GY 112 Lecture Notes
Evolution of the Earth's Atmosphere and Hydrosphere

Lecture Goals:
A) The Early Atmosphere
B) The Oceans and Hydrosphere
C) The Change

Textbook reference: Levin 7th edition (2003), Chapter 6; Levin 8th edition (2006), Chapter 8

A) The Early Atmosphere

We have spent considerable time mentioning that the early Earth was very different from today. The same can be said about the early atmosphere. Today, our atmosphere contains only a few major gases:

O_2: 21%; N_2; 78%; Ar: 1%; CO_2; 0.03% (but rising!)

When the Earth was first forming (refer to an earlier lecture) it is likely that there was a primordial atmosphere of some sort. During the Early Hadean Eon, the atmosphere might have consisted of water vapor, nitrogen, argon, carbon dioxide etc. There might also have been some hydrogen and helium (left over from the initial formation of the solar system), but most of these gases would have been blown away when the sun ignited and the solar wind began. In addition, gases like hydrogen and helium can largely escape the Earth's gravity well anyway, so they would not have hung around for any great length of time.

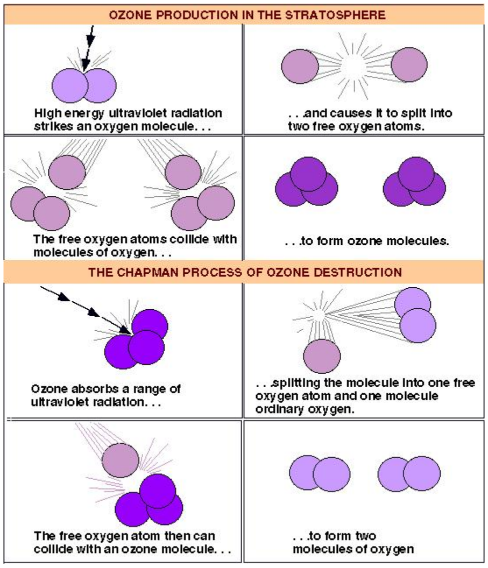
Well all this begs the question, "Where did our "modern" atmosphere come from?" The most likely source is volcanoes. During the Hadean, volcanic activity would have been extreme. Volcanoes were literally everywhere and volcanic eruptions must have been occurring non-stop. Volcanic eruptions produce a lot more than lava and ask. They produce tremendous amount of gas and it is quite likely that the early Earth's atmosphere was primarily derived from these volcanic eruptions. Today volcanic eruptions produce H_2O, CO_2, H_2S, SO_2, NO_2, N_2O (generally written as N_xO_y), HCl and several other gases (most of which smell bad). To the best of my knowledge, volcanic eruptions generally do not produce much CH_4 or N_2, but we suspect that these gases were also in the Earth's early atmosphere. Perhaps they managed to hang around from the primordial solar nebula or they leaked into the atmosphere from the interior of the Earth through other mechanisms. One thing is clear however, the water vapor that was produced from the volcanic eruptions eventually condensed in the atmosphere to form water droplets (clouds) and rainfall. The oceans almost certainly formed from this rainfall. Incidentally, rain for the first several million years would have been extremely acidic. Water combines with CO_2, SO_2, HCl and N_xO_y to form many strong acids:

$H_2O + CO_2 = H_2CO_3$ (**carbonic acid**; weak)
$H_2O + SO_2 = H_2SO_3$ (sulfurous acid; weak)
$H_2O + SO_3 = H_2SO_4$ (**sulfuric acid**; strong)
$H_2O + NO_x = HNO_3$ (**nitric acid**; strong)
$H_2O + HCl = HCl$ (**hydrochloric acid**; strong)

Given the acidity of the rain that fell on the early Earth, it is reasonable to assume that chemical weathering of the rocks was widespread. Many minerals would have dissolved, and the dissolved ions would have then been carried away by streams into the oceans. The ionic soup that we today call seawater may have been produced gradually by acid rain reacting with rocks.

The one ingredient missing from both the oceans and the atmosphere at this time was oxygen. The entire Earth **hydrosphere** (the total volume of water on the planet; atmosphere, oceans, lakes, rivers, ice) was anaerobic. We have already discussed the origin of life on this planet, but a refresher is probably called for here. The first prokaryotic life forms were probably anaerobic meaning that they preferred environments free of oxygen. But they also had one other hurtle to overcome; **ultraviolet radiation. UV** radiation is constantly emitted from stars and it is exceptionally hazardous to all life forms (aerobic and anaerobic alike). The only reason that we can survive on the Earth today is that we have a shield of **ozone** (**O_3**) in the upper atmosphere that prevents UV radiation from making it to the surface of the Earth where we live. The early atmosphere did not have any free oxygen and it is likely that it did not have much ozone either. The first life forms probably lived in deep parts of the oceans (the deep water protected them). They could not live in shallower water just yet. Ozone had to build up first.

Ozone is produced in the upper atmosphere through photochemical reactions involving UV radiation and water:



$$2H_2O + \text{uv radiation} = 2H_2 + O_2$$

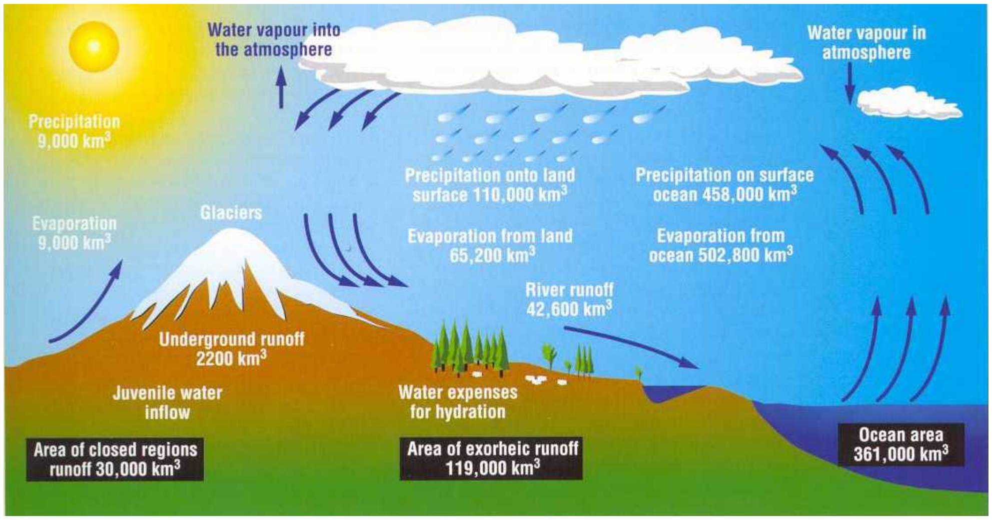
and

$$2O_2 + \text{uv radiation} = O_3 + O$$

and

$$O + O_2 = O_3$$

Nitrogen oxides (the main constituents of smog) are formed through the same process. When water is first dissociated, it forms hydrogen gas and some oxygen. The hydrogen escapes into space while the oxygen forms ozone. You might think that the oxygen that we find in today's atmosphere came from UV **photochemical dissociation** of water, but experimentation suggests that this was not the case. We owe our present atmospheric constituents to microscopic beasties.

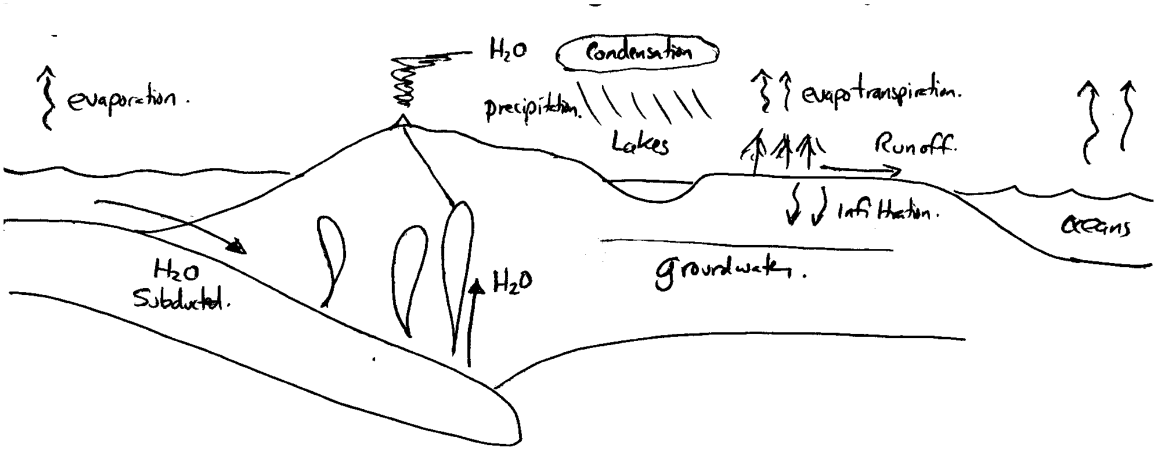


B) The Oceans and the Hydrosphere

Before we discuss the change that occurred in the atmosphere, it is sensible to first discuss how water on the Earth evolved. As we discussed earlier, the oceans probably formed through condensation of volcanic gases erupted from volcanoes. I read recently of a new possible source of oceanic waters that I'd like to pass on to you. I believe that I read it in *New* Scientist, an excellent British weekly science news review magazine. A scientist had observed dull flashes of light in the upper atmosphere which gave off the spectrum of water. He interpreted these flashes as records of "snowball" impacts on the upper atmosphere. He hypothesized that space is full of small, loosely packed snowball comets and that they regularly impact the upper atmosphere of the Earth. They lack any real substance and consequently, could never make it through the atmosphere. But he feels that they might have contributed a lot of water to the Earth over geological time. Who knows, maybe they did.

Regardless of how the water got on the Earth (volcanoes or snowballs or both), it is clear that we have been recycling the water for a longtime. The Earth's hydrosphere is largely a **closed system.** This means that you neither lose nor gain water. This isn't exactly true. You lose and gain some water through the Earth's interaction with space, but not too much, that is, if you don't accept the snowball hypothesis).

There are 5 major **reservoirs** that comprise the Earth's hydrosphere. They are 1) the oceans, 2) the polar ice caps, 3) groundwater, 4) rivers and lakes and 5) the atmosphere. The water is circulated between reservoirs through the **hydrological cycle**. This involves the processes of **evaporation, condensation, precipitation, infiltration, evapotranspiration** and **runoff.** The following cartoon is the best way to illustrate the cycle.

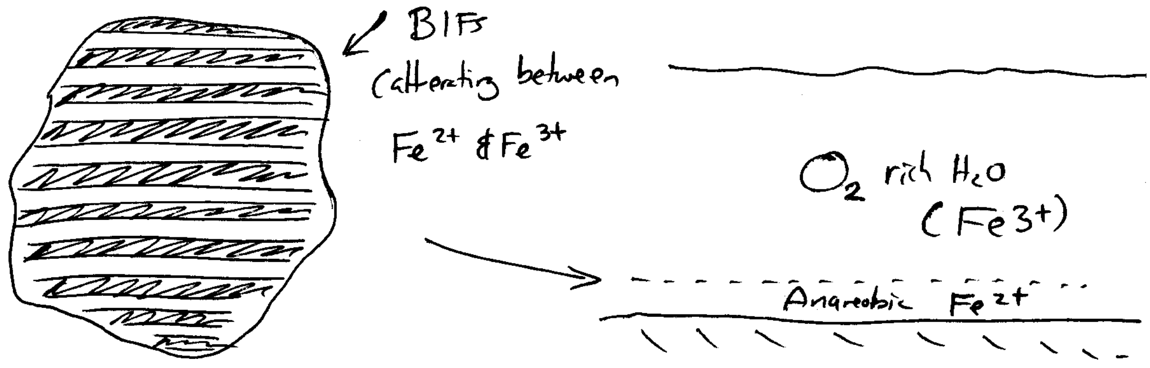


The water that we today see erupting from volcanoes is not "new" water. It is recycled along with the lithosphere that is subducted at convergent plate boundaries. It has been calculated that the entire volume of ocean water can be recycled through this process every 200 million years. I find this fascinating. Given the recycling that goes on in the hydrosphere (including along convergent plate boundaries), it is likely that the bottled water you just drank has been through a number of different reservoirs. It could have been ocean water, a cloud, a glacier, a geyser and/or the bodily fluids of a dinosaur. So much for "mountain pure". I can think of one or two good Budweiser commercials based on this premise (and yes they both involve frogs and lizards and their kidneys).

By the way, there is "new" water available to the Earth's hydrosphere, it's just not all that accessible. The Earth's mantle is apparently full of water (albeit incorporated into minerals), but it is trapped below the lithosphere. Right now it is destined to stay there.

C) The Change

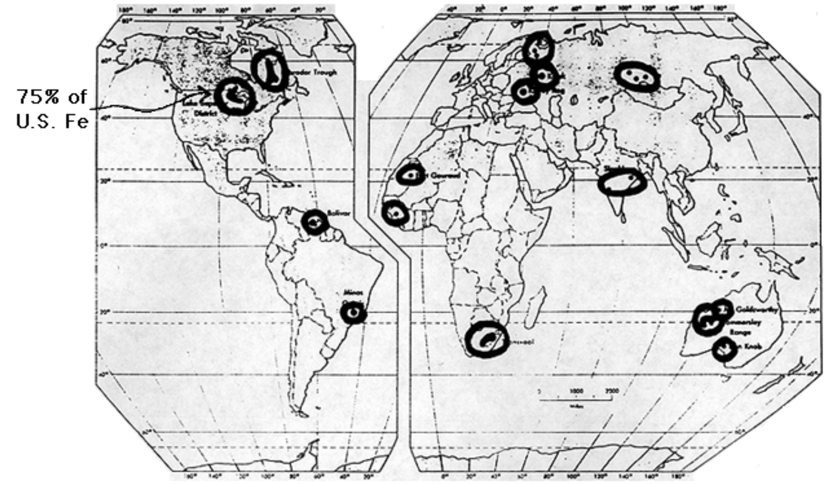
Alright, when last we visited the atmosphere (and the oceans) they were anaerobic. Prokaryotic life was in the deeper portions of the ocean and all was peaceful. As the ozone layer built up, the micro-beasties (including photosynthetic cyanobacteria) spread into shallower water (remember, they could not live here until they had protection from the UV radiation). Eventually they must have dominated the world's oceans. Since they were photosynthetic, they took in CO_2 and produce O_2 as a waste product. Overtime, they "polluted" their environment with oxygen. As they lived in a marine environment, the pollution was initially confined to the oceans. The first evidence of increasing oxygen in seawater is found in marine sedimentary rocks called **banded iron formations** or **BIF's** (see image to right from http://www.uni-tuebingen.de/uni/qvo/pm/pm2005/gifs/pm-05-100-01gr.jpg). These are curious rocks that are prized by rock collectors for their intricate banding. They consist of finely laminated bands of red, green and/or silver-colored minerals each about 1 to 2 mm thick. The red and silver bands are chert containing hematite (earthy - red; specular - silver). The chemical formula of hematite is Fe_2O_3 which indicates that the iron has a +3 charge. Fe^{3+} is **ferric** iron and only forms in **oxidizing** environments. The green bands are also iron-rich chert, but they are **ferrous** in nature (i.e., Fe^{2+}) suggesting that they formed in anaerobic or **reducing** environments.



The green-red alterations suggest fluctuations between oxidizing and reducing conditions. Alterations between earthy and specular hematite probably occurred entirely during oxidizing conditions, but we are not certain about this. There are even iron formations that are unbanded. They are mostly composed of earthy hematite (Red Mountain in Birmingham is an example of an unbanded **iron formation**, but it is much younger than the Archean examples that we have been discussing - Red Mountain formed through groundwater alteration which is a form of **diagenesis** in the Paleozoic.

Archean banded iron formations are reasonably common around the world and comprise the majority of many country's iron ore supply (e.g., USA, Canada and Australia; see map below from http://www.ldeo.columbia.edu/edu/dees/)

Precambrian Banded Iron Formations



Location of the major Precambrian banded iron formations of the Lake Superior type. These ores assure abundant iron resources for centuries ahead.

The origin of the iron in these BIFs is kind of still debated. Iron isn't all that soluble in seawater under normal conditions, so the fact that it formed extensive BIF's at all is intriguing. Some believe that intensive underwater volcanic activity was responsible for the increased iron deposits. It is also possible that high acidity and/or UV radiation made the iron more soluble in the past. We will probably never know for certain. We can however, date when the transition from anaerobic to aerobic oceanic conditions occurred. Green-red BIFs date back to about 3.1 GA suggesting that the Earth's oceans were starting to go aerobic well back in the Archean. Unbanded iron formations are mostly younger that 2.0 GA which suggests fully aerobic marine conditions during the Paleoproterozoic.

But what of the atmosphere? We find a similar transition from green to red (this time in terrestrial shales), that dates back to about 1.8 GA. Many geologists believe that this was the start of an oxidizing atmosphere and that O_2 has been gradually added ever since. It is important that you realize that without oxygen in the oceans and in the atmosphere, higher forms of life could not have evolved on this planet. Where it not for prokaryotic bacteria, you would not exist.

Important terms/concepts from today's lecture

(Google any terms that you are not familiar with)

Carbonic acid
Sulfuric acid
Nitric acid
Hydrochloric acid
Hydrosphere
Photochemical dissociation
Ultraviolet radiation (UV)
Closed system
Ozone, O_3
Reservoir
Hydrological cycle
Evaporation
Condensation
Precipitation
Runoff
Infiltration
Banded iron formations (BIFs)
Iron Formations
Ferric
Ferrous
Reducing
Oxidizing
diagenesis