History of Primitive Atmosphere

- When Earth formed 4.6 billion years ago from a hot mix of gases and solids, it had almost no atmosphere.
- The atmosphere formed mainly from gases spewed from volcanoes. This mainly included water vapors as a major fraction (95-97%), 10-200 times of CO_2, hydrogen sulfide, SO_2, and other gases.
- Thus it was a reducing atmosphere with little or no oxygen.
- The surface was molten which get solidified when the cooled and form the thin layer over the surface
- The water vapors condensed enough to form the water bodies i.e., oceans, rivers etc.

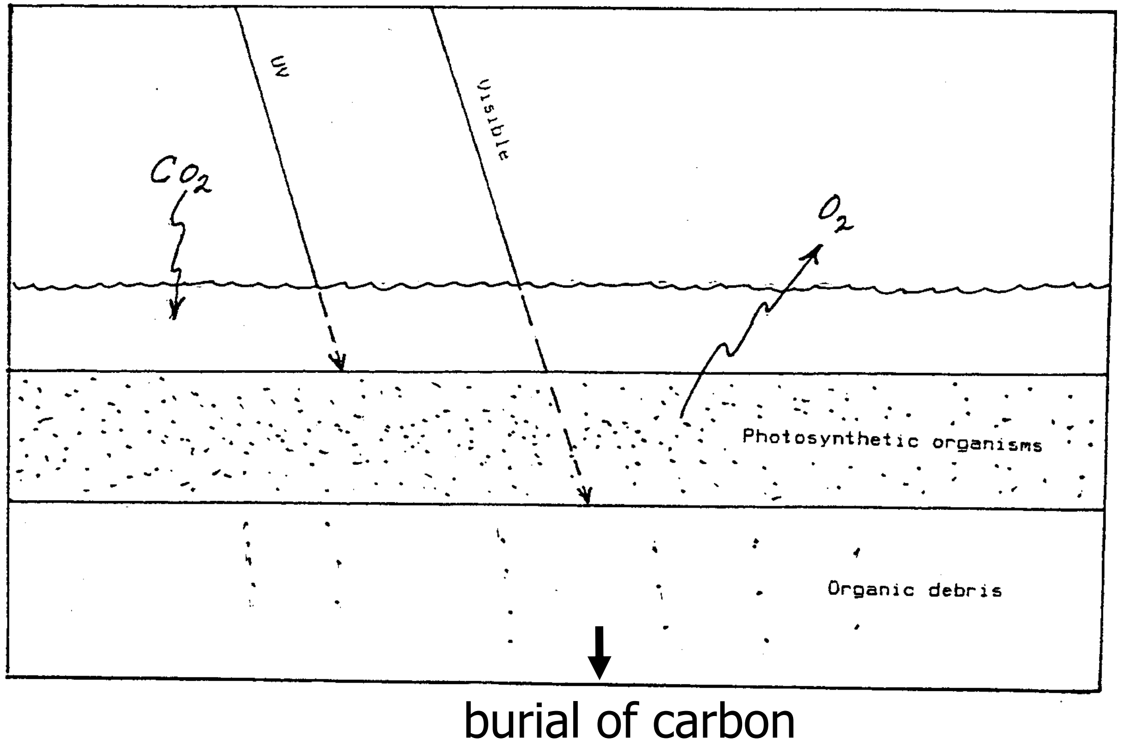
How did the earth's atmosphere get the way it is? (a theory)

- Volcanic emissions believed to be the major source of gaseous in the atmosphere.
- Volcanic emissions consisted of : 85% H_2O vapor, 10% CO_2, a few percent of nitrogen and sulfur compounds, traces of noble gases and other species,
- **However, O_2 was absent**.

Then Where did all the O_2 come from?

Concepts on development of Oxygen molecules

- As the surface cooled, water condensed
- CO_2 dissolved in the newly formed ocean and precipitated (limestone, dolomite rock)
- CO_2 combined with H_2 and give rise to formation of organic species which is an important substrate for life to occur



$$CO_2 + 2H_2 \xrightarrow{UV+catalyst} CH_3OH$$

$$CO + H_2 \xrightarrow{UV+catalyst} HCHO$$

- It is believed that certain life-forms (Algae) in the ocean slowly developed the ability to photo-synthetically produce organic molecules and free O_2.

$$H_2O + CO_2 \xrightarrow{UV+organism} CH_2O + O_2$$

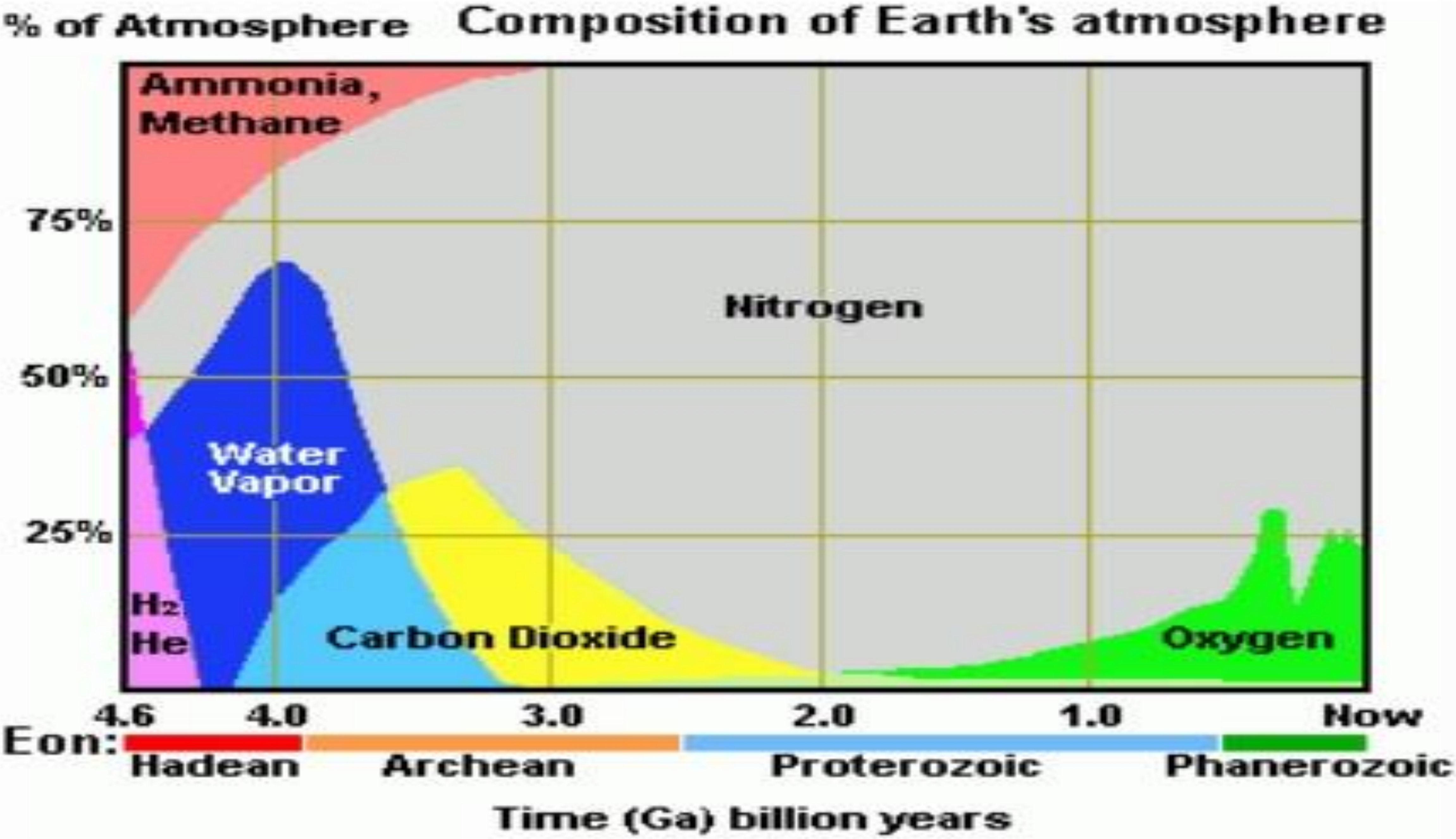
Build-up of Atmospheric Oxygen

- This enriched the molecule of O_2 by replacing CO_2 from the atmosphere. & resulted decrease in the CO_2 fraction.

- Initially the rate of **O_2 increase would have been slower** because it was used for oxidizing surface minerals which, gradually builds up in the atmosphere.

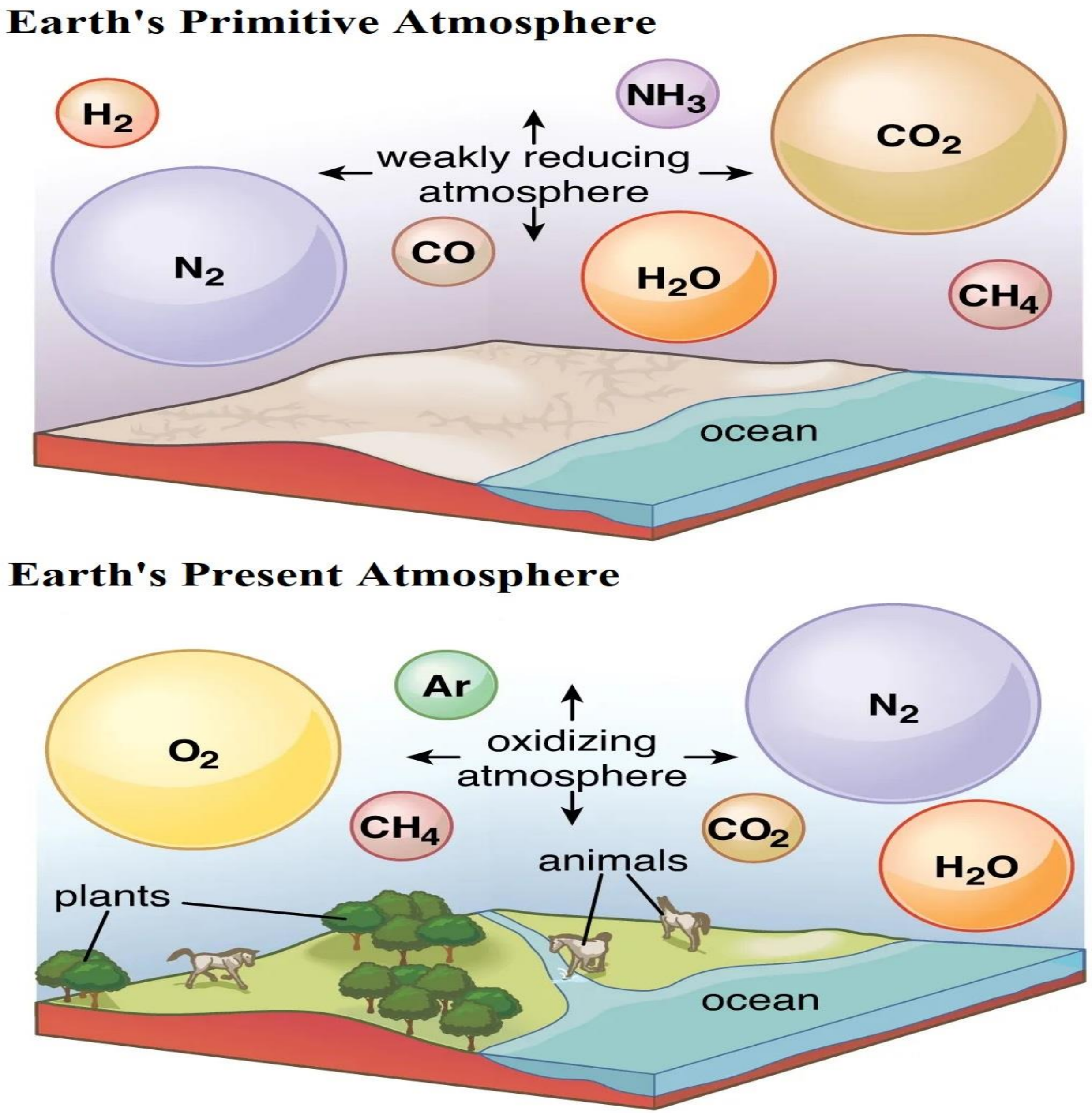
- While **N_2 being not very reactive; get accumulated** and became a larger fraction of the earth's gas composition.

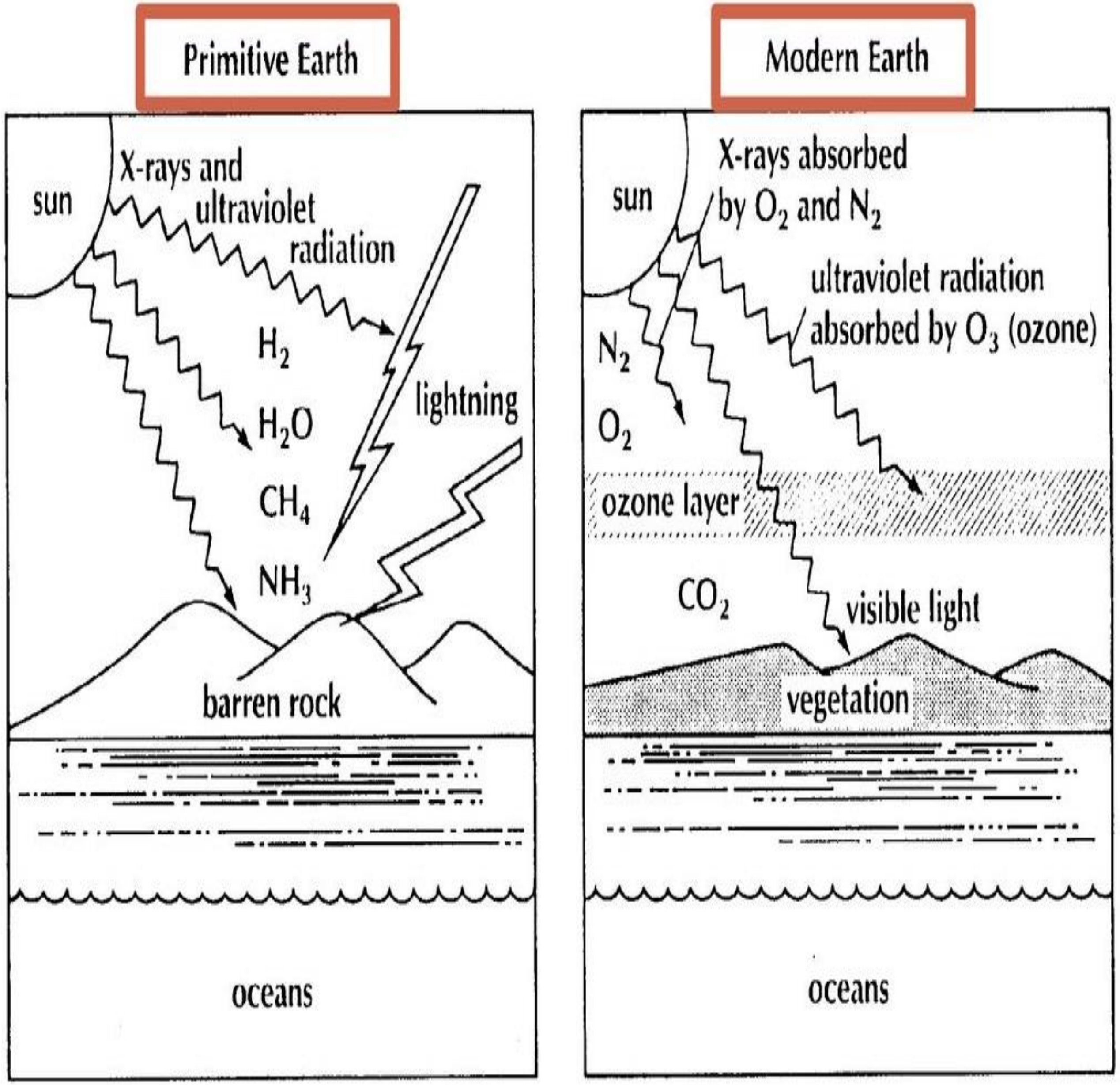
- This is how our primitive atmosphere converted into present atmosphere



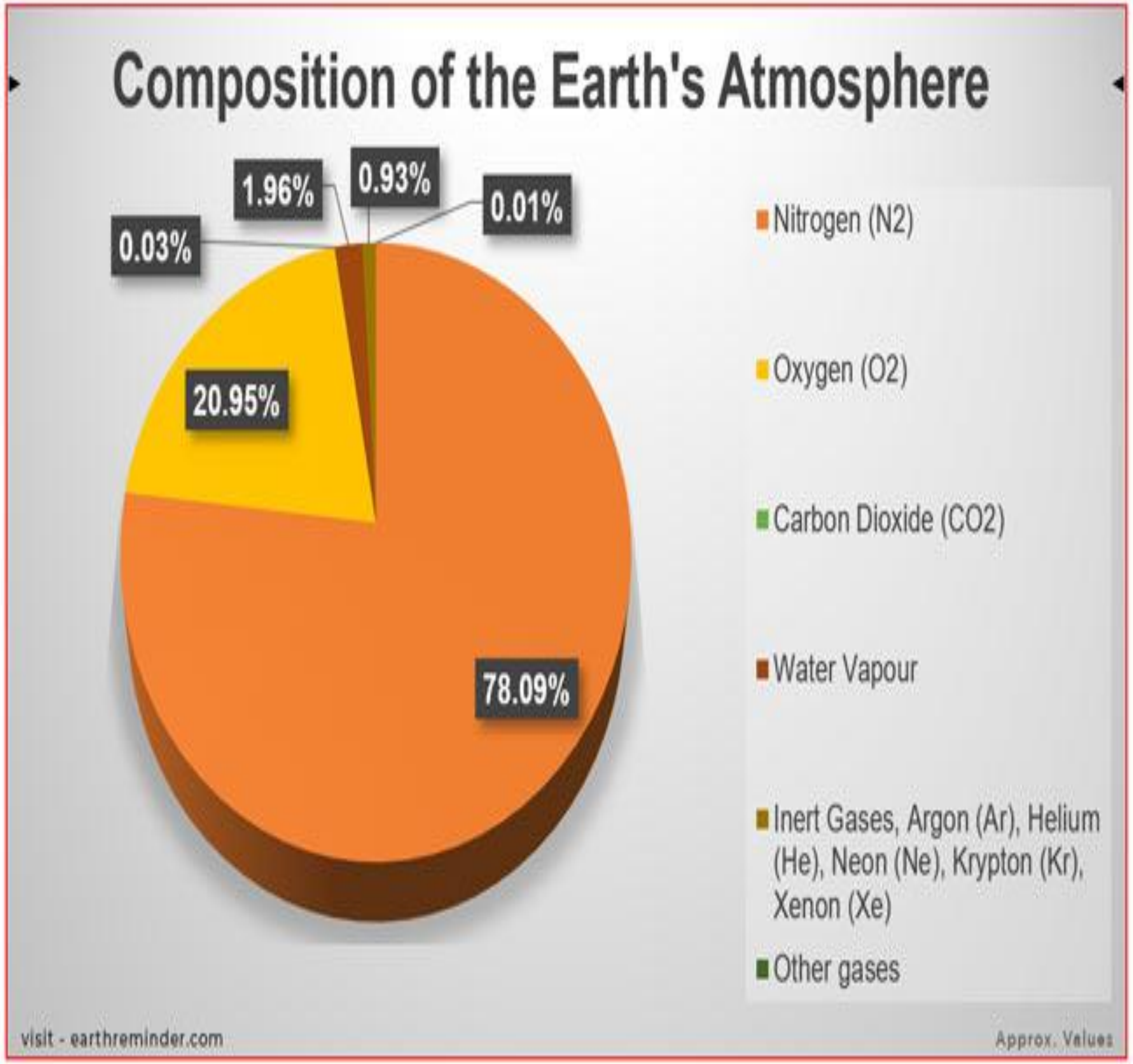
% of Atmosphere
Composition of Earth's atmosphere
Ammonia,
Methane
75%
50%
25%
Nitrogen
Water
Vapor
H2
He
Carbon Dioxide
Oxygen
4.6
4.0
3.0
2.0
1.0
Now
Eon:
Hadean
Archean
Proterozoic
Phanerozoic
Time (Ga) billion years

Primitive Atmosphere Vs Present Atmosphere



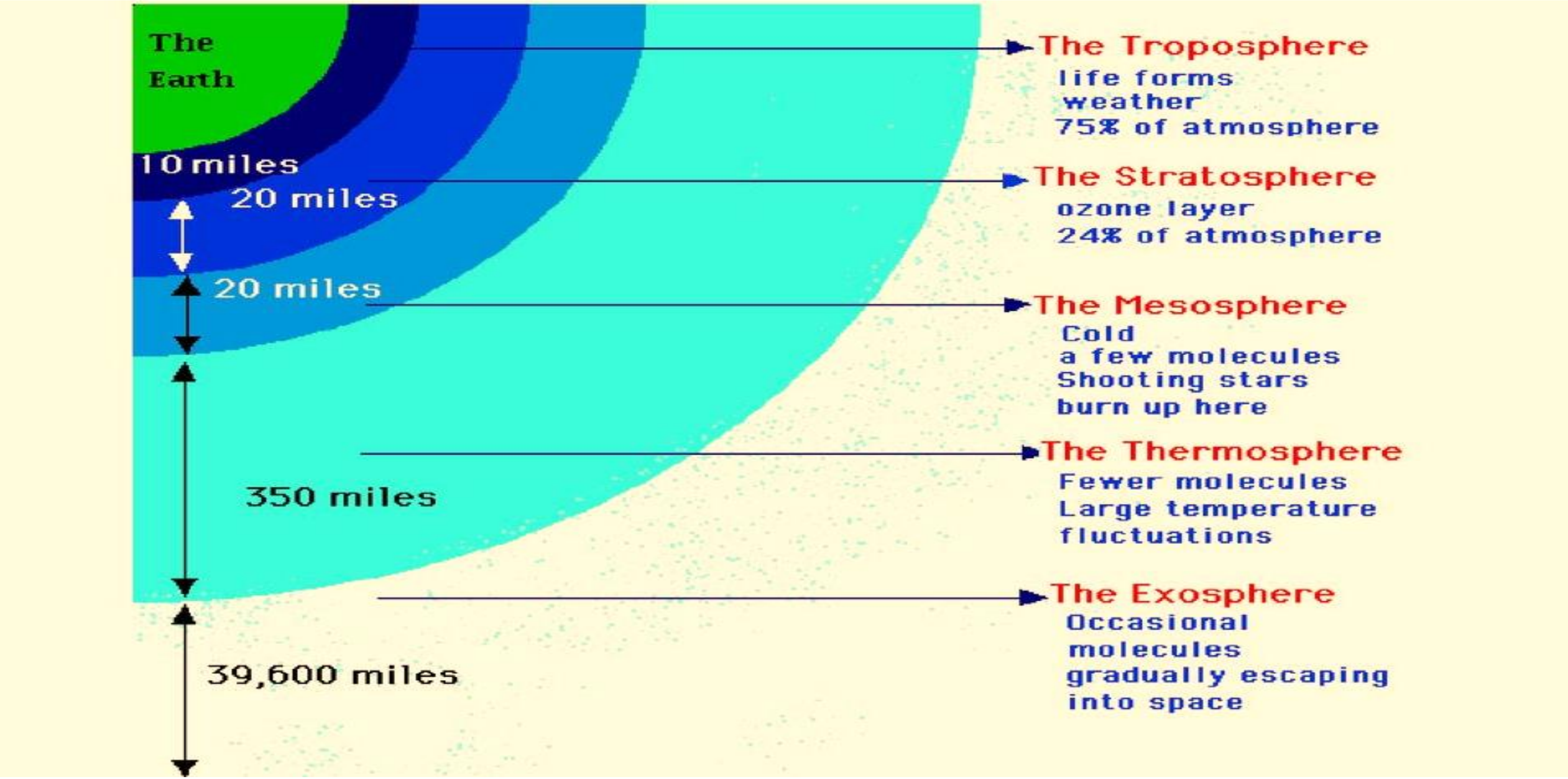


Composition of the Present Atmosphere (Well-Mixed Gases)



CONSTITUENT	CHEMICAL SYMBOL	MOLE PERCENT
Nitrogen	N_2	78.084
Oxygen	O_2	20.947
Argon	Ar	0.934
Carbon Dioxide	CO_2	0.035
Neon	Ne	0.00182
Helium	He	0.00052
Methane	CH_4	0.00017
Krypton	Kr	0.00011
Hydrogen	H_2	0.00005
Nitrous Oxide	N_2O	0.00003
Xenon	Xe	0.00001
Ozone	O_3	trace to 0.00080

Stratification of present atmosphere



Solar Radiation

- Source of most of the earth's energy
- Energy emitted by **black body** at temperature of **6000 ^{o}K**
- Energy received by the earth at a constant rate
  - ✓**Energy flux of solar radiation on extraterrestrial surface = 1370 W/m^2.**
  - ✓**Energy flux of solar radiation on earth surface = 343 W/m^2.**

What is "black body"?

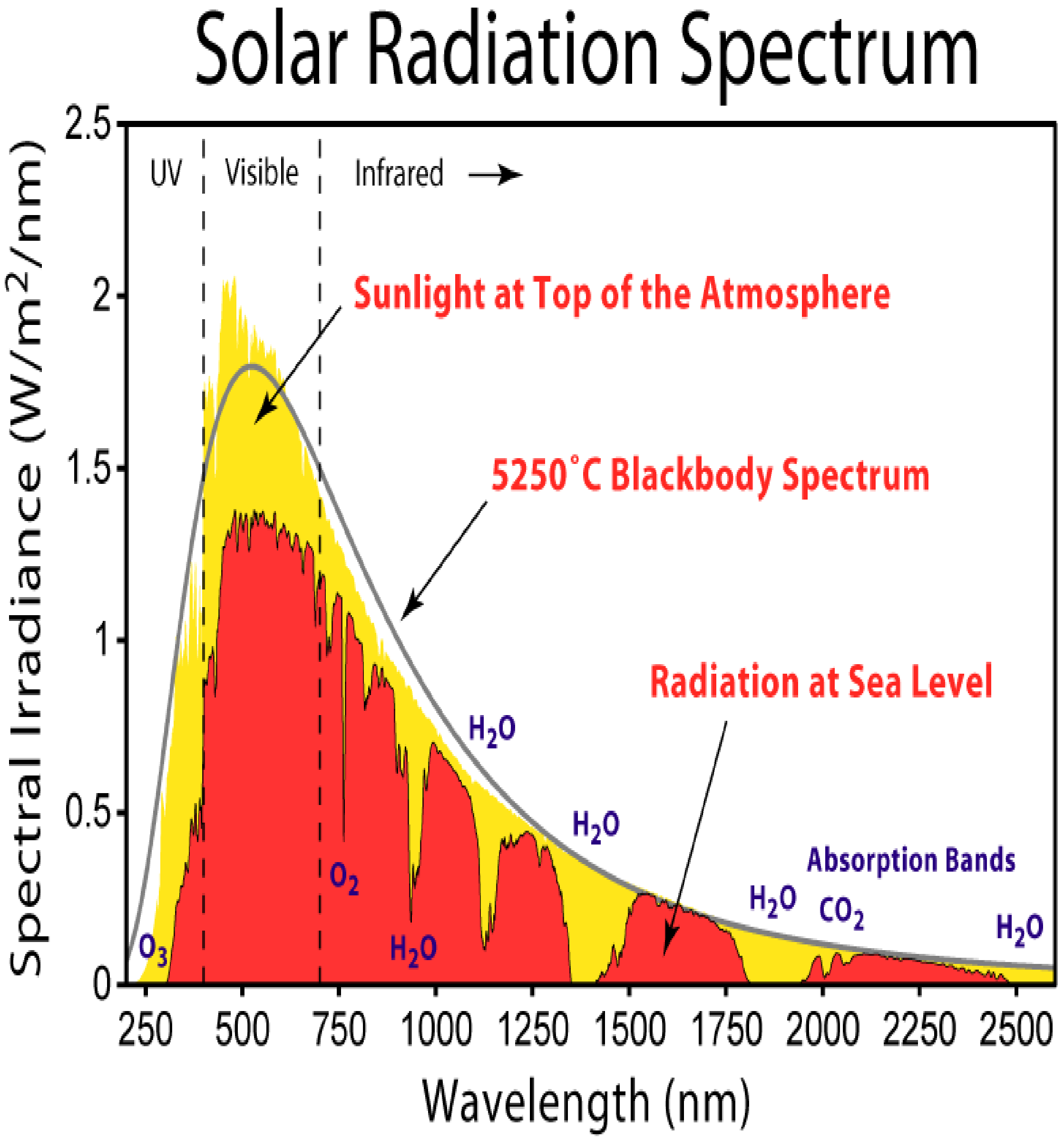
a surface that absorbs all radiant energy falling on it. Because incident visible light will be absorbed rather than reflected, and therefore the surface will appear black.

What happened to the difference?

Radiant energy (sometimes referred to as *radiant intensity*) decreases at the rate of the inverse square of the distance from the source.

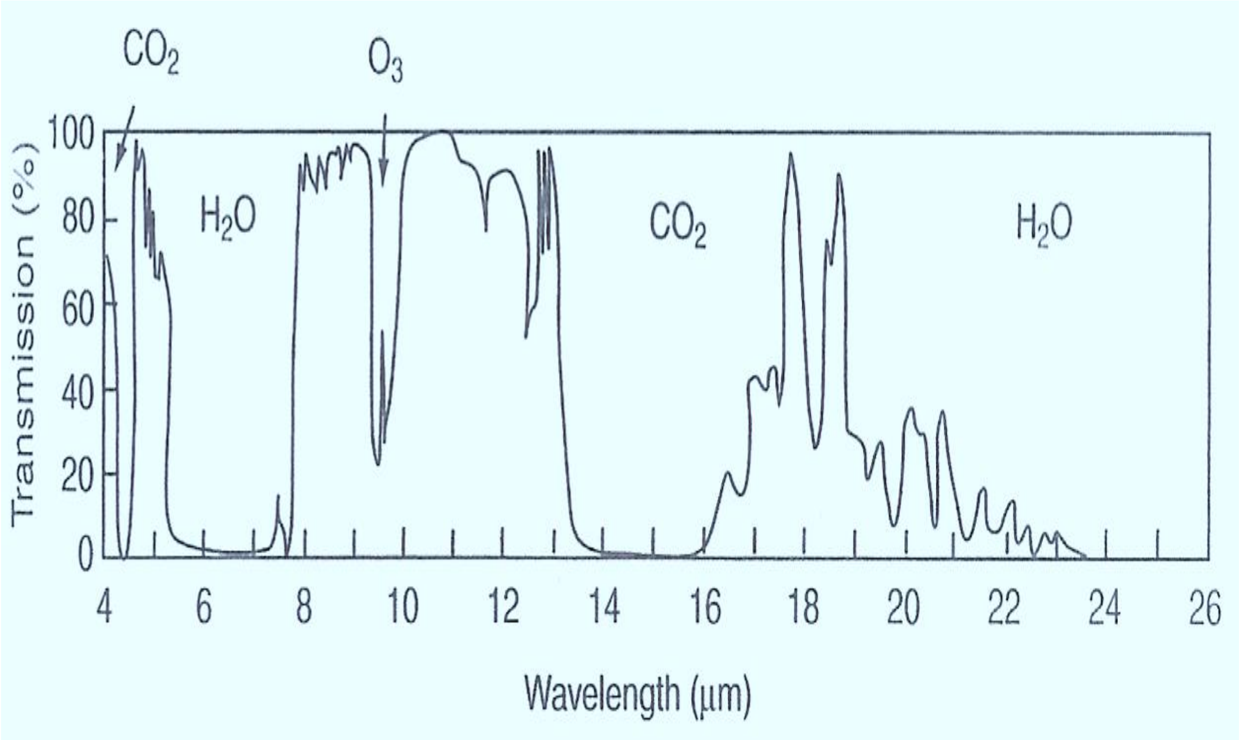
Solar Spectrum

- Most energy in the UV wavelength region (0.15- 4 μm) is absorbed by O_3 and O_2 absorb much of the UV irradiance below 300 nm at higher altitude mostly in the stratosphere.
  - UV radiation < 0.18 μm absorbed by O_2 at 100 km;
  - While UV radiation of wavelength 0.2-0.3 μm is being absorbed by O_3 below 60 km.
- About half of the energy is in the visible wavelengths below 0.7 μm and a significant fraction of the visible irradiance is scattered by clouds and aerosol.
- The rest of the energy is in the form of Infrared-large wavelength bands > 750 nm which are absorbed by water vapor, CO2, and O3.



Thermal Radiation

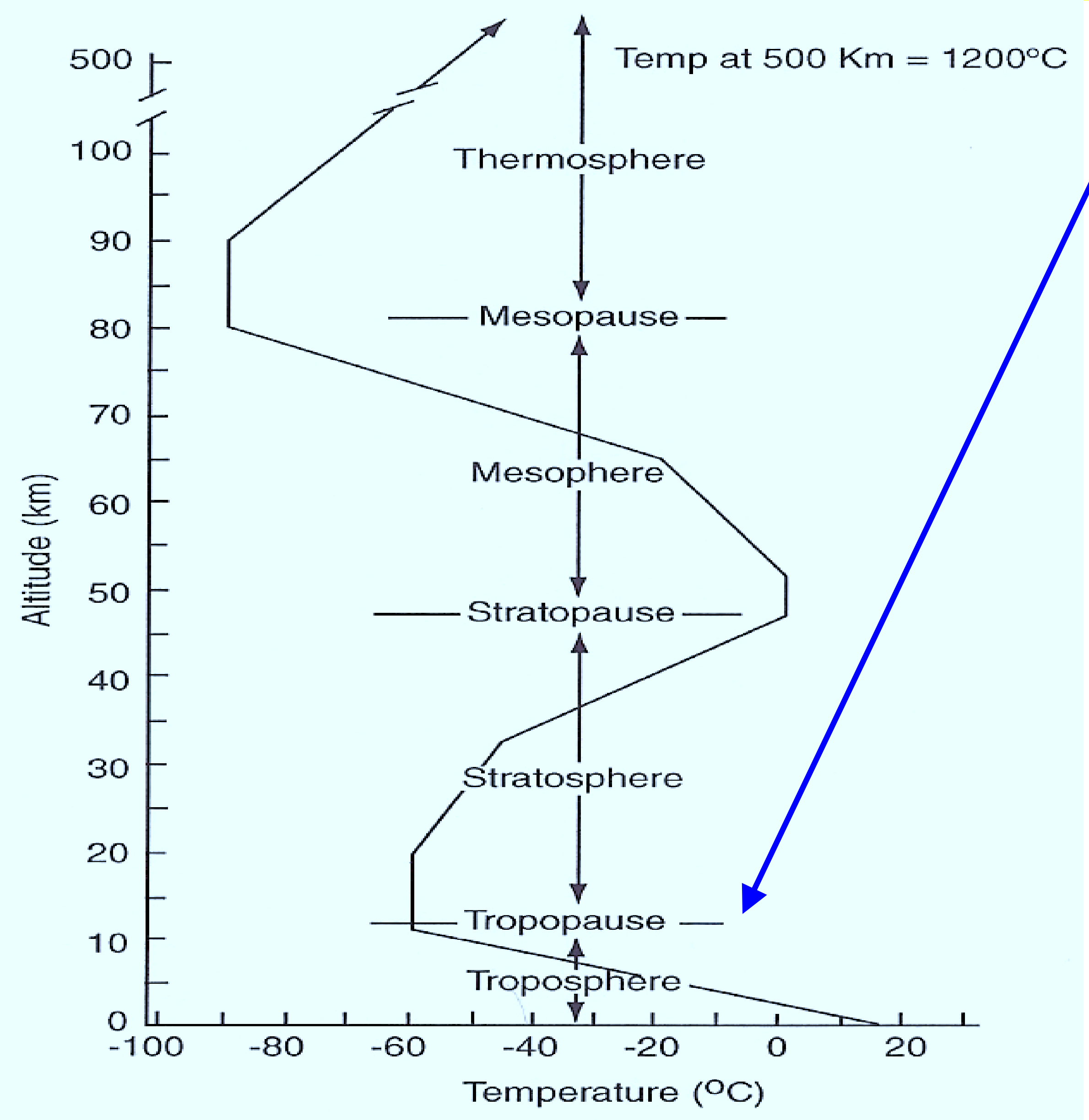
- Earth absorbs solar radiation and re-emits longer infra-red wavelengths particularly in the 1-30 μm spectral region
- It radiates as **black body** at 290ºK
- H_2O, CO_2, and other greenhouse gases present in the atmosphere absorbs these solar energy



Surface Air Temperatures

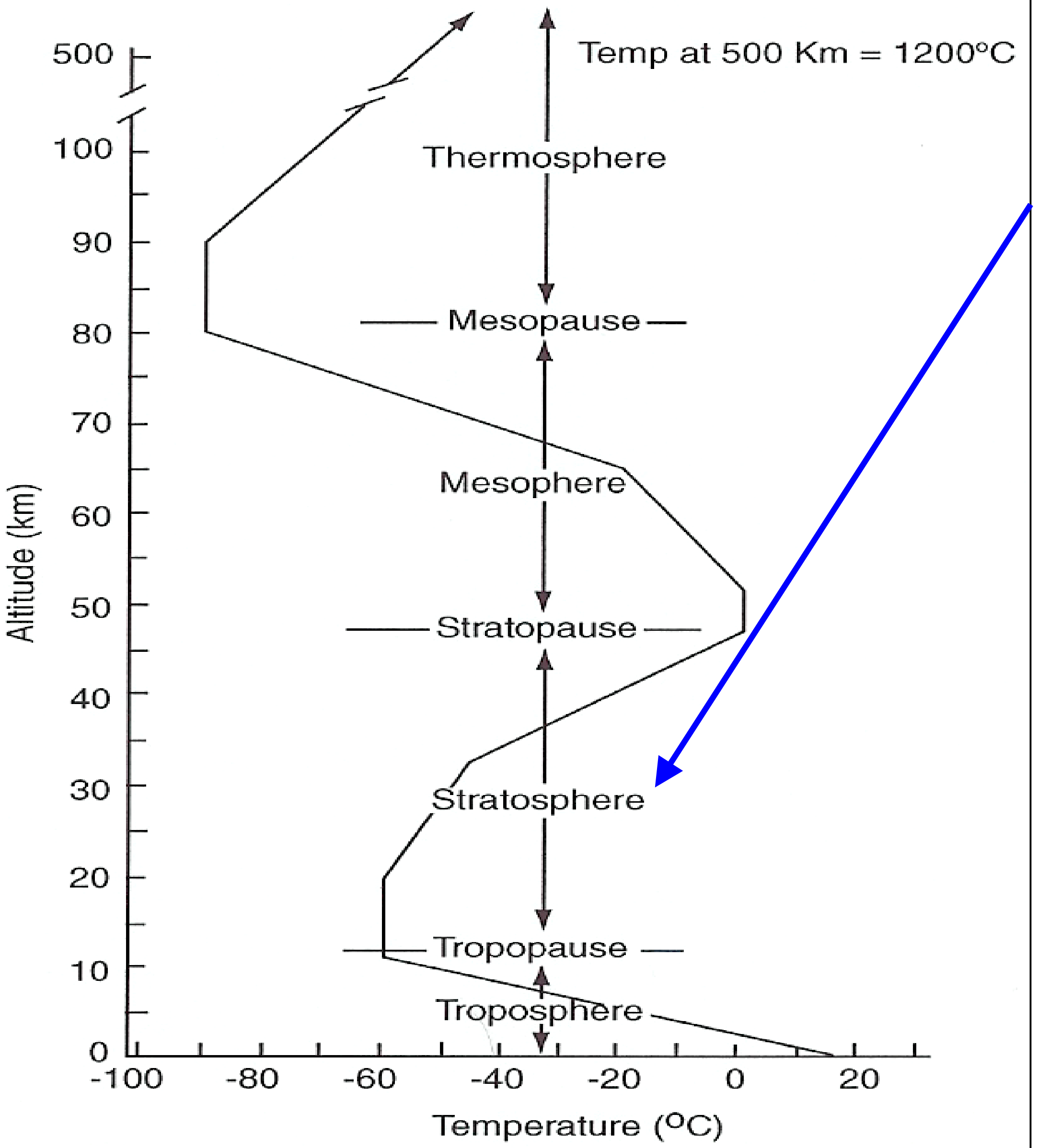
- Average surface air temperature (~ 15^{o}C to 20^{o}C)
- Temp. vary regionally due to the unequal distribution of solar radiation
- Equatorial regions gets higher radiation compared to the polar region
- This difference results in energy transport by air and ocean currents
- Heat generated is dissipated through cloud formation, evaporation and condensation
- Warmer air currents generated in the equatorial region moves towards polar region while cold currents generated at polar region moves towards equator to balance the heat
- The temperature changes significantly with height. This change in Vertical temperature profile describe atmosphere into various zones or layers

Vertical Temperatures and Zones (Troposphere)



- This is the lowest layer of atmosphere
- Depth varies from 8-18 km
  - Less at the poles, more at equator
- Characterized by 2 regions
  - **Planetary boundary layer (~ 1 km depth)**
  - **Free troposphere**
- Temperature decreases with height on average - 6.5 °C/km – temp lapse rate: positive
- Highly unstable condition exist due to temp. and velocity gradient
- Vertical and horizontal air motion; cloud formation, condensation, evaporation etc. Forms the "weather"
- Isothermal condition exist at tropopause above 12 km

Vertical Temperatures and Zones (Stratosphere)



Temperature increases with height to altitude of 45-55 km

❖**Temp. lapse rate is : Negative**

❖ Temperature reaches to 0°C at 30-35 km

❖Relatively Stable Region: Horizontally it is very stable region with little vertical mixing

❖ Few clouds/no weather

❖ Warmer temperatures due to absorption of UV radiation

❖ Complex chemistry occurs NO, $OH^{\cdot}$, NH_3, O, O_2, O_3, Cl and other species.

❖ Chapman Reactions:

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

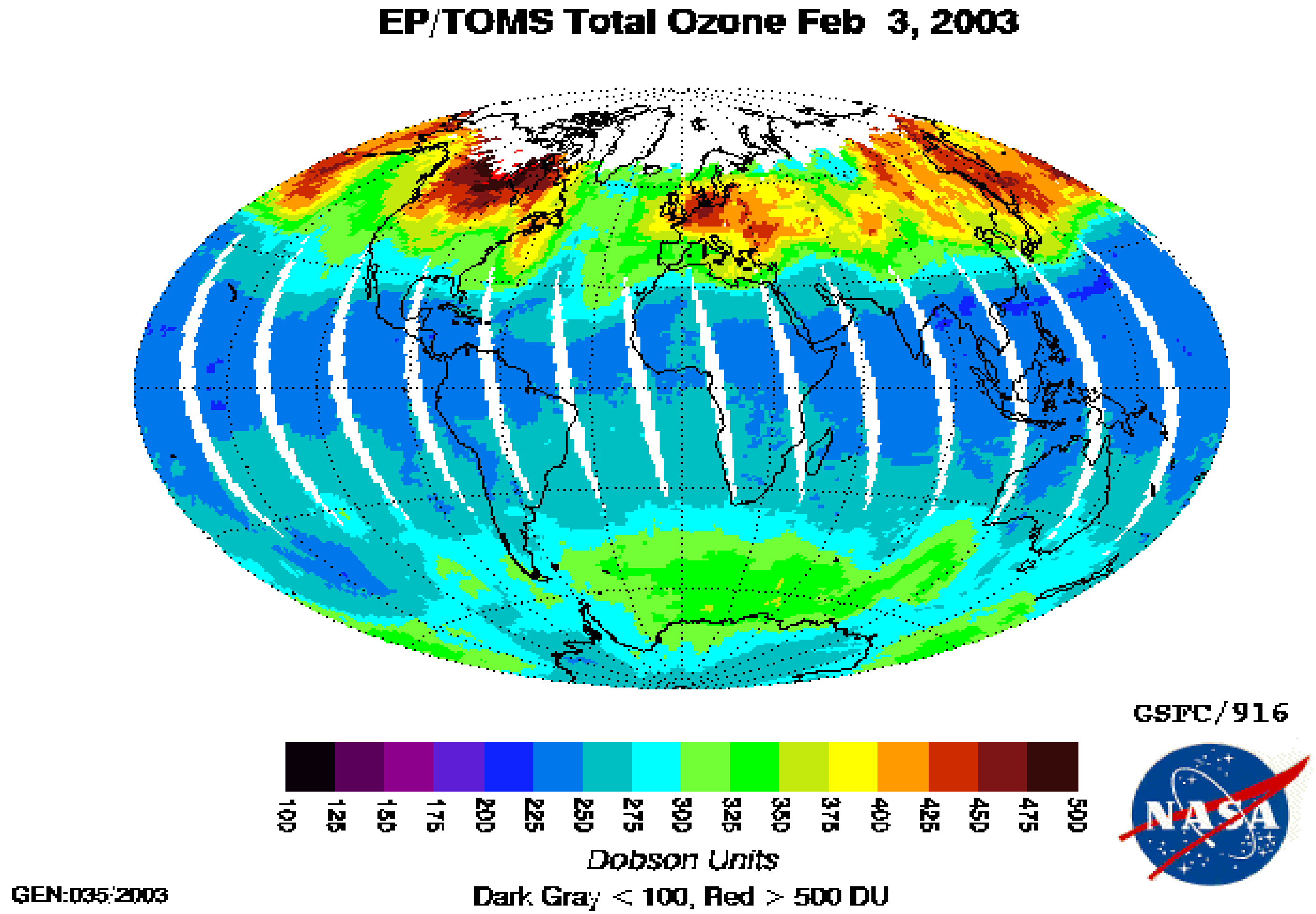
$O + O + M \rightarrow O_2 + M$

$O_3 + h\nu \rightarrow O_2 + O + \text{Heat}$

for $h\nu$ corresponding to $0.24 \leq \lambda \leq 0.30\ \mu m$

Maximum O_3 at 25-40 km

STRATOSPHERIC OZONE LAYER



1 "Dobson Unit (DU)" = 0.01 mm ozone at STP = 2.69×10^{16} molecules cm^{-2}

THICKNESS OF OZONE LAYER IS MEASURED AS A COLUMN CONCENTRATION

Importance of Stratospheric Ozone

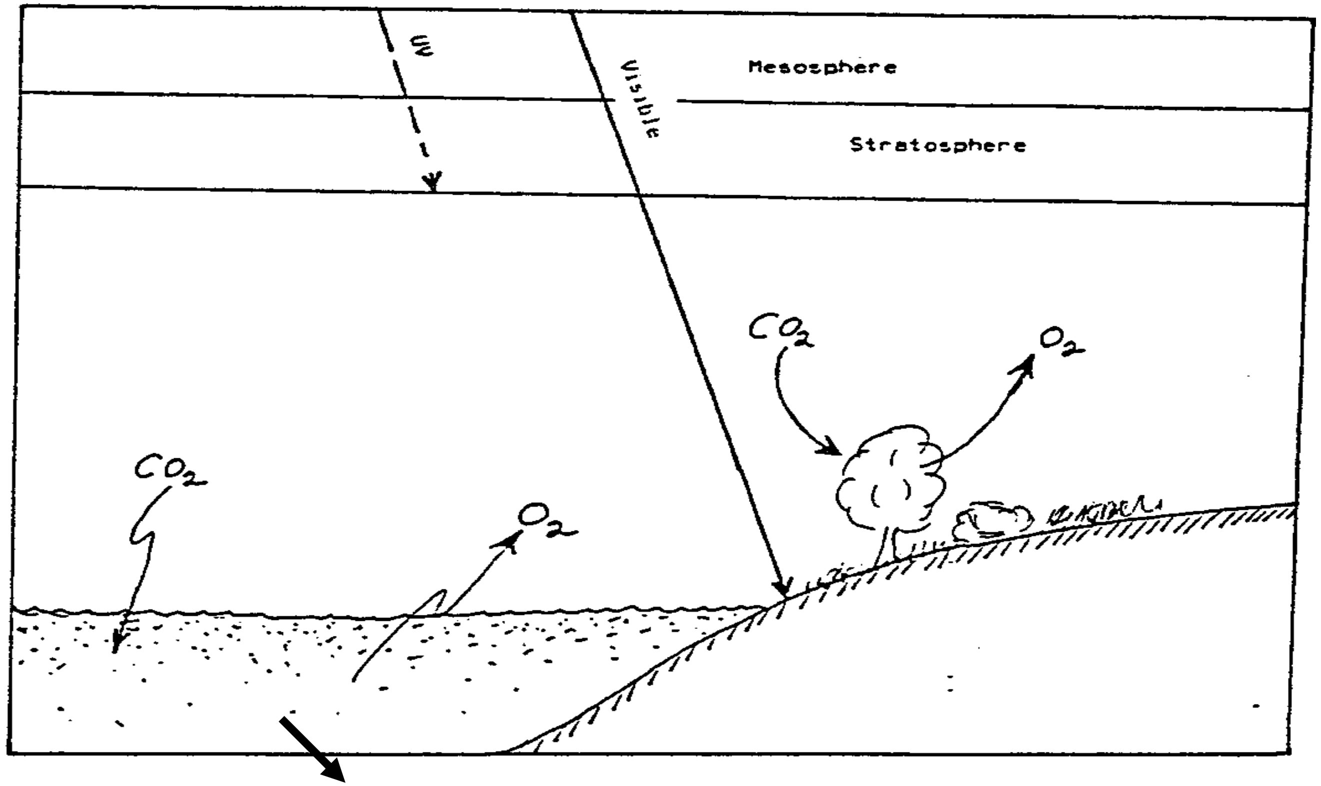
- anthropogenic sources emits CO_2 in the atmosphere which is partially dissolved in the ocean and also is used in Photosynthesis
- Photosynthesis process evolve O_2.
- This O_2 builds in the atmosphere and get converted into O_3 in the stratosphere

$O_2 + h\nu \rightarrow 2O$

$O_2 + O + M \rightarrow O_3$

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

- This reduces the penetration of UV light to the surface & prevents our health from its negative effects



burial of carbon