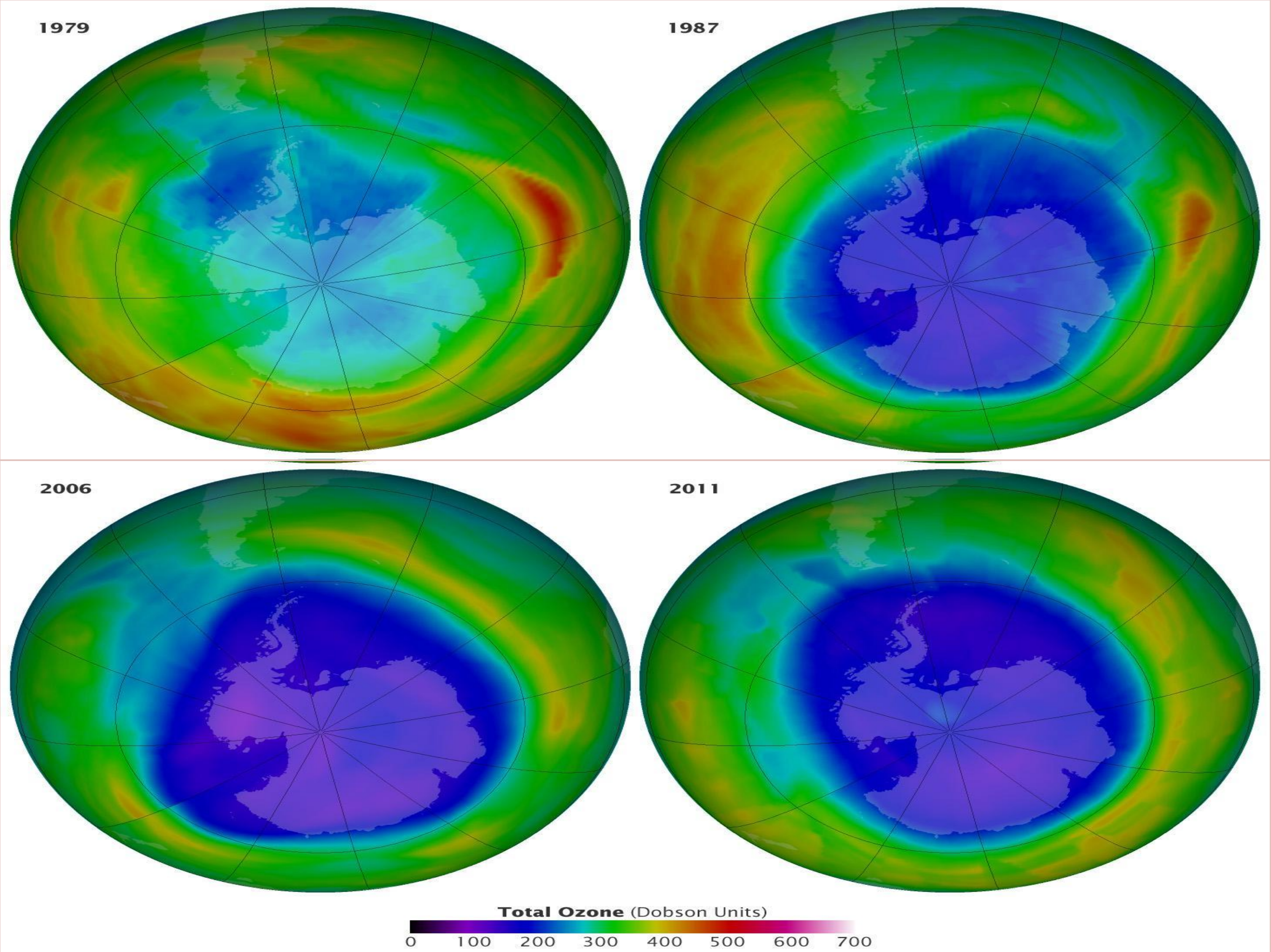
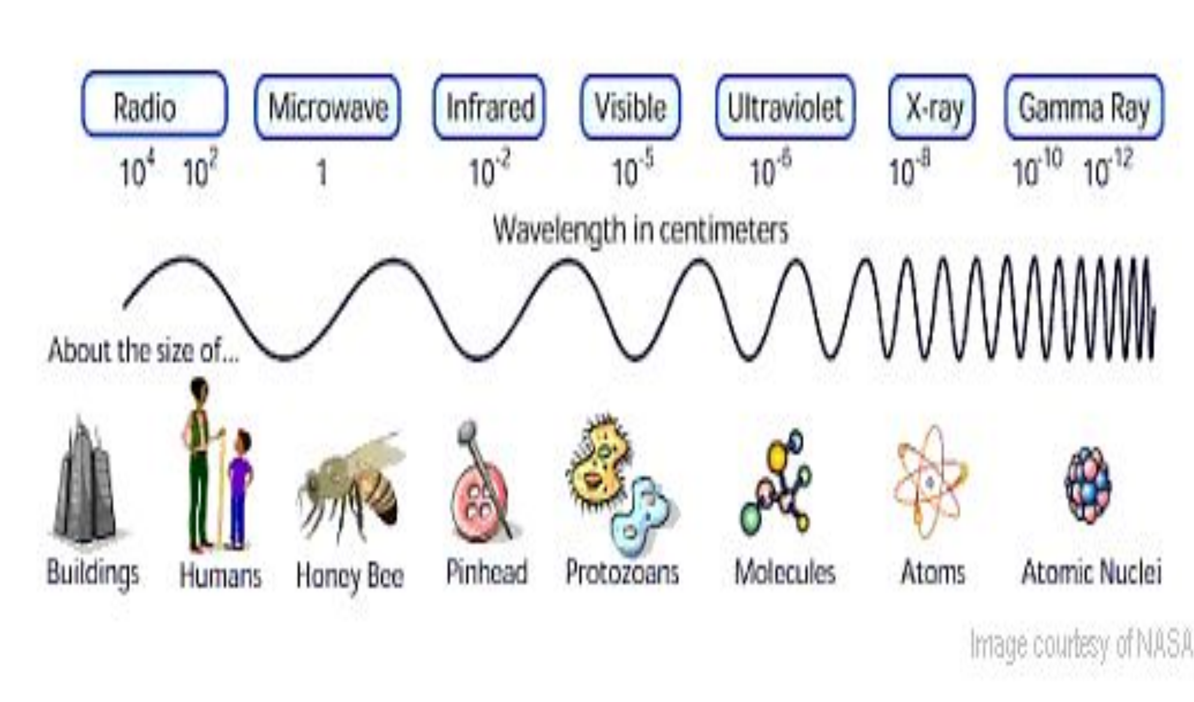
Ozone Depletion

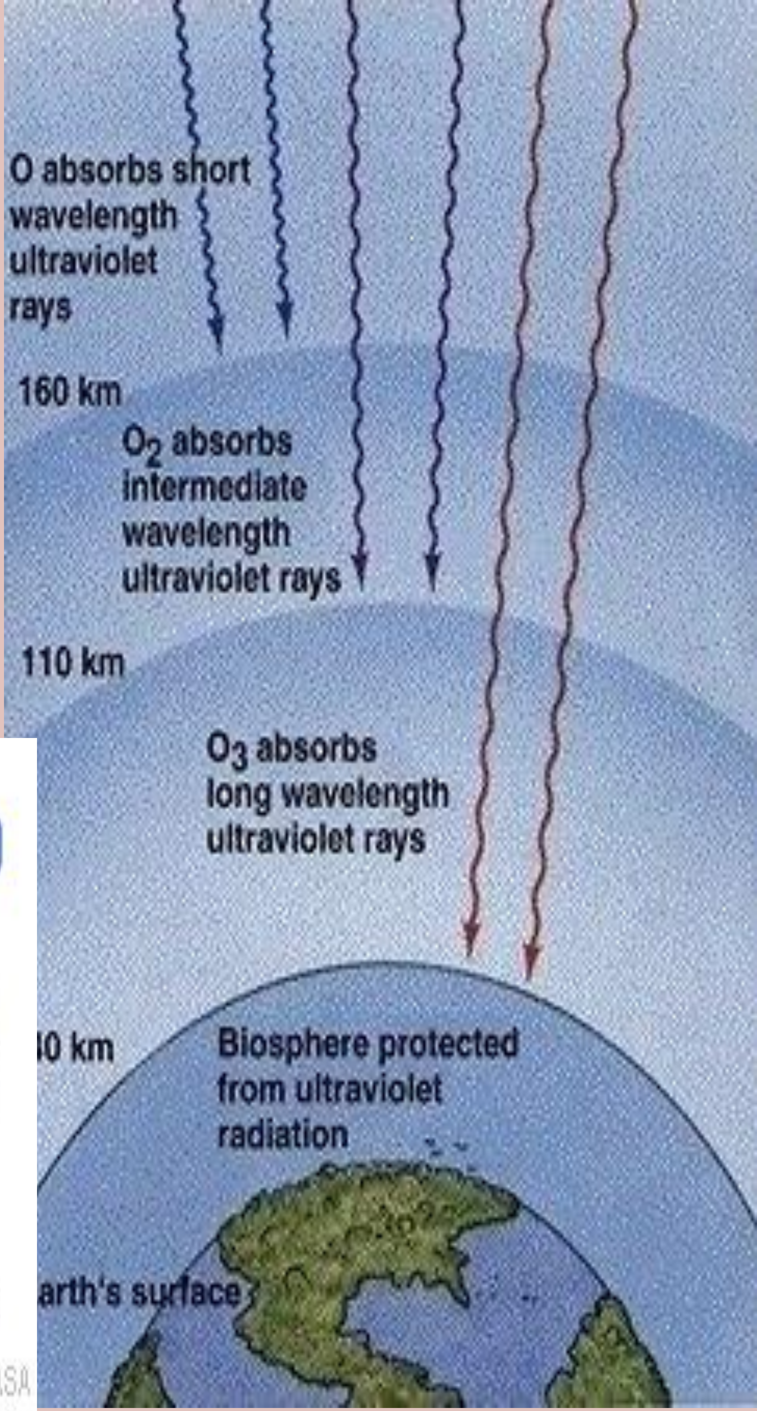


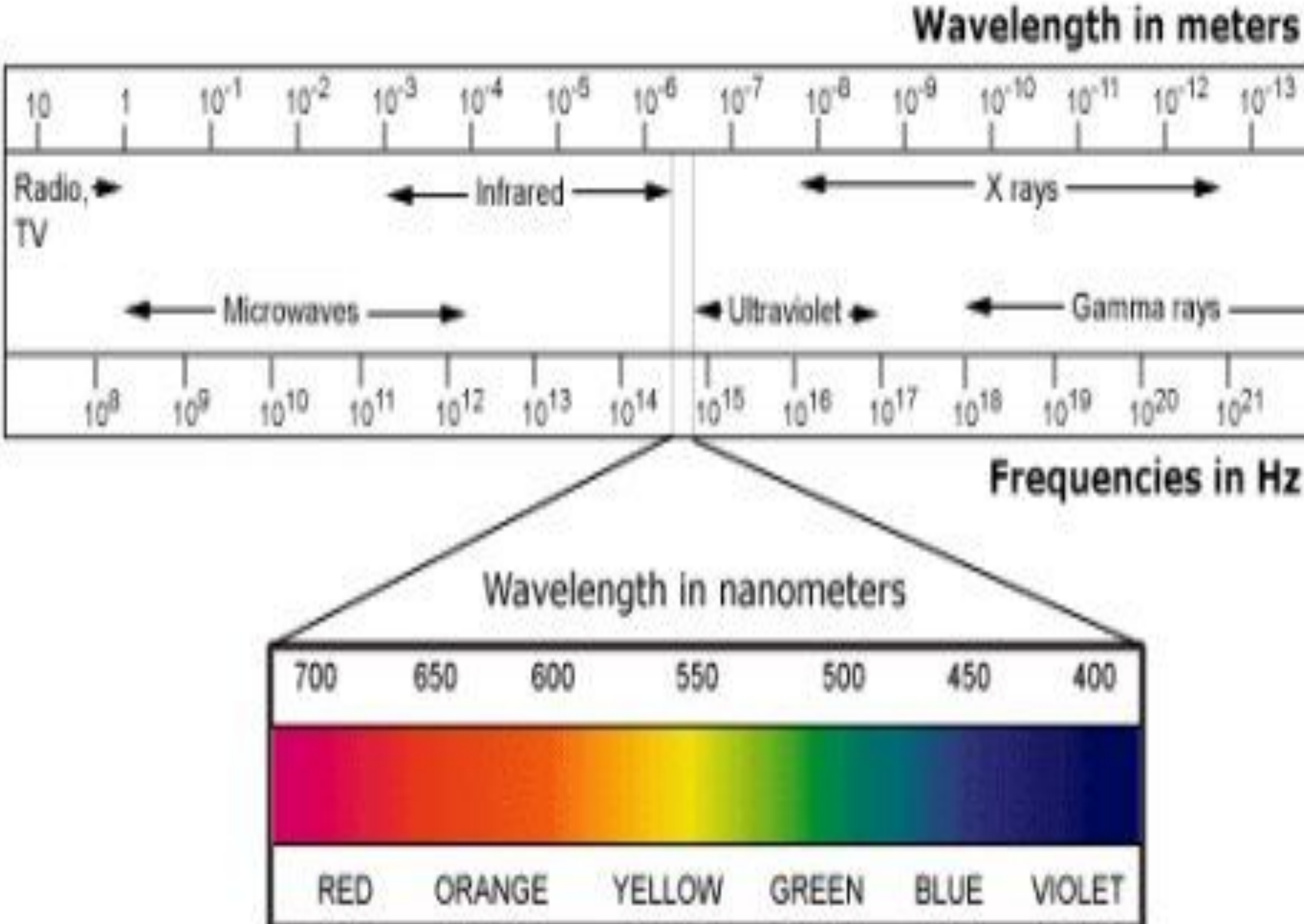
Images by NASA on the status of the Antarctic Ozone Hole on September 16 of the years 1979,1987,2006& 2011

Ozone

- About 90% of Ozone resides in the stratosphere
- It protects us from UV radiations
- Increase in the Troposphere ozone can contribute to raising global temperature
- Ozone is continuously created in the stratosphere by absorption of UV radiation, while it is continuously being removed by various chemical reactions that convert it back to molecular oxygen


Radio
Microwave
Infrared
Visible
Ultraviolet
X-ray
Gamma Ray
10^4 10^2
1
10^{-2}
10^{-5}
10^{-6}
10^{-8}
10^{-10} 10^{-12}
Wavelength in centimeters
About the size of...
Buildings
Humans
Honey Bee
Pinhead
Protozoans
Molecules
Atoms
Atomic Nuclei
Image courtesy of NASA


O absorbs short wavelength ultraviolet rays
160 km
O_2 absorbs intermediate wavelength ultraviolet rays
110 km
O_3 absorbs long wavelength ultraviolet rays
Biosphere protected from ultraviolet radiation


Wavelength in meters
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{-12}
10^{-13}
Radio, TV
Infrared
X rays
Microwaves
Ultraviolet
Gamma rays
10^{8}
10^{9}
10^{10}
10^{11}
10^{12}
10^{13}
10^{14}
10^{15}
10^{16}
10^{17}
10^{18}
10^{19}
10^{20}
10^{21}
Frequencies in Hz
Wavelength in nanometers
700
650
600
550
500
450
400
RED
ORANGE
YELLOW
GREEN
BLUE
VIOLET

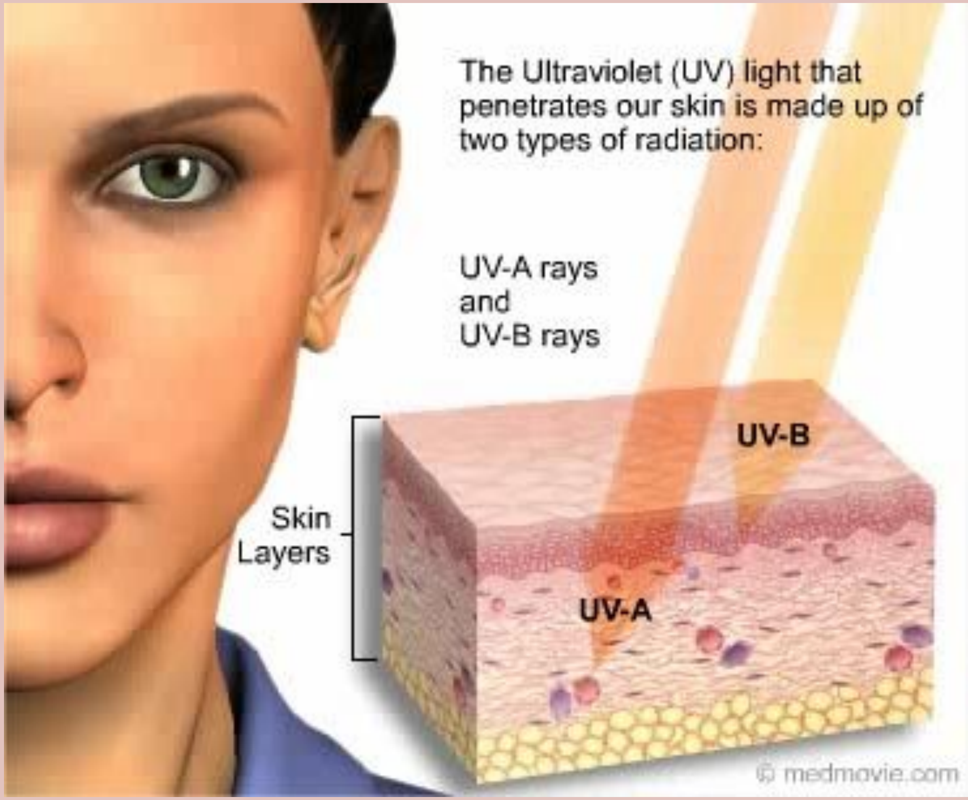
Classification of UV Rays

Name	Abbr.	λ range in nm	Energy/ photon (eV)
UV A, long wave, or black light	UVA	400 –315	3.10–3.94
Near	NUV	400 –300	3.10–4.13
UV B or medium wave	UVB	315 –280	3.94–4.43
Middle	MUV	300 –200	4.13–6.20
UV C, short wave, or germicidal	UVC	280 –100	4.43–12.4
Far	FUV	200 –122	6.20–10.2
Vacuum	VUV	200 –100	6.20–12.4
Low	LUV	100 –88	12.4–14.1
Super	SUV	150 –10	8.28–124
Extreme	EUV	121 –10	10.2–124

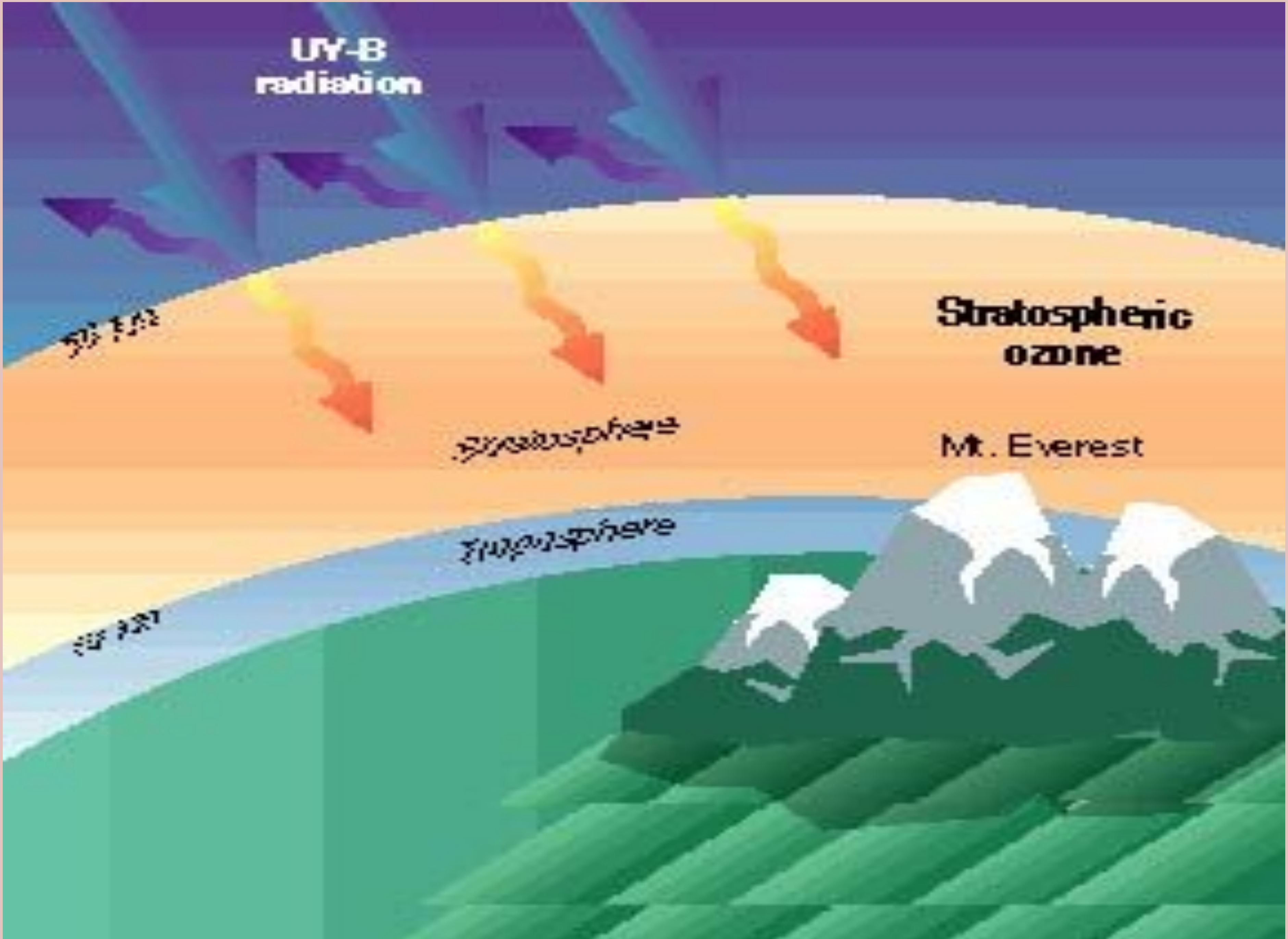
UV Skin Penetration

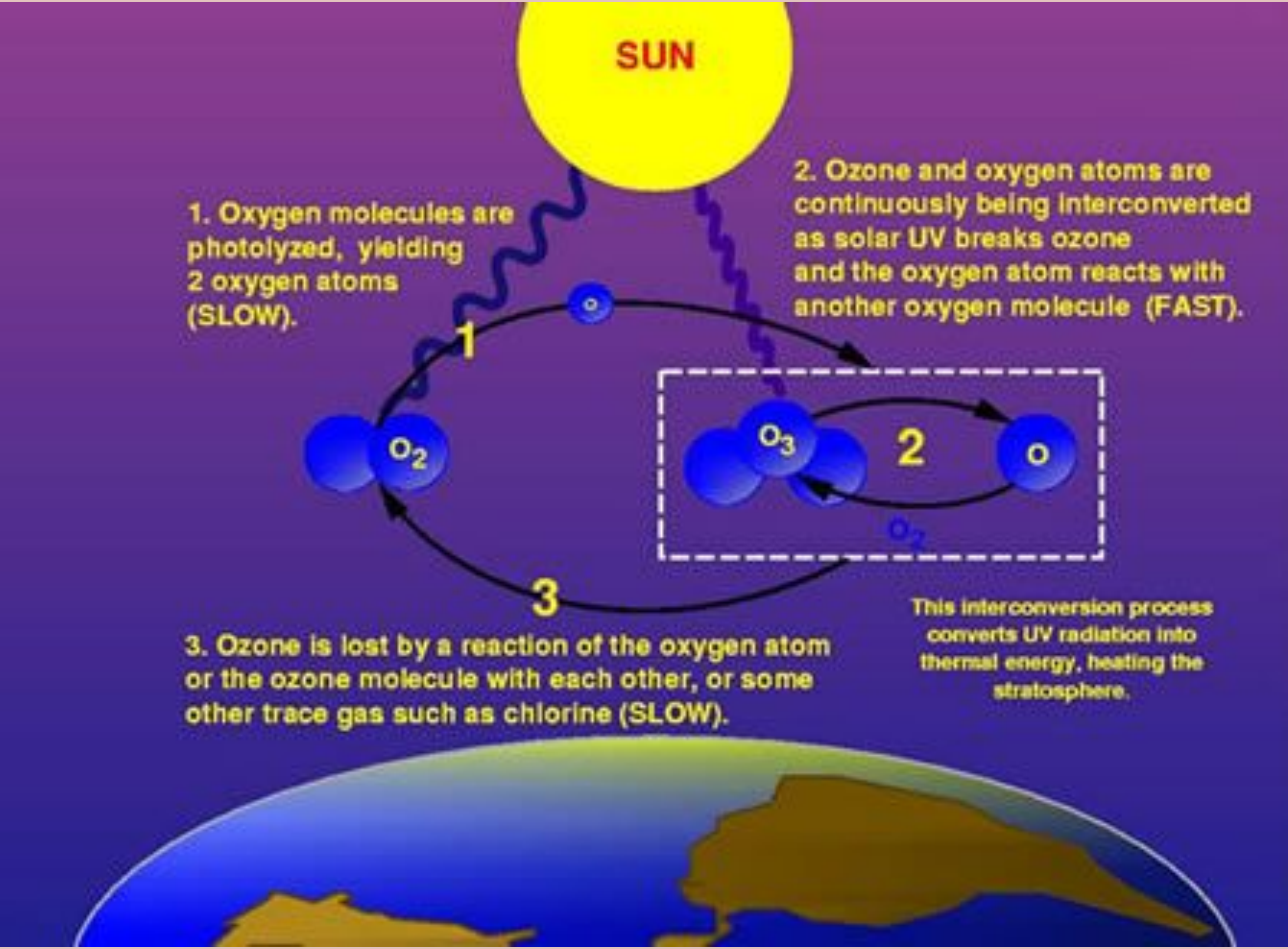
- UVC and much of UVB rays are absorbed by the Earth's ozone layer.
- UVA and some UVB rays are transmitted through the atmosphere,
- UVB rays (short wavelength) reach only the outer layer of your skin (the epidermis)
- UVA rays (longer wavelength) and can penetrate the middle layer of your skin (the dermis).
- Both Cause sunburns.

Sunburn—Skin damage due to UV



- UVB radiation (280 - 320) has been linked to skin cancer, cataracts, damage to materials like plastics, and harm to certain crops and marine organisms. Although some UVB reaches the surface without ozone depletion, its harmful effects will increase as a result of this problem.


UV-B
radiation
Stratospheric
ozone
Mt. Everest


SUN
1. Oxygen molecules are photolyzed, yielding 2 oxygen atoms (SLOW).
2. Ozone and oxygen atoms are continuously being interconverted as solar UV breaks ozone and the oxygen atom reacts with another oxygen molecule (FAST).
O
1
O_2
O_3
2
O
O_2
3
This interconversion process converts UV radiation into thermal energy, heating the stratosphere.
3. Ozone is lost by a reaction of the oxygen atom or the ozone molecule with each other, or some other trace gas such as chlorine (SLOW).

Natural Formation and Removal of Ozone

Ozone Formation:

$$O_2 + h\nu \rightarrow 2\,O^* \ldots\ldots\ldots\ldots\ldots\ (\lambda < 240\text{ nm})$$

$$O^* + O_2 \rightarrow O_3$$

Ozone Removal:

$$O_3 + h\nu \rightarrow O^* + O_2 \ldots\ldots\ldots\ldots\ (\,200\text{ nm} < \lambda < 310)$$

$$O_3 + O^* \rightarrow 2\,O_2$$

Catalytic Ozone Removal (by Cl, Br, OH^*, NO^*):

The catalysts can be anthropogenic or natural

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

$$ClO + O_3 \rightarrow Cl + 2\,O_2 \ldots\ldots\text{catalyst regenerated.}$$

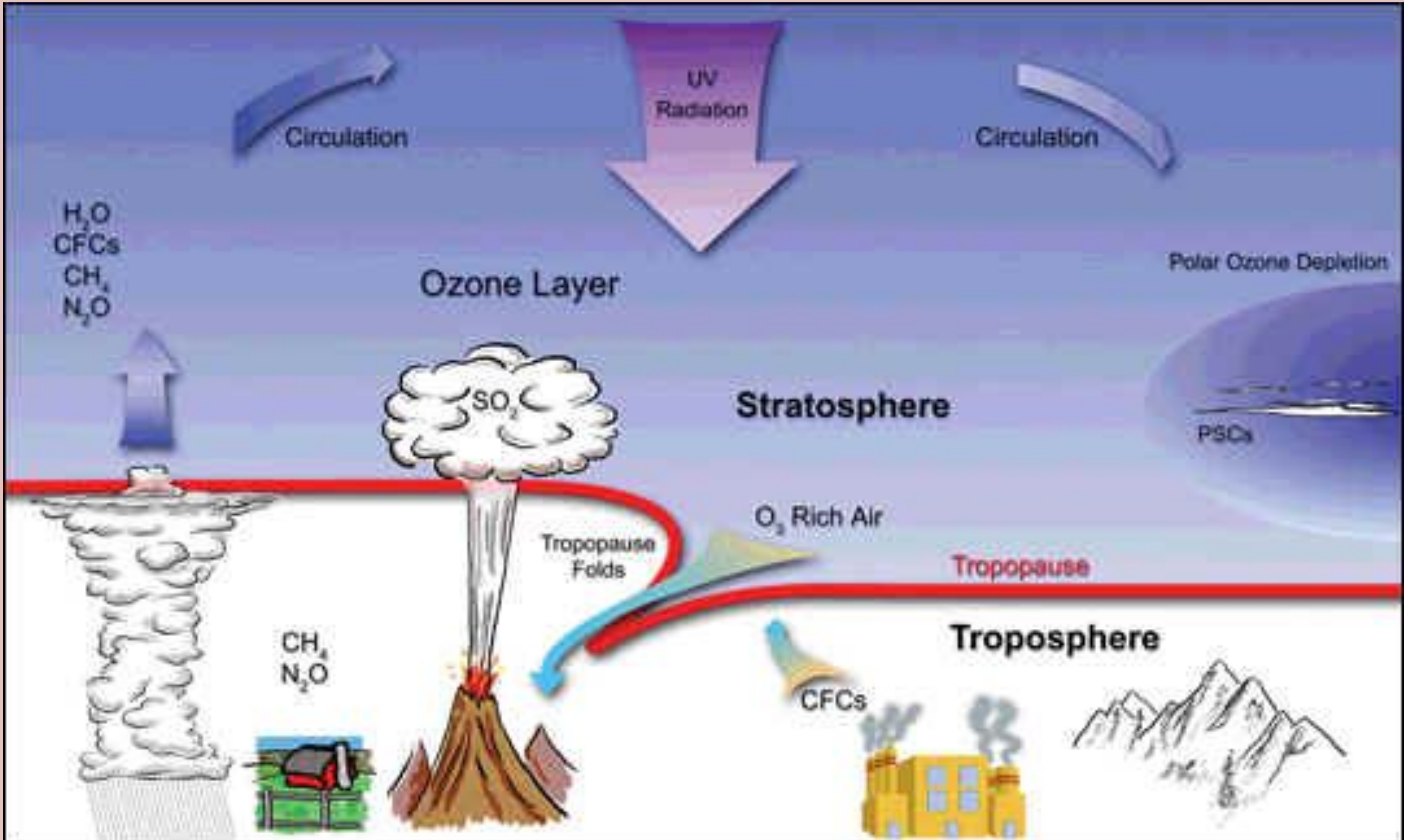
Anthropogenic Ozone Depletion

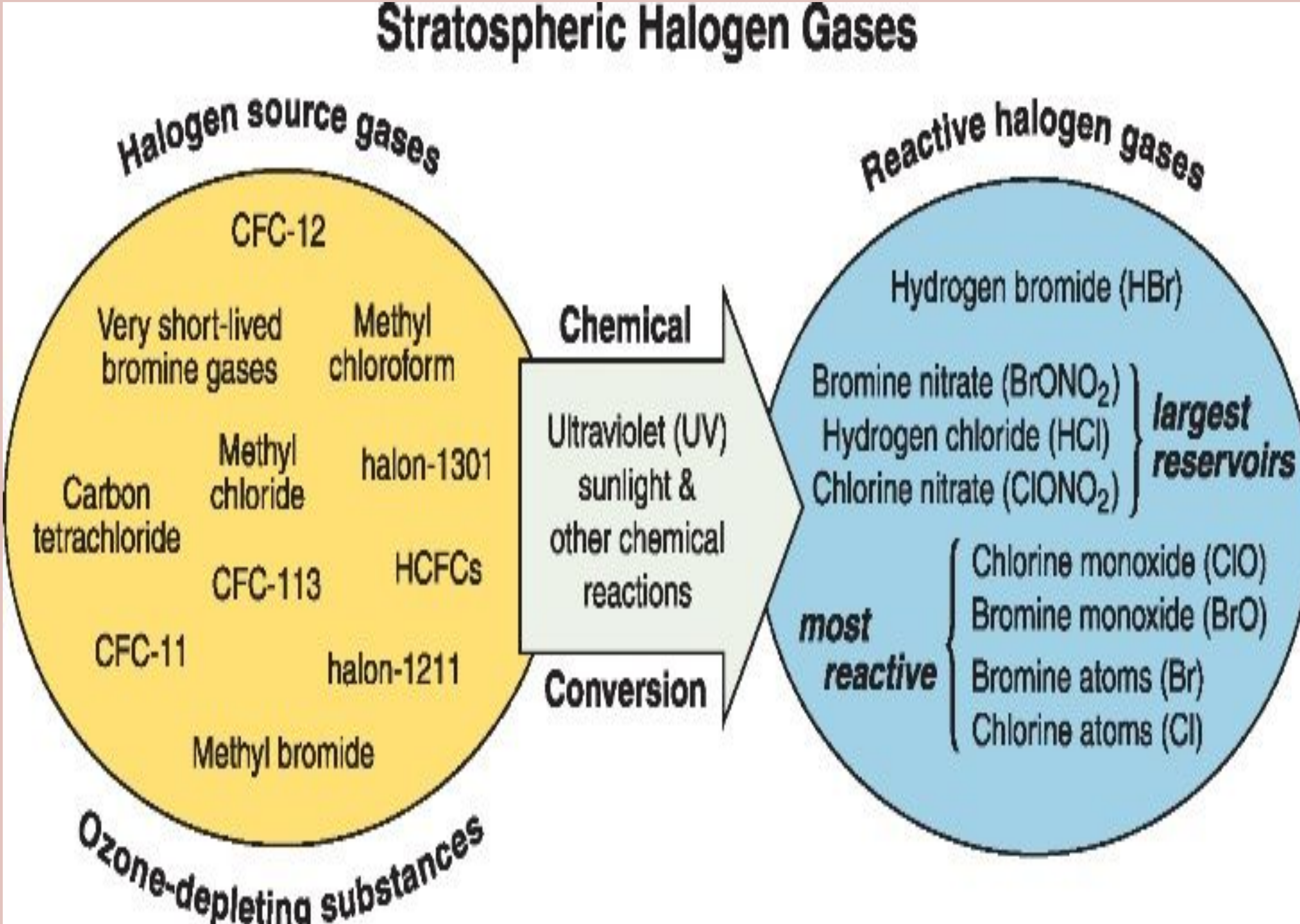
- Emission of chlorofluorocarbons and other ozone depleting substances.
- These molecules are inert and non water soluble,
- They are not destroyed through atmospheric chemical reactions in the troposphere or removed with precipitation.
- They rise to the stratosphere and are broken down to yield Cl, Br. e.g.

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

- This results in a drastically higher concentration of ozone-destroying catalysts (Cl, Br) in the stratosphere.
- Accelerates the catalytic destruction of ozone.
- A single chlorine molecule can break down tens of thousands of ozone molecules before it gets deactivated.

Ozone Depletion





Stratospheric Halogen Gases
Halogen source gases
CFC-12
Very short-lived bromine gases
Methyl chloroform
Methyl chloride
halon-1301
Carbon tetrachloride
CFC-113
HCFCs
CFC-11
halon-1211
Methyl bromide
Ozone-depleting substances
Chemical
Ultraviolet (UV) sunlight & other chemical reactions
Conversion
Reactive halogen gases
Hydrogen bromide (HBr)
Bromine nitrate ($BrONO_2$)
Hydrogen chloride (HCl)
Chlorine nitrate ($ClONO_2$)
largest reservoirs
Chlorine monoxide (ClO)
Bromine monoxide (BrO)
Bromine atoms (Br)
Chlorine atoms (Cl)
most reactive

Chemical	**Application**	**O_3 Dep. Pot.**
CFC	Stable in troposphere. Rise to the stratosphere, break down in presence of UV-B and attack O_3.	0.6-1
CCl_4	Wide industrial uses: CFC manufacture, solvent and catalyst. Potent carcinogen.	1.2.
Halons	Contain Br, F, C. Fire extinguishing agent. Production Stopped in the U.S. ended on 12/31/93. Br is many times more effective at destroying ozone than Cl	
HCFC	CFC-replacements. Lesser depletion potential.	0.01- 0.1.
HFC	CFC replacements. Because they do not contain chlorine or bromine, they do not deplete the ozone layer.	0.
MeBr	CH_3Br Methyl Bromide. Pesticide for soil and many agricultural products. Production stopped in the U.S. on 12/31/2000.	0.6.
CH_3CCl_3	Methyl Chloroform. Industrial solvent.	0.11.
HBFC	Hydrobromofluorocarbon Class I substances.	

Chlorofluorocarbons

- CFCs can last in stratosphere > 100 yr.
- Production ban since December 31, 1995.
- Only recycled and stockpiled CFCs can now be used on a limited basis.
- CFCs are also a “greenhouse gas”
- Class I substances have an ozone-depletion potential of 0.2 or higher. These include CFCs, halons, carbon tetrachloride, methyl chloroform, HBFC and methyl bromide.

Hydrochlorofluorocarbons

- HCFCs and hydroflurocarbons (HFC) are safer.
- Less stable in the atmosphere
- Less likely to reach the stratosphere to affect the ozone layer.
- HFCs even lack Cl and hence are safer.
- But HCFCs an HFCs are highly potent greenhouse gasses.

Measurement of Ozone: Dobson Unit

- Measurement of stratospheric ozone columnar density: Dobson unit (DU)
  - Gordon Dobson, University of Oxford researcher.
  - 1920s, he built the Dobson ozone spectrophotometer.
- 1 DU = a layer of ozone that would be 10 μm thick under standard temperature and pressure. 2.69×10^{16} ozone molecules/ sq. cm
- 300 DU of ozone brought down to the surface of the Earth (atmospheric pressure) at 0°C would occupy a layer only 3 mm thick.
- Ozone hole: Layer < 220 DU

Global warming and Ozone –Depletion impacts of CFCs

- Fully halogenated CFCs have long atmospheric lifetimes,
- They contain relatively large amounts of chlorine
- They absorb strongly within the 7 to 13 micron atmospheric window
- Therefore, they have considerable potential for both global warming and ozone depletion.
- **They are 15000 times potent than carbon dioxide when compared to carbon dioxide!**

India & CFC's

- According to UNEP, in 2008, India produced almost all the CFC in the world, and the amount it officially exported was far lower than the amount reported by other countries to be imported from India.
- However, CFC's are still the most smuggled commodity, next to drugs.
- India and South Korea are the two major manufacturers that still produce CFC's, but are sold on the black market.

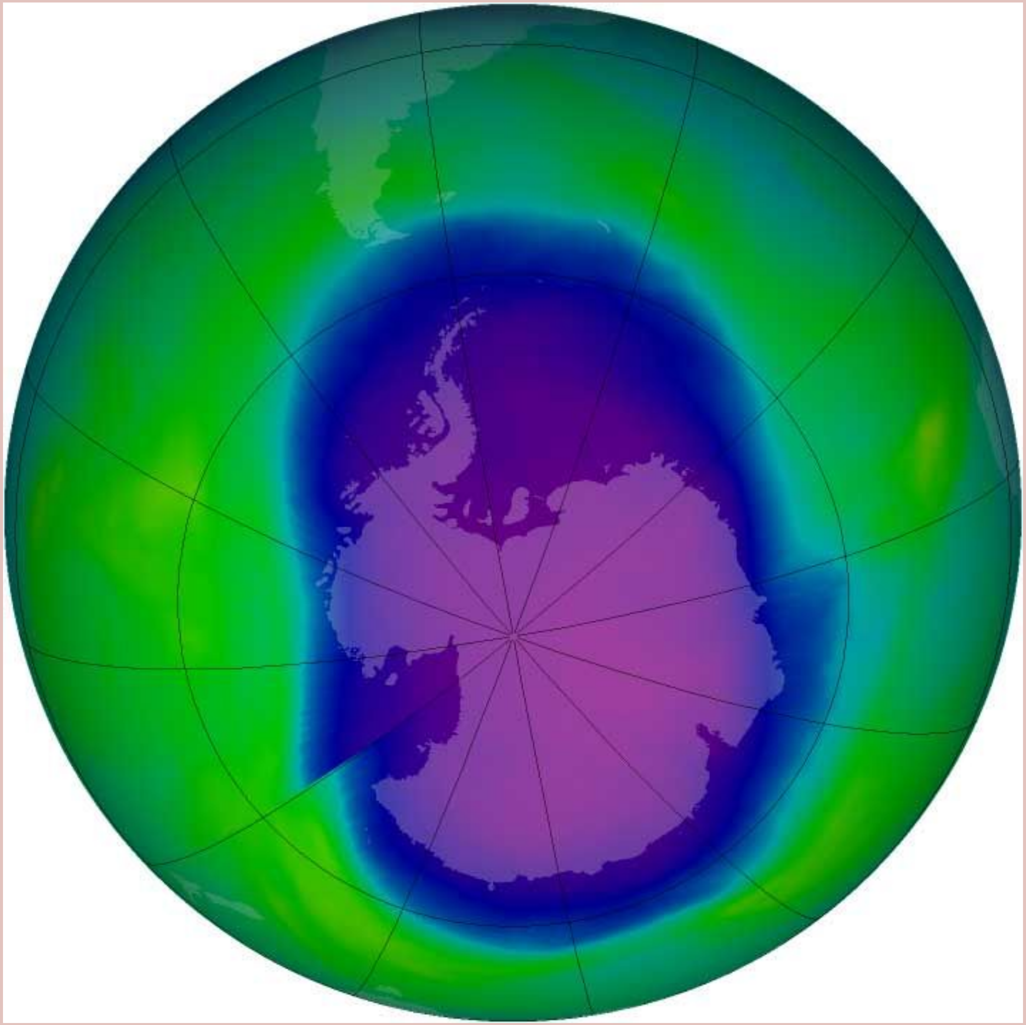
- In 2008, UNEP estimated these two countries accounted for over 70 per cent of global CFC production, which has come down from a million tonnes a year to 50,000.
- All developed nations have already banned CFC production, and India officially banned CFC's in late 2008, after signing the Montreal Protocol.

Homogenous and Heterogeneous Ozone Depletion

- Homogeneous:
  - the depletion occuring more or less uniformly all over the globe (in the statosphere.
- Heterogeneous: Ozone hole
  - Excessive depletion of the ozone layer above the poles especially during the spring season.

(http://www.epa.gov/ozone/science/hole/whyant.html)

Ozone Hole



Largest observed ozone hole, September 21-30 Sept, 2006 (10.6 mi. sq miles). The blue and purple colors are where there is the least ozone, and the greens, yellows, and reds are where there is more ozone. Credit: NASA

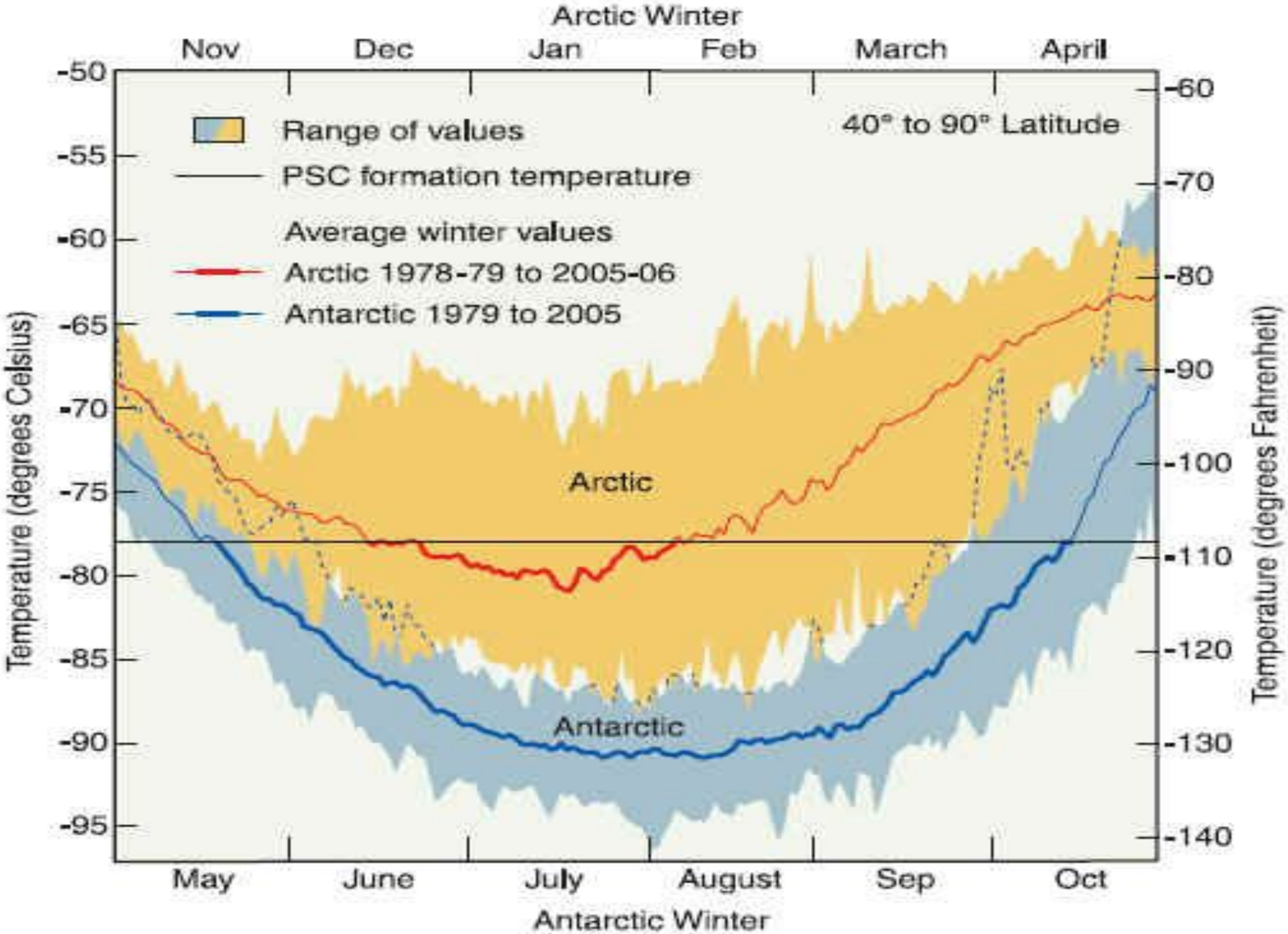
Watch NASA video on Ozone Depletion

Antarctic Ozone Hole

- In the 3-month long dark polar winter, **the Polar Vortex develop** (http://science.nasa.gov/headlines/y2000/ast02oct_1.htm)
- It is more pronounced in the southern hemisphere due to fewer land masses.
- It traps and chills the polar stratosphere to <–80 °C.
- **Polar Stratospheric Clouds (PSCs)** form at these temperatures.
- Chlorine accumulates on these ice crystals in the form of reservoir compounds like **$ClONO_2$, HOCl**

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + NO_2 \rightarrow ClONO_2$$

Minimum Air temperatures in the Polar Lower Stratosphere

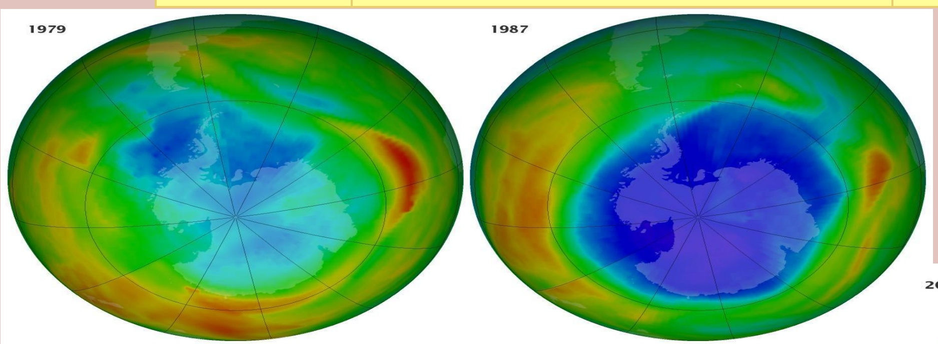


Antarctic Ozone Hole

- In the spring, solar radiation triggers the release of massive quantities of Cl from the reservoir compounds.
- The released Cl causes a rapid catalytic degradation of ozone in a short span.
- This leads to the formation of the ozone hole.
- By mid-December (in the Antarctic), the polar vortex breaks up, PSCs disappear, and ozone from lower latitudes comes in and the ozone hole shuts down.

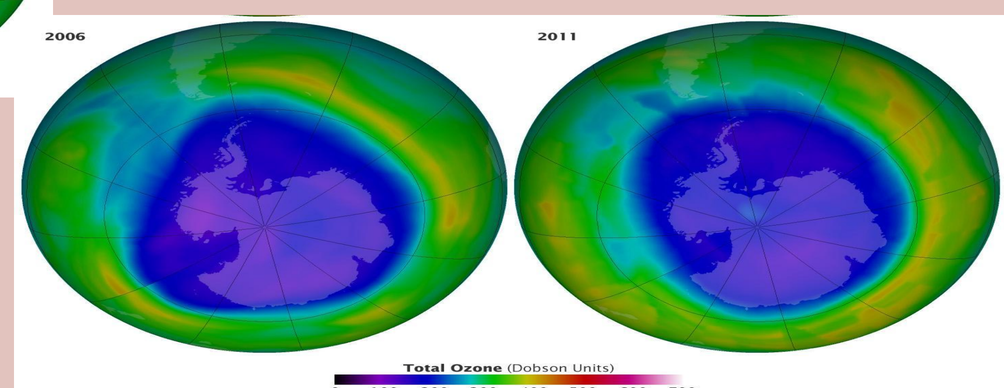
Temporal status of Ozone

Year	Area of O_3 Hole (in million km^2)	Concentration of O_3 (in DU)
1979	11.1	194
1987	22.4	109
2006	29.6	84
2011	26	95



Credit: https://earthobservatory.nasa.gov/IOTD/view.php?id=79198

Images by NASA on the status of the Antarctic Ozone Hole on September 16 of the years 1979,1987,2006& 2011



Montreal Protocol on Substances that Deplete the Ozone Layer

- International treaty with a mission to protect Ozone layer by regulating production of ozone-depleting substances (ODSs)

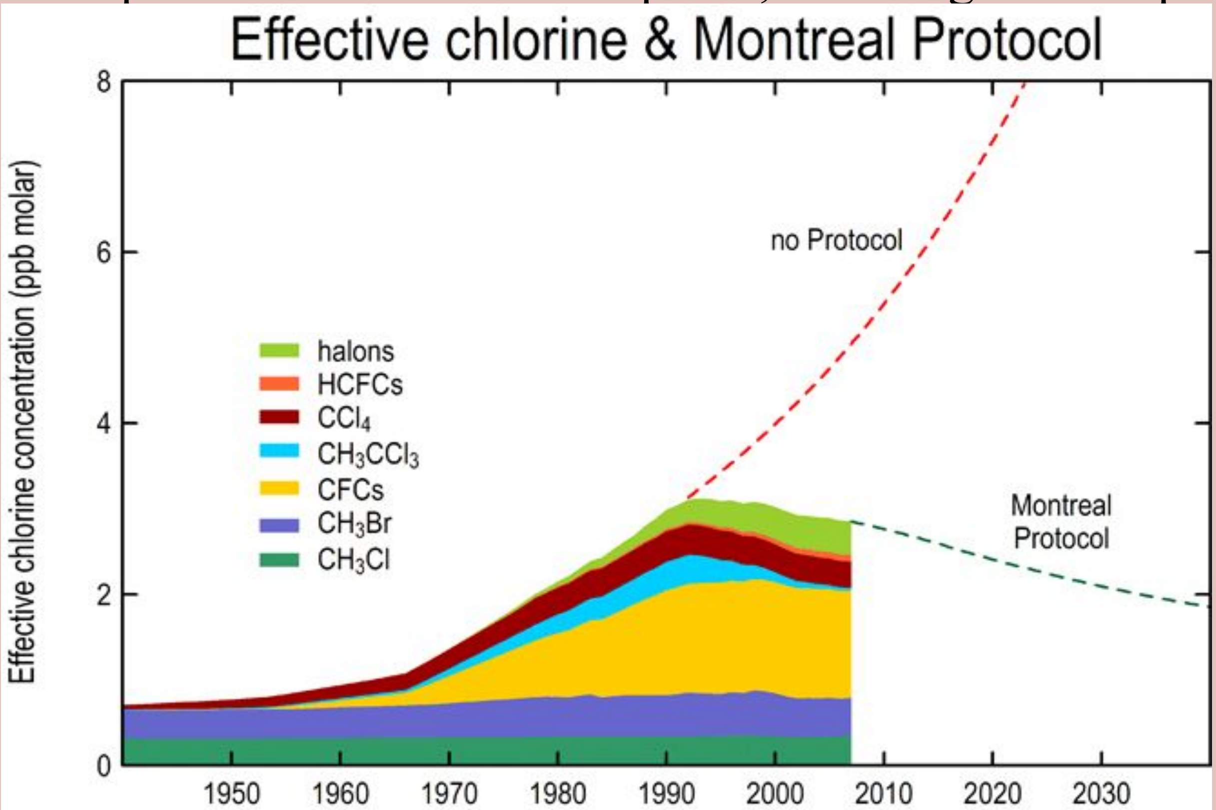
- It was initiated on 16 September 1987, and entered into force on 1 January 1989; 197 countries participated in the ratification process thereafter

- It is believed that if the international agreement is adhered to, the ozone layer is expected to recover by 2050.

"Perhaps the single most successful international environmental agreement to date has been the Montreal Protocol" Kofi Annan (Former Secretary-General of the United Nations)

How has the Montreal Protocol been a success story?

The treaty with the international cooperation has effectively phased-out the production and consumption of several major Ozone Depleting Substances (ODSs) in the lower atmosphere and in the stratosphere, enabling staratospheric ozone recovery.

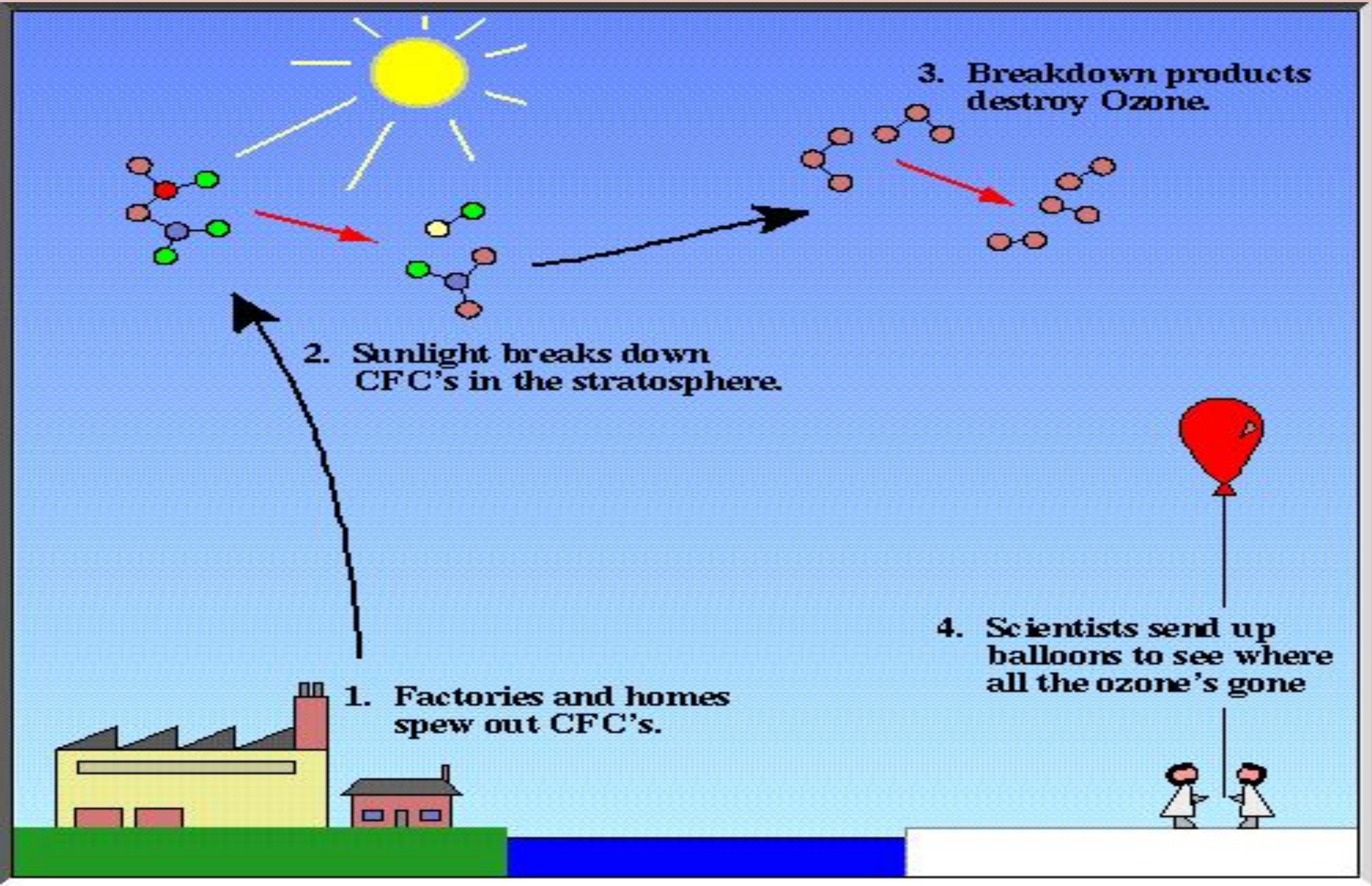


Graphical illustration by CSIRO Marine and Atmosphere Research on global impact of the Montreal Protocol on the levels of ODSs in the atmosphere, and suggest the impact by 2050

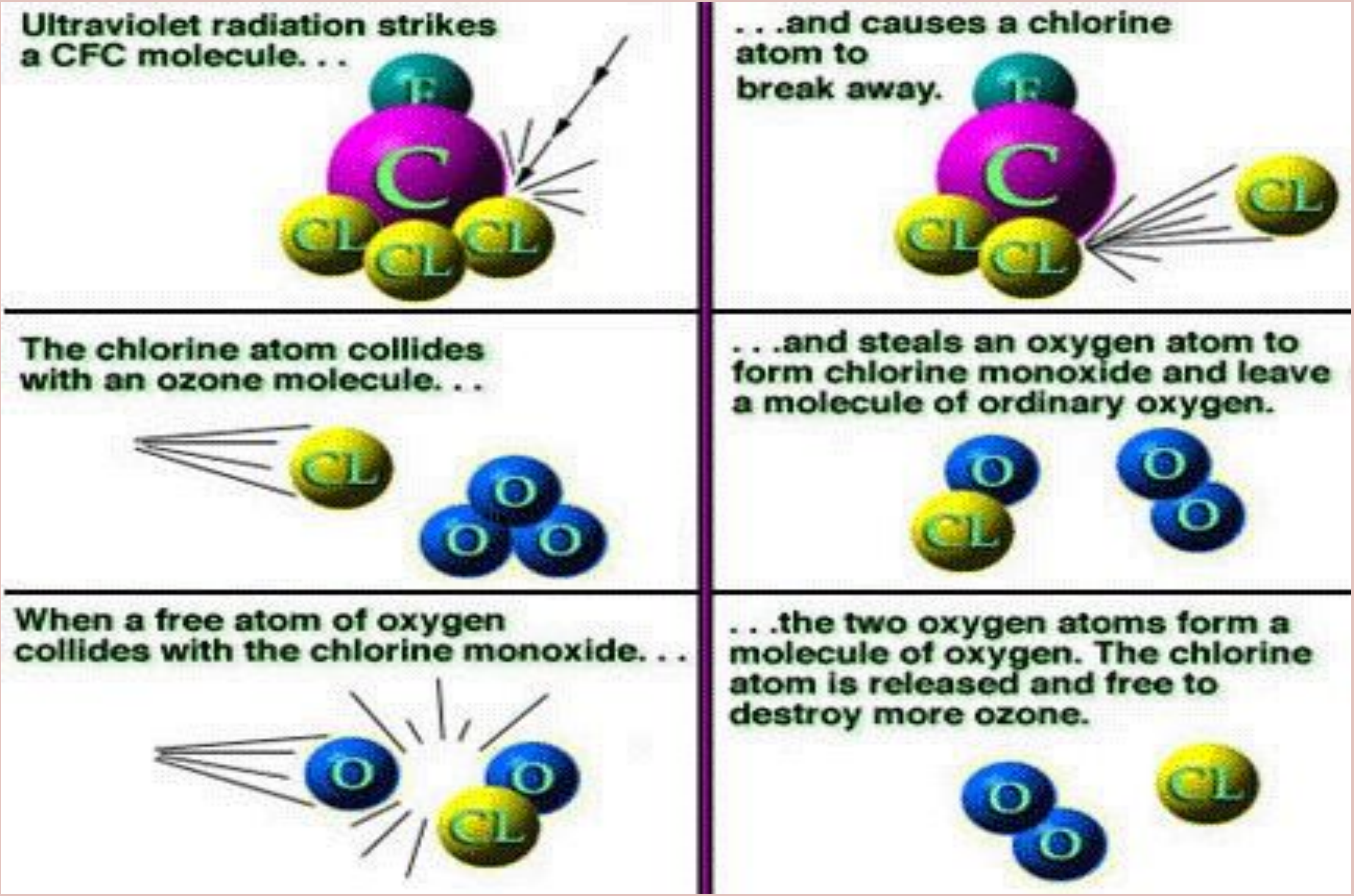
Never doubt that a small group of thoughtful, committed citizens can change the world indeed it's the only thing that ever has

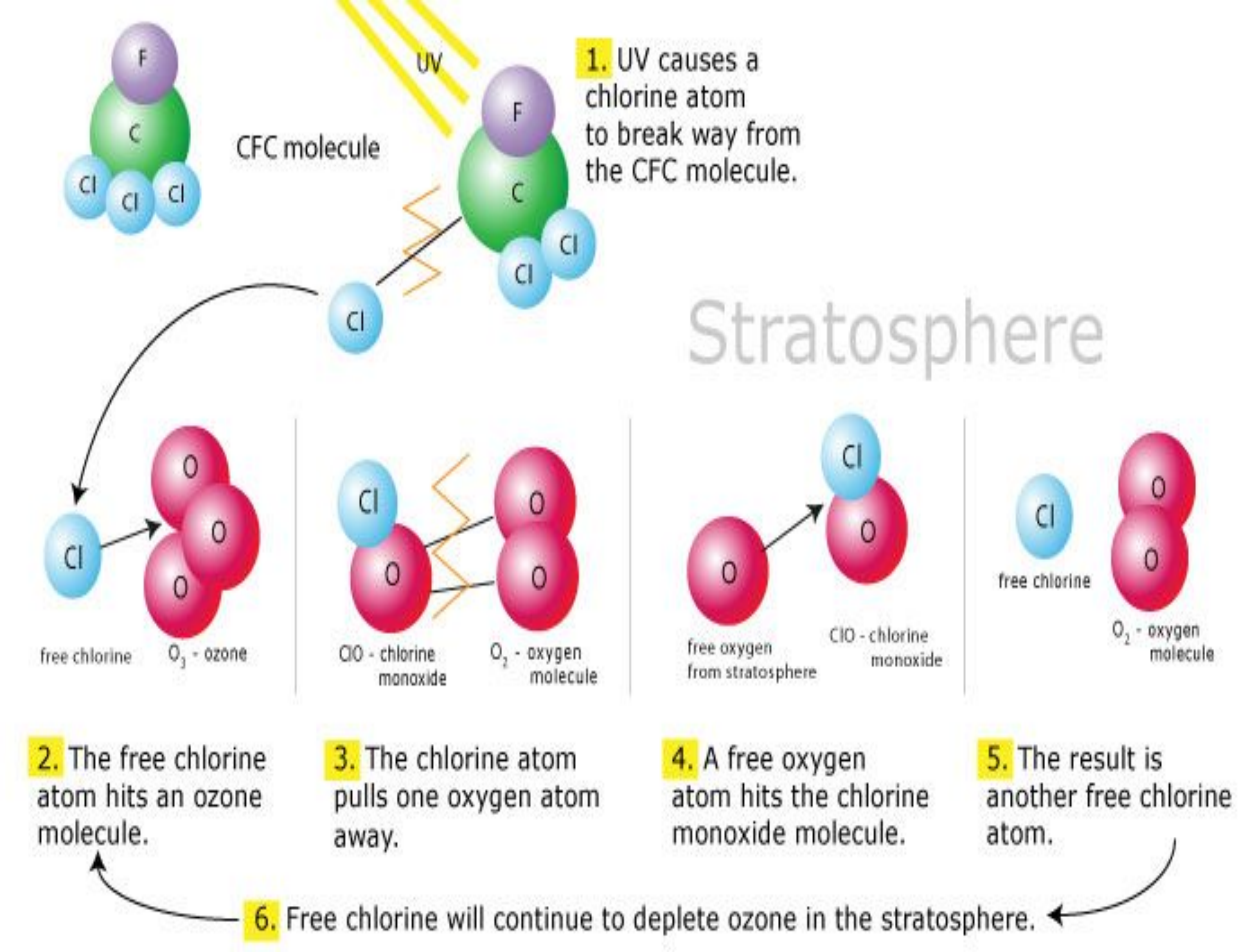
- Margaret Meed

Extra slides

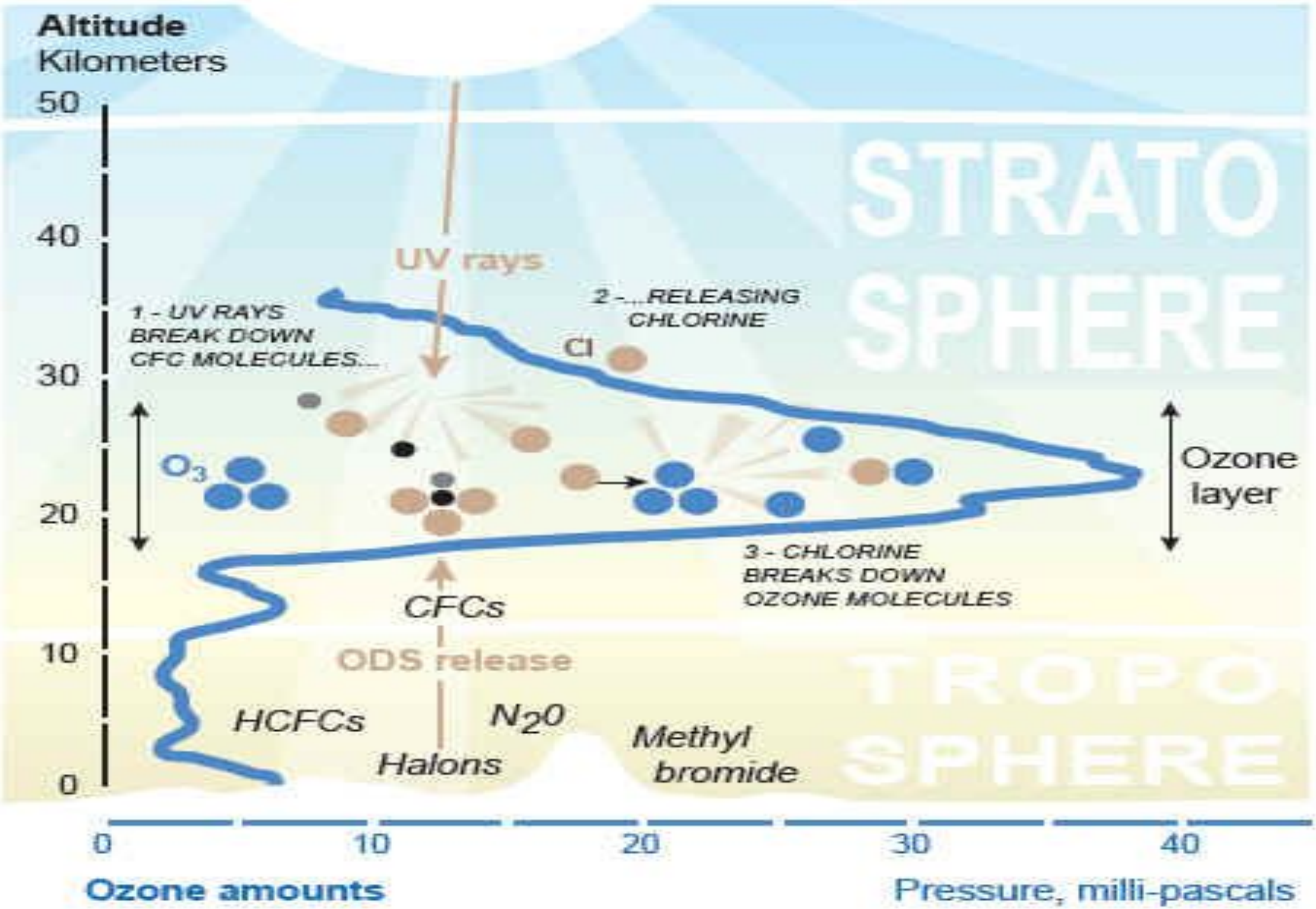


How ozone is destroyed by CFCs




CFC molecule
F
C
Cl
Cl
Cl
UV
F
C
Cl
Cl
Cl
1. UV causes a chlorine atom to break way from the CFC molecule.
Stratosphere
Cl
O
O
O
free chlorine
O3 - ozone
Cl
O
O
O
ClO - chlorine monoxide
O2 - oxygen molecule
O
Cl
O
free oxygen from stratosphere
ClO - chlorine monoxide
Cl
O
O
free chlorine
O2 - oxygen molecule
2. The free chlorine atom hits an ozone molecule.
3. The chlorine atom pulls one oxygen atom away.
4. A free oxygen atom hits the chlorine monoxide molecule.
5. The result is another free chlorine atom.
6. Free chlorine will continue to deplete ozone in the stratosphere.

CHEMICAL OZONE DESTRUCTION PROCESS IN THE STRATOSPHERE



Ozone layer as protective shield

Atomic oxygen is produced by the photolytic decomposition of molecular oxygen

$$O_2 + h\nu \longrightarrow O + O$$

Atomic oxygen, in turn, reacts rapidly with molecular oxygen to form ozone

$$O + O_2 + M \longrightarrow O_3 + M$$

where M represents a third atom (Nitrogen or oxygen)

- Ozone removal by photo dissociation

$$O_3 + h\nu \longrightarrow O_2 + O$$

$$H_2O + ClONO_2 \longrightarrow HOCl + HNO_3$$

The sun light frees Cl from HOCl by photolysis

$$HOCl + h\upsilon \longrightarrow Cl + OH$$

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$OH + O_3 \longrightarrow HO_2 + O_2$$

Impacts of other greenhouse gases

Methane helps to remove ozone destroying chlorine

$$Cl + CH_4 \longrightarrow HCl + CH_3$$

$$CH_3 + O_2 \longrightarrow CH_3O_2$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$$

$$NO_2 + h\upsilon \longrightarrow NO + O$$

$$M + O + O_2 \longrightarrow O_3 + M$$