Atmospheric Chemistry

Spring 2014

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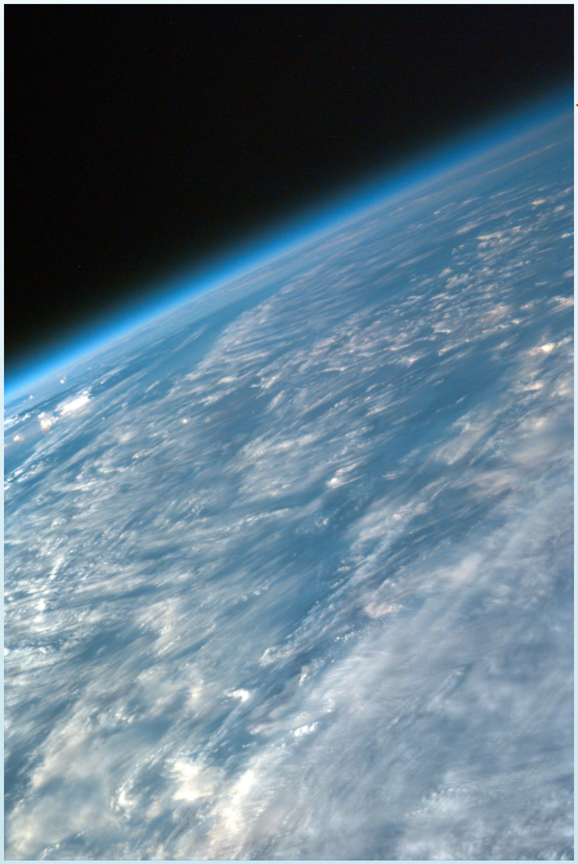
Research Professor

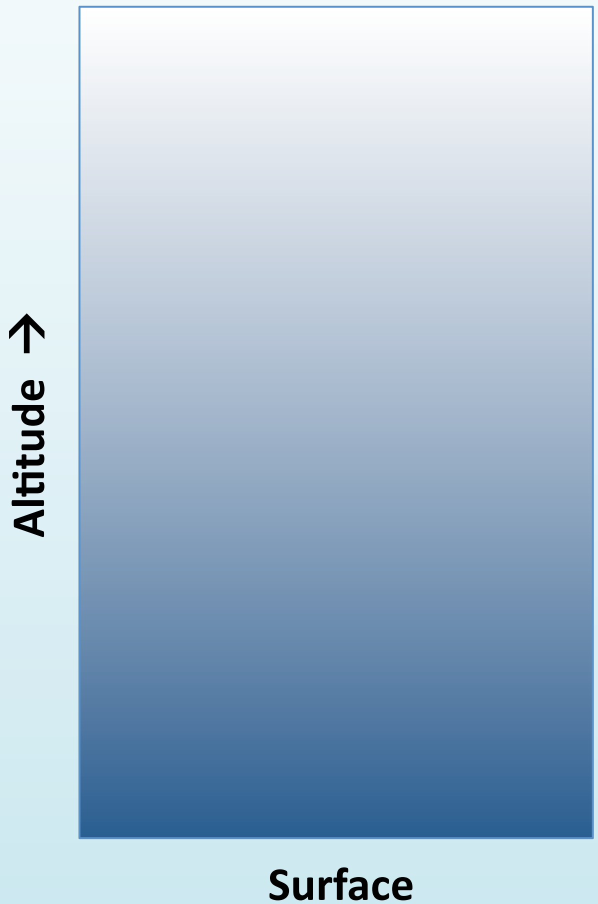
Cook's Tour of the Atmosphere:
from an atmospheric chemist's perspective



The atmosphere is a thin spherical shell around the Earth

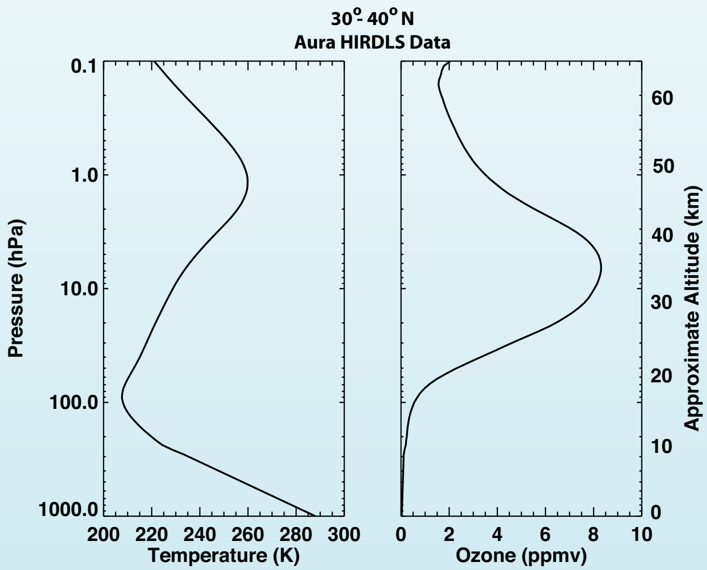
At surface pressure it would be only 8 km thick while the radius of the Earth is 6300 km

Internal Structure of the Atmosphere



- Pressure and density decrease exponentially with increasing altitude
- This is a consequence of the gravitational attraction of the Earth
- The prime constituents, N_2(78%), O_2(21%), and Ar(1%) are well-mixed up to about 100 km altitude

Temperature Structure of the Atmosphere



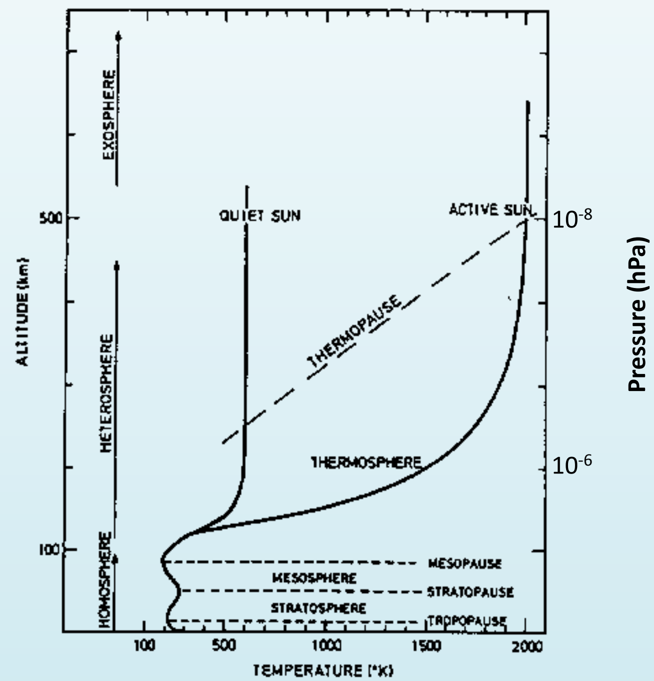
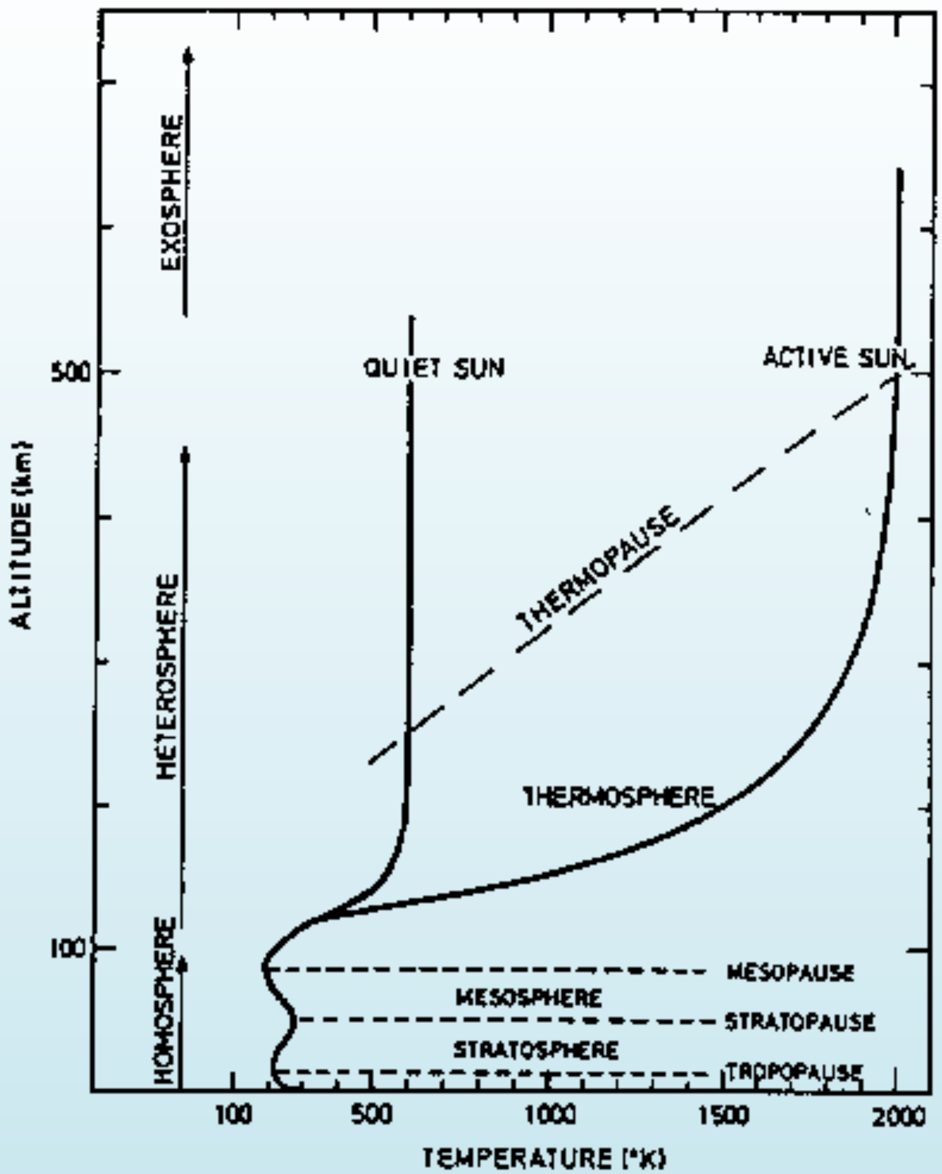


Fig 2. Vertical temperature distribution in the earth's atmosphere with emphasis on the thermosphere. (After P. M. Banks and G. Kockarts, "Aeronomy," Academic Press, New York, 1973, Part A, p. 3.)



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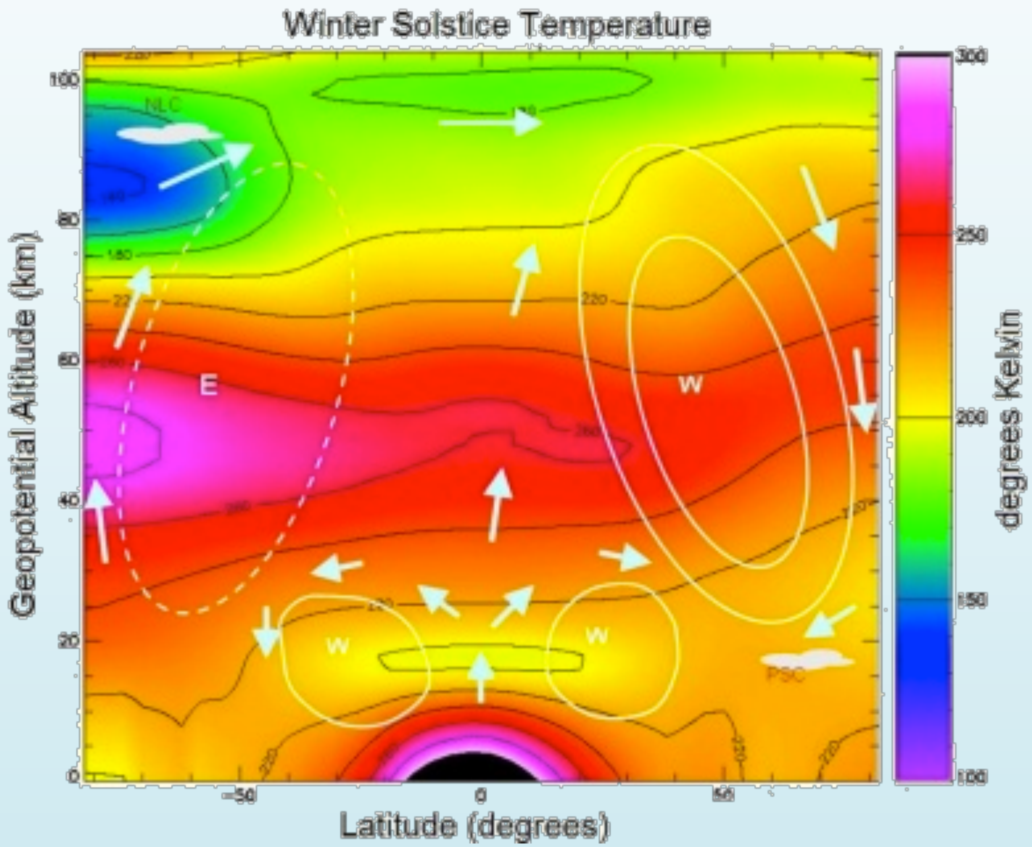
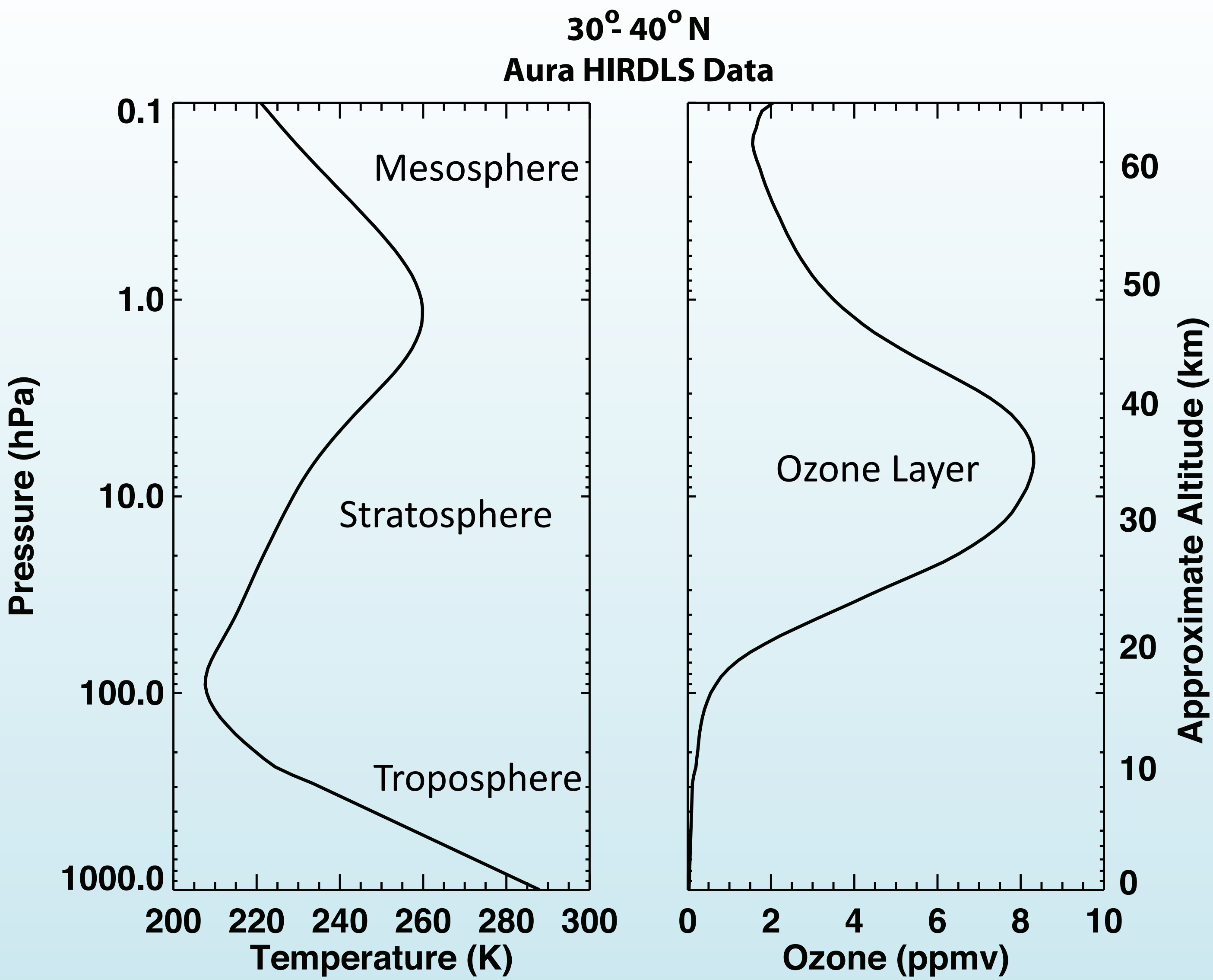
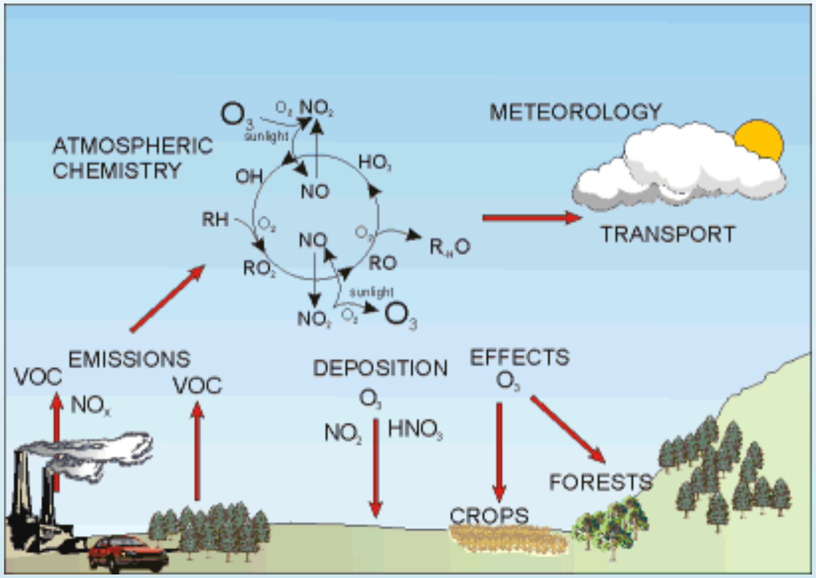
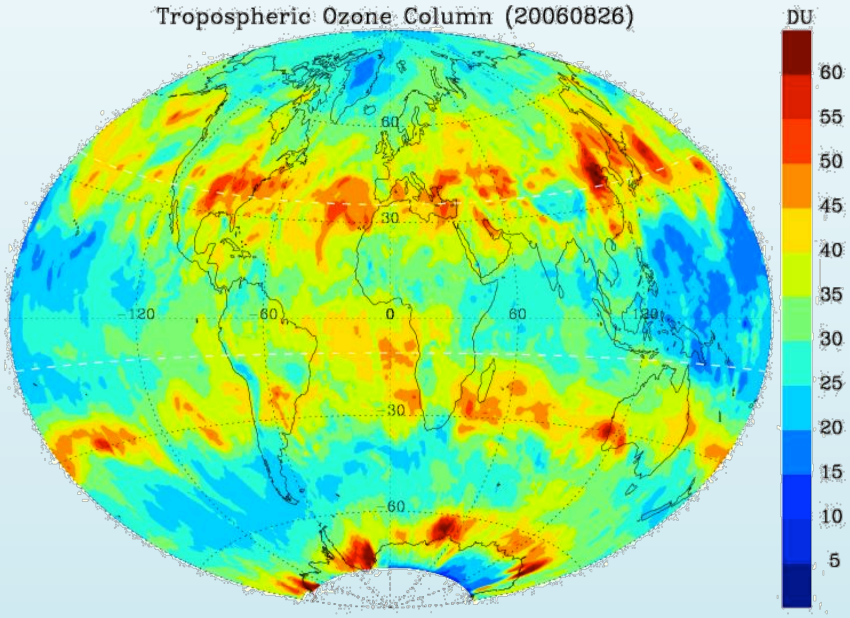

Winter Solstice Temperature
Geopotential Altitude (km)
Latitude (degrees)
degrees Kelvin
NLC
PSC
E
W
W
W
0
20
40
60
80
100
-50
0
50
100
150
200
250
300

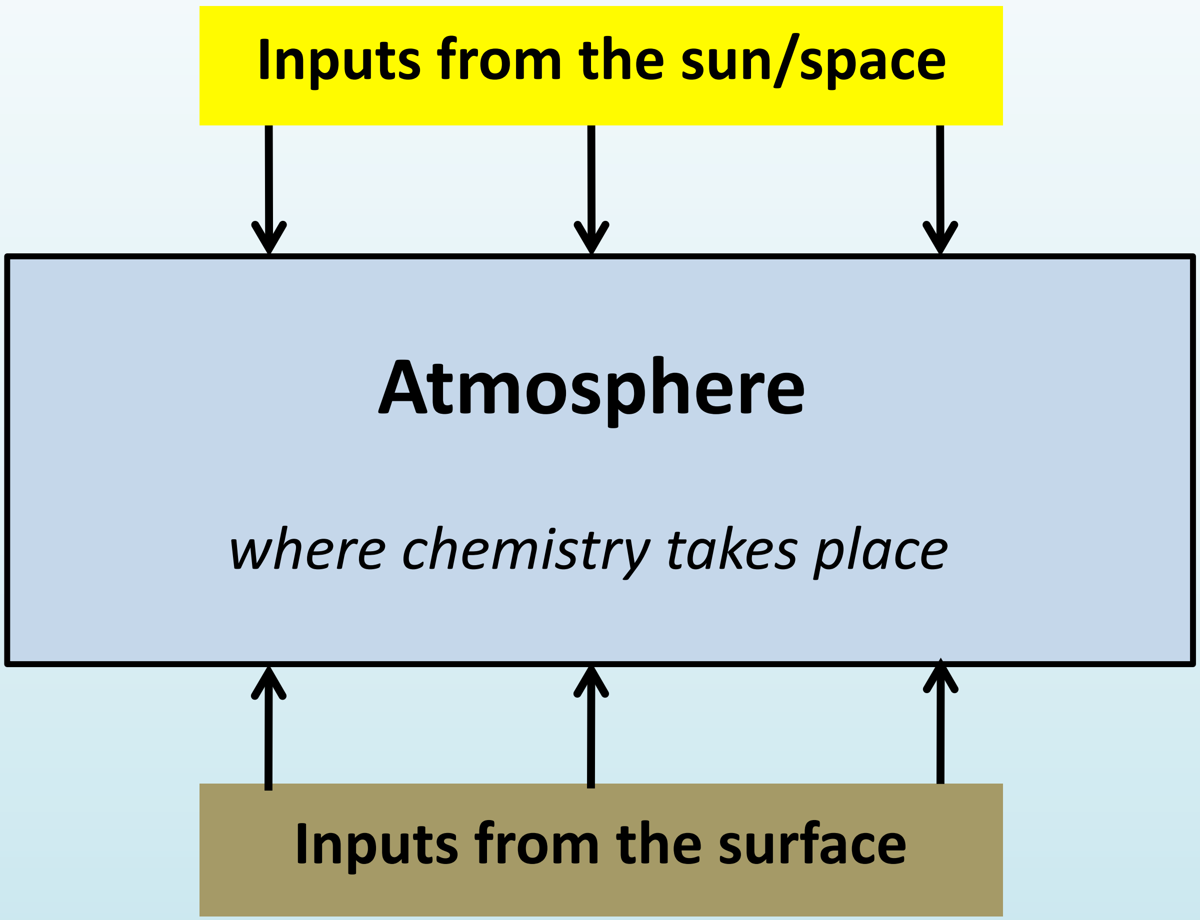

30° - 40° N
Aura HIRDLS Data
0.1
1.0
10.0
100.0
1000.0
Pressure (hPa)
Mesosphere
Stratosphere
Troposphere
200 220 240 260 280 300
Temperature (K)
Ozone Layer
0 2 4 6 8 10
Ozone (ppmv)
60
50
40
30
20
10
0
Approximate Altitude (km)

Tropospheric Ozone

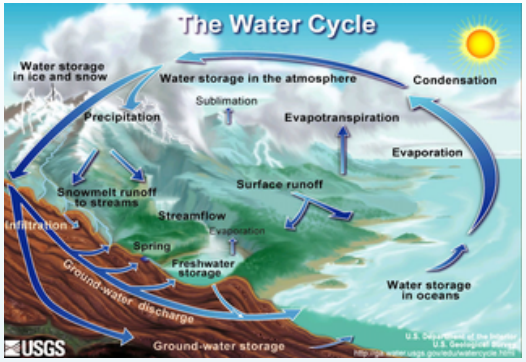


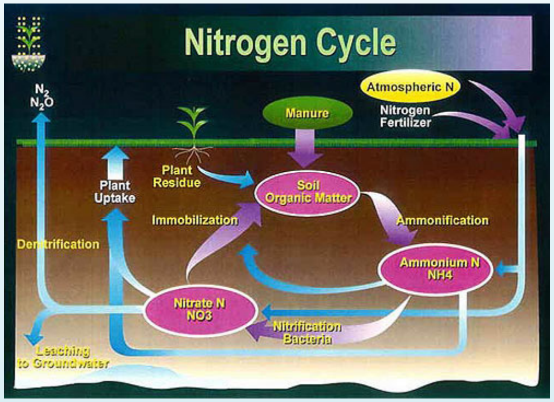


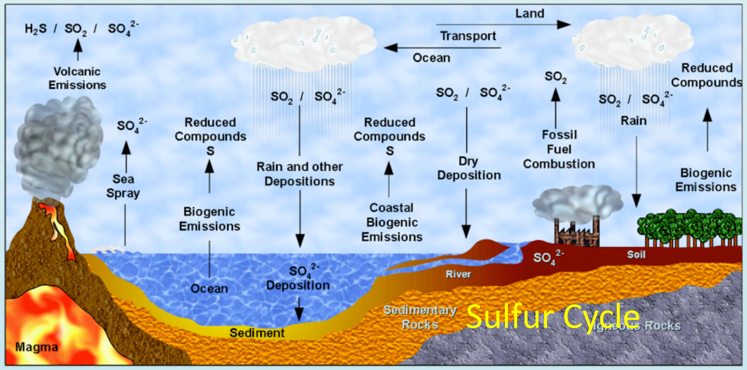
Think of the atmosphere as a single box



Inputs from the surface

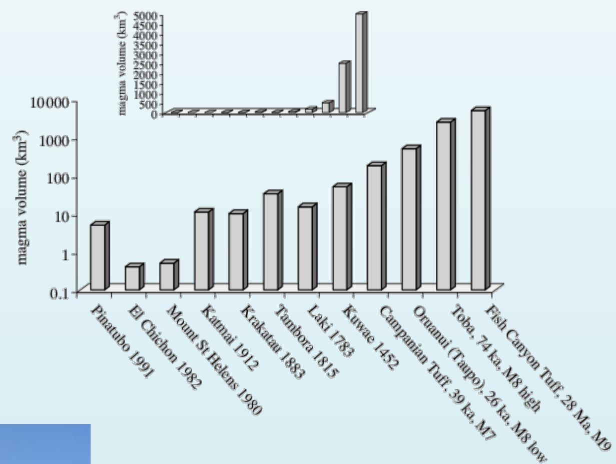


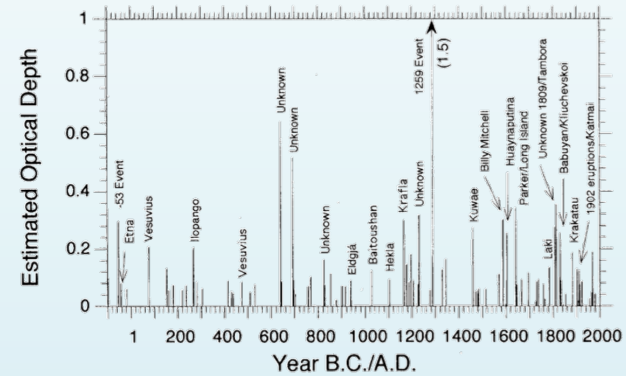


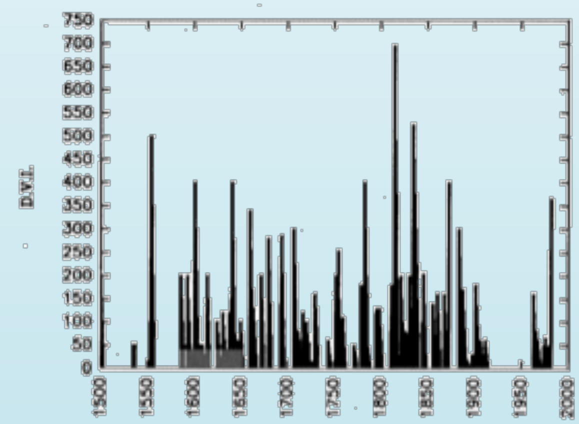


- Water evaporates from oceans, lakes, etc. (hydrological cycle)
- Biogeochemical cycling of nitrogen, sulfur, hydrocarbons, etc. connects to atmosphere
- Volcanoes and fumarole vents inject magmatic gases
- Industrial chemicals are vented to atmosphere

Explosive Volcanic Eruptions







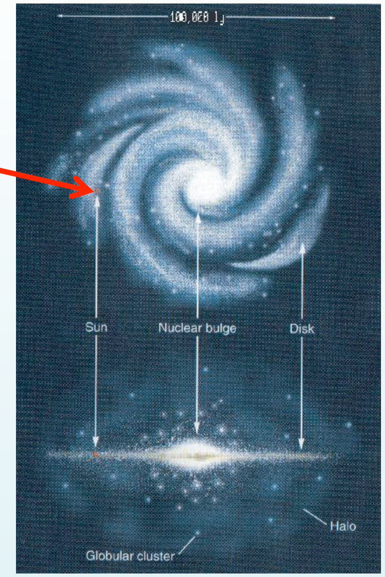
Fumaroles

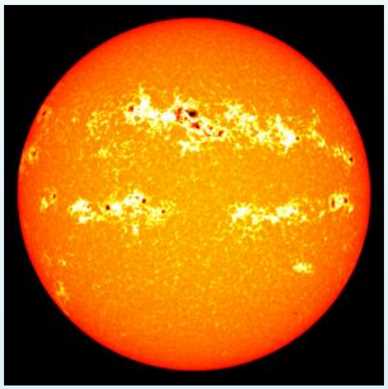
Inputs from the sun/space

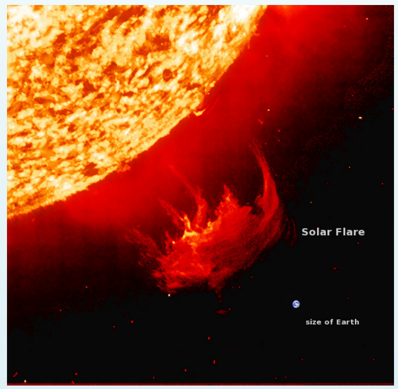
- Solar radiation (IR, visible, UV, extreme UV)
- Particles from the sun (protons, high energy electrons)
- Galactic cosmic rays
- Meteoritic dust

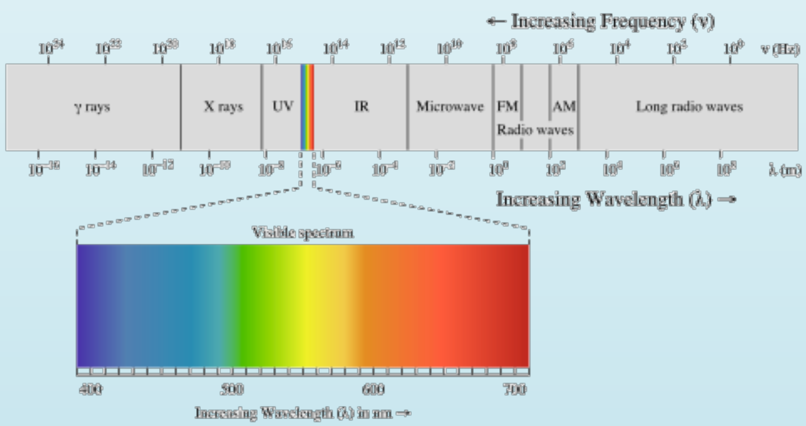
The Sun: a G2 Star in the Milky Way Galaxy

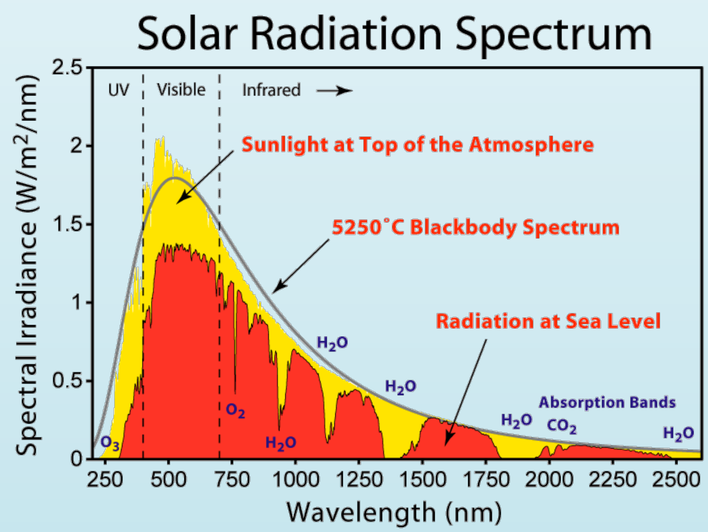
(~100 million stars)



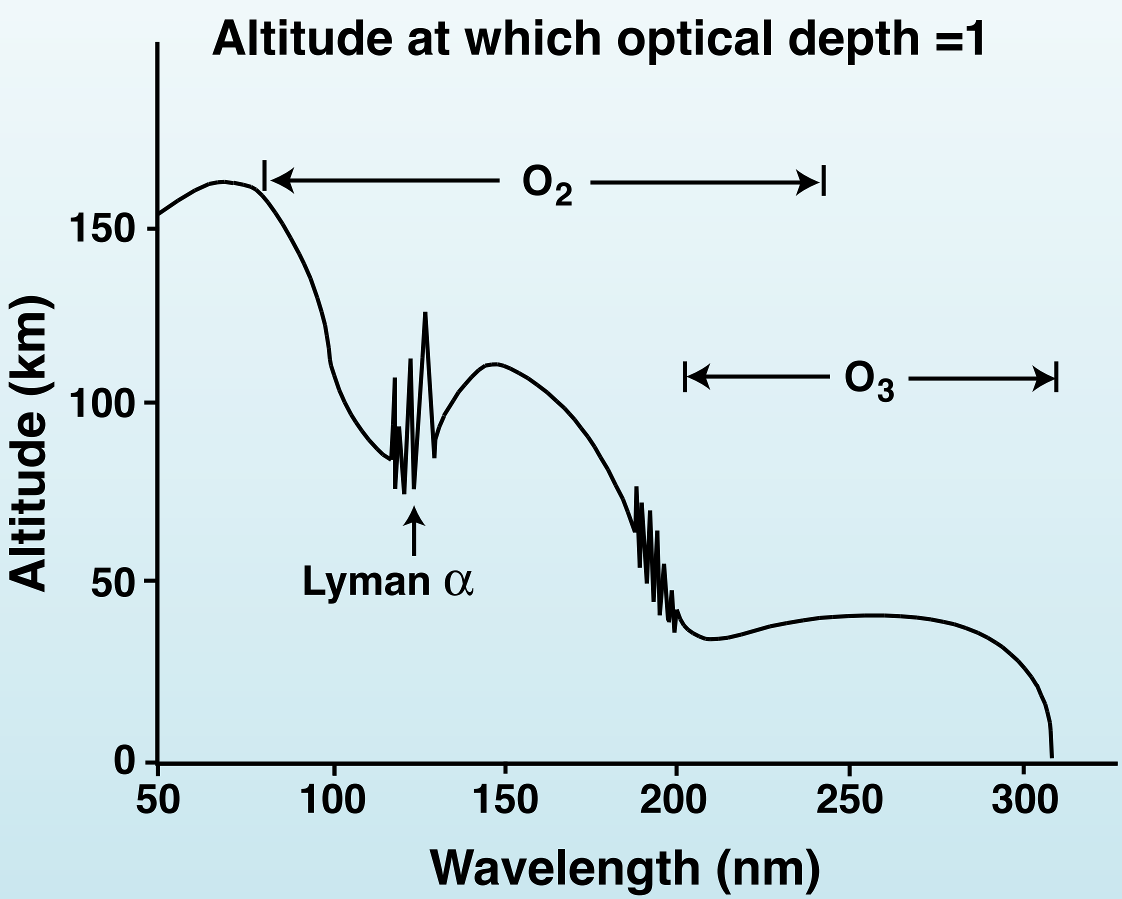




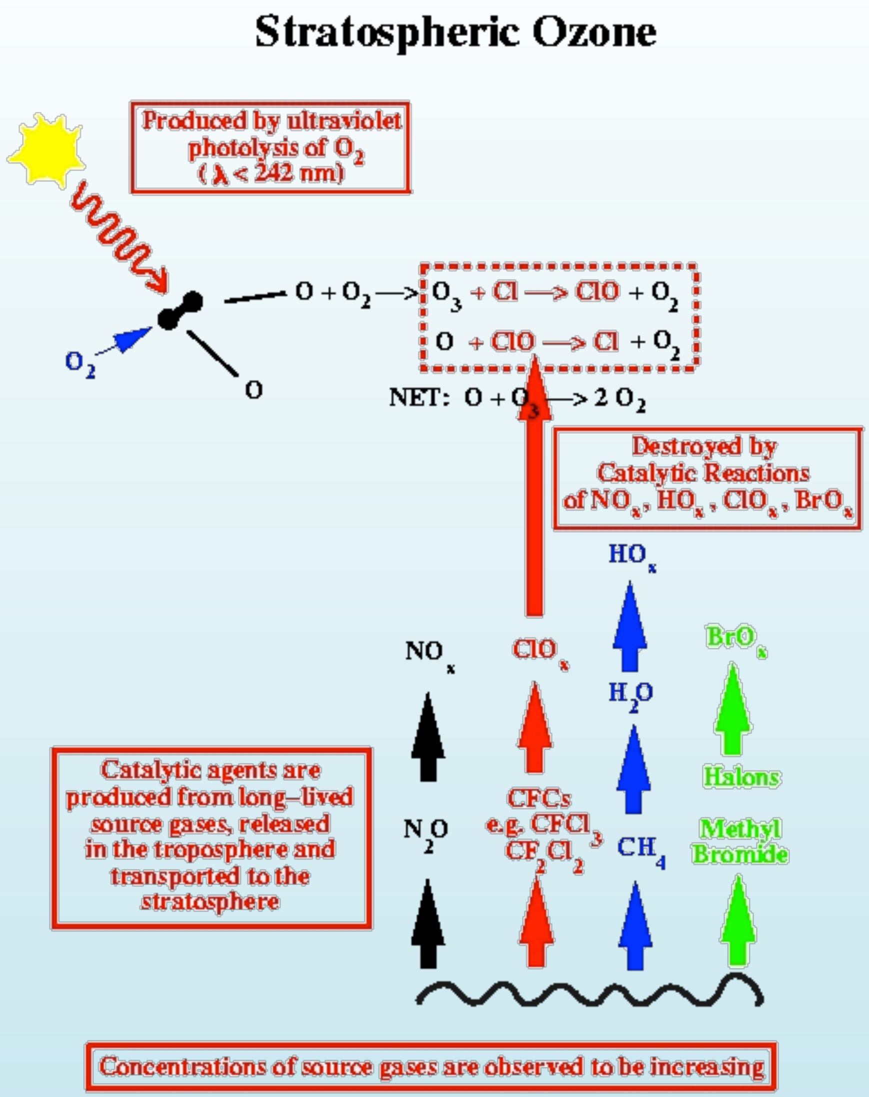




Penetration of Solar Radiation into the Atmosphere

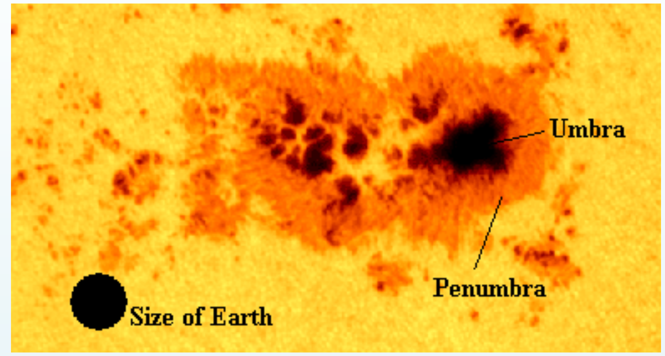


Description of Basic Stratospheric Chemistry

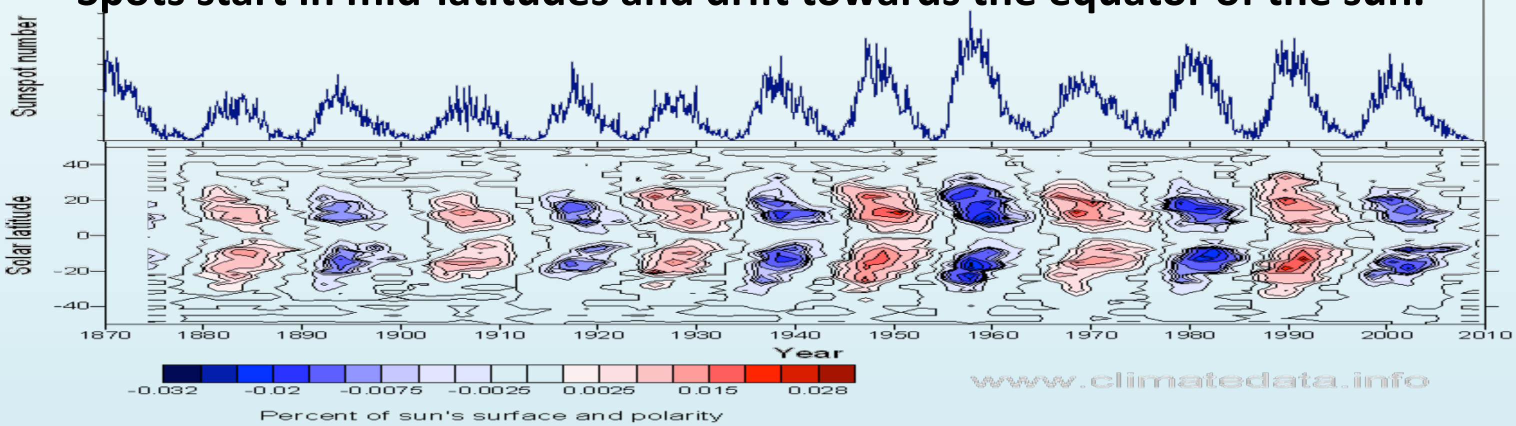


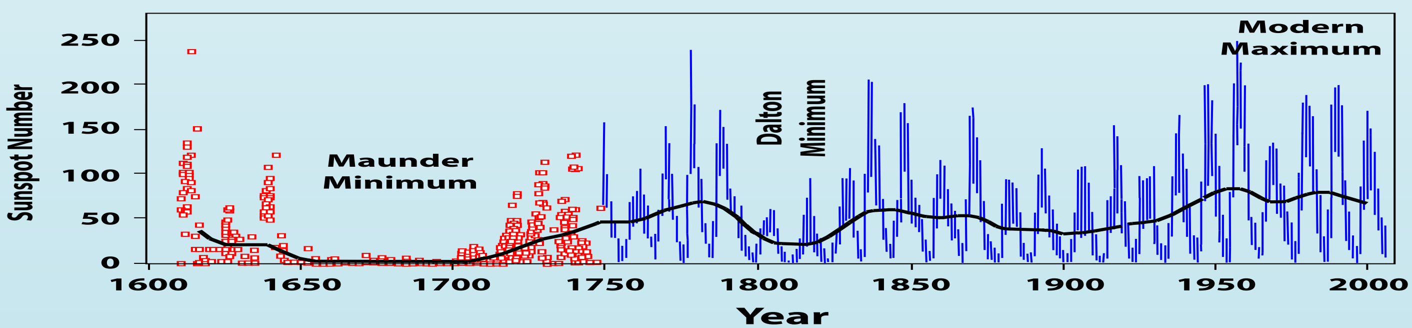
The 11-Year Sunspot Cycle

Sunspots are associated with large magnetic outbursts on the surface of the sun. The dark umbra is surrounded by a brighter penumbra.

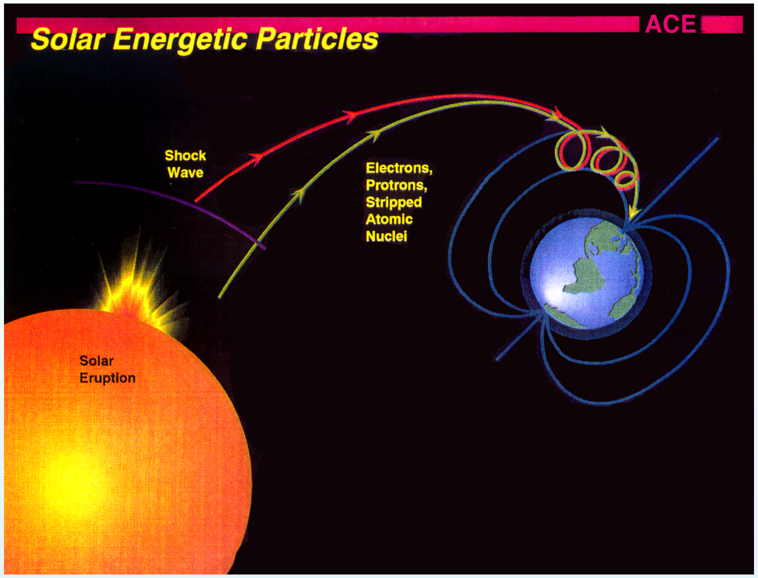


Spots start in mid-latitudes and drift towards the equator of the sun.





Solar Particles



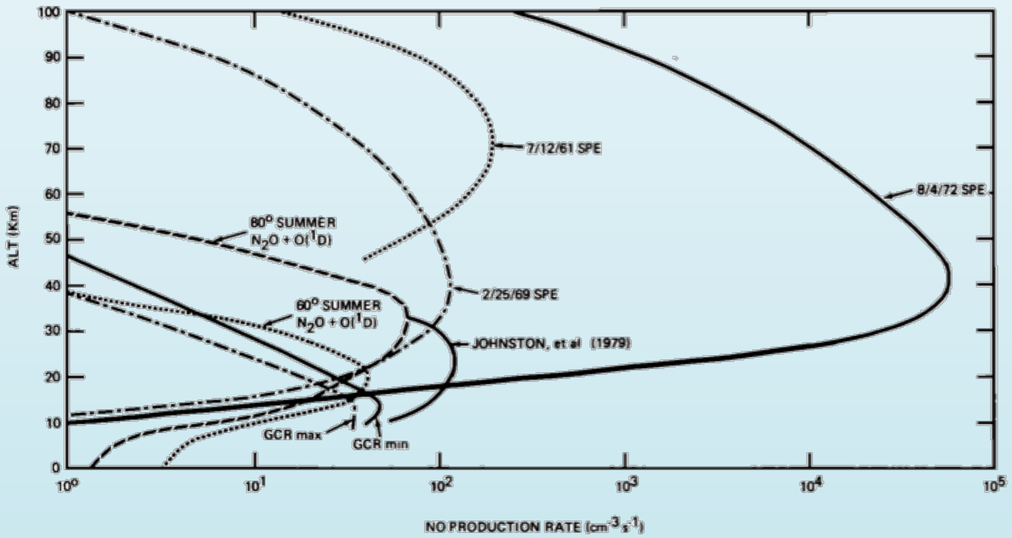
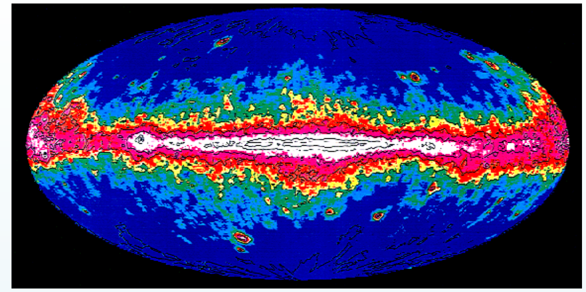
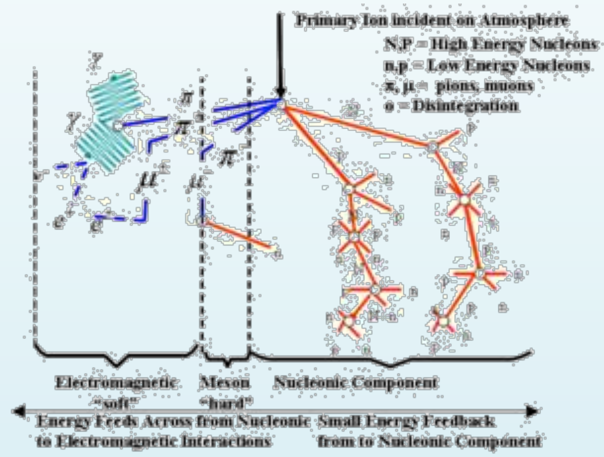


Fig. 4. Instantaneous nitric oxide production rates for GCRs (at solar maximum and minimum), SPEs (July 12, 1961, February 25, 1969, August 4, 1972), and oxidation of nitrous oxide (60° summer, 80° summer and *Johnston et al.* [1979] at 60° summer).

Galactic Cosmic Rays

- Origin in galaxy shown by isotropic distribution; Earth near edge of galaxy and no variation with Earth rotation to face either galactic center or galactic edge
- Galaxy can only contain GCRs below about 10^{17}ev; energies above that are intergalactic cosmic rays
- Magnetic heliosheath expands and contracts with solar activity causing anti-correlation of GCRs arriving at Earth with solar activity
- Primary GCR ionizes atmosphere creating a cosmic ray shower composed of many kinds of particles including so-called secondary electrons and neutrons. Secondary electrons deposit energy with maximum in lower stratosphere. Also generate NO_x from dissociation of N_2
- Carbon-14 (^{14}C) created from neutrons in cosmic ray shower interacting with nitrogen: $n + {}^{14}N \rightarrow p + {}^{14}C$. Half-life of ^{14}C is 5700 years; used in carbon dating





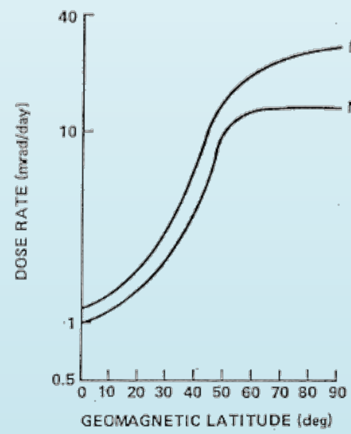


Figure 7. GCR dose rate as a function of latitude and solar cycle.

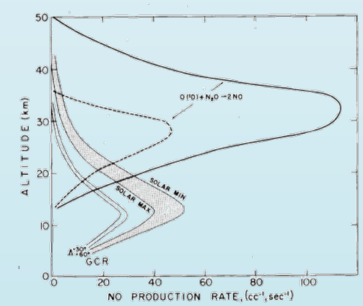


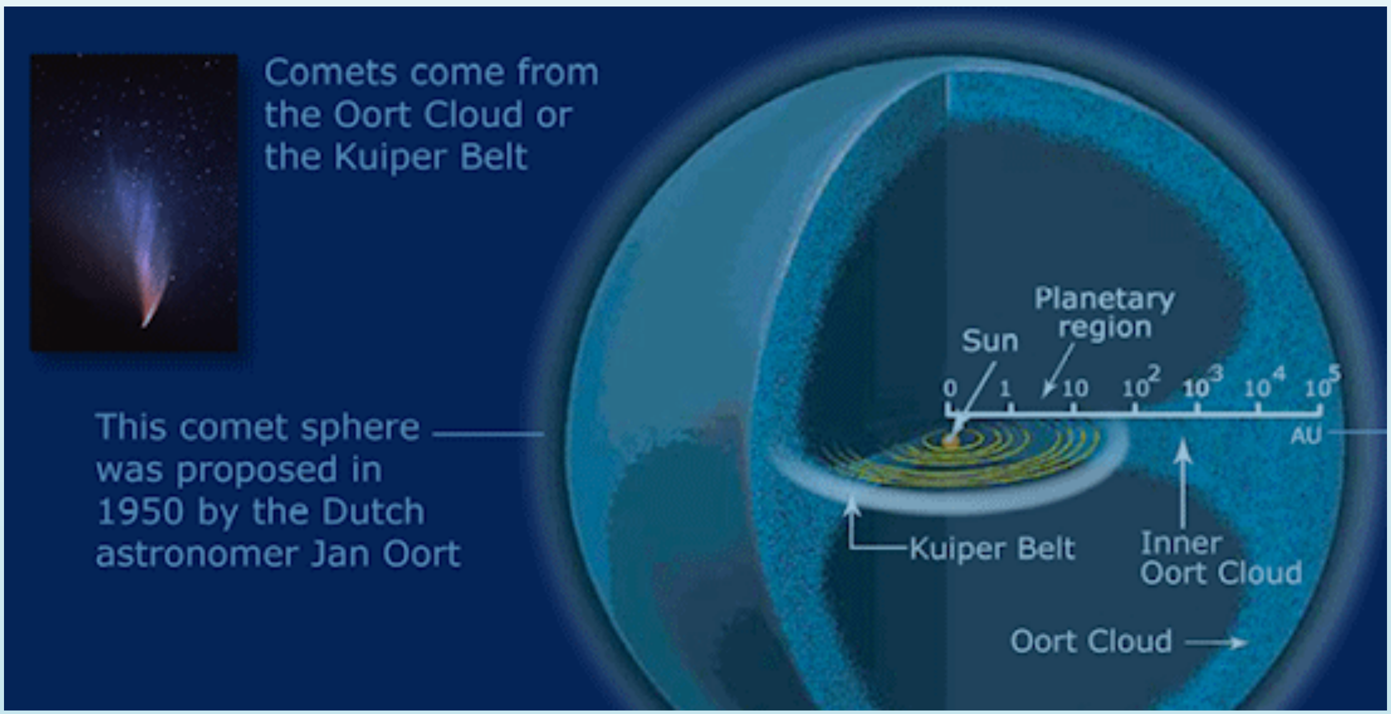
Figure 5

A comparison between the altitude profile of NO production by galactic cosmic radiation and the oxidation of terrestrial N_2O. The range of GCR production over the solar cycle is shown for both 30° and 60° invariant latitudes. The two curves for the N_2O source represent the extreme values given by Brasseur and Nicolet (1963) due to uncertainties in the vertical eddy diffusion coefficient and the production of $O(^1D)$ atoms.

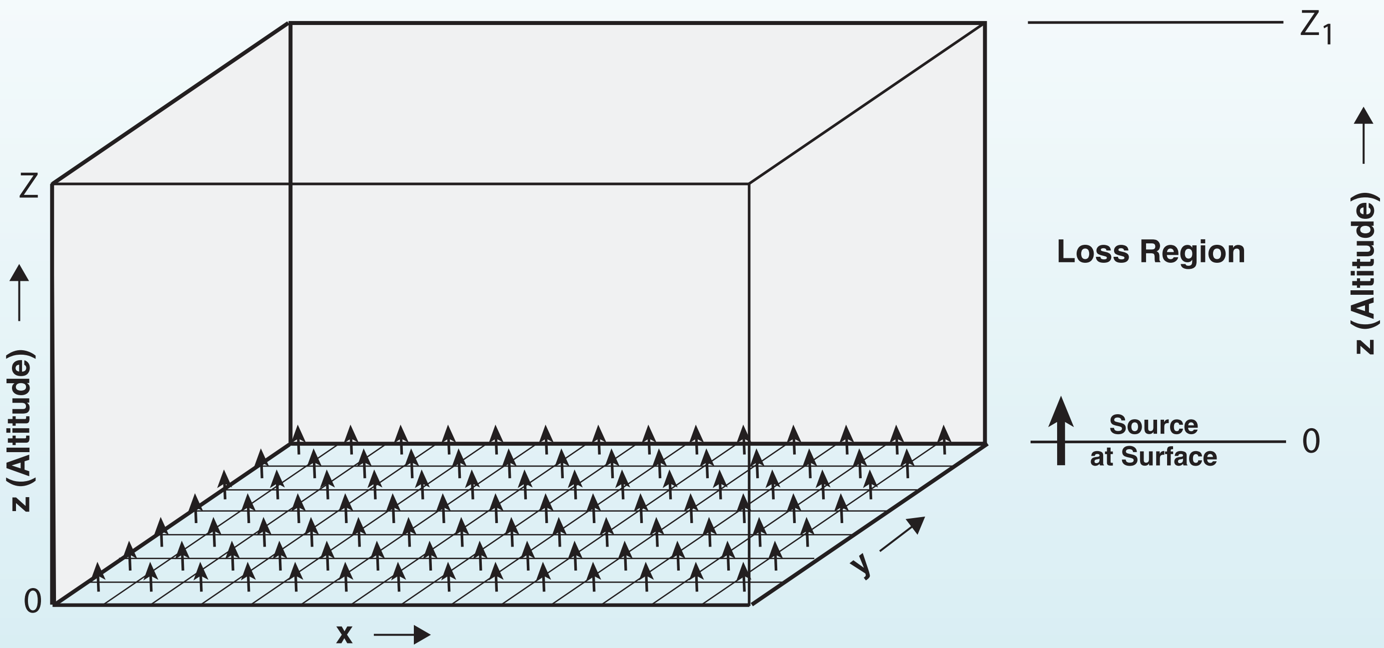
Cosmic Dust

Comets originate in the Kuiper belt and the Oort cloud. They disintegrate over time and leave a debris field of small particles that form "Cosmic Dust"

- Jupiter family comets (short-term <20 years, orbits controlled by Jupiter)
- Kuiper belt objects (medium-period (20 -200 years)
- Halley type comets (long-period > 200 years)



Simple One-Box Model of Atmosphere



$$\textit{Total Flux into Box (molecules/sec)} \quad F(t) = \int\int f(x,y,t) \cdot dxdy$$

$$\textit{Total Molecules in Box} \quad N(t) = \int\int\int n(x,y,z,t) \cdot dxdydz$$

Continuity Equation

$$\frac{dN(t)}{dt} = F(t)$$

Solution for constant flux, F_o

$$N(t) = \int_{t=t_0}^{t=t} F_0 \cdot dt = F_0 \cdot (t - t_0)$$

Loss Processes in the Atmosphere

Loss generally proportional to density $$l = l_f \cdot n$$

l = *loss in molecules/cm³/sec* ; l_f = *loss frequency in sec⁻¹*

Loss integrated over entire atmosphere

$$L = \int\int\int l \cdot dxdydz = l_f \int\int\int n \cdot dxdydz = l_f \cdot N$$

Continuity Equation with Loss term

$$\frac{dN}{dt} = F - l_f \cdot N$$

Simple Solutions of the Continuity Equation

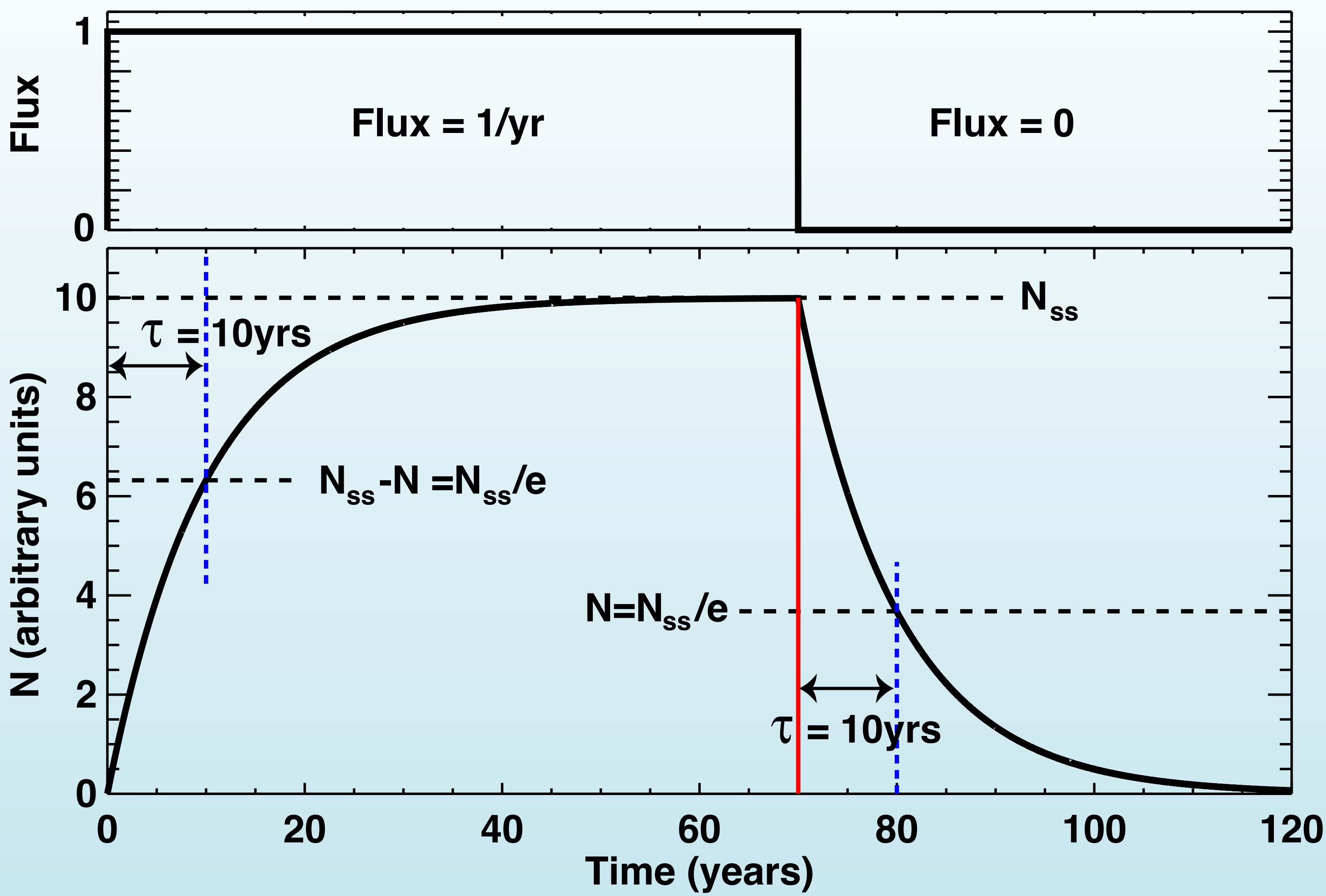
Steady-state; dN/dt = 0 ; $$N_{ss} = F_0 \cdot \frac{1}{l_f} = F_0 \cdot \tau$$

Defines lifetime, τ ; $$\tau = \frac{N_{ss}}{F_0}$$

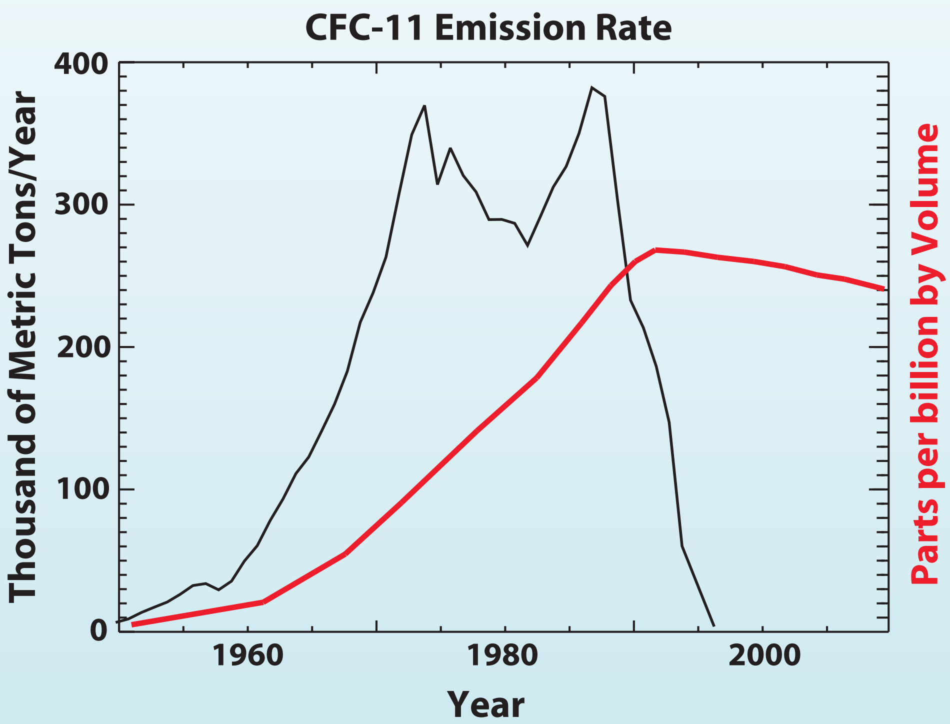
Set flux to zero ; $$\frac{dN(t)}{dt} = -l_f \cdot N(t)$$

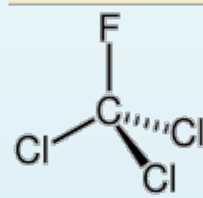
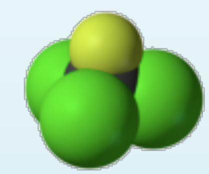
Solution ; $$N(t) = N_{ss} e^{-l_f \cdot t} = N_{ss} e^{-t/\tau}$$

The Atmosphere as a Simple Box Model



Example: CFC11 = $CFCl_3$



Trichlorofluoromethane	
	
IUPAC name	Trichlorofluoromethane
Other names	Trichloro(fluoro)methane, Fluorotrichloromethane, Fluorochloroform, Freon 11, CFC 11, R 11, Arcton 9, Freon 11A, Freon 11B, Freon HE, Freon MF

Summary Lecture 1

- **Descriptive overview of atmosphere from the point of view of its chemistry/composition**
- **Simple box model to illustrate fundamental concepts**
  - **flux into atmosphere**
  - **loss within atmosphere**
  - **continuity equation**
  - **steady-state; definition of lifetime**
  - **exponential decay; meaning of lifetime**