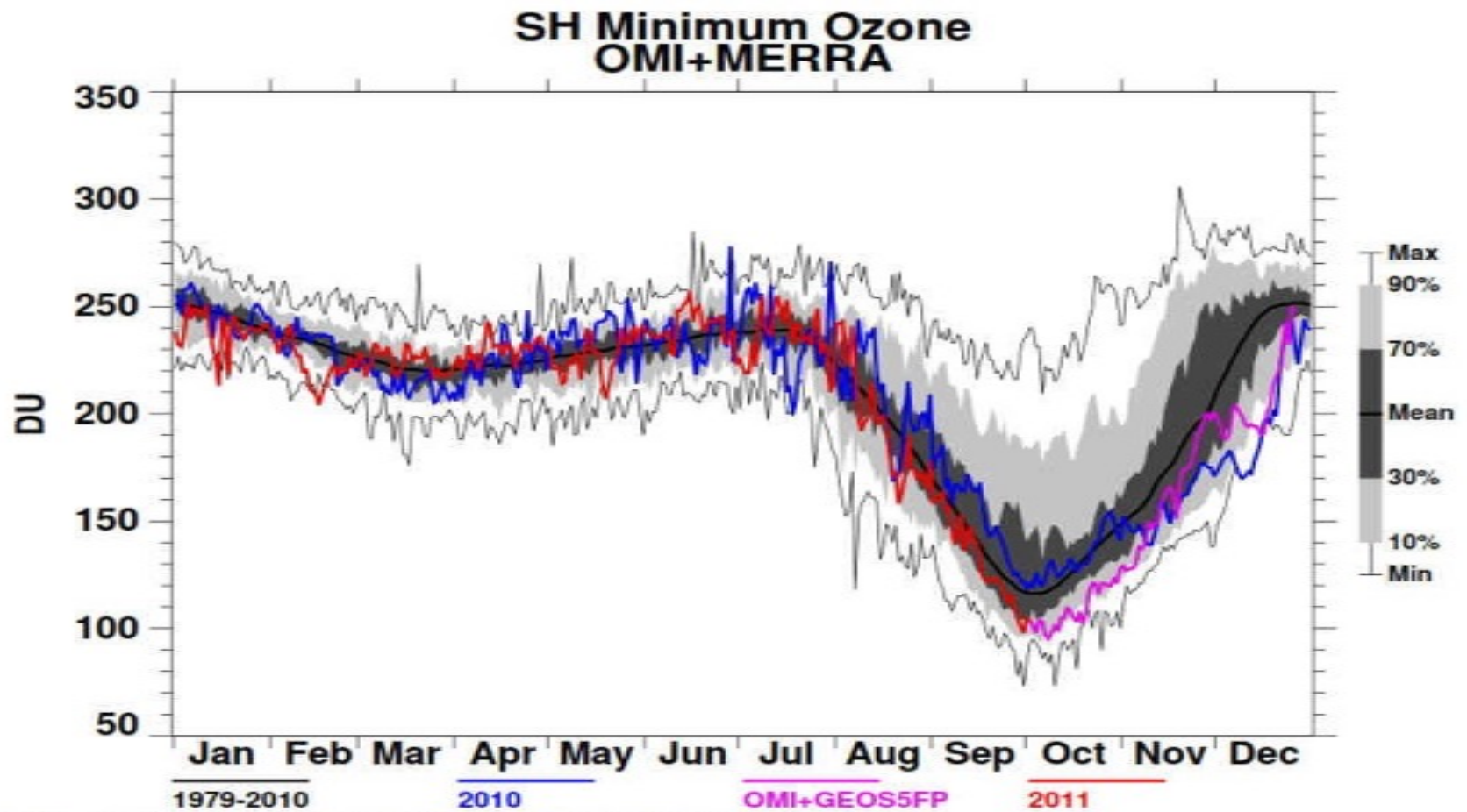
it develops in austral spring (September-October) and is gone by December



Isolated concentric region around Antarctic continent is called the *polar vortex*.  
Strong westerly winds, little meridional transport

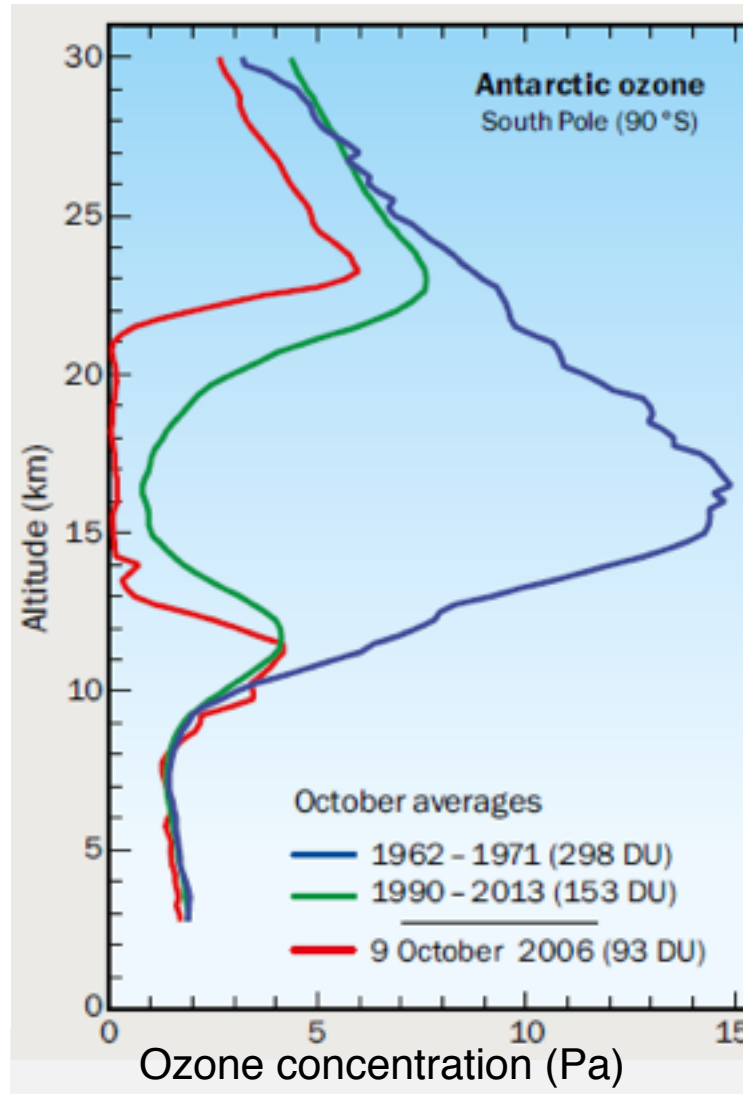
<http://ozonewatch.gsfc.nasa.gov/>

# Magnitude of springtime ozone depletion in ozone hole



P. Newman (NASA), E. Nash (SSAI), S. Pawson (NASA), R. McPeters (NASA)

# Vertical structure of ozone hole: near-total depletion in lower stratosphere

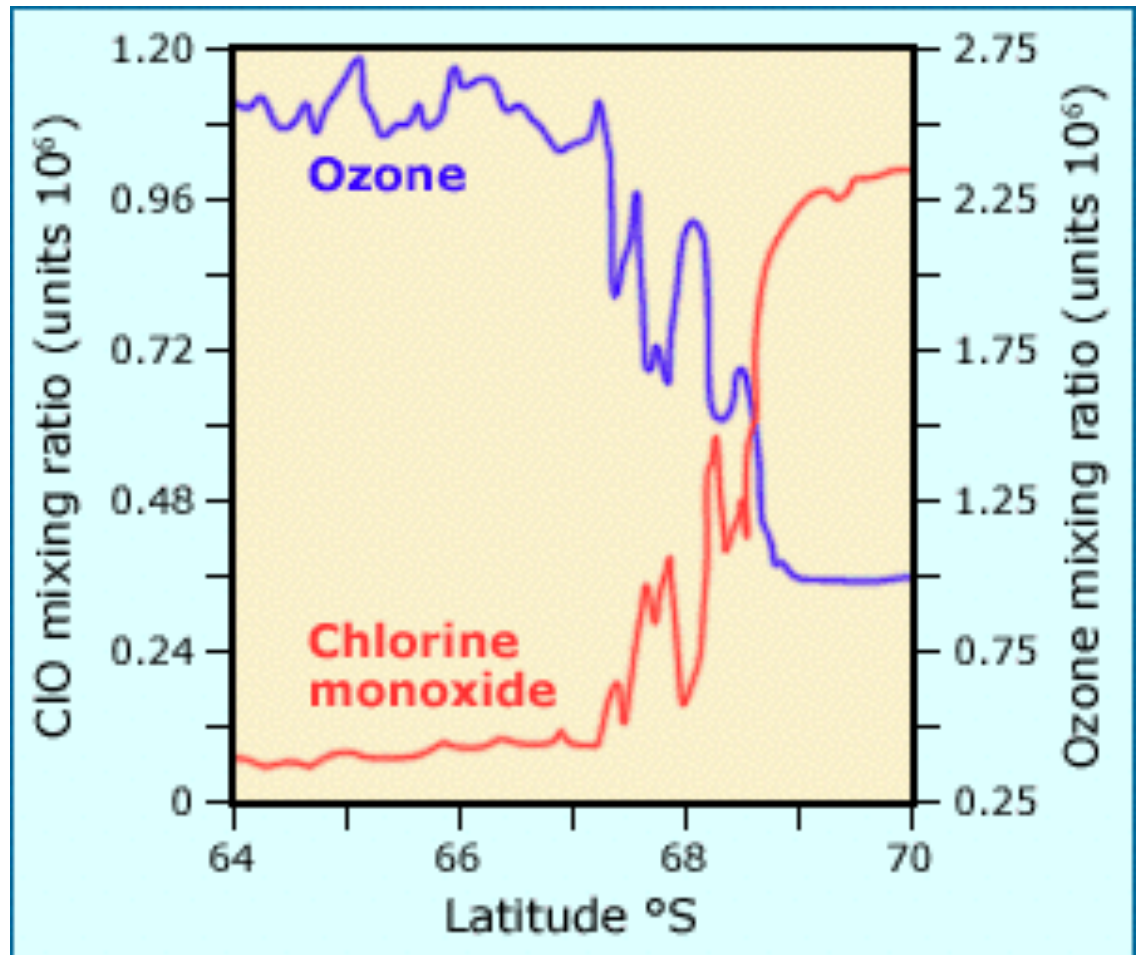


# What is the cause of the ozone hole?

Spring 1987 NASA ER-2 mission  
from Punta Arenas, Chile

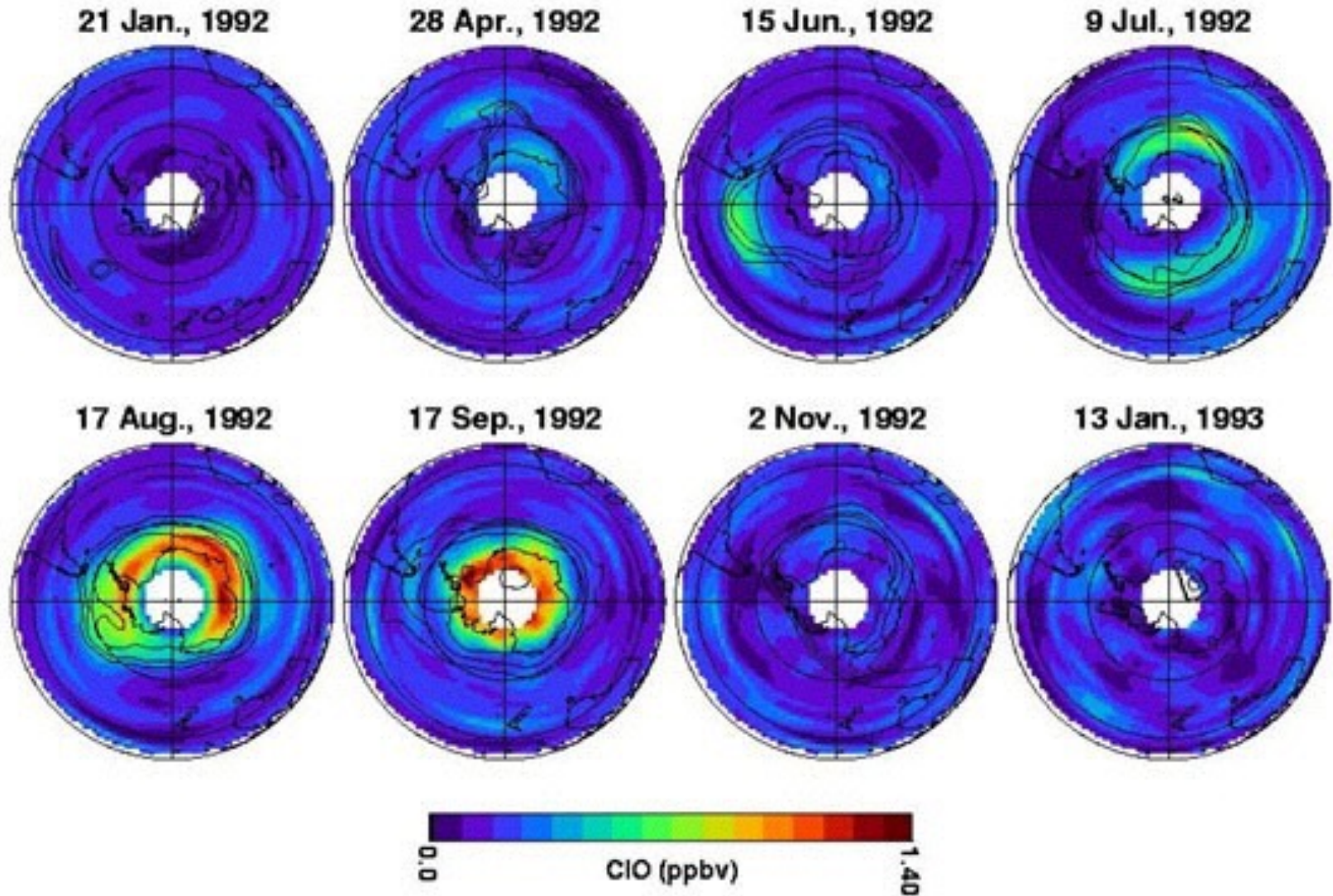


Ozone-destroying chlorine produced from CFCs

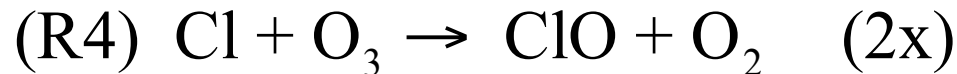
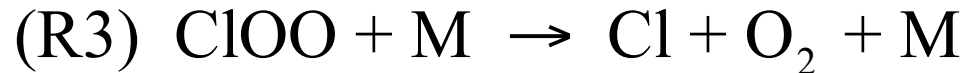
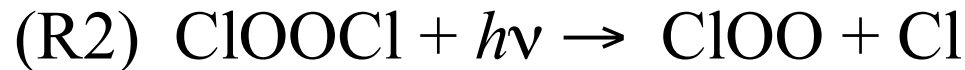


# SATELLITE OBSERVATIONS OF ClO IN THE SOUTHERN HEMISPHERE STRATOSPHERE

## MLS ClO 20 km



## Mechanism for ozone depletion when ClO is high



Ozone loss rate: 
$$-\frac{d[\text{O}_3]}{dt} = 2k_1[\text{ClO}]^2[\text{M}]$$

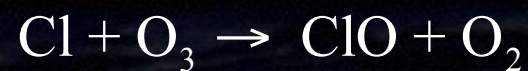
# Conversion of Cl reservoirs to ClO in polar stratospheric clouds (PSCs)

HCl, ClNO<sub>3</sub>

Cl<sub>2</sub>  $\xrightarrow[\text{fast}]{h\nu}$

Cl

ozone  
destruction

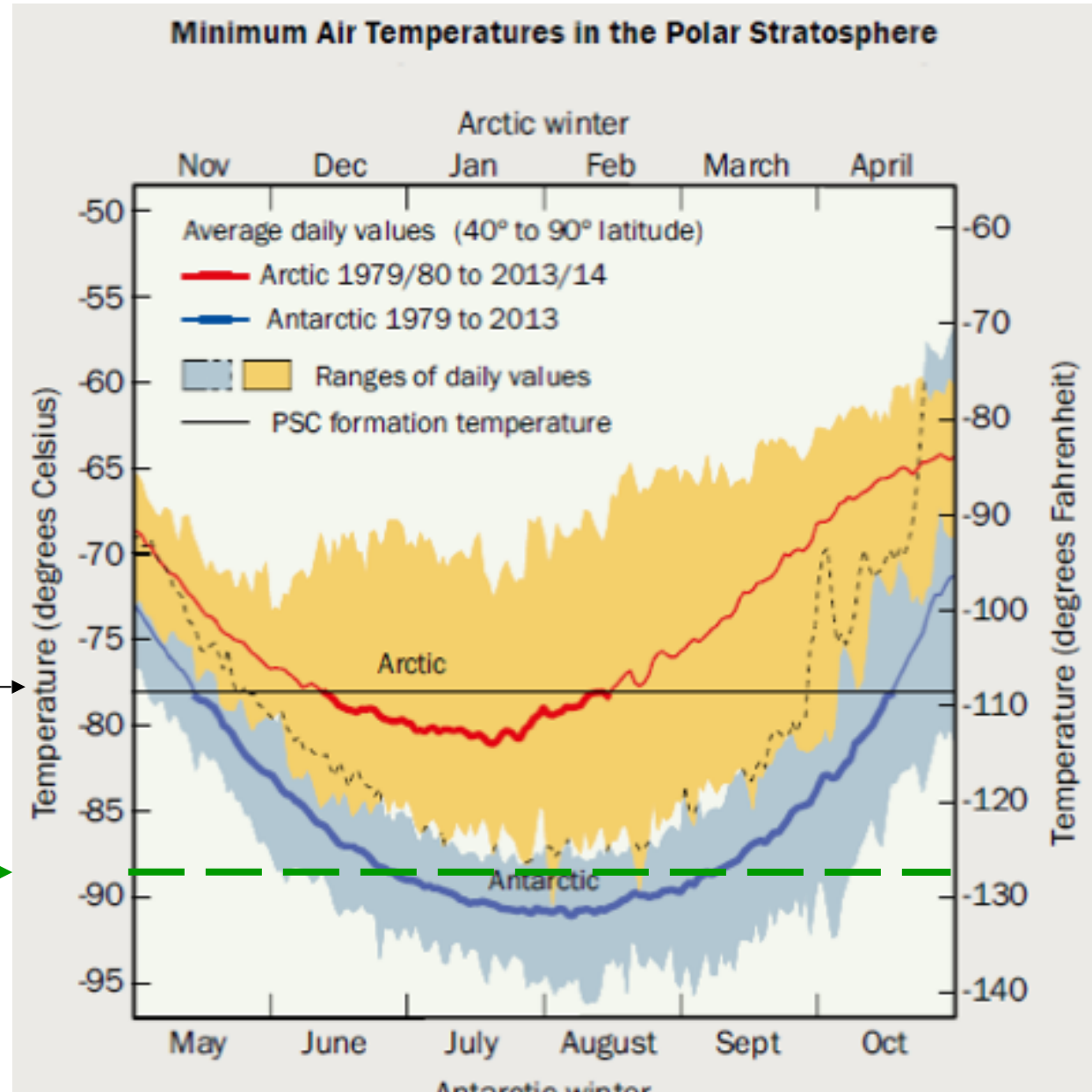


...

Polar stratospheric clouds  
over McMurdo, Antarctica



Polar stratospheric clouds require very cold conditions, found mainly in Antarctic stratosphere in winter

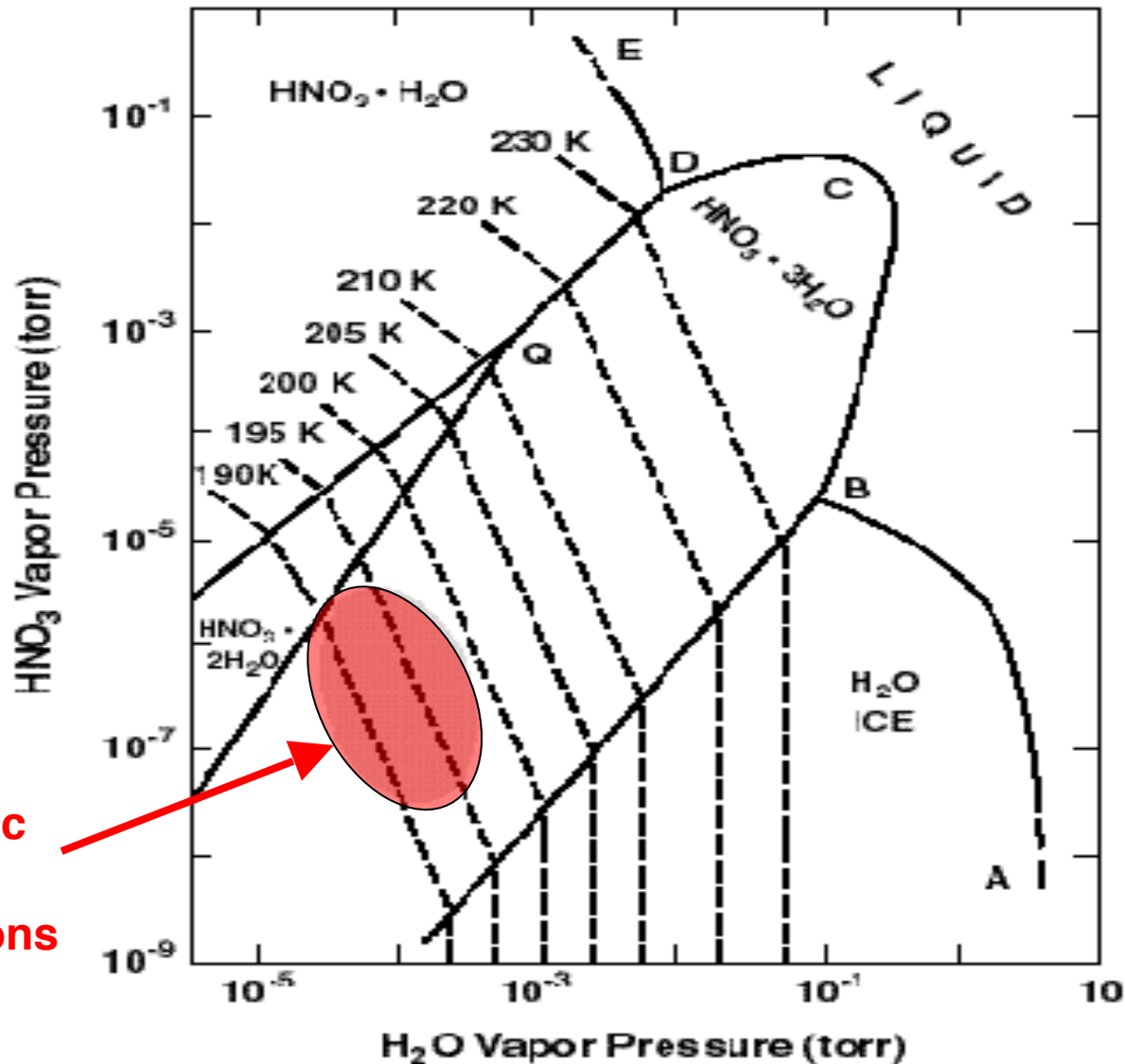


PSC formation →

Frost point of water →

# HOW DO PSCs START FORMING AT 195K?

## HNO<sub>3</sub>-H<sub>2</sub>O PHASE DIAGRAM



Antarctic  
vortex  
conditions

PSCs are not water but nitric acid trihydrate (NAT) clouds

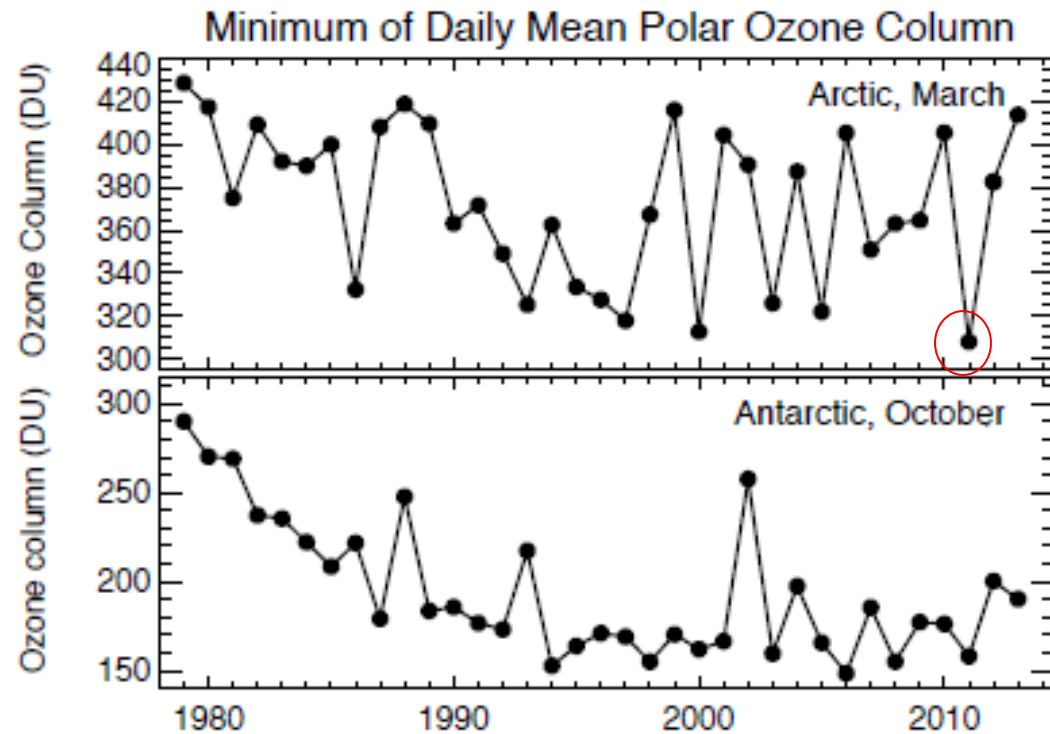
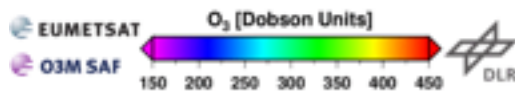
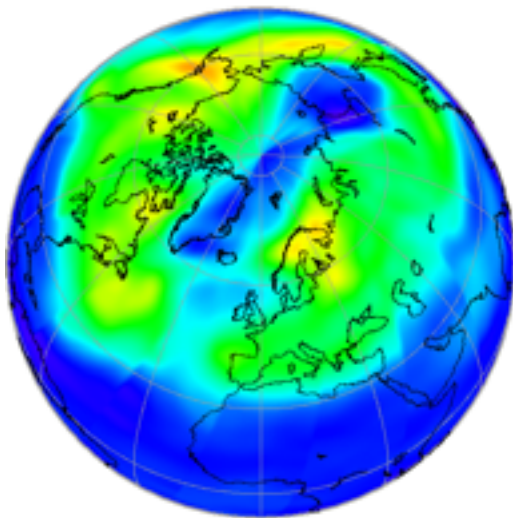
**Polar stratospheric clouds occur in Arctic too  
but much more rarely**



# Embryo of ozone hole is occasionally seen in Arctic following cold winters

GOME-2/METOP-A Ozone 2011-03-23

<http://atmos.caf.dlr.de/gome2>

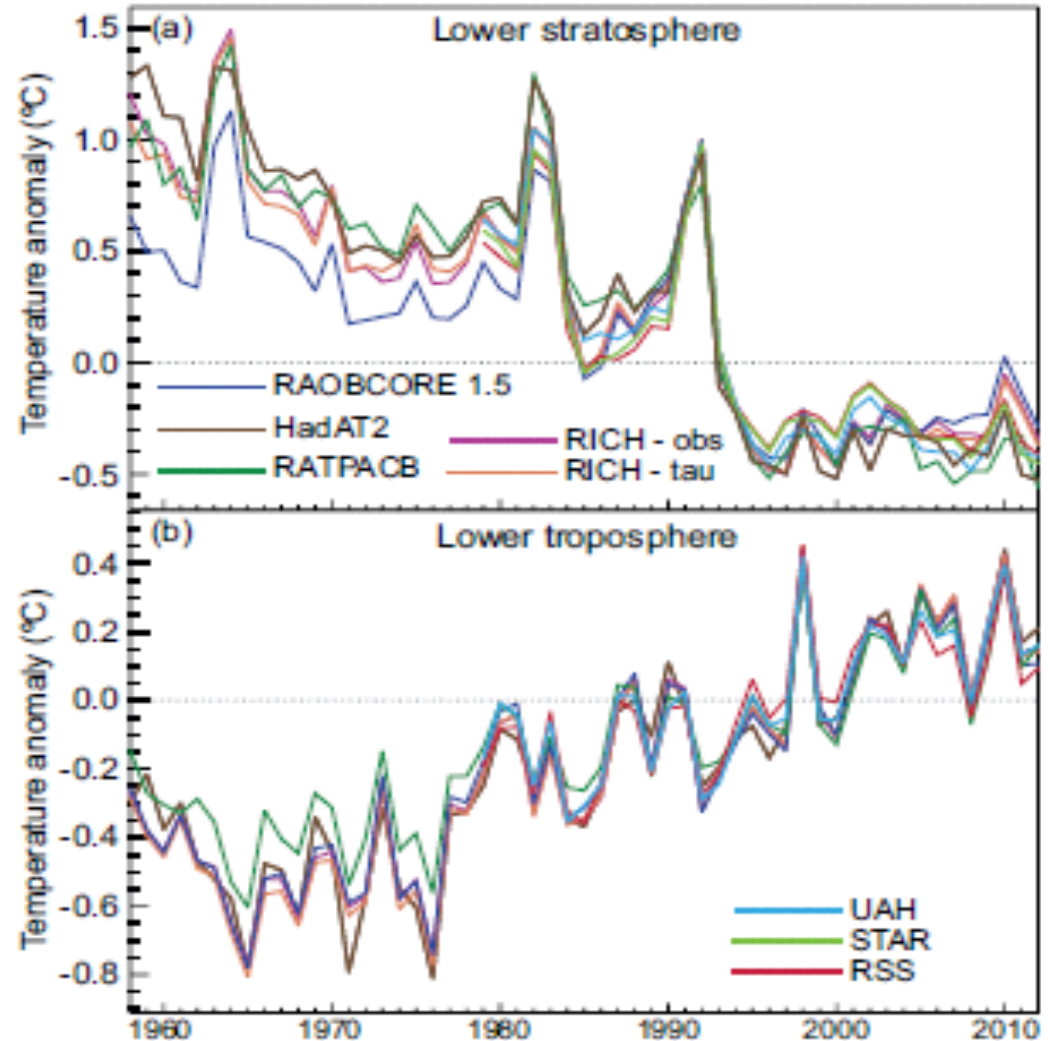
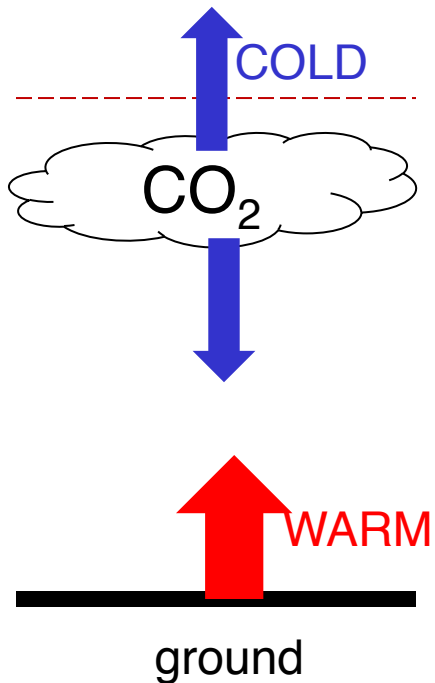


# Rising CO<sub>2</sub> warms the surface but cools the stratosphere

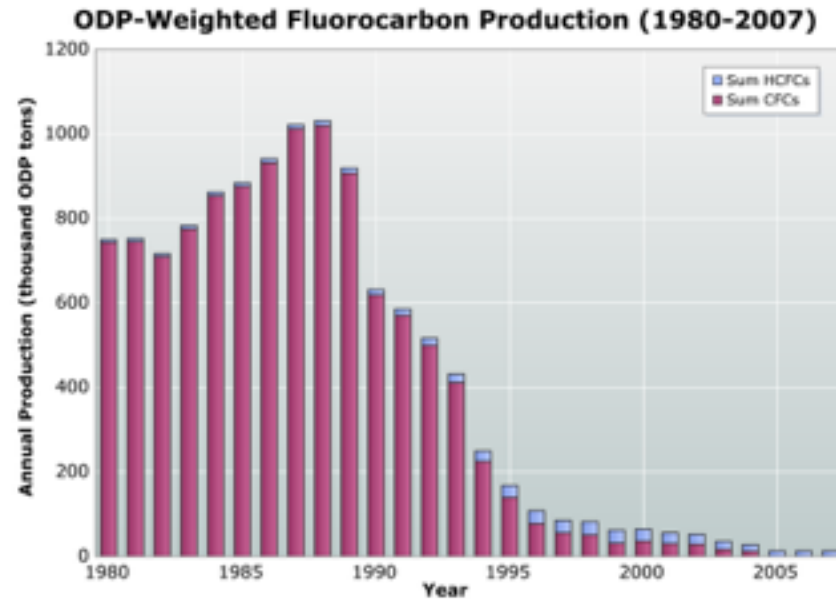
stratosphere

tropopause

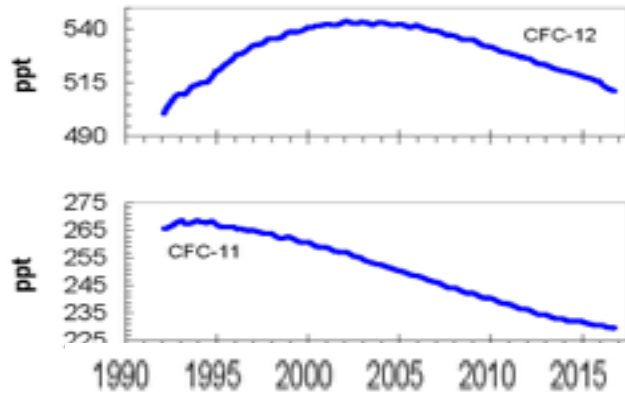
troposphere



# Montreal Protocol (1987-1996): global ban of CFC production

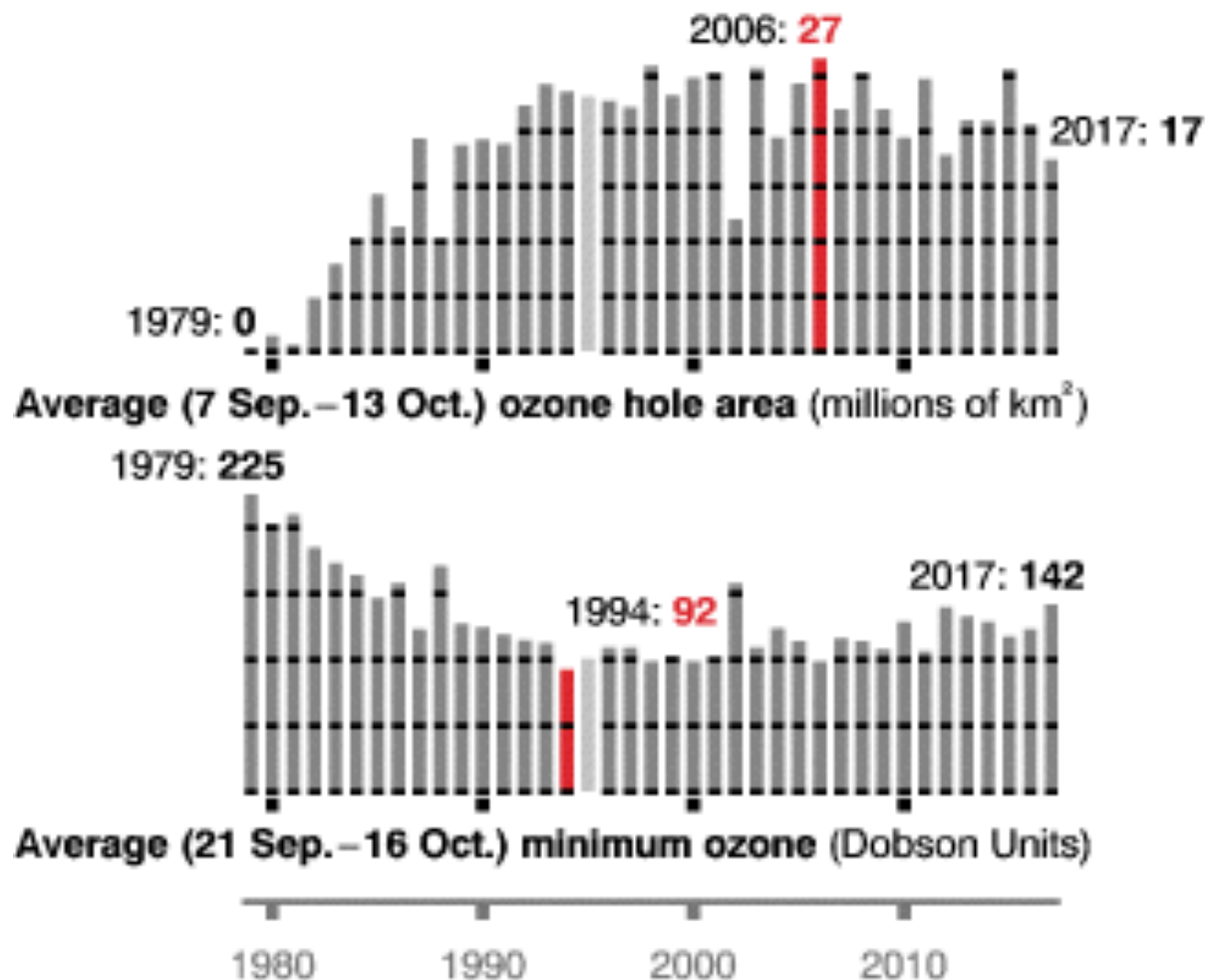


...but CFCs have long lifetimes in the atmosphere so ozone hole will remain for decades



Atmospheric CFC concentrations  
(NOAA ESRL data)

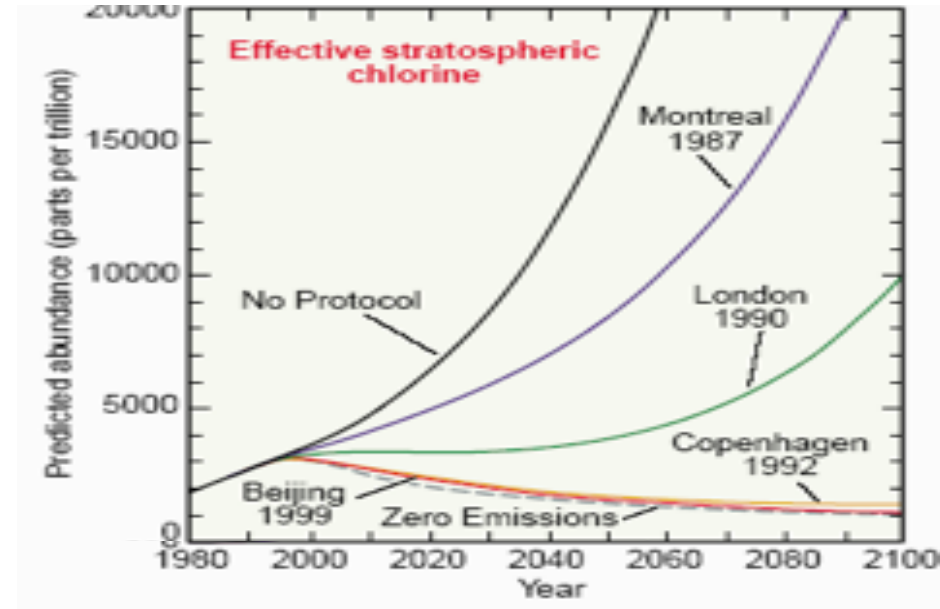
There is tentative evidence that Antarctic ozone recovery has begun



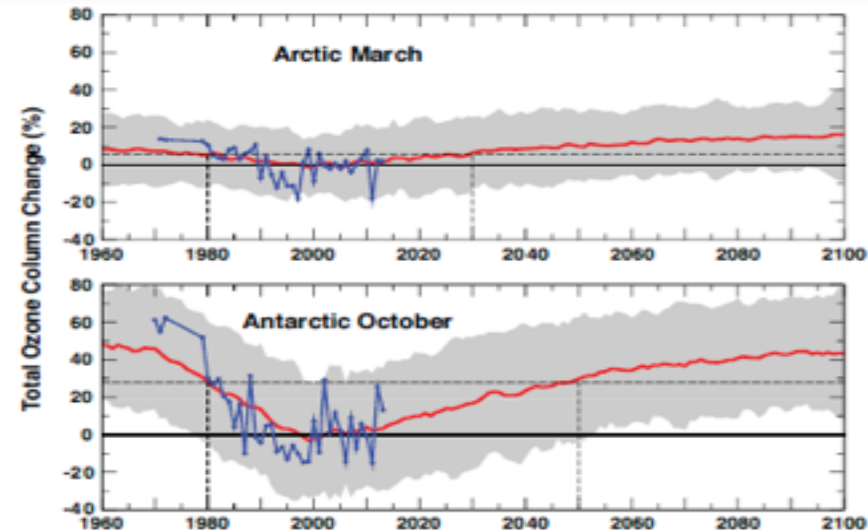
**Note:** No data were acquired during the 1995 season

# Montreal Protocol as model for successful global environmental action

Montreal Protocol and its amendments have reversed the stratospheric chlorine trend



Antarctic ozone hole is on its way to recovery, Arctic ozone hole appears to have been avoided





# Questions

1. If temperatures in the wintertime Antarctic stratosphere were not so cold, the ClO dimer would thermally decompose by  $\text{ClOOCI} + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M}$  rather than photolyze. What would be the effect of this thermolysis on Antarctic ozone depletion?
2. Satellite observations of ClO in the Antarctic stratosphere in the middle of winter show a “collar” of maximum values around 60°S. Why isn't ClO highest over the South Pole, where temperatures would be lowest?