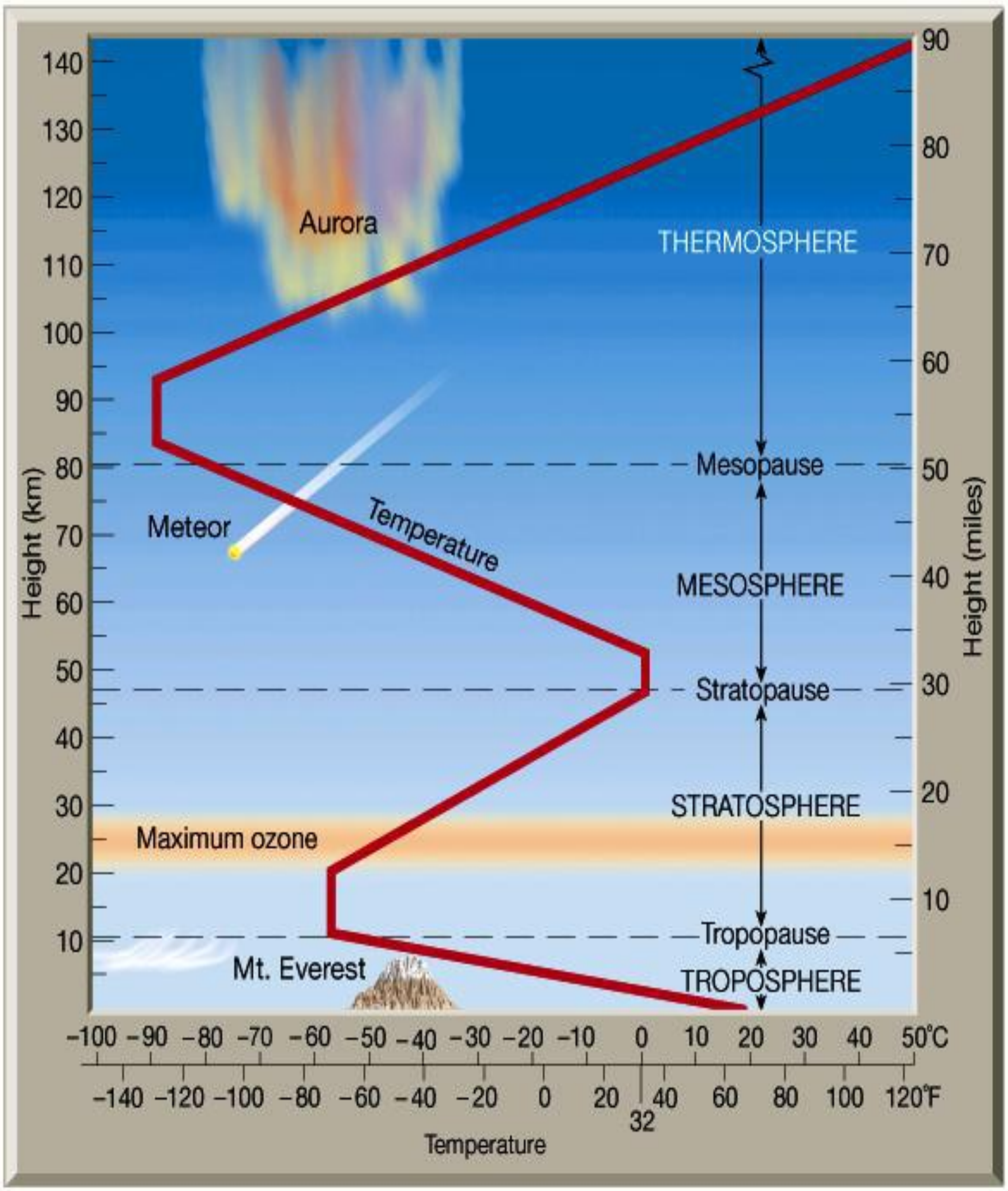
II. Atmosphere---Composition and Origin:

A. The standard atmosphere is created by averaging from equator to pole, from winter to summer, from day to night, from land to sea.

B. The standard atmosphere has 4 layers, distinguished by how temperature varies with height.



1. The **Troposphere** is the lowest layer, nearest to the ground.

a. Troposphere is from the Greek turning sphere, turning implying change, implying the weather. It's our weather sphere.

b. It extends from sea level up about 12 kilometers or 7.5 miles or so.

c. We remember that surface pressure is 1000 millibars, and the pressure at the top of the troposphere, which we call the "**tropopause**," is about 200 millibars. This represents 80% of the Earth's atmospheric mass because pressure is proportional to mass.

d. Temperature decreases quickly with height. From 60°F or 16°C, at bottom, on average, to -80°F, or -62°C, at the top. The troposphere is heated from below.

2. Next up is the **stratosphere**, from the Latin to spread horizontally.

a. This is a layer of great stability, which impedes vertical motions.

b. The top of the stratosphere is called the "**stratopause**".

i) We find it at 50 kilometers or 30 miles on average above sea level.

ii) The pressure there is about a millibar.

c. Temperature increases with height instead of decreasing.

i) Some incoming solar radiation is absorbed there, and further, harmful ultraviolet radiation is absorbed by oxygen and ozone.

ii) The stratosphere to us is the ozone layer.

d. The troposphere and stratosphere together already account for 99.9% of the mass of the atmosphere.

3. Next up is the **mesosphere,** Greek for middle sphere.

a. It is distinguished by temperature resuming its decrease with height.

b. The top of the mesosphere is the **mesopause**, 85 km, or 55 miles, above sea level.

c. The pressure is 0.01 millibars.

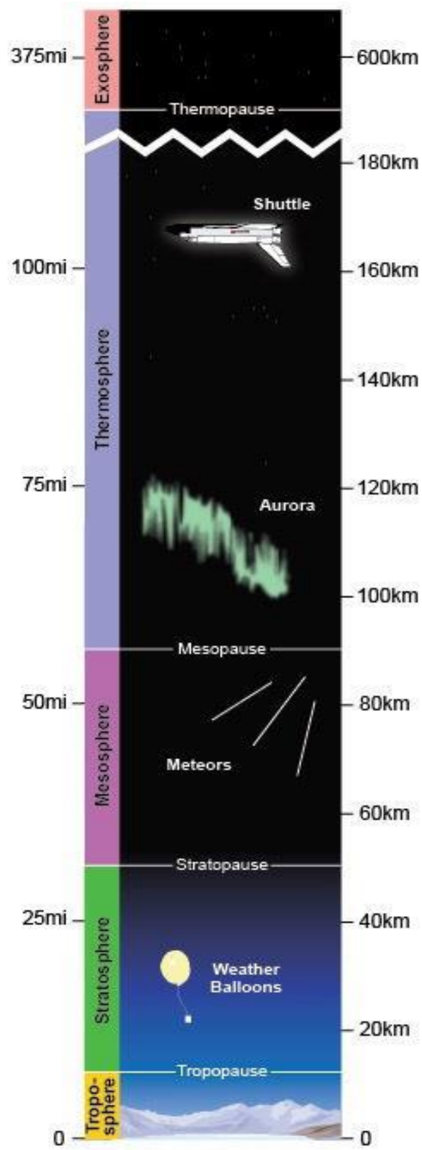
4. Finally, the **thermosphere** extends from 55 miles up to where the atmosphere just fades away.

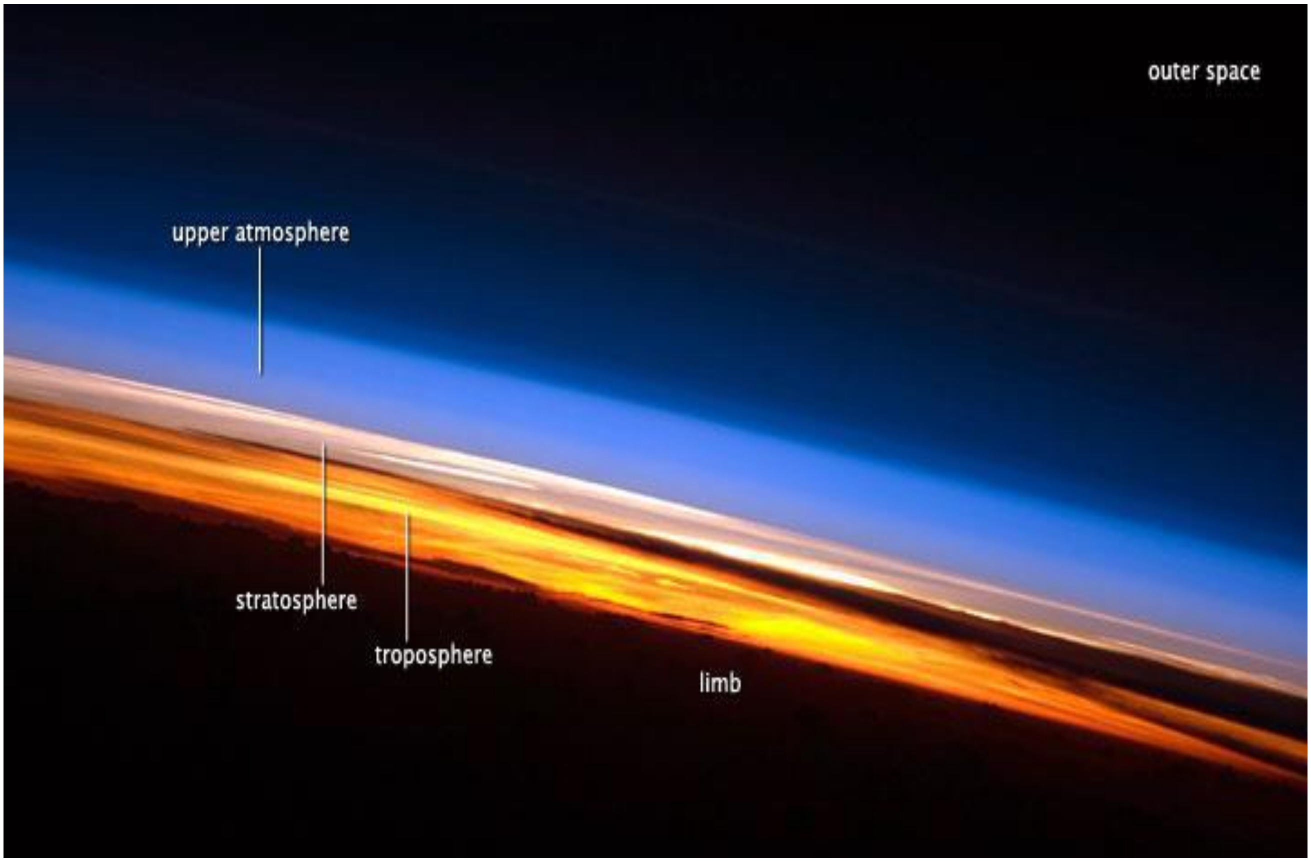
a. Temperatures there can be thousands of degrees, and yet it is also a strangely cold place.

b. There's virtually no mass in the thermosphere, but it's a very deep layer, (very, very low density).

c. Suppose you were unfortunate enough to find yourself in the thermosphere, with your back facing the Sun and your belly facing the Earth. You would have the absolutely unique sensation of freezing and frying at the same time.

C. What is the actual thickness of the atmosphere?





D. What is air?

1. Dry air: (Fixed in quantity and well mixed through the atmosphere)

a. Dry air is 78% nitrogen in the form N_2

i) 2 nitrogen atoms---together they combine a diatomic nitrogen molecule.

ii) Nitrogen is removed from the atmosphere by bacteria is soil, and it's returned when plants and animals decay.

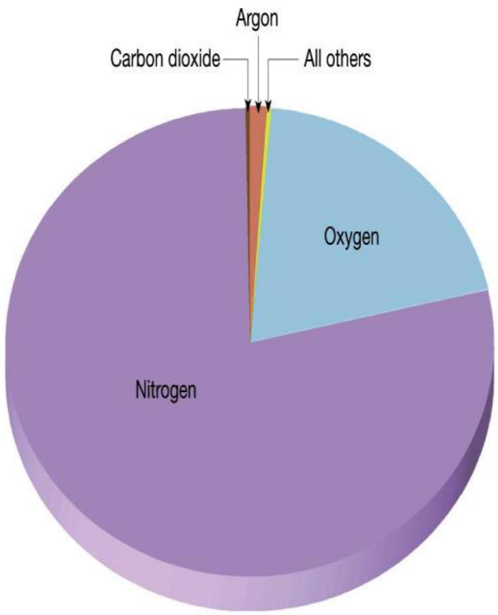


TABLE 2.1
Gases Composing Dry Air in the Lower Atmosphere (below 80 km)

Gas	% by Volume	Parts per Million
Nitrogen (N_2)	78.08	780,840.0
Oxygen (O_2)	20.95	209,460.0
Argon (Ar)	0.93	9,340.0
Carbon dioxide (CO_2)	0.03890	389.0
Neon (Ne)	0.00180	18.0
Helium (He)	0.00052	5.2
Methane (CH_4)	0.00014	1.4
Krypton (Kr)	0.00010	1.0
Nitrous oxide (N_2O)	0.00005	0.5
Hydrogen (H)	0.00005	0.5
Xenon (Xe)	0.000009	0.09
Ozone (O_3)	0.000007	0.07

b. A further 21% of the dry atmospheric mass is oxygen in the form O_2.

i) Oxygen is removed by plant and animal decay and also by the process of oxidation, in which oxygen combines with other elements.

ii) It's added back to the atmosphere through plant photosynthesis.

c. About 1% of the dry atmospheric mass is argon, one of the nonreactive noble gases.

i) You can think of argon as just lying around, doing nothing. (Greek word for lazy)

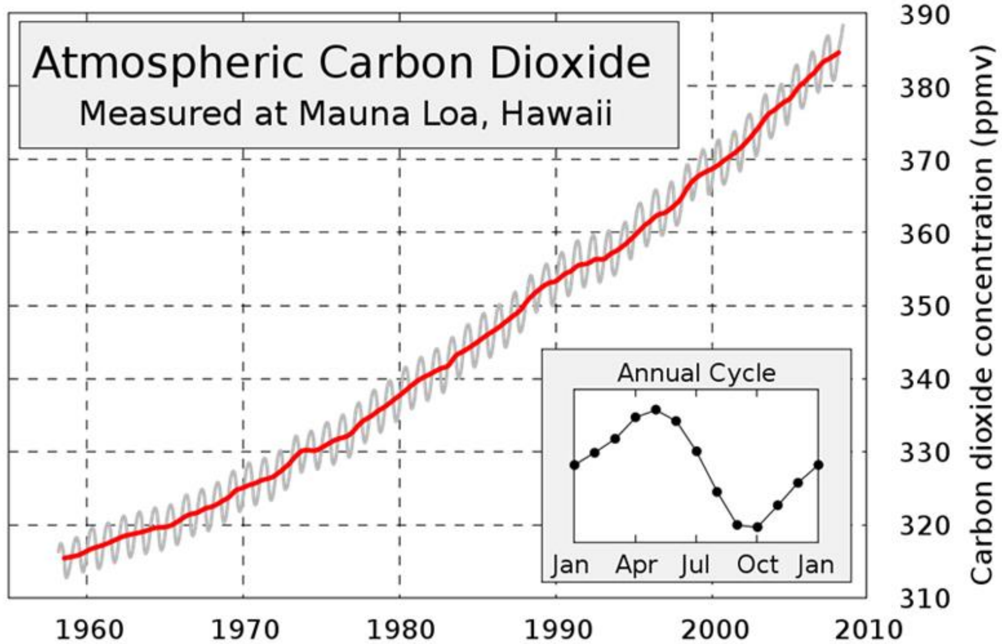
d. Carbon dioxide represents 0.0387% of the dry atmospheric mass, and you know it's rising. (That's only 387 molecules out of every million).

i) It plays a major role in regulating the temperature of the Earth's surface. [H_2O is earth's biggest greenhouse gas].

ii) CO_2 concentrations are rising, due in large part to fossil fuel burning.

iii) CO_2 concentrations in the atmosphere have increased 20 % over the last 50 years.

iv) The Keeling curve: (The horizontal axis is time in years, and the vertical axis is carbon dioxide concentration in parts per million.) Note the saw-tooth nature of this curve. There's an annual cycle superimposed on a clearly distinct upward trend. [The data were collected at Mauna Loa, Hawaii]



v) Biological activity of plants removes CO_2 from the air, so therefore atmospheric concentration should be lowest after periods of the highest plant activity, so that means the summer and into the early autumn. This demonstrates that Nature provides an important sink for carbon dioxide, and the sink is not large enough to compensate our activity.

e. Another minor constituent in the dry atmospheric mass include methane, CH_4, which is about 2 parts per million. It's added to the atmosphere by 6 distinct sources.

i) Swamps, rice paddies, landfills, and areas like that.

ii) Methane is added by ruminants, like cattle and sheep.

iii) Insects like termites

iv) Biomass burning

v) Oceans

vi) Volcanic activity

{Methane is highly reactive, and it is removed by oxidizers, but is 25x more potent per unit weight the carbon dioxide as a greenhouse gas}

f. The next minor constituent is nitrous oxide, N_2O, about 300 parts per billion.

i) It's about 300x more potent a greenhouse gas by unit weight than CO_2.

ii) Nitrous oxide is produced in the soil by bacteria, and destroyed by sunlight, principally in the stratosphere. (Also increasing in time)

g. Our next minor constituent is ozone, O_3, 3 oxygen atoms together to produce an ozone molecule.

i)Ozone represents about 40 parts per billion.

ii) Near the surface, it is a dangerous pollutant that damages plants and contributes to smog, and ozone literally eats rubber.

iii) Ozone is created by lightning and it contributes to the peculiar fresh odor we sometimes detect in the vicinity of thunderstorms.

iv) The vast majority of ozone is located in the stratosphere where local concentrations are 250x larger than they are in the entire atmosphere as a whole.

v) In the stratosphere, ozone is produced after oxygen molecules absorb incoming solar radiation, and it's destroyed on reaction with atomic oxygen. Ozone itself also absorbs harmful radiation that would otherwise survive to reach the ground. Let's look at the natural **stratospheric ozone cycle.**

vi) Consider an oxygen molecule, that's O_2, and it absorbs ultraviolet radiation. This act causes the molecule to split apart into its individual oxygen atoms, but oxygen atoms don't last long in the atmosphere. Oxygen is far too reactive and an oxygen atom will find a nearby O_2 molecule to react with to make O_3, which is ozone. Next, ozone also absorbs ultraviolet which splits it apart. Note in this process that ozone is both created and destroyed, but there's no net loss. Also, 2 Ultraviolet absorption events have occurred, and that's harmful radiation that doesn't reach the ground.

vii) The ozone hole is an area of depleted stratospheric ozone, residing over the South Pole. It has a very strong annual cycle, and is most pronounced in October, which is spring in the Southern Hemisphere. It is a natural phenomenon, but has become much more severe in recent years.

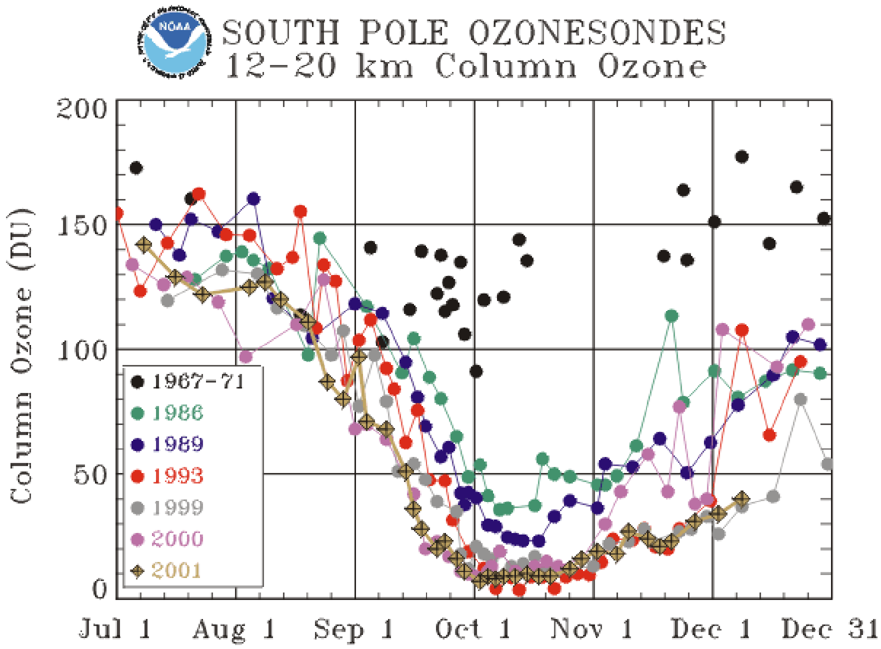
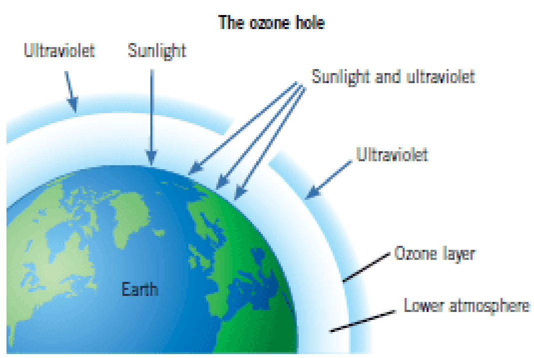


Figure 8. Column ozone between 12 and 20 km as measured by ozonesondes at the South Pole for selected recent years and 1967-'71 when there was very little ozone depletion.

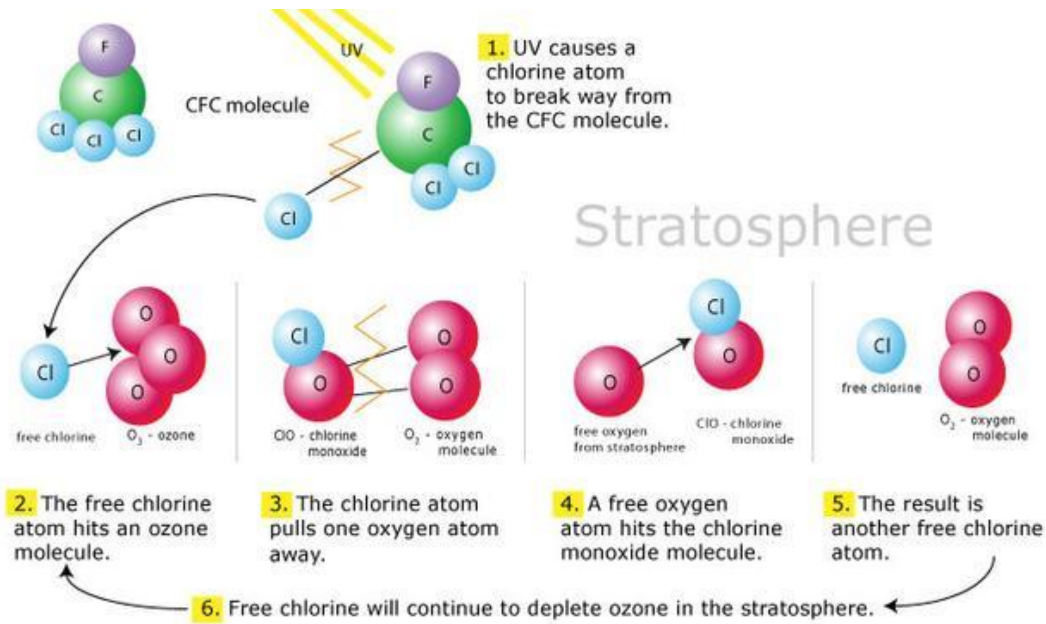
viii) The culprit in the excessive ozone hole expansion includes something called "chlorofluorocarbons", which I'll call "CFCs".



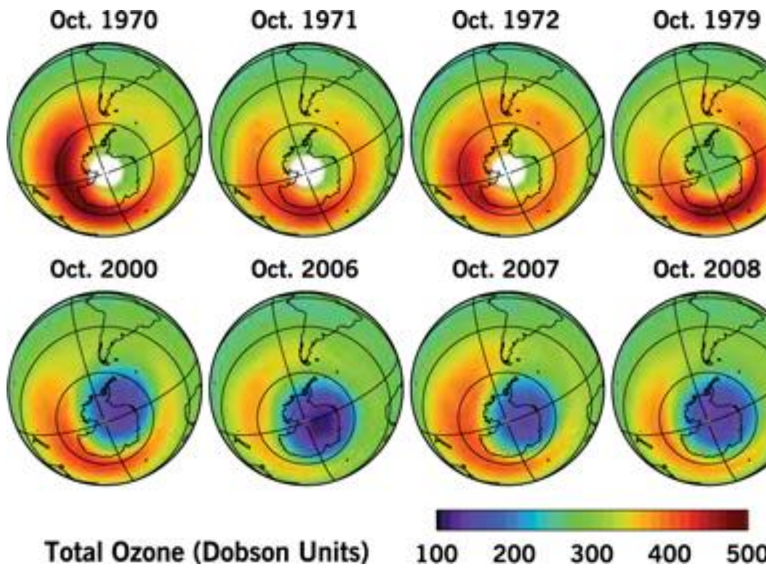
g. CFCs are very rare in the stratosphere, amounting to only 1-2 parts per 10 billion, but CFCs play a dual role as greenhouse molecules and also destroyers of stratospheric ozone.

i) CFCs have anthropogenic sources. They were used as propellants in spray cans, but also coolants in refrigerators and in air conditioners, as solvents and in fire extinguishers.

ii) The problem is CFCs are chemically inert, which leads to them having very, very long lifetimes in the atmosphere. This long lifetime allows CFCs released at the surface to spread globally and loft far upwards, reaching the stratosphere. In particular, they can work their way to the Southern Hemisphere, where they become trapped in an intense vortex of winds that encircles Antarctica during its long and sunless winter season. When sunlight returns to the region in the Antarctic spring, intense ultraviolet radiation from the Sun can break the CFC molecules apart, liberating the chlorine atoms. Ultimately, these chlorine atoms become involved in reactions that destroy ozone, but also restore the free chlorine back to the atmosphere, leaving those chlorine atoms free to destroy even more ozone.



iii) First, free chlorine reacts with ozone, creating chlorine oxide, ClO, and molecular oxygen, but then chlorine oxide encounters a free oxygen atom. Remember, those oxygen atoms were just floating around, and when they encounter one, it gives up its oxygen to the oxygen atom. So we see that the free chlorine is liberated and lives yet again to attack yet another ozone molecule. Eventually, the chlorine atom is removed from the atmosphere, but before it has been, it can destroy many, many thousands of ozone molecules.



iv) The 1995 Nobel Prize for Chemistry went to 3 scientists for explaining stratospheric ozone processes, including the role of CFCs in the destruction. In 1987, the Montreal protocol, an international treaty dedicated to phasing out the production of ozone-depleting substance like CFCs, was initiated and was one of the most successful international treaties ever. [The new replacements don't deplete the ozone layer but adds to additional greenhouse gases].

2. Wet air: (water vapor)

a. Water vapor is literally the fuel of thunderstorms and hurricanes.

b. Water vapor represents zero to 4% of the total atmospheric mass, but is extremely variable in space and time.

c. Water vapor is concentrated near the Earth's surface and the lower troposphere, and there are 3 reasons for that:

i) Water has a surface source like soil, plants, and surface water, such as rivers, lakes, and obviously the oceans.

ii) An efficient mechanism for returning water to its surface origin exists, (precipitation).

iii) The ability of air to hold water vapor is a very strong function of temperature.

d. Warm air can hold much more water vapor than cold air.

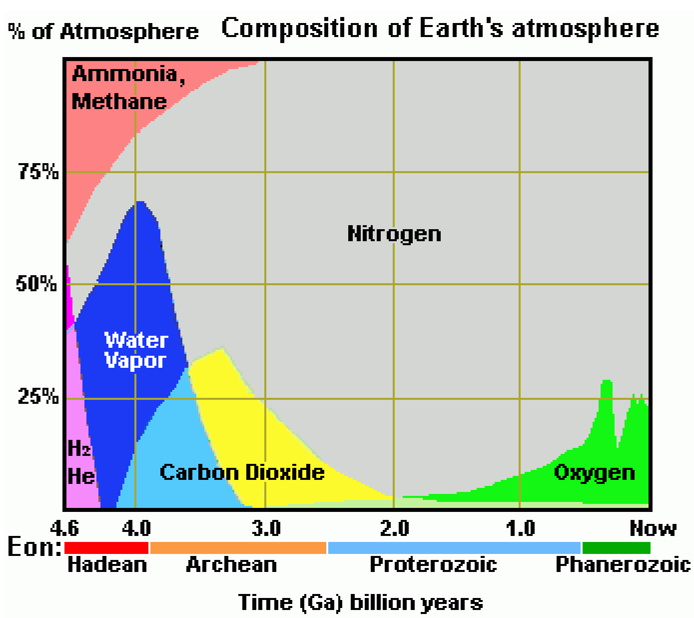
i) At sea level, 90°F air can hold more than 7x more vapor than air at freezing, and temperature decreases rapidly with height in the lower atmosphere. As you go higher in the atmosphere, it becomes too cold to permit much vapor to accumulate.

E. The Early Atmosphere:

1. When the Earth was still cooling, it probably had an atmosphere of hydrogen and helium.

a. Those are the 2 most abundant constituents of the universe. But Earth's mass is not great enough, it's gravity is not strong enough, to retain those elements, and that early atmosphere was lost to space.

b. Subsequently, Earth developed an atmosphere that had significantly more CO_2 than our present atmosphere, and that atmosphere had plenty of water vapor, nitrogen, sulfur, and ammonia, but the distinctive thing was that the atmosphere had virtually no oxygen. This atmosphere was produced by volcanic activity and crustal outgassing.



2. Where did all that CO_2 go?

a. All that CO_2 is largely bound up in rocks, especially carbonates such as limestone.

3. Where did our oxygen come from?

a. In our atmosphere, the first free oxygen probably resulted from photo-dissociation of water vapor by intense solar radiation.

b. Radiation came in and blasted H_2O molecules apart, liberating the oxygen into the atmosphere, but this is a very, very slow process, so actually, significant oxygen concentrations had to await the evolution of photosynthesis, which converts CO_2 and water into sugar, as well as oxygen.

c. Even then, oxygen concentration increases in the atmosphere were slow, limited by oxygen's highly reactive nature. So a large amount of the oxygen produced by plants and bacteria didn't get into the atmosphere or didn't stay there very long because they become bound up with iron in the soils.

F. Summary:

1. The atmosphere has 4 layers. Most important for us is the troposphere, our weather sphere, and stratosphere, which hosts the ozone layer.

2. In the troposphere, temperature decreases very, very quickly with height. Temperature drops 140°F over a vertical distance of only 7 to 8 miles. But the troposphere never overturns.

3. The cold air at the tropopause is also much less dense than the air at sea level.

4. Less dense air rises, more dens air sinks.

5. Air is mainly N_2 and O_2, nitrogen and oxygen, and a little bit of argon. The rest are just minor constituents that don't even add up to 1%. But, these minor constituents are very, very important.

6. One of those trace gases, CO_2, is a greenhouse gas, and it's increasing in concentration over time.

7. Other even rarer gases are even more potent at regulating Earth's surface temperature, including methane and nitrous oxide, because they're greenhouse gases as well, and they represent the thermostat of the Earth/atmosphere/ocean system.

8. Ozone protects us by absorbing harmful radiation that otherwise would have reached the surface.

9. Manmade chemicals, like the now banned CFCs, destroyed stratospheric ozone, especially in the infamous ozone hole over the South Pole.

F. Questions:

1. We have all heard the saying warm air rises and cold air sinks. Is that always true? Explain.

2. Could something that comprises only 4 out of every 10,000 molecules in air really make a difference? Explain.

3. What good is the ozone layer?

4. How did a chemical used in common spray cans damage the ozone layer?

5. Why does the ozone hole disappear in summertime?

6. The ionosphere is not an atmospheric layer, but rather a region that extends from the upper mesosphere up to 400 kilometers or so. The structure of this region varies dramatically from day to night. Strong solar radiation ionizes atoms, creating layers that absorb AM radio signals but disappear at night. At what time of day do you expect to be most successful at receiving a distant AM station on you radio? Explain.

7. What are the 3 main components of dry air and their %?

8. What are the sources of Methane in our atmosphere?

9. Why is water vapor common in the troposphere of the earth?

10. Where did all the oxygen come from in the atmosphere?

11. What was the chemistry of our atmosphere in the Precambrian time period?