Lecture 35

Differentiation of Planet Earth

Today
1. Evolution of the atmosphere

Earth Differentiation: the Atmosphere

Interesting questions regarding the formation and evolution of Earth's atmosphere include:

★ When did volatiles segregate from the silicate earth?
★ How has the composition of Earth's gas envelope changed over geological time
★ How and when did the present atmosphere-hydrosphere system form?
Earth's atmosphere today

It is useful to review the features of our modern atmosphere, as a point of reference.

Our modern atmosphere:

- 78% N₂, 21% O₂, 0.93% Ar, 0.039% CO₂, plus small amounts of other gases, including N, S, and other C species.
- physically and chemically stratified; for example, above and below the tropopause.

Most of what we think of as weather is caused by air movements within the lowest part of the atmosphere, the troposphere. This is also the part of the atmosphere that is most directly related to the hydrosphere.

Earth's atmosphere today

It is useful to review the features of our modern atmosphere, as a point of reference.

- Water vapor from the hydrologic cycle does not travel freely above the tropopause because of a temperature inflection that causes significant crystallization of H₂O to ice.

There is water above the tropopause but most of it is produced and destroyed through photochemical oxidation of methane in the stratosphere (and similar reactions)

\[ \text{CH}_4 + 2\text{O}_2 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} \]

View across the tropopause from a high flying research aircraft. Below are tropospheric clouds, above are rare nacreous clouds formed at the low temperatures of the tropopause and lower stratosphere. Imaged by Paul Newman of NASA Goddard Space Flight Center. http://www.atoptics.co.uk/highsky/hitrop.htm
Earth's atmosphere today

The structure of our modern atmosphere is shown below. The tropopause is highlighted with an arrow:

![Diagram of the Earth's atmosphere with highlighted tropopause]

Composition of the modern atmosphere

The lower atmosphere is composed of:

a. constituents that are constant in composition throughout

b. naturally variable components. These reflect photochemical reactions (especially above the tropopause) and exchanges with the geosphere-biosphere-hydrosphere) below the tropopause:

- water vapor
- N and C species produced by biological and human activity on the earth’s surface
- S species from volcanic, biologic and human sources
- O₃ from photochemical reactions and human activities
- very trace quantities of organic molecules of both natural and human origins.
Evolution of Earth's atmosphere

In the early stages of accretion, our proto-atmosphere very likely had low $E_H$ because of the higher $H_2$ abundance. Probable gases were $CO_2$, $N_2$, $H_2O$, $Ar$, and possibly $NH_3$. A potentially important equilibrium was

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$

high temp. low temp.

The extent to which this reaction occurred depends on the time-temperature path of accretion and on when the Earth lost most of its nebular $H_2$. This reaction is also affected by $N_2$-$NH_3$ equilibrium.

In any case, the earliest atmosphere was probably at least somewhat reducing and dominated by C, whereas now it has only ~0.039% C and is oxidizing.

Evolution of Earth's atmosphere

Early estimates suggested the primordial atmosphere was poised at a pE set by the "QFI" buffer (quartz-fayalite-iron); i.e., near the $Fe^0/Fe^{2+}$ couple.

Many magmatic systems are poised at or near the "QFM" (quartz-fayalite-magnetite) buffer; that is, near the $Fe^{2+}/Fe^{3+}$ couple.

The relationship of $O_2$ fugacity vs. T for these two reactions has been determined experimentally. 

(Recall that fugacity is a measure of pressure that includes a non-ideality correction, in the same way that aqueous activity is related to molarity.)

Using these buffers and estimates of total abundance for each element, we can predict what form the atmospheric gases will be in at each pE as a f(T). See next page for a sample calculation.
Given the following simple conditions, let’s calculate the gas content (P, for each phase) of a closed system of magma and gas at equilibrium with the QFM buffer:

**Initial conditions:**
- Magma temperature: 1100°K
- Pressure (P_m): 1 atm
- C:H ratio: 0.65
- Allowable gaseous species (for simplicity): O_2, H_2, H_2O, CO, CO_2

We have 5 unknowns, so we need 5 equations for a unique solution. **See below**

To solve for the five unknowns, we must write five equations. Two of these follow directly from the bulk chemistry of the system. Because total pressure is 1.0 atm, we know that

\[ \text{H}_2 + p\text{H}_2\text{O} + p\text{CO} + p\text{CO}_2 + p\text{O}_2 = 1.0. \]

Because the atomic ratio C:H is 0.65, we also know that

\[ p\text{CO} + p\text{CO}_2/(p\text{H}_2 + p\text{H}_2\text{O}) = 0.1. \]

The partial pressure of O_2 is defined by the QFM buffer at the temperature specified. An empirical equation commonly used for this purpose

\[ \log f_0 = 9.00 - (25738/T), \]

where T is the temperature in Kelvin. In this example, then,

\[ f_0 = 1.8 \times 10^{-6}. \]

Assuming ideality, this is also the partial pressure of O_2 in atmospheres.

The final two equations are based on the stoichiometry of the gas species. From the potential reaction

\[ 2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2, \]

we calculate that

\[ f_{\text{CO}_2}/f_{\text{CO}} = (f_{\text{O}_2}/K_e)^{1/2}, \]

in which \( K_e \) is the equilibrium constant for this reaction between carbon species. It has a value, under these conditions, of \( 3.79 \times 10^{-11} \). The other independent chemical reaction that can be written is

\[ 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2, \]

from which

\[ f_{\text{H}_2\text{O}}/f_{\text{H}_2} = (f_{\text{O}_2}/K_e)^{1/2}. \]

The equilibrium constant, \( K_e \), has the value of \( 8.82 \times 10^{-14} \) at 1373 K.

The equations can be solved simultaneously to yield

\[ P_{\text{H}_2} = 1.97 \times 10^{-2} \text{ atm}, \]

\[ P_{\text{H}_2\text{O}} = 0.60 \text{ atm}, \]

\[ P_{\text{CO}} = 4.00 \times 10^{-4} \text{ atm}, \]

\[ P_{\text{CO}_2} = 8.70 \times 10^{-4} \text{ atm}. \]

**Evolution of Earth’s atmosphere**

Today’s atmosphere is **far more oxidizing**. This is both a result of and a key indicator of life, particularly **photosynthetic life**.

The compositions and magnitude of chemical exchanges between the atmosphere, biosphere, crust, and deep Earth have been **modified considerably** by biological evolution, and by climatic and tectonic cycles.

This caused the **transition** from a **somewhat reducing** to a **strongly oxidizing atmosphere**.
Evolution of Earth's atmosphere

Important events and processes that affected this transition:

1. Early loss of light elements and “blow off” of the proto-atmosphere.
2. Degassing from the planet’s interior.
3. Regulation of CO\(_2\) by liquid H\(_2\)O, allowing it to go into rocks via the Urey reaction (not storing CO\(_2\) in rocks is a main reason why Venus so different from Earth):
   \[
   \text{CaSiO}_3(s) + \text{CO}_2(g) \xrightleftharpoons{\text{H}_2\text{O}} \text{CaCO}_3(s) + \text{SiO}_2(s)
   \]
4. Evolution of photosynthetic life and the buildup of atmospheric O\(_2\) and O\(_3\).
5. Poising by the S\(^2-\)/S\(^4+\) and Fe\(^{2+}\)/Fe\(^{3+}\) redox couples.

Essentially, Earth's atmosphere went from one dominated by CO\(_2\) to one dominated by O\(_2\). This is an older representation of the change.
Evolution of Earth's atmosphere

A more recent and speculative rendering of the history of O2 accumulation in Earth’s atmosphere.

The “current” view (Kump 2008) of atmospheric oxygen through time.

PAL = “present atmospheric level”

The great oxidation event

Rapid rise in O₂ between at about 2.5 Ga
this rendering suggest a more sudden onset of O₂ change
Evolution of Earth's atmosphere

At the same time, CO$_2$ has dropped many orders of magnitude

Isotopic variation due to photochemical reactions in the more energetic lower atmosphere before earth had an ozone layer

BIF = banded iron formation

Oxygenated atmosphere with an ozone layer promotes S isotope homogeneity
Evolution of Earth's atmosphere

Taking inventory of our planetary volatiles requires looking to other parts of the rock record as well:

The total inventory of volatiles in the atmosphere today shows that it is significantly depleted in most gaseous elements relative to the 90%-10% chondritic bulk-Earth model.

The atmosphere today is also significantly less dense than predicted by the 90%-10% chondritic bulk-Earth model.

Furthermore, volatile element inventories “stored” in the oceans, sediments, and rocks don’t account for the difference.

<table>
<thead>
<tr>
<th>Volatiles</th>
<th>Total Quantity (grams)</th>
<th>Atmosphere (grams)</th>
<th>Oceans (grams)</th>
<th>Sediments (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>1.6 x 10^{24}</td>
<td>1.7 x 10^{19}</td>
<td>1.4 x 10^{24}</td>
<td>1.9 x 10^{24}</td>
</tr>
<tr>
<td></td>
<td>(0.001%)</td>
<td>(88%)</td>
<td>(12%)</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>2.4 x 10^{23}</td>
<td>2.5 x 10^{18}</td>
<td>0.4 x 10^{20}</td>
<td>2.4 x 10^{24}</td>
</tr>
<tr>
<td></td>
<td>(0.001%)</td>
<td>(0.06%)</td>
<td>(99.9%)</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>4.9 x 10^{21}</td>
<td>3.9 x 10^{21}</td>
<td>2.2 x 10^{19}</td>
<td>1.0 x 10^{21}</td>
</tr>
<tr>
<td></td>
<td>(79.5%)</td>
<td>(0.5%)</td>
<td>(20%)</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>3.1 x 10^{22}</td>
<td>5.0 x 10^{12}</td>
<td>2.6 x 10^{22}</td>
<td>5.0 x 10^{21}</td>
</tr>
<tr>
<td></td>
<td>(0%)</td>
<td>(84%)</td>
<td>(10%)</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>5.2 x 10^{21}</td>
<td>5.0 x 10^{12}</td>
<td>1.2 x 10^{21}</td>
<td>4.0 x 10^{21}</td>
</tr>
<tr>
<td></td>
<td>(0%)</td>
<td>(23%)</td>
<td>(77%)</td>
<td></td>
</tr>
</tbody>
</table>

* The amounts are given as the mass of H₂O, CO₂, N (nitrogen-atom equivalents), Cl (chlorine-atom equivalents), or S (sulfur-atom equivalents).
Evolution of Earth's atmosphere

Most geochemists argue that the primordial atmosphere, or Stage 1 atmosphere, was removed ("blown off") early in the planet's evolution. This proto atmosphere was replaced by a secondary, or Stage 2 atmosphere, which subsequently evolved into our present one.

Primary causes of stage 1 atmosphere blow-off would have been:

a. late-stage giant impacts (the largest of which was apparently Thela)

b. strong young star solar winds (T Tauri phase).

Evidence for early atmospheric removal:

1. From accretion models, we expect nitrogen to be 275-400 times as abundant as it actually is.

This implies that 99.6% to 99.8% of our early atmosphere was lost.

Evolution of Earth's atmosphere

More evidence for early atmospheric removal

2. Another line of evidence for significant early loss of volatiles comes from xenon isotopes (discussed a few lectures ago).

\[ \frac{^{129}\text{Xe}}{^{132}\text{Xe}}_{\text{mantle}} > \frac{^{129}\text{Xe}}{^{132}\text{Xe}}_{\text{atmosphere}} \]

This tells observation that some \(^{129}\text{I}\) \((t_{1/2} = 15.7\ \text{Myr})\), which is non-volatile and decays to \(^{129}\text{Xe}\), was still "alive" in the mantle when most of the primordial atmosphere was removed.

Later, additional \(^{129}\text{Xe}\) outgassed from the mantle into the Stage 2 atmosphere.

(a little bit is still outgassing today).
Evolution of Earth's atmosphere

More evidence for early atmospheric removal

3. Argon is a rare gas, like Xe.

Once Ar is outgassed from the interior it stays in the atmosphere.

\[ ^{40}\text{Ar} \] forms by radioactive decay of \( ^{40}\text{K} \) \((t_{1/2} = 1.25 \text{ Gyr})\), whereas \( ^{36}\text{Ar} \) is non-radiogenic.

\[ \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \text{mantle} \gg \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \text{atmosphere} \]

- The \( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \) ratio produced by nucleosynthesis is \(~0.005\).
- The Ar isotopic composition of today's atmosphere is \( ^{40}\text{Ar}/^{36}\text{Ar} = 295.5 \).
- The \( ^{40}\text{Ar}/^{36}\text{Ar} \) coming from the mantle in volcanic systems today is 2000-5000.

These values indicate early loss of most of the Earth's \( ^{36}\text{Ar} \), before much \( ^{40}\text{Ar} \) had built up by \( ^{40}\text{K} \) decay and degassed from the interior.

Evolution of Earth's atmosphere

How much gas has been lost after the blow-off of the Stage 1 atmosphere?

Gas escape to space is governed by the mass and kinetic energy of an atom or molecule, and the mass of the planet. One estimate of escape times versus mass for Earth, Mars, Venus and the Moon is discussed below:

To escape the planet, a species must have sufficient energy to exceed the planet's gravitational pull.

The effective escape times of different gaseous species are calculated by comparing the number of gaseous atoms or molecules with sufficient velocity given the population distribution of gases at a given kinetic energy, to that required for escape. \( V_{\text{escape}}^2 = 2 Gm/R \) (where \( G \), \( M \) and \( R \) = Earth's gravitational field, mass, and radius, respectively)

The number of gas particles above \( V_{\text{escape}} \) has changed over Earth history since kinetic energy \((= \frac{1}{2} mv^2)\) is a function of temperature \((3/2 kT)\) \((m= \text{mass of the gas, } V= \text{average velocity of gas particles, } k = \text{Boltzman's constant, } 1.3807 \times 10^{-23}\text{ J/K})\)

\( \frac{1}{2} mv^2 = 3/2kT \), so \( v = (3/2 kT/m)^{1/2} \), so \( v \) is proportional to \( T^{1/2} \) and \( (1/m)^{1/2} \)

The dashed horizontal line at the age of the solar system \((4.55 \times 10^9 \text{ yrs})\) intersects Earth's curve at mass \(-5\). Only species less massive than this \((\text{H}, ^2\text{H}, ^3\text{H}, ^4\text{He}, \text{and the mixed isotope H}_2 \text{ species})\) will have significantly escaped the Earth over its history.

Venus, Mars and the Moon have seen more escape of more massive elements over this time period (Venus because it is closer to the sun and has more energetic atmospheric gas molecules and Mars and the Moon because they are cooler but smaller than Earth).
Evolution of Earth’s atmosphere

Temperatures may have been high very early in the evolution of the Stage 2 atmosphere, and some heavier gases may have been lost. However, by at least 4 Ga sediments deposited from liquid H₂O were being formed, which implies similar surface temperatures to today. The pattern of rare-gas abundances below provides additional information.

The “expected” solar-to-Earth ratios are based on solar abundances, temperatures allowing liquid water within the first 0.2-0.3 Gyr of Earth history, and the expected rate of early degassing from estimates of accretion rate.

Values below the “expected” curve indicate retention; values above it indicate loss. All of these gases are below the curve.

H, C, O and N are all well below the curve because they were partially bound in heavier molecules that were retained in the Earth. Ar is also in significant excess because much ⁴⁰Ar has been produced by decay of ⁴⁰K over time.

Evolution of Earth’s Stage 2 atmosphere

When liquid water first condensed on the Earth, surface rocks and the atmosphere must have had an E₉ low enough to sustain Fe²⁺, because we don’t find evidence for significant Fe³⁺ in early Archean rocks. And because of the high abundance of iron in surface rocks, iron must have regulated the pE of the early atmosphere.

The oxidizing atmosphere developed later.

The primary abiotic O₂ source is photo-dissociation of water

\[ \text{H}_2\text{O} + \text{hv} \leftrightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \]

This reaction produces only a small amount of O₂, which must have gone into oxidizing Fe²⁺ to Fe³⁺ (and/or oxidizing other reduced chemicals) in the crust.

It’s currently estimated that the prebiotic atmosphere had pO₂ < 10⁻¹² atm (and pCO₂ > 1 atm).

The main source of O₂ is photosynthesis. Once photosynthesizing organisms evolved (i.e., cyanobacteria or blue-green algae) and began producing significant amounts of O₂, Fe²⁺ in surface rocks and waters was oxidized and pE atm began to slowly increase.
Evolution of Earth’s Stage 2 atmosphere

Permian = trees
Cambrian explosion
Ozone layer and Multi-cellular life
Paleosols with Fe
BIFs
ΔS^{34} variation stops

Evolution of Earth’s Stage 2 atmosphere – the narrative

3.8 Ga: oldest unrefuted evidence for life (from C isotopes in biogenic apatite).

3.5 Ga: oldest fossils (bacteria in Australian sediments). Good evidence exists for cyanobacteria by at least 3.0 Ga (stromatolites – see modern example from Australia in image at right); large-scale O_{2} production underway. Life was likely restricted to aquatic forms, because of intense UV radiation (which water absorbs) reaching the surface.

3-2.7 Ga: variations in S isotopes – early S^{2}/S^{4} poising of atmosphere/hydrosphere, followed by Fe II/Fe III poising, when most banded iron formations (BIFs) are deposited.

2.6-2.3 Ga: globally significant deposits of BIFs and other Fe-rich sandstones, which also contain significant concentrations of Mn.

Both images from http://www.amnh.org/learn/resources/earth_resource1.php

GG325 L35, F2013
**Evolution of Earth’s Stage 2 atmosphere – the narrative**

2.3 Ga: BIFs no longer forming in large quantities; $p_{O_2}/p_{CO_2} \approx 10^{-5}$.

Atmospheric $O_2$ must have reached about 0.5% of the modern concentration by this time, in order for dissolved $Fe^{2+}$ and $Mn^{2+}$ to become insoluble and be deposited regularly in sediments. U concentrations in sedimentary rocks also went down as $pE$ rose; $U^{4+}$ (insoluble) converted to $U^{6+}$ (soluble).

2.0 Ga and later: paleosols (fossil soils) now contain significant Fe (all as $Fe^{3+}$).

Older soils had essentially no Fe because it was leached away as soluble $Fe^{2+}$. ●

[Image: Paleosol preserved between two lava flows on the Isle of Skye, Scotland](http://www.uwgb.edu/dutchs/EarthSC202Slides/soilslid.htm)

It took another ~1.3 Gyr for multicellular life to evolve near the end of the Proterozoic Eon of the Precambrian (at about 700 Ma).

Probably by about 1 Ga, the protective stratospheric ozone layer probably started building up, allowing more complex life forms to begin to evolve.●

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**Evolution of Earth’s Stage 2 atmosphere**

$O_2$ continued to build up, to ~5% of the modern value by ~545 Ma, coinciding with the “Cambrian explosion” of higher organisms having differentiated cells.

The continued buildup of the $O_3$ layer allowed land plants and animals to begin to evolve. By about 430 Ma, things were starting to look pretty familiar (from our perspective). ●

By the end of the Paleozoic (Permian), forests had covered the land and then been buried, giving rise to enormous coal deposits in the Carboniferous. ●

$O_2$ continued to increase. It may even have been several percent higher in the Carboniferous and Cretaceous atmosphere than today.

$CO_2$ levels fluctuated throughout, generally dropping, from the controls we’ve already discussed.●

[Image: Permian forest, news.discovery.com]