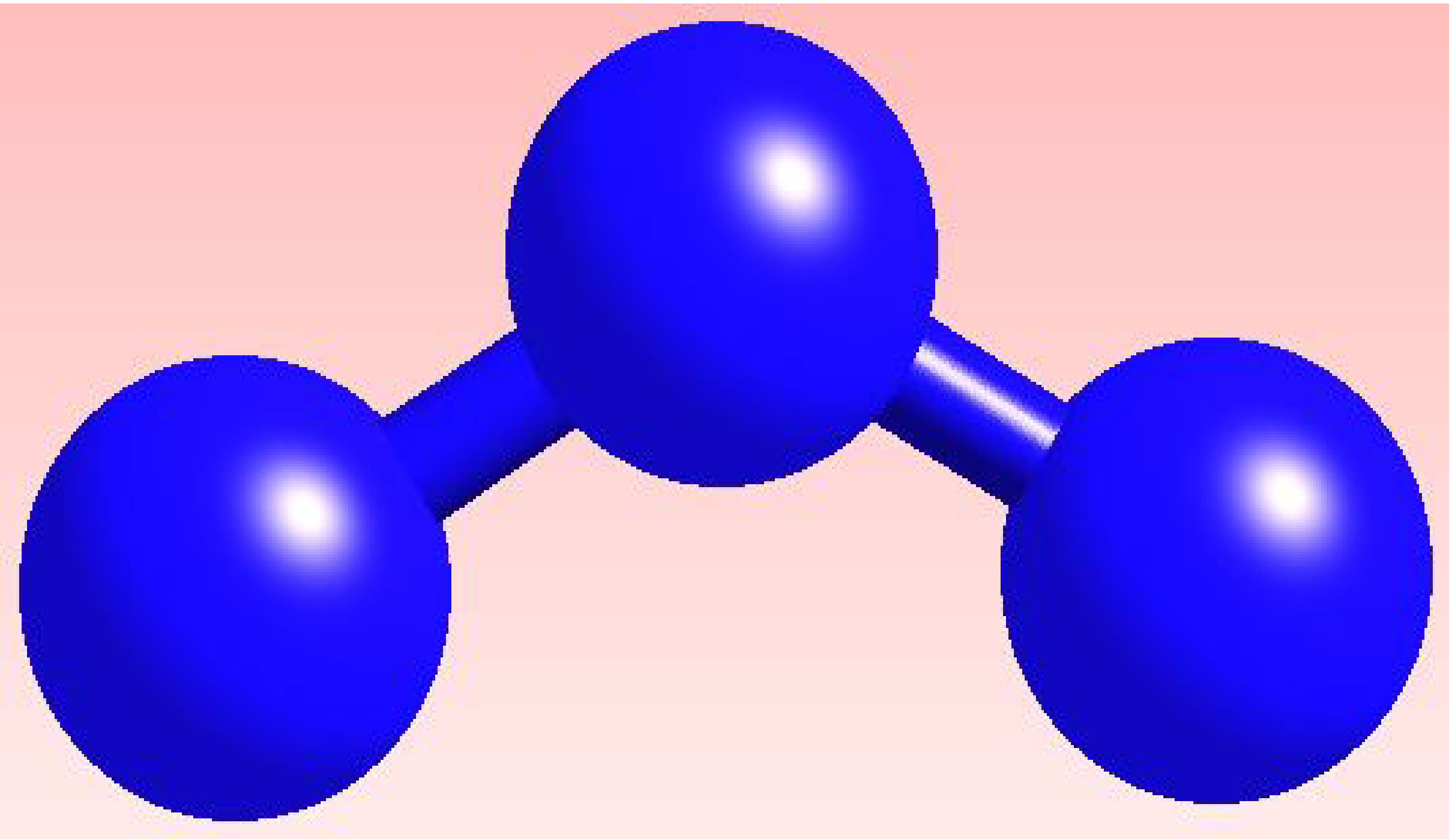
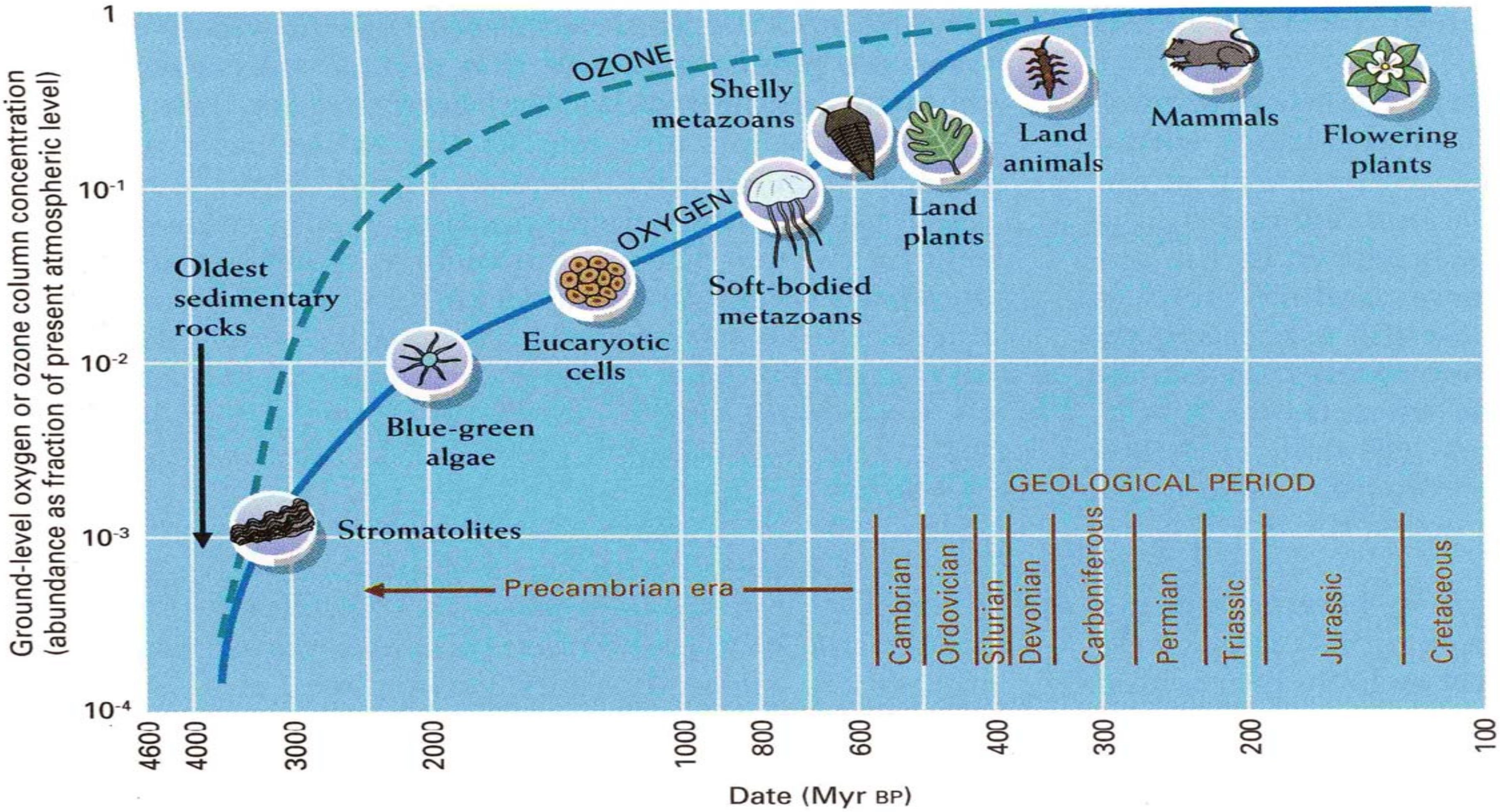
# Lecture 5

# Ozone, Ozone Hole, and Climate



# Molecular Oxygen ($O_2$, O—O)

- 2 BY ($10^9$ yrs): atmopheric $O_2$ reach 1% of present value
- 700 MY ($10^6$ yrs): atmospheric $O_2$ reach 10% of present value
- 350 MY ($10^6$ yrs): atmopheric $O_2$ reach 100% of present value



**A reconstruction of the evolutionary development of oxygen and ozone in Earth’s atmosphere. Land-based life could not have become established without sufficient ozone to provide protection against ultraviolet radiation. The oxygen curve is based on evidence from rocks and fossils; the ozone curve was developed from a photo-chemical computer model..**

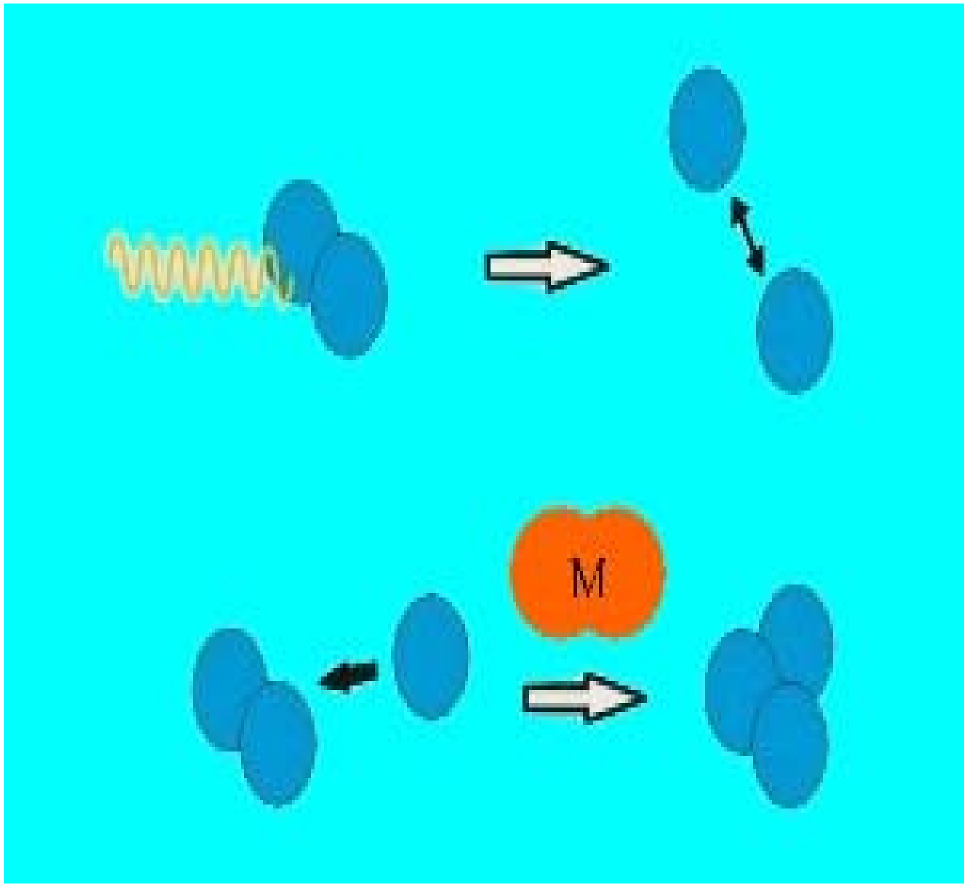
$\tilde{\nu}$

# Photon of Energy

$E = h\tilde{\nu} = hc/\lambda$ (Planck law)

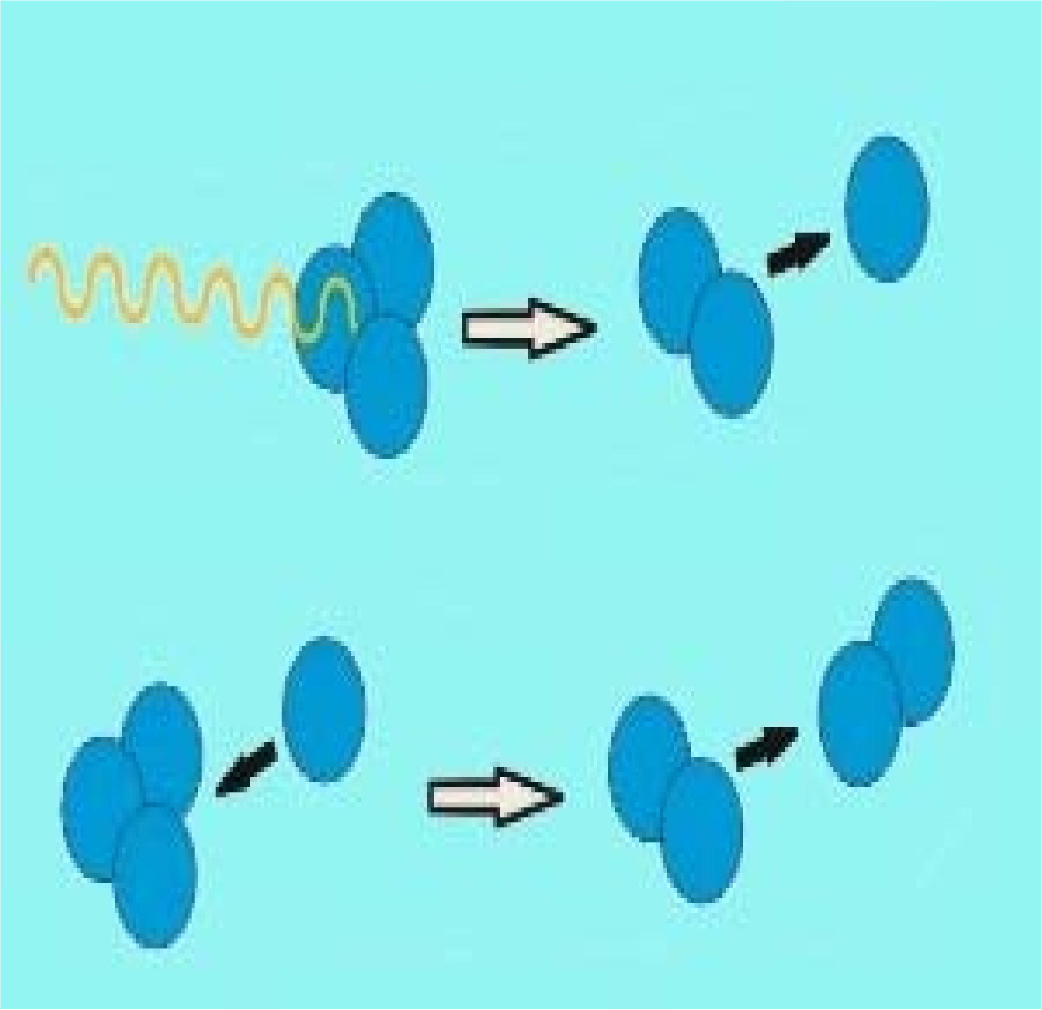
where

$h$ = Planck constant = $6.626 \times 10^{-34}$ J sec
$\tilde{\nu}$ = frequency
$c$ = velocity of light ~ $10^{8}$ m/sec
$\lambda$ = wavelength



# Ozone formation and destruction

Two forms of oxygen are found in the stratosphere. Molecular oxygen ($O_2$), which is made up of two atoms of oxygen (O), and ozone ($O_3$) which, as you can see from its chemical formula, is made up of three oxygen atoms. Ozone is formed when intensive ultra-violet radiation from the Sun breaks down $O_2$ into two oxygen atoms. These highly reactive oxygen atoms can then react with more $O_2$ to form $O_3$.



In a similar way, ozone is destroyed by solar radiation. Ultraviolet radiation hits ozone and breaks it back down into molecular oxygen ($O_2$) and atomic oxygen (O). The oxygen atom O then reacts with another ozone molecule to form two oxygen molecules.

The UV-light is symbolized by violet flashes, which split the oxygen molecule ($O_2$) into two O atoms. The free O atoms each pair themselves up with another oxygen molecule, to form tri-atomic ozone ($O_3$) molecules. These ozone molecules can also be split up again by the ultra-violet light.

# Ozone Formation and Destruction (Stratosphere, 90%)

$$O_2 + h\tilde{\nu} \dashrightarrow O + O$$

$$O_2 + O + M \dashrightarrow O_3 + M$$

$$O_3 + h\tilde{\nu} \dashrightarrow O + O_2$$

$$O_3 + O \dashrightarrow 2\,O_2$$

# Destruction of $O_3$ (man-made effect)

$$X^* + O_3 \;{-}{-}\!\!\rightarrow\; XO^* + O_2$$

$$O_3 + h\tilde{\nu} \;{-}{-}\!\!\rightarrow\; O + O_2$$

$$O + XO^* \;{-}{-}\!\!\rightarrow\; X^* + O_2$$

Net Result: $2\,O_3 \;{-}{-}\!\!\rightarrow\; 3\,O_2$

Note: X* and XO* are free radicals (molecular fragments)
* denotes odd # of electrons, highly reactive

# Sources of Free Radicals

**$O_3$ + $h\tilde{\nu}$** (highly energetic photons, $\lambda < 0.31\ \mu m$)
--→ **$O_2$ + $O^*$** (highly excited, unstable)

1. Water vapor ($H_2O$)

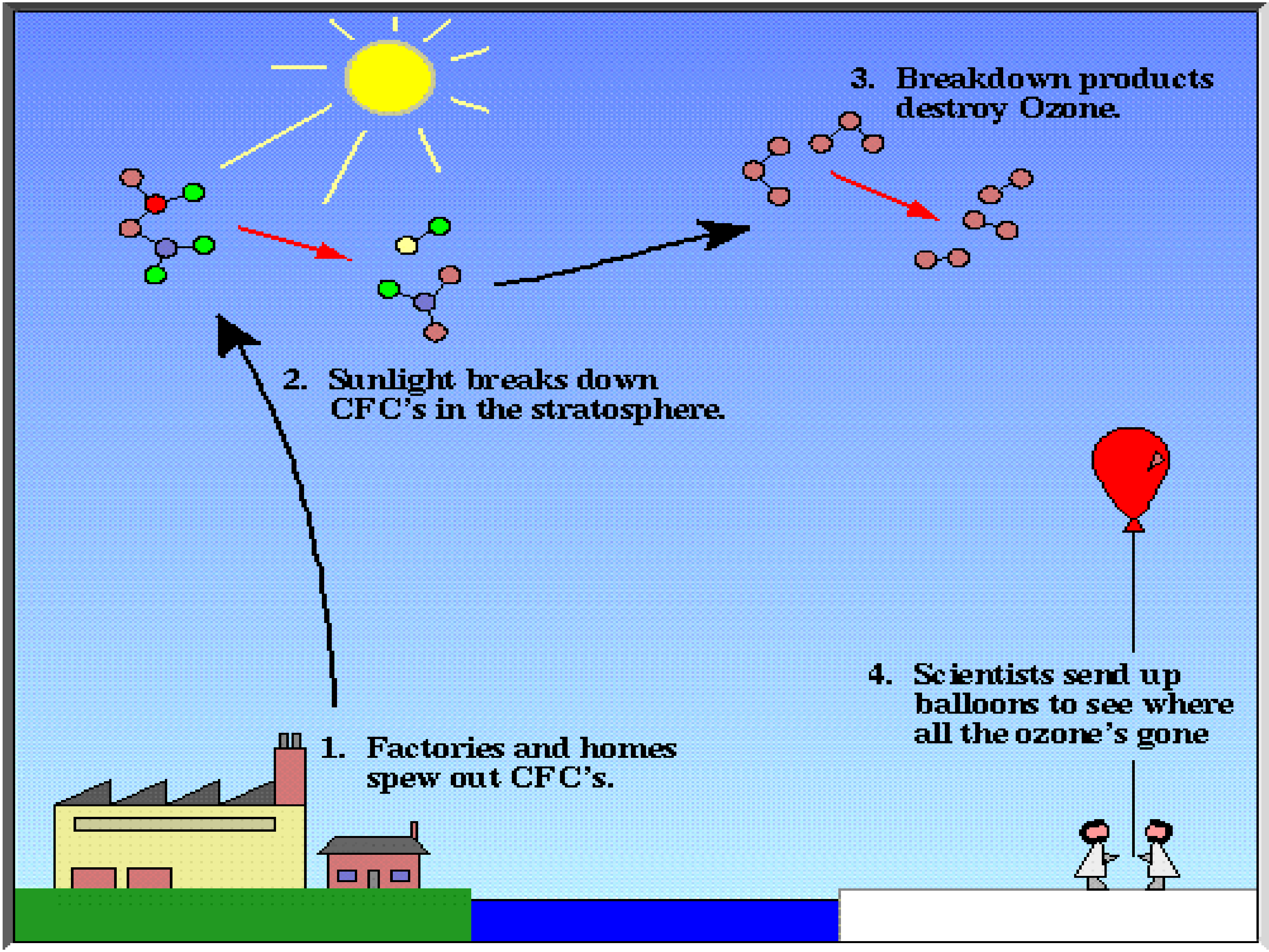
   **$H_2O$ + $O^*$ --→ 2 $HO^*$** (hydroxyl radicals)

2. Nitrogen dioxide ($N_2O$): microbiological processes in solids/oceans)

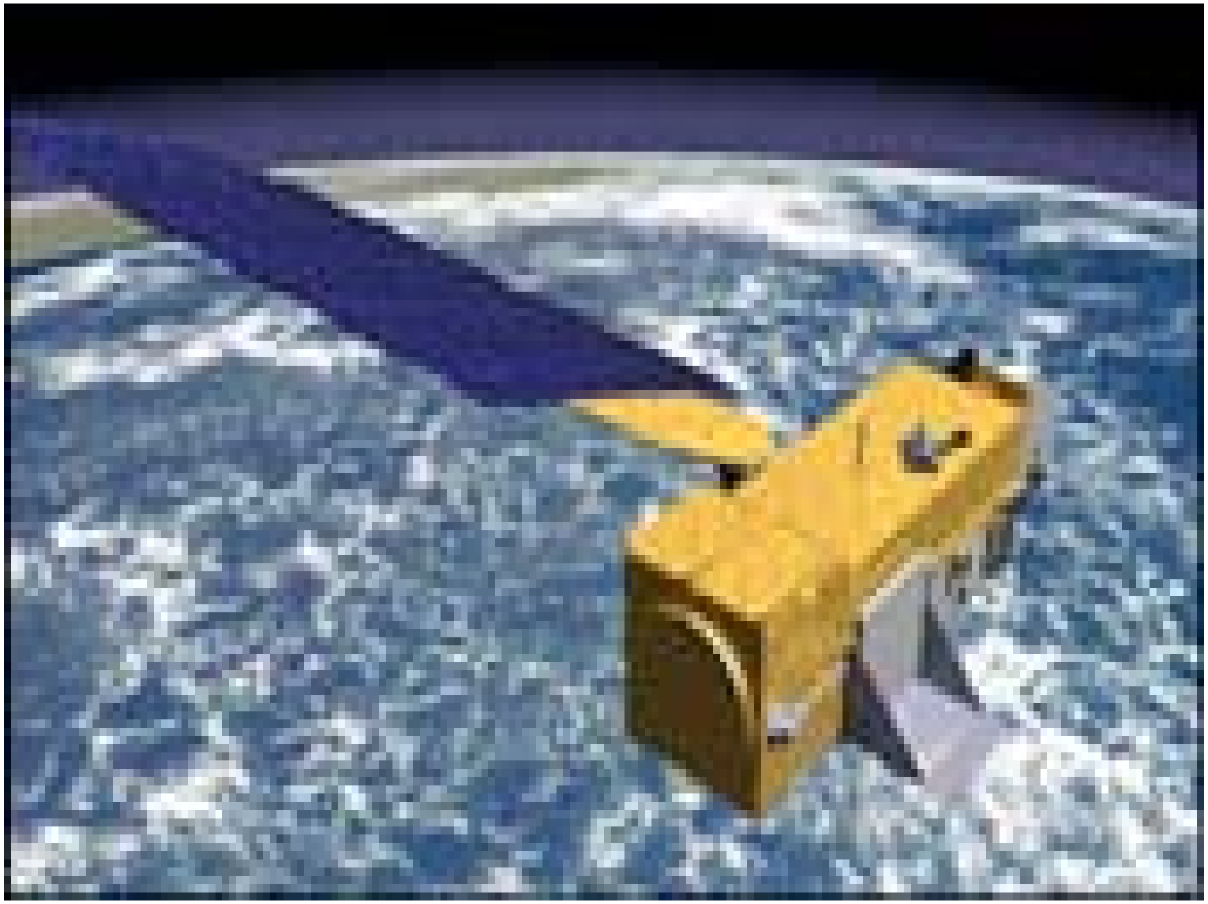
   **$N_2O$ + $O^*$ --→ 2 NO** (nitric oxide)

3. Chlorine (**Cl**): man-made chlorofluorocarbons (**CFCs**)

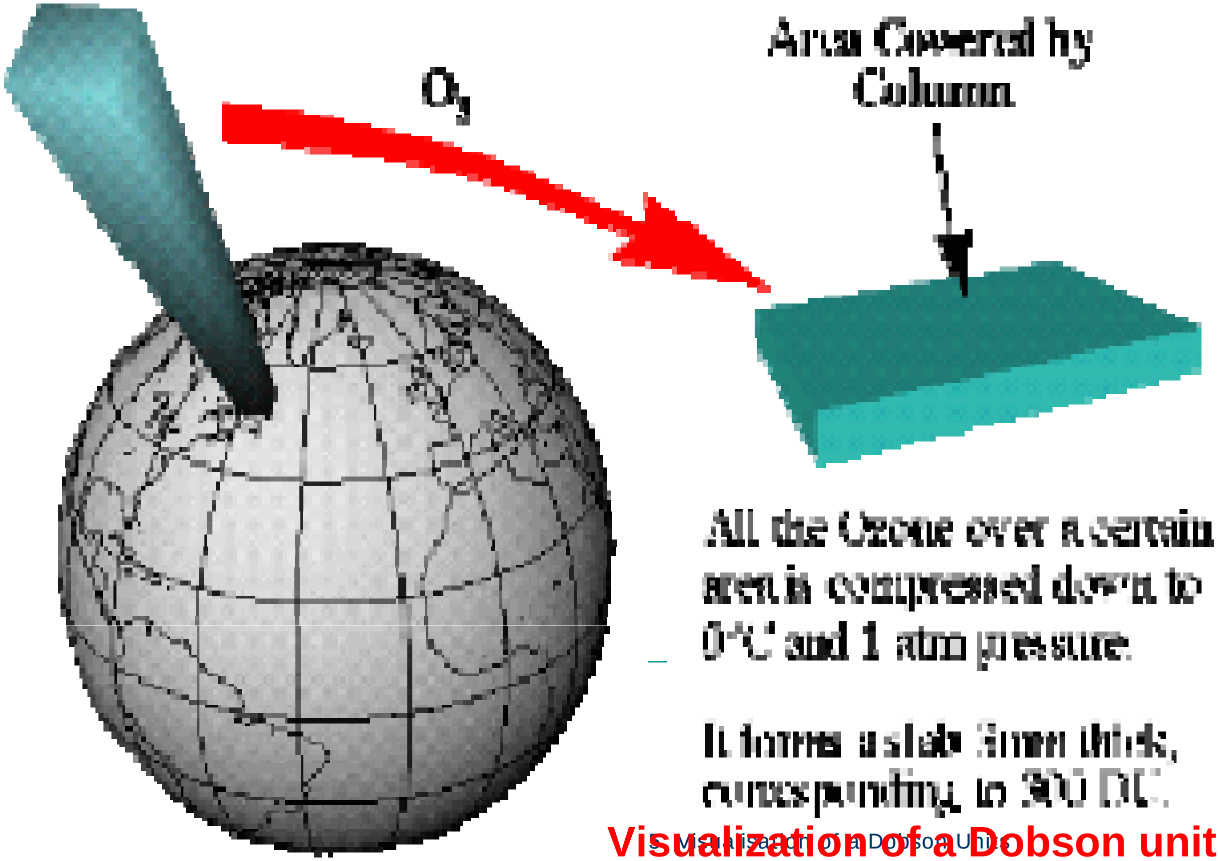
Note: **$X^*$ = Cl, NO, and HO**



1. Factories and homes spew out CFC’s.
2. Sunlight breaks down CFC’s in the stratosphere.
3. Breakdown products destroy Ozone.
4. Scientists send up balloons to see where all the ozone’s gone



**Satellite Observation of ozone**: NASA's Aura satellite launched in 2004 will observe the composition, chemistry and dynamics of the Earth's upper and lower atmosphere, including temperatures and ozone amounts.



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

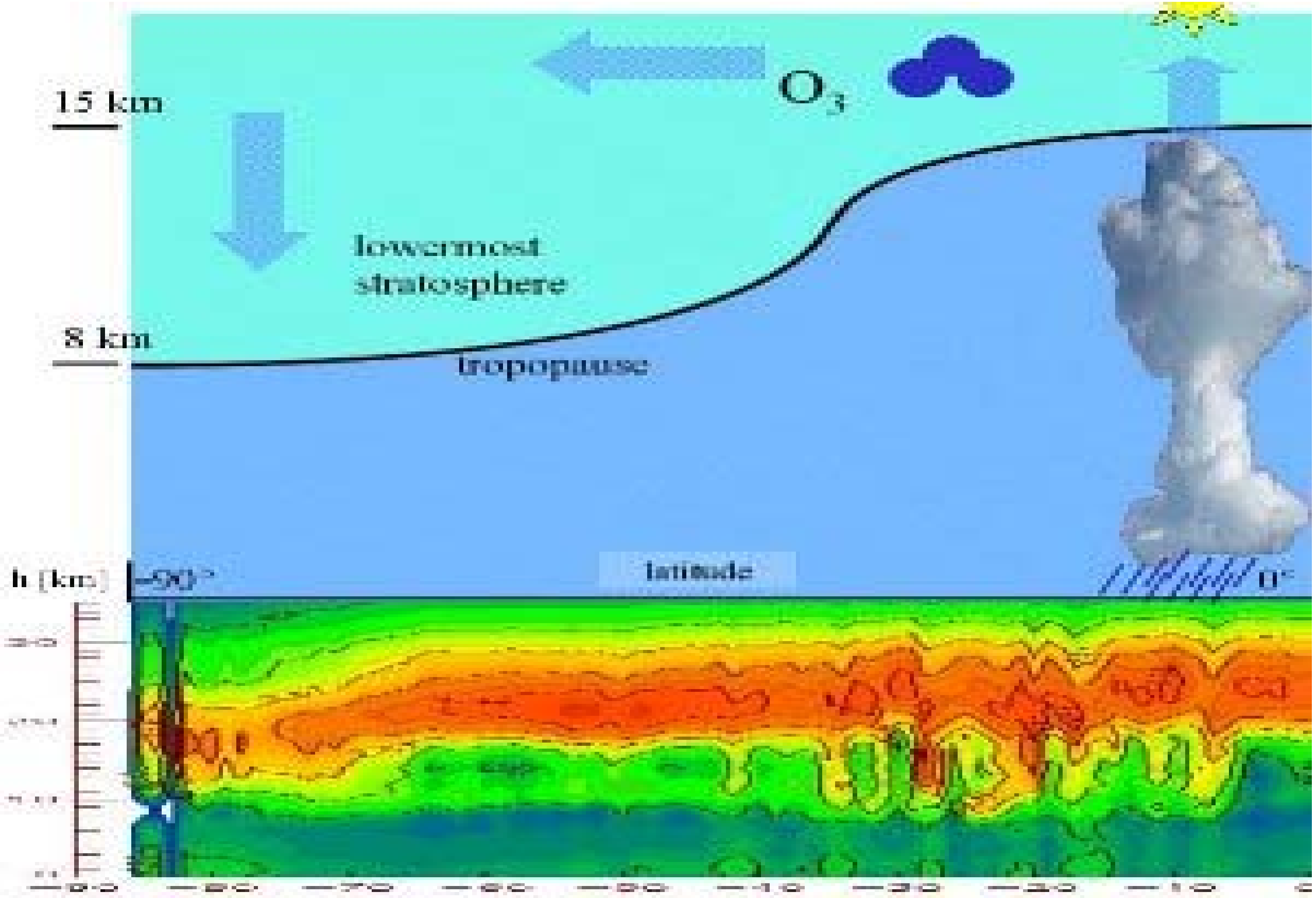
It forms a slab 3mm thick, corresponding to 300 DU.

Visualization of a Dobson units

5. Visualisation of a Dobson Units

## Dobson units (DU)

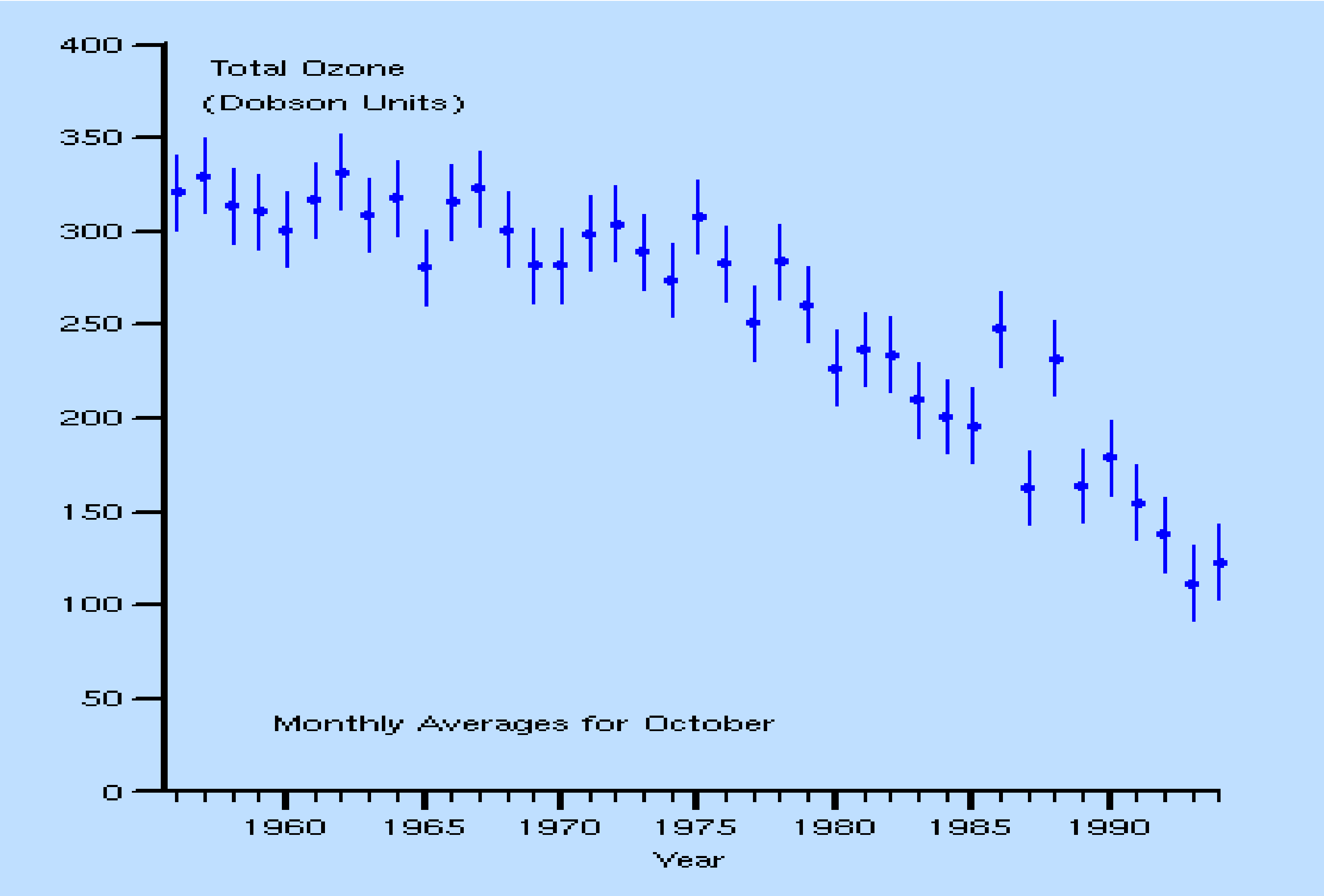
**300 DU is a typical ozone value. But what does this mean? If we assume that all the ozone molecules in the atmosphere were concentrated in a small layer at the ground, then thickness of this layer would be about 3 mm. Since 1 DU is equivalent to a layer of pure ozone molecules 0.01 mm thick, a 3 mm layer of ozone is equivalent to a value of 300 DU.**



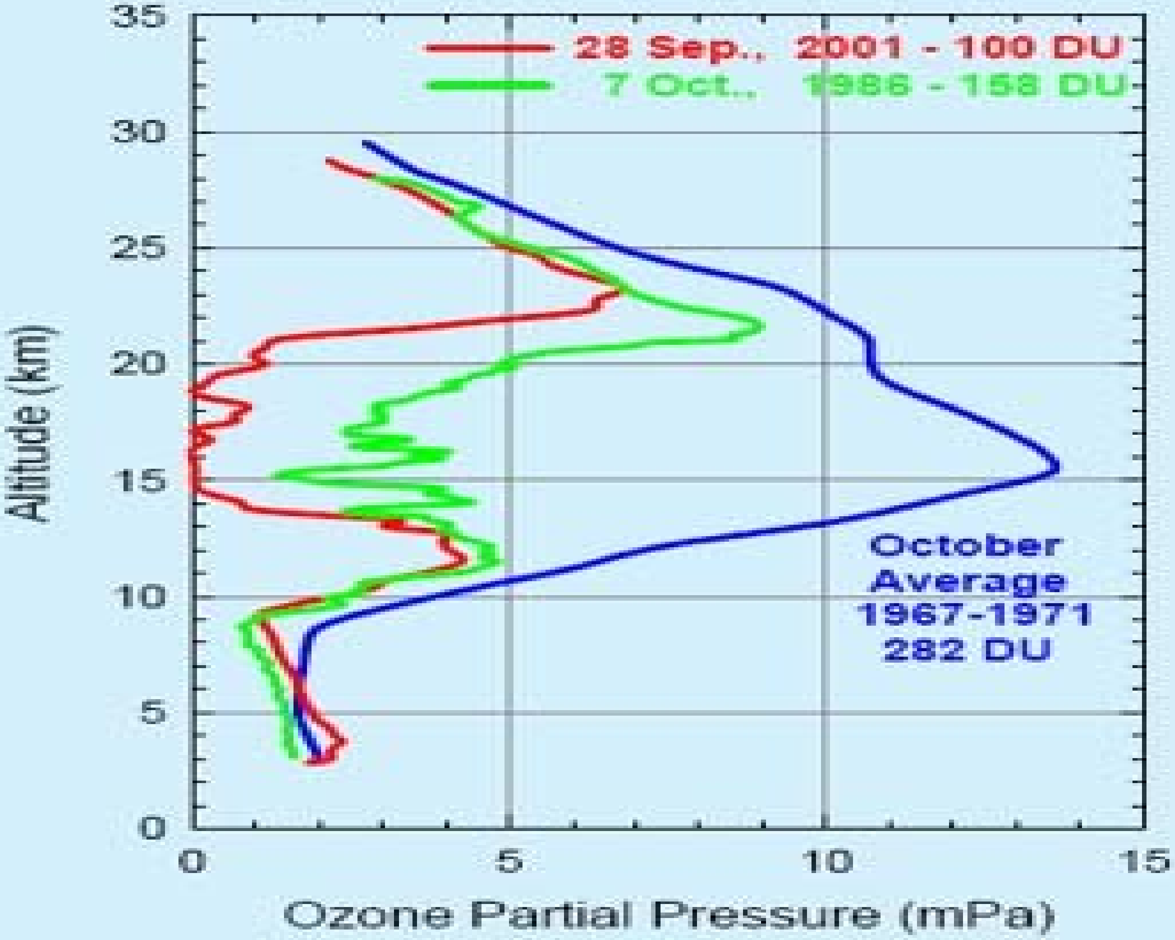
This scheme shows ozone transport and how measured ozone concentrations vary between the poles and the equator (low values = blue, high values = red). It also shows air containing low ozone levels rising at the equator to high latitudes.

# Ozone Hole

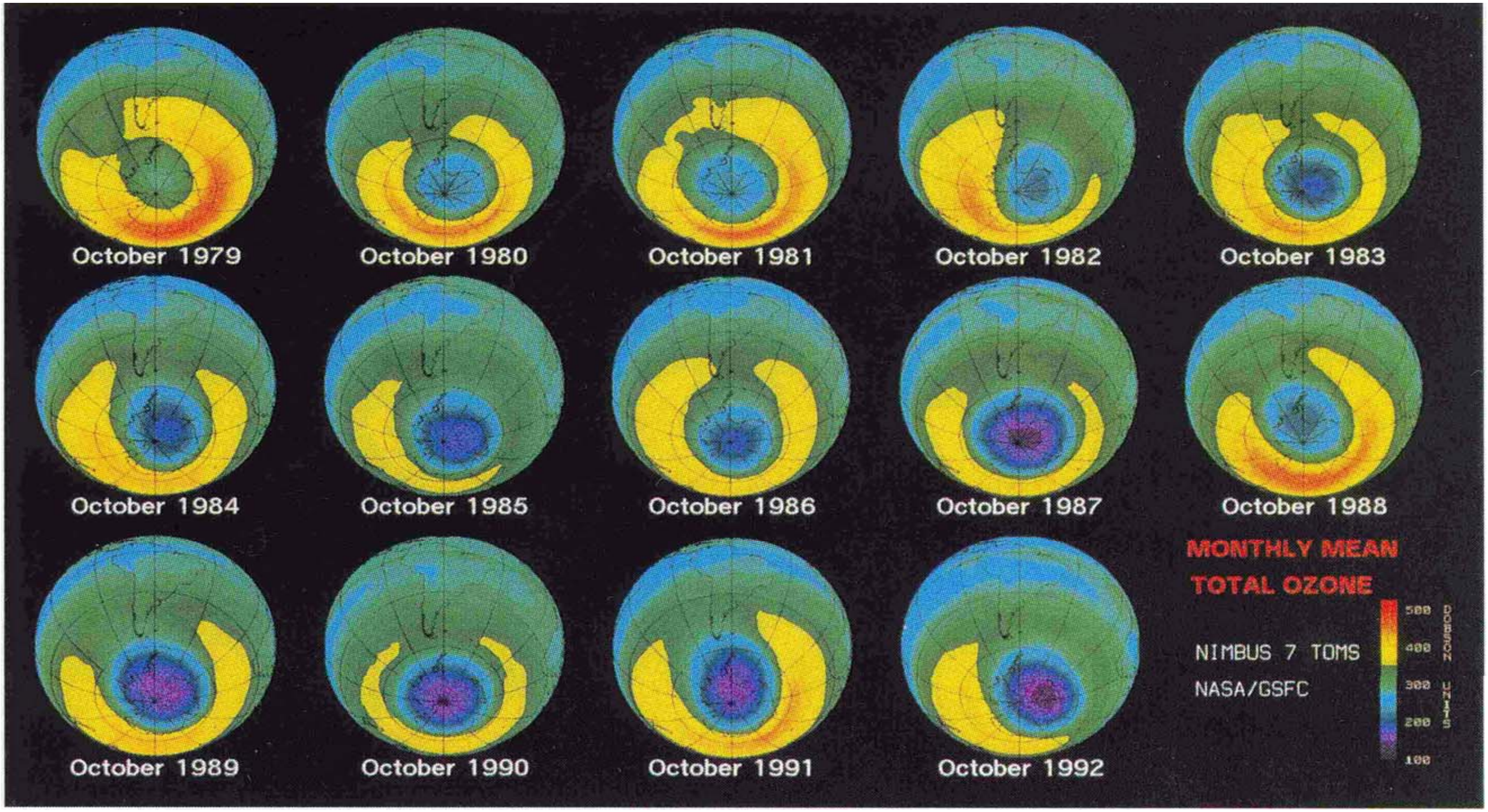
Because of peculiar meteorological conditions (polar vortex), ozone destruction by CFCs and others is particularly severe over Antarctica, giving rise to an "**Ozone Hole**"



**Monthly mean values (horizontal lines) and ranges (vertical bars) of total ozone over Halley Bay, Antarctica, as measured by the British Antarctic Survey and NASA 5 total ozone monitoring experiment for October of the years 1957 through 1993.**



**South Pole ozone at maximum depletion.**



**Total Ozone Mapping Spectrometer (TOMS) satellite observations graphically depict the decline of atmospheric ozone over the South Pole between October 1979 and October 1992: green represents an average amount of ozone, blue less, and purple still less. Ozone concentrations fell by more than 50% in this period.**

# Ozone Hole and Polar Stratospheric Clouds (very cold temperature in Antarctica, $T < -80^{o}C$)

**1st step**, nitric acid ($HNO_3$) and/or $H_2O$ ice surfaces

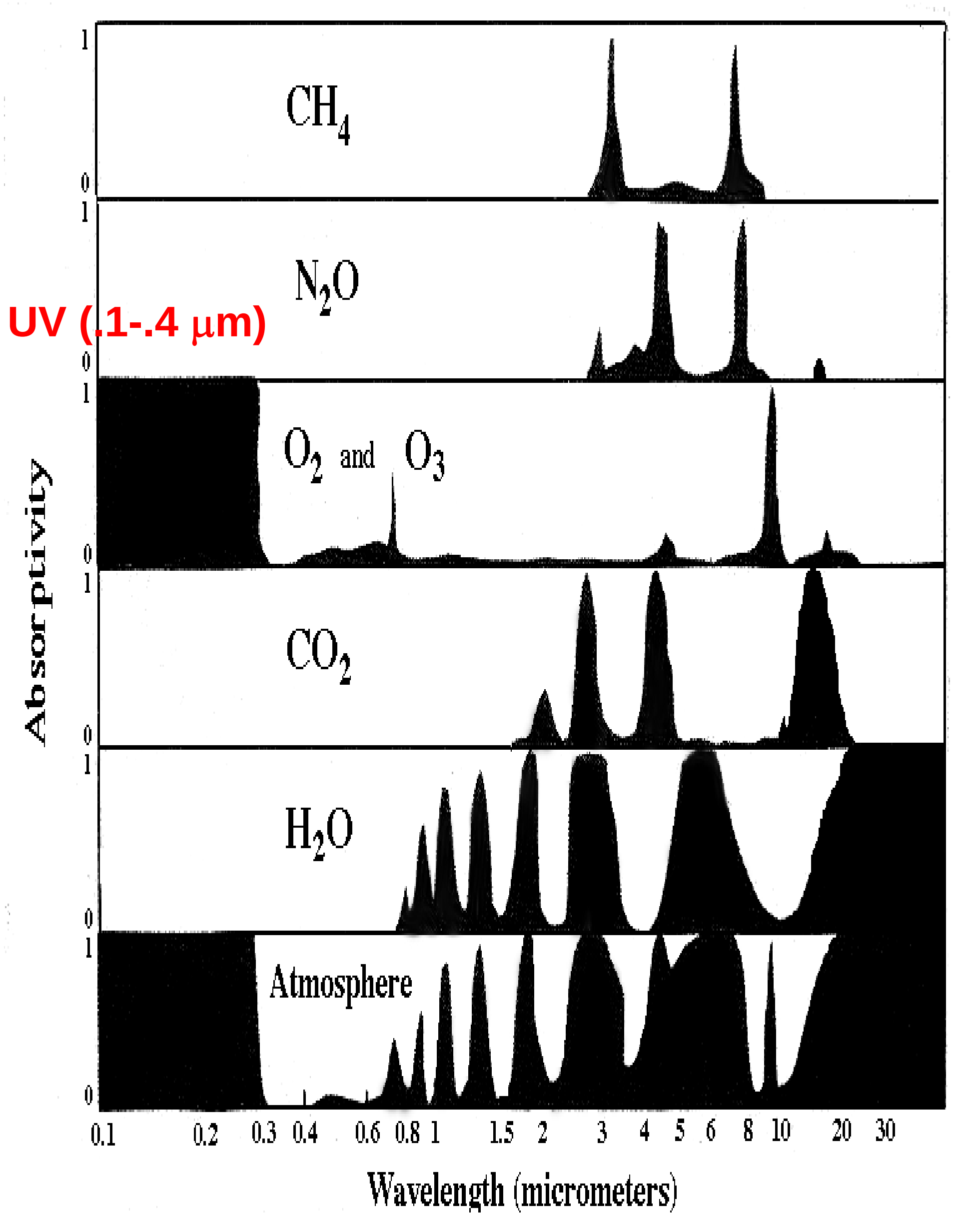
$$ClONO_2 + HCl \;{-}{-}\!\rightarrow\; Cl_2\,(gas) + NHO_3\,(ice)$$

**2nd step**, Sunlight (Spring, SH) $Cl_2 + h\tilde{\nu} \;{-}{-}\!\rightarrow\; 2\,Cl^*$

**3rd step**, Catalytic destruction cycle

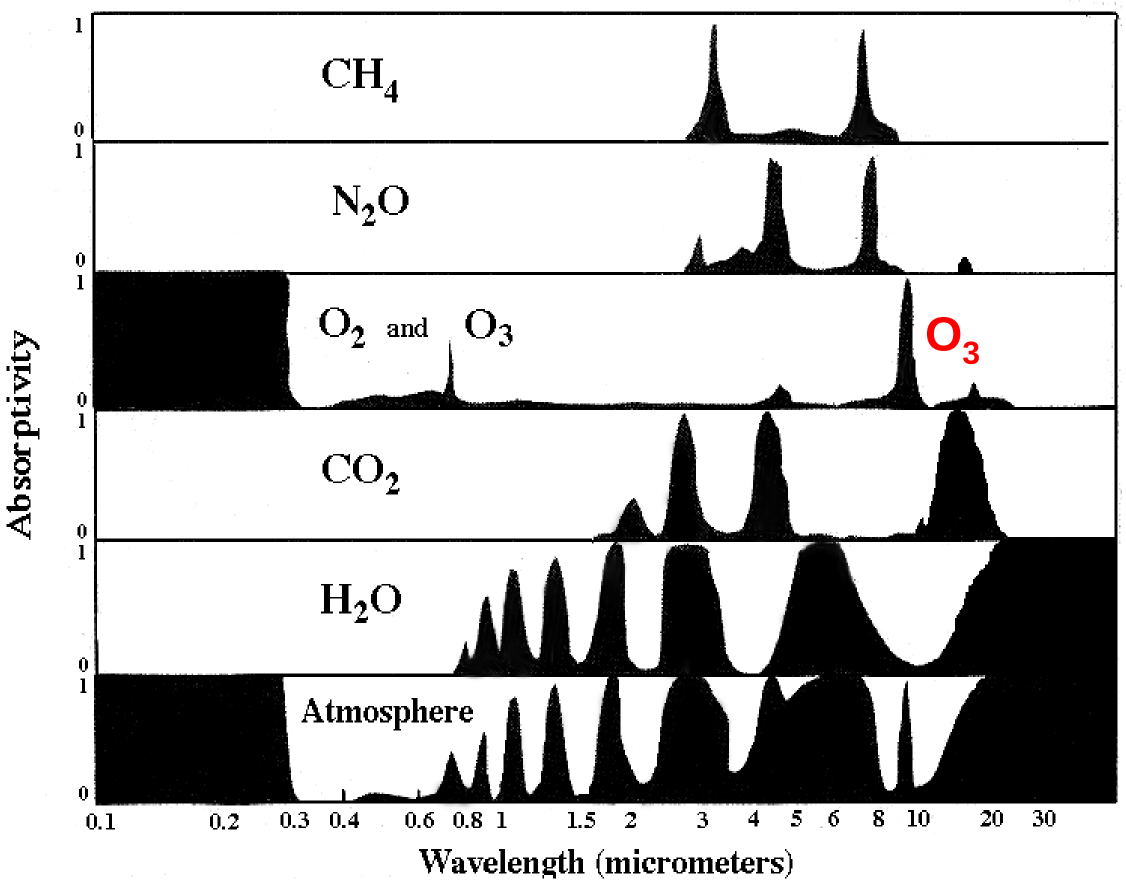
$$\left.\begin{array}{l} Cl^* + O_3 \;{-}{-}\!\rightarrow\; ClO + O_2 \\ O_3 + h\tilde{\nu} \;{-}{-}\!\rightarrow\; O + O \\ O + ClO \;{-}{-}\!\rightarrow\; Cl + O_2 \end{array}\right\} \text{Net result: } 2\,O_3 \;{-}{-}\!\rightarrow\; 3\,O_2$$

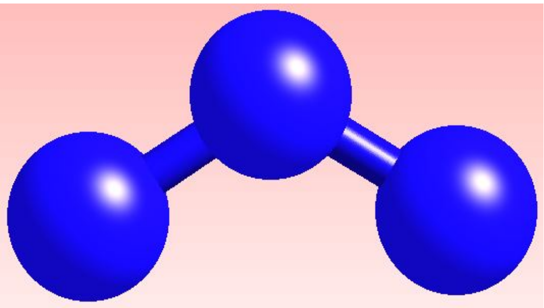
Reading: Course Reader, pp 35-39 and pp104-111.



**Absorption of harmful ultraviolet radiation by ozone (UV-B, 290-320 nm):** Absorption of these wavelengths damages DNA molecules. The organisms are more sensitive to shorter wavelengths associated with higher energy photons. Any significant decrease in $O_3$ causes large increase in ground-level UV-B, leading to DNA damage (adaptation).

# Greenhouse Effect of Ozone (Absorption of Infrared Radiation in the troposphere)





**Vibrational and rotational transitions at the 9.6 μm area**

# Greenhouse Gases (part 1)

- Carbon dioxide ($CO_2$ ): ~0.4% / yr, fossil fuel combustion, photosynthesis, and ocean, ~380 ppmv, present value
- Water vapor ($H_2O$): via temperature feedback
- Ozone ($O_3$): in the troposphere (~10 %)

# Greenhouse Gases (related to $O_3$)

- Methane ($CH_4$): increasing human and animal populations, and change in land use (~ 1–2%/yr, ~1.7 ppmv)

  $CH_4 + 4O_2 \rightarrow CH_2O + H_2O + 2O_3$ (OH, NO)

- Nitrous Oxide ($N_2O$): Fossil fuel combustion and fertilizer denitrification (~ 0.2%/yr)

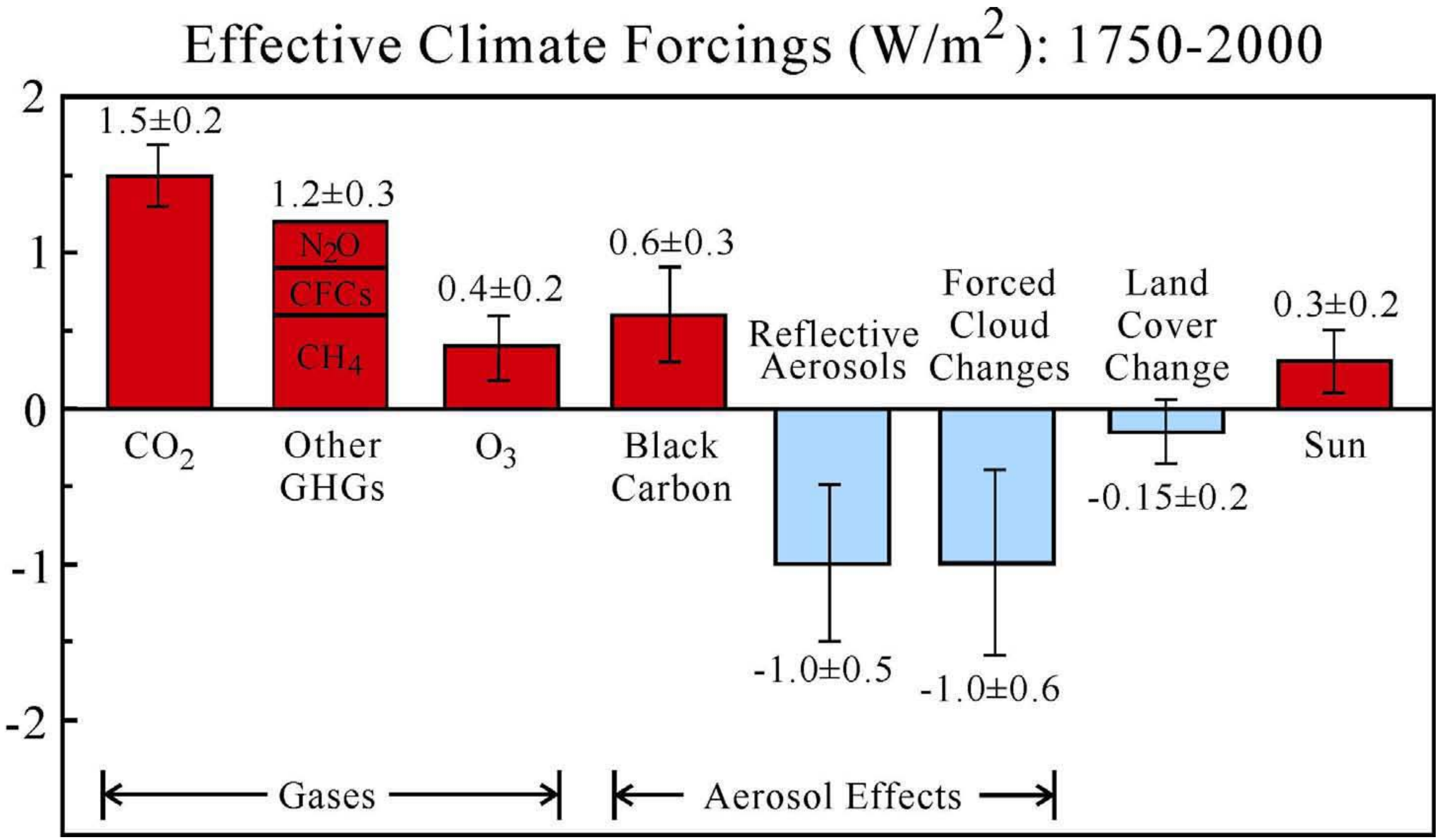
  Tropophere ($NO_x$ = NO, $NO_2$, ~ $O_3$)

- Chlorofluorocarbons (CFCs): aerosol spray cans & refrigerant (Montreal Protocol, 1987)

  $Cl + O_3 \rightarrow ClO + O_2$ $ClO + O \rightarrow Cl + O_2$

- Carbon Monoxide (CO): transportation, fossil fuel combustion, deforestation, biomass burning, and $CH_4$

  $CO \rightarrow OH \rightarrow CH_4$ $CO \rightarrow CO_2$



**Climate forcing agents in the industrial era**. “Effective” forcing accounts for “efficacy” of the forcing mechanism

*Source:* Hansen et al., JGR, **110**, D18104, 2005.