Origin and Early Evolution of an Equilibrium Earth Atmosphere
Mars is an equilibrium planet, and it is dead.

Venus is an equilibrium planet, and it is dead.

The Earth is a non-equilibrium planet, and it is alive.
Mars is an equilibrium planet, and it is dead

Venus is an equilibrium planet, and it is dead

But, it probably started off more like Venus, . . . or Mars.
4. The atmosphere is oxygen rich even though oxygen is extremely chemically reactive. Left alone all oxygen would disappear in less than 1000 years. Something is actively maintaining an oxygen rich atmosphere.

Unique things about the Earth we need to explain

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Nitrogen</td>
<td>79%</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Oxygen</td>
<td>19%</td>
<td>Helium</td>
</tr>
<tr>
<td>CO2</td>
<td>0.03%</td>
<td>Methane (CH4)</td>
</tr>
<tr>
<td>Argon</td>
<td>1.0%</td>
<td>Ammonia (NH3)</td>
</tr>
<tr>
<td>Water vapor</td>
<td>variable</td>
<td>Water ice</td>
</tr>
</tbody>
</table>

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<td>95.3%</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6%</td>
<td>Water vapor</td>
</tr>
</tbody>
</table>

Earth  
Saturn  
Mars
### Planetary Fractionation

#### Composition of the Jovian Planets

The gas planets have a composition very similar to that in the sun, meaning they have undergone almost no fractionation.

#### Abundances of Elements in the Solar Spectrum

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent of atoms</th>
<th>Percent of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>91.2</td>
<td>71.0</td>
</tr>
<tr>
<td>Helium</td>
<td>8.7</td>
<td>27.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.078</td>
<td>0.97</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.043</td>
<td>0.40</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0088</td>
<td>0.096</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.0045</td>
<td>0.099</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.0038</td>
<td>0.076</td>
</tr>
<tr>
<td>Neon</td>
<td>0.0035</td>
<td>0.058</td>
</tr>
<tr>
<td>Iron</td>
<td>0.0030</td>
<td>0.14</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.0015</td>
<td>0.040</td>
</tr>
</tbody>
</table>

#### Abundances of Elements in Saturn

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent of atoms</th>
<th>Percent of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>25%</td>
<td></td>
</tr>
<tr>
<td>Methane (CH4)</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>Ammonia (NH3)</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>Water ice</td>
<td>trace</td>
<td></td>
</tr>
</tbody>
</table>

At depth hydrogen becomes liquid hydrogen, then liquid metallic hydrogen. At the center is an iron and rock core.

#### Abundances of Elements in Jupiter

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent of atoms</th>
<th>Percent of mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>~90%</td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>~10%</td>
<td></td>
</tr>
<tr>
<td>Methane (CH4)</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>Ammonia (NH3)</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>Water ice</td>
<td>trace</td>
<td></td>
</tr>
</tbody>
</table>

In the center is a rocky core about 10-15 times the mass of the Earth, and at about 20,000 degrees centigrade (3x hotter than Earth’s core).
## Origin of Atmosphere and Oceans

By Fractionation

But, even though the Earth has a markedly different atmosphere today than the other terrestrial planets . . . .

### Comparison With Other Terrestrial Planets

<table>
<thead>
<tr>
<th>Abundances of Gasses in Earth’s Atmosphere</th>
<th>Abundances of Gasses in Mar’s Atmosphere</th>
<th>Abundances of Gasses in Venus’s Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen 79%</td>
<td>CO₂ 95.3%</td>
<td>CO₂ 96.5%</td>
</tr>
<tr>
<td>Oxygen 19%</td>
<td>Nitrogen 2.7%</td>
<td>Nitrogen 3.5%</td>
</tr>
<tr>
<td>CO₂ 0.03%</td>
<td>Argon 1.6%</td>
<td>SO₂ 150 ppm</td>
</tr>
<tr>
<td>Argon trace</td>
<td>Oxygen 0.15%</td>
<td>Argon 70 ppm</td>
</tr>
<tr>
<td>Water vapor variable</td>
<td>Water vapor 0.03%</td>
<td>Water vapor 20 ppm</td>
</tr>
<tr>
<td>Atmospheric Pressure 1.0</td>
<td>Atmospheric Pressure 0.064</td>
<td>Atmospheric Pressure 92</td>
</tr>
<tr>
<td>Temperature 13 C</td>
<td>Temperature -23 C</td>
<td>~1300 #/in²</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperature 462 C</td>
</tr>
</tbody>
</table>
Origin of Atmosphere and Oceans By Fractionation

It almost certainly began more like the other terrestrial planets, and has evolved to its present non-equilibrium state through history.

Comparison of Earth With Itself at 4 Billion Years Ago

<table>
<thead>
<tr>
<th>Abundances of Gasses in Earth’s Atmosphere</th>
<th>Original Composition of Earth’s Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nitrogen</strong></td>
<td><strong>CO₂</strong></td>
</tr>
<tr>
<td>79%</td>
<td>98.%</td>
</tr>
<tr>
<td><strong>Oxygen</strong></td>
<td><strong>Nitrogen</strong></td>
</tr>
<tr>
<td>19%</td>
<td>1.9%</td>
</tr>
<tr>
<td><strong>CO₂</strong></td>
<td><strong>Oxygen</strong></td>
</tr>
<tr>
<td>0.03%</td>
<td>trace</td>
</tr>
<tr>
<td><strong>Argon</strong></td>
<td><strong>Argon</strong></td>
</tr>
<tr>
<td>1.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td><strong>Water vapor</strong></td>
<td><strong>Water vapor</strong></td>
</tr>
<tr>
<td>variable</td>
<td>variable</td>
</tr>
<tr>
<td><strong>Atmospheric Pressure</strong></td>
<td><strong>Atmospheric Pressure</strong></td>
</tr>
<tr>
<td>1.0</td>
<td>60</td>
</tr>
</tbody>
</table>
From its early planetary state the Earth could have evolved in the direction of Venus

Fiery hot (477° C), a dense, choking atmosphere of acid, weighing about 90 times more than the Earth’s atmosphere.
Or, it *could* have evolved in the direction of Mars.

*Bitter cold (-53°C), dry, with an atmosphere weighing only 0.06 times the Earth’s.*
Because Mars once had liquid water on its surface

Millions of years ago, Mars may have hosted rivers and lakes like those depicted in this artist's rendition.

http://www.lbl.gov/Science-Articles/Archive/SB-ESD-hunting-for-martians.html

http://science.nasa.gov/headlines/y2001/ast05jan_1.htm

http://www.lcusd.net/rop/bb2000/1/mars.htm
The Case of the Missing Mars Water

http://science.nasa.gov/headlines/y2001/ast05jan_1.htm

http://www.esa.int/esaCP/GGG33G3UGEC_Life_1.html

http://www.marsdaily.com/water.html

http://zebu.uoregon.edu/~imamura/121/lecture-11/lecture-11.html

http://www.astro.virginia.edu/class/oconnell/astr121/marsimages.html

http://www.marsdaily.com/water.html
... even though Mars is cold and dry now.
Part of the Mars-Earth differences can be explained by their different sizes.

Earth and Mars compared
Mars’ diameter is half that of the Earth's
It has ten percent the mass
If you weigh 180 pounds on Earth, you would weigh only 68 pounds on Mars
Mars is half again further from the Sun than the Earth

http://www.arcadiastreet.com/cgvistas/mars_002.htm
But, size differences cannot be used to explain the Venus-Earth differences.

Earth and Venus compared
Venus' diameter is 86% that of the Earth's
It has 82% the mass.
While Venus is roughly the same size and density as the Earth, it is otherwise a very different world. Earth's surface is a varied one, with liquid water covering three quarters of its surface. Those areas not under water have been highly modified by plate tectonics, weather, and life itself. Venus on the other hand is far too hot to host liquid water. Volcanoes, massive lava flows and the occasional impact crater characterize its surface.
### Comparison With Other Terrestrial Planets

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<td><strong>Nitrogen</strong></td>
</tr>
<tr>
<td>19%</td>
<td>2.7%</td>
<td>3.5%</td>
</tr>
<tr>
<td><strong>CO₂</strong></td>
<td><strong>Argon</strong></td>
<td><strong>SO₂</strong></td>
</tr>
<tr>
<td>0.03%</td>
<td>1.6%</td>
<td>150 ppm</td>
</tr>
<tr>
<td><strong>Argon</strong></td>
<td><strong>Oxygen</strong></td>
<td><strong>Argon</strong></td>
</tr>
<tr>
<td>trace</td>
<td>0.15%</td>
<td>70 ppm</td>
</tr>
<tr>
<td><strong>Water vapor</strong></td>
<td><strong>Water vapor</strong></td>
<td><strong>Water vapor</strong></td>
</tr>
<tr>
<td>variable</td>
<td>0.03%</td>
<td>20 ppm</td>
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**Atmospheric Pressure**
- Earth: 1.0
- Mars: 0.064
- Venus: 92 (≈1300 #/in²)

**Temperature**
- Earth: 13°C
- Mars: -23°C
- Venus: 462°C

Mars is so cold now in part because it is far from the sun, and in part because its atmosphere is so thin there is no Greenhouse effect.

Venus is so hot now because it is closer to the sun, and its atmosphere is so thick with CO₂ that the Greenhouse effect is powerful.
Origin of Atmosphere and Oceans
By Fractionation

A Deductive Argument:

_IF, . . . the Earth and other terrestrial planets lost whatever solar atmosphere they had early in the solar system’s development,

_AND, IF, . . . the Earth had an initial atmosphere similar to those of Venus and Mars,

THEN, . . . the Earth’s present atmosphere must be the result of some kind of evolutionary processes.

> Nitrogen must increase from 1.9% to 79%
> Carbon dioxide must decrease from 98% to 0.03%
> Oxygen must increase from a trace to 19%
> Plus, there is a lot of sulfur in the atmosphere (like Venus)
> And, the pressure must reduce from 60 atmos. to 1 atmos.

This is not a simple story . . . And it will take us some time to tell it.
**Evolution of the Earliest Atmospheres of Mars and Earth**

**Volcanic Outgassing Evolving to Equilibrium Atmosphere**

- **Primary Components**:
  - **H₂O** (Abundant)
  - **CO₂** (Abundant)
  - **H₂** (Common)
  - **N₂** (< 10%)
  - **S** (few %)

- **Losses**:
  - Uv radiation (photo-dissociation)

- **Ocean Sink**:

- **Final Mars/Earth/Venus Equilibrium Atmosphere**
  - **CO₂** ~ 95%
  - **N₂** few %
  - **S** traces

- **Closed, dead, equilibrium systems**

- **Banded Iron Formation**
- **Sediment Sequestering**
This is the way the world ends
This is the way the world ends
This is the way the world ends
Not with a bang but a whimper.

The Hollow Men
T. S. Eliot (1925)

But this is not what happened
The Influence of Life on the Earth
JUST HOW LONG IS EARTH HISTORY? AND WHEN DID THE IMPORTANT THINGS HAPPEN?

Billions of Years

4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

Hadean
Archaean
Proterozoic
Phanero

Oldest Rocks
First Fossils
Grenville

Origin of Earth 4.5-4.0
First Record Of liquid Water

Origin of Continents
Plate Tectonic Processes
With the addition of life we now add a new energy source to the Earth System.

Biological \rightarrow Organic chemistry, plus biological modifications of environments
Life Energy

All life forms from the simplest known to the most complex use ATP as the mediator of biochemical reactions.

\[
\text{ATP} \rightarrow e^- + \text{ADP} + P
\]

High energy electrons are used to break and make chemical bonds during biochemical reactions.

A major attractor of life, and the path’s of its evolution, is about the procurement or manufacture of ATP.
Life as an Energy Dissipating System
The structure of Adenosine Tri Phosphate

3rd phosphate split off

 ATP now becomes Adenosine DiPhosphate

High energy electron released to mediate other chemical reactions.
Life as an Energy Dissipating System
The structure of Adenosine Tri Phosphate

ADP does not have enough energy to split off another phosphate and release another high energy electron.

To reconstruct it as an energy source a high energy electron obtained from the environment or a food source is used to reconnect the third phosphate back on to the ADP.

ADP is now back to being ATP

The issue is, . . . Where do the high energy electrons come from to reconstruct the ATP??
Life as an Energy Dissipating System

Life Energy has two modalities:
1. **Environmental Energy** – tectonic and/or solar.
2. **Biochemical Energy** - derived from or internal to life itself (i.e. some things eat other things).

Ultimately on Earth all energy is derived environmentally, meaning it comes down to either tectonic or solar energy.

The story of the evolution of life is how it . . .

- Extracts environmental energy, and . . .
- Mediates between these environmental and biochemical energy sources.

And, how those mediations have influenced both the evolution of life itself and the Earth.
The Most Basic Forms of Life are . . . ?
Universal Tree of Life
And Earth’s Earliest Life Forms
Extremophiles are the rule breakers of biology. These organisms live in the harshest environments on earth—boiling water holes in Italy, the ice of Antarctic seas, and hydrothermal vents at the bottom of the ocean. They not only survive but also thrive under conditions previously thought to prohibit all forms of life. In recent years, scientists have begun to mine the genomes of extremophiles for information that might lead to new technologies, such as heat-resistant molecules for commercial uses, and to breakthroughs in medicine and the environmental sciences.

The first extremophile to be sequenced was *Methanococcus jannaschii*, an organism straight out of science fiction. The single-celled microbe lives near hydrothermal vents 2,600 meters below sea level, where temperatures approach the boiling point of water and the pressure is sufficient to crush an ordinary submarine. There, *M. jannaschii* survives on carbon dioxide, hydrogen and a few mineral salts. It cannot tolerate oxygen and takes care of its energy needs by producing methane.
Archaebacteria - Extremophiles

1. Extreme Thermophiles - live in hot springs and black smokers.

Boiling hot springs in Yellowstone National Park are colored by colonies of thermophilic cyanobacteria, eubacteria and archaebacteria. *Thermus aquaticus* survives in temperatures too high for photosynthetic bacteria, up to 80 degrees Celsius (176 degrees F). *Thermus aquaticus* is heterotrophic and survives on minute amounts of organic matter in the water.
Archaebacteria - Extremophiles

1. Extreme Thermophiles--live in hot springs and black smokers.

Links to videos of active smokers and vent environments
Archaebacteria - Extremophiles

1. Extreme Thermophiles--live in hot springs and black smokers.
Giant tube worms living in the vent communities. These have no mouth or digestive system, but survive symbiotically on the bacteria that live in their bodies.
These bacteria live in very hot, acid habitats of 60-80 °C and pH 2-4, like the photo of a "Hot springs" below, the red stain on the rocks are the prokaryotic cells.
Archaebacteria - Extremophiles

1. Extreme Thermophiles -- live in hot springs and black smokers.

2. Extreme Halophiles – live in saturated brine and salt crust.

The bacteria thrive in saturated brine up to 30 percent salinity (9 times the salinity of sea water). They can also be found embedded in the thick, pinkish-red salt crust literally baking in the desert sun. In fact, they cannot survive if the salt concentration drops below 10 percent.

The vivid red brine (teaming with halophilic archaebacteria) of Owens Lake contrasts sharply with the gleaming white deposits of soda ash (sodium carbonate). The picturesque Inyo Range can be seen in the distance.

http://waynesword.palomar.edu/ploct97.htm
**Archaebacteria - Extremophiles**

1. Extreme Thermophiles -- live in hot springs and black smokers.

2. Extreme Halophiles -- live in saturated brine and salt crust.

3. Extreme Acidophiles - live in waters with a pH below 7, and as low as 0.0.

Despite the extreme environment on the waste dump acid-loving algae/bacteria colonies live in puddles on the waste dumps where the pH can be extremely low. Some acidophiles thrive in water with a pH of 0.0.
Archaebacteria - Extremophiles

1. Extreme Thermophiles--live in hot springs and black smokers.
2. Extreme Halophiles--live in saturated brine and salt crust.
3. Extreme Acidophiles and acid mine drainage
Where and how did/do these extremophile organisms live on Earth?
Microbial Mat Communities

The modern mats to the right are much what an Archaean community was like. In fact, it is almost exactly what they were like – except for a few forms that will evolve during the Proterozoic.
Microbial Mat Communities

Microbial Mats from a Hydrothermal System

Up close the mats look like tangled, chaotic, slimy messes.

But, they are a complex ecosystem of different species living symbiotically.

http://www-eaps.mit.edu/geobiology/research/hydrothermal.html
Microbial Mat Communities

The Connection Between Tectonic Energy and Biological Redox in Bacterial Mat Communities

*Hot vent bacterial mat*

These early extremophile bacteria obtained their energy by utilizing the oxidation-reduction chemical reactions driven by difference between the thermal highly reduced water and the less reduced Archaean sea water.

\[
H_2S + FeS = FeS_2 + H_2 + e^-
\]

Hydrogen sulfide  Pyrite
Archaean Archaea Matt Communities

Stromatolites

http://www.spaceprime.com/early-earth.html
Modern Bacterial Matt Communities

Stromatolites

~ 3.6 Ga

http://www.spaceprime.com/early-earth.html
Early Biochemical Pathways for Obtaining Energy
ChemoLithoAutotrophy

- Using or facilitating exothermic chemical reactions that release high energy electrons.

\[ \text{H}_2\text{S} + \text{FeS} = \text{FeS}_2 + \text{H}_2 + \text{e}^- \]

- A common reaction in smokers and volcanic environments.
- Many similar reactions are known involving sulfur, sulfate, carbon dioxide, etc.
- Release high energy electrons captured by bacteria
1. Extreme Thermophiles--live in hot springs and black smokers.
Methanogenic Generating Archaea

*Methanococcus jannischii* was originally isolated from a "white smoker" chimney at an oceanic depth of 2,600 meters. It can be grown in a mineral medium containing only $H_2$ and $CO_2$ as sources of energy and carbon for growth within a temperature range of 50 to 86 degrees centigrade.

\[
4H_2 + CO_2 \rightarrow CH_4 + 2H_2O
\]

To atmosphere

e$^-$ Used to convert ADP to ATP

Today methanogens live in almost all anoxic environments on Earth.
Methanogenesis

Methanogens (methane-producers)--responsible for swamp gas.
Methanogenesis

H₂, CO₂, CH₄

Extremophiles (Methanogens)

4H₂ + CO₂ → 2H₂O + CH₄

Basalt Weathering Reaction

2FeO + 3CO₂ + H₂O → Fe₂CO₃ + H

Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. CO₂ (carbon) is sequestered in sediments as petroleum or natural gas.
Fermentation

- Breaking a larger organic molecule into two smaller pieces releasing high energy electrons.
- Pyruvic fermentation is the best known.

Sugar $\rightarrow$ 2 lactic acids

2 e$^-$ Used to convert ADP to ATP

- This takes place only in the absence of oxygen.
Pyruvic fermentation is widespread today, but pretty inefficient – each fermentation results in only two ATP molecules, and a lot of energy remains in the remaining waste molecules.

It also does not provide a direct path to new sources of energy.
Anaerobic Respiration and the Invention of Electron Transport Chains

VI – Desulfovibrios
Sulfur Reducing Bacteria

Respiration (in general)

Respiration using oxygen is fundamental to the life of higher plants and animals. Possibly, it is the only kind of respiration we are aware of.

Lactic Acid  + O₂ → CO₂ + H₂O  + ATP

- Known as the Krebs or Citric Acid cycle.
- In plants and animals this is the only pathway of respiration.

But, oxygen respiration is only one of dozens of respiration pathways, many of which are more important than oxygen respiration.
Anaerobic Respiration

Respiration: the process of breaking down food molecules where the electrons released are finally transferred to an inorganic molecule for neutralization.

- In oxygen respiration (aerobic respiration) oxygen is the final electron receptor.
- In anaerobic respiration the final electron receptor is an inorganic molecule other than oxygen.

\[ \text{SO}_4^{2-} + e^- \rightarrow \text{H}_2\text{S} \]

- sulfate → sulfide

- Almost any reduced molecule can serve as the electron acceptor.

\[ \text{NO}_3^- \quad \text{NO}_2^- \quad \text{NO} \quad \text{Fe}^{+2} \quad \text{Mn}^{+2} \quad \text{Etc.} \quad \text{Etc.} \quad \text{Etc.} \]
Desulfovibrios likely invented the electron transport chain very early in the Earth’s history.

- At the end of the chain the high energy electron is disposed of by passing it to a sulfate anion, reducing it to sulfide ($S^{2-}$), forming either $H_2S$, or some other smelly compound.
Methanogenesis

\[ \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 \]

Extremophiles

4\( \text{H}_2 + \text{CO}_2 \rightarrow 2\text{H}_2\text{O} + \text{CH}_4 \)

Basalt Weathering Reaction

2\( \text{FeO} + 3\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{CO}_3 + \text{H}_2\text{O} \)

Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. CO\(_2\) (carbon) is sequestered in sediments as petroleum or natural gas.
Green/Purple Sulfur Bacteria

Anaerobic Photosynthesis

\[
\begin{align*}
\text{bacteriochlorophyll} \\
\text{H}_2\text{S} & \rightarrow 2\text{H}^+ + \text{S} \\
& \text{goes to } \text{S}^{-2} \text{ (sulfide) like FeS}_2 \text{ (pyrite)} \\
& + \text{CO}_2 \rightarrow \text{Sugar} \\
\end{align*}
\]

\text{H} \text{ reduces } \text{CO}_2 \text{ To form sugar}

http://www.humboldt.edu/~pls13/BacThome.html

A photogenic purple sulfur bacterial mat (Thiopedia)
Green/Purple Sulfur Bacteria

Anaerobic Photosynthesis

The two step sugar production, the first-hydrogen generation-along the thylacoid membranes, the second-CO$_2$ reduction-in the stroma space outside the thylacoids (Calvin-Benson Reaction). If the membranes are disturbed the reactions cease.
**Methanogenesis**

\[ 4H_2 + CO_2 \rightarrow 2H_2O + CH_4 \]

**Extremophiles (Methanogens)**

Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. CO₂ (carbon) is sequestered in sediments as petroleum or natural gas.

**Fermentation + Anaerobic Respir**

\[ H_2 + H_2S \rightarrow \text{Lactic Acid} + \text{Acetic Acid} + \text{Energy} \]

\[ SO_4^{2-} + H_2 \rightarrow H_2S + H_2O \]

**Desulfovibrios**

In fermenting food molecules, use sulfate to neutralize a high energy electron, putting hydrogen sulfide and water into the atmosphere. Organic matter (C from CO₂) sequestered in sediments.

**Basalt Weathering Reaction**

\[ 2FeO + 3CO_2 + H_2O \rightarrow Fe_2CO_3 + H \]

**Stored**
Aerobic Photosynthesis
Precursor Blue Green Algae

Photosynthesis in General

• The traditional photosynthetic equation most of us grew up with is

\[ 6 \text{CO}_2 + 6 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 \]

• In the history of the photosynthetic biochemical strategy atmospheric \( \text{CO}_2 \) has always been the source of carbon. The major problem has been finding a source of hydrogen.

• The preceding equation can be made more general by substituting "A" for the oxygen ("O") since what is essential here for photosynthesis is the reducing power of the hydrogen. The oxygen is just incidental.

\[ \text{CO}_2 + \text{H}_2\text{A} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{A} \]
Precursor Blue-Green Algae

Aerobic photosynthesis and Oxygen Sequestering

The Precursor Blue-Green algae initially solved the problem by taking advantage of an environmental convenience.

For the first two billion years of Earth history weathering released a lot of iron from igneous rock forming minerals like pyroxene and biotite. In these minerals most of the iron is in the ferrous state.

\[ \text{Fe}^{+2} \]

On weathering, and in the absence of oxygen the ferrous iron combines with readily available anions.

\[ 2\text{FeO} + 3\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{CO}_3 + \text{H}_2 \]

This is the basalt weathering reaction, likely one of the most common geological reactions on the early Earth, and results in iron carbonate as a product.

During the Archaean the oceans were supersaturated with this dissolved iron carbonate.
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\[ \text{Fe}_2\text{CO}_3 + \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \]

Magnetite
Banded Iron Formation – Peak abundance

2500 Ma • Peak development of Banded Iron formations world-wide:

http://www.eps.harvard.edu/people/faculty/hoffman/snowball_paper.html

http://www.humboldt.edu/~natmus/lifeThroughTime/PreCam.web/

PreCambrian Record of Life And Associated Geologic Deposits

Banded Iron Formation – South Africa

http://web.uct.ac.za/depts/geolsci/dlr/hons1999/
PreCambrian Record of Life And Associated Geologic Deposits

Banded Iron Formation – South Africa

**Methanogenesis**

\[4H_2 + CO_2 \rightarrow 2H_2O + CH_4\]

- Extremophiles

**Fermentation + Anaerob Respir**

- Desulfovibrios

\[\text{Lactic acid} \rightarrow \text{Acetic Acid} + \text{Energy}\]

\[\text{SO}_4^{2-} + H_2 \rightarrow H_2S + H_2O\]

\[H_2S \rightarrow H_2 + S\]

- Green & Purple Sulfur Bacteria

\[H_2 + CO_2 \rightarrow \text{Sugar}\]

**Anaerobic Photo.**

\[CO_2\]

- Organic matter to sediments

**Stored in Sediment**

- Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. CO₂ (carbon) is sequestered in sediments as petroleum or natural gas.

- In fermenting food molecules use sulfate to neutralize a high energy electron, putting hydrogen sulfide and water into the atmosphere. Organic matter (C from CO₂) sequestered in sediments.

- Suck down hydrogen sulfide and CO₂ from atmosphere to manufacture sugar. Sequester sulfur and carbon from organic matter in the sediments.
Every advance leads to a limitation

Hydrogen (H$_2$S) shortage

As the population of green and purple sulfur bacteria increased across the world, and as they moved away from the hydrothermal vents, they soon ran up against a wall...

- A shortage of hydrogen from H$_2$S to reduce CO$_2$ to produce sugar.

Another energy strategy had to be invented.
Every limitation is an opportunity

Invention of Aerobic Photosynthesis

Precursor Blue Green Algae

Photosynthesis in General

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• The preceding equation can be made more general by substituting "A" for the oxygen ("O") since what is essential here for photosynthesis is the reducing power of the hydrogen. The oxygen is just incidental.

\[ \text{CO}_2 + \text{H}_2\text{A} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 2\text{A} \]
Green/purple sulfur bacteria photosynthetic reactions require hydrogen sulfide. In its absence these organisms wither and die from lack of energy.

\[ \text{H}_2\text{S} \]

There does exist, however, an unlimited supply of hydrogen, it is just that it is tightly bound up with other atoms. The key to the next step was finding a source of energy large enough to remove the hydrogen from . . .

\[ \text{H}_2\text{O} \]
Precursor Blue-Green Algae

Aerobic Photosynthesis and Oxygen Sequestering

To access the hydrogen available in water the Precursor Blue-Green algae invented or incorporated from an earlier form a second form of chlorophyll and housed it in a new Reaction Center II. This chlorophyll absorbs a shorter wave length of light, that results in a more highly energized molecule, which results in a higher energy electron. This higher energy electron is used to split water.

The down side to this reaction is that it releases free oxygen, and in an anoxic world this is bad news. It would be like us breathing hydrogen cyanide gas – almost instant death.

**Oxygen Generation and Release**
Every advance leads to a limitation and sometimes unintended consequences.

**Oxygen Cataclysm**

This spilling of toxic wastes into the environment precipitated one of the most severe environmental crises the Earth and the life on it experienced.

*Life has three choices during such a crisis.*

1. Go extinct
2. Move to a safe environment
3. Adapt to new conditions
Blue-green algae are not true algae, but are more properly photosynthetic bacteria and can also be called cyanobacteria. They are commonly found in lakes, ponds, wetlands, and marine environments.
Stromatolites: Shark Bay, Australia

http://www-eaps.mit.edu/geobiology/biomarkers/whatis.html

http://www.nirgal.net/graphics/stromatolite_moderne.jpg
Stromatolite formation in Hamlin Pool, Shark Bay, western Australia. This is one of the few places in the world today where stromatolites form as commonly as they did on the proto-Atlantic DCM. Top picture is a close up of the stromatolite mounds; lower right intertidal region with tide in; lower left region with tide out. Good images of what Virginia looked like in the mid to late Cambrian.

**Methanogensis**

$\text{H}_2$, $\text{CO}_2$, $\text{CH}_4$

**Fermentation + Anaerob Respir**

$\text{H}_2$, $\text{H}_2\text{S}$

**Anaerobic Photo.**

$\text{CO}_2$

**Aerobic Photo-1**

$\text{H}_2$, $\text{CO}_2$, $\text{Sugar}$

---

**Extremophiles (Methanogensi)**

$4\text{H}_2 + \text{CO}_2 \rightarrow 2\text{H}_2\text{O} + \text{CH}_4$

**Desulfovibrios**

Lactic acid $\rightarrow$ Acetic Acid $+ \text{Energy}$

$\text{SO}_4^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{H}_2\text{O}$

---

**Green & Purple Sulfur Bacteria**

$\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S}^0$

$\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$

**Precursor BGA (Blue Green Algae)**

$\text{H}_2 + \text{CO}_2 \rightarrow \text{Sugar}$

$\text{BIF} \rightarrow \text{Fe}_3\text{O}_4 + \text{O}_2$

---

**Stored in Sediments**

Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. $\text{CO}_2$ (carbon) is sequestered in sediments as petroleum or natural gas.

In fermenting food molecules use sulfate to neutralize a high energy electron, putting hydrogen sulfide and water into the atmosphere. Organic matter ($\text{C}$ from $\text{CO}_2$) sequestered in sediments.

Suck down hydrogen sulfide and $\text{CO}_2$ from atmosphere to manufacture sugar. Sequester sulfur and carbon from organic matter in the sediments.

Suck down $\text{CO}_2$ from atmosphere and water from environment to manufacture sugar. Waste oxygen is combined with iron and sequestered as Banded Iron Formation. Organic matter to sediments.
Proterozoic Cleansing of Methane Smog

Reducing Atmosphere
Deep UV penetration sky orange from methane smog

Oxidizing Atmosphere - blue sky

Relative Gas Concentration

CO₂

methane

oxygen

1st red beds:

CO₂

methane

oxygen

The Cleansing of the Methane Smog

Saturn shimmers through the haze above the dense, orangish smog that obscures the surface of Titan. Above the clouds and haze, there may be a level in Titan's atmosphere where a blue sky color can be seen.

The haze of an atmospheric layer on Saturn's moon, Titan. With an atmosphere thicker than Earth's, and composed of many biochemically interesting molecules (methane, hydrogen and carbon), Titan's rich chemistry will continue to interest astrobiologists as they look forward to landing a probe on its surface in 2004-5. Credit: Voyager Project, JPL, NASA
THE CLEANSING OF THE METHANE SMOG
Invention of Oxygenic Respiration

X – Mitochondria and the Krebs Cycle

ATP Generating Biochemical Pathways

Organotrophy – energy is derived from organic processes rather than inorganic processes.

**Aerobis; a.k.a. Respiration, or the Krebs cycle**

- This is the most efficient and abundant source of energy for living systems.

\[ 2 \text{H}_2\text{O} \rightarrow 2 \text{H}^+ + \text{O}_2 \]

\[ \text{Lactic Acid} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 36 \text{ATP} \]
Methanogens – Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. CO2 (carbon) is sequestered in sediments as petroleum or natural gas.

\[4H_2 + CO_2 = CH_4 + 2H_2O\]

Sulfur Reducing Bacteria (Desulfovibrius) – In fermenting food molecules use sulfate to neutralize a high energy electron, putting hydrogen sulfide and water into the atmosphere. Organic matter (C from CO2) sequestered in sediments.

\[SO_4^{2-} + H_2 \rightarrow H_2S + H_2O\]

Anaerobic Photosynthesis (Green/Purple Sulfur Bacteria) – Suck down hydrogen sulfide and CO2 from atmosphere to manufacture sugar. Sequester sulfur and carbon from organic matter in the sediments.

\[H_2S + CO_2 \rightarrow \text{Sugar} + S\]
Aerobic Photosynthesis-1 (Precursor BGA) – Suck down CO2 from atmosphere and water from environment to manufacture sugar. Waste oxygen is combined with iron and sequestered as Banded Iron Formation. Organic matter to sediments.

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Sugar} + \text{O}_2 \]

\[ \text{Fe}_2\text{CO}_3 \rightarrow \text{Fe}_3\text{O}_4 \text{ (BIF)} \]

Aerobic Photosynthesis-2 (BGA) – Suck down CO2 from atmosphere and water from environment to manufacture sugar. Waste oxygen is released into the atmosphere. Organic matter to sediments.

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Sugar} + \text{O}_2 \]

To atmosphere
**Organic smog - orange sky**

**Methanogenesis**

\[
\begin{align*}
H_2 + CO_2 &\rightarrow CH_4 + CO_2 \\
\text{Extremophiles (Methanogens)} &\rightarrow 4H_2 + CO_2 \rightarrow 2H_2O + CH_4
\end{align*}
\]

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**Fermentation + Anaerob Respir**

\[
\begin{align*}
H_2 + CO_2 &\rightarrow H_2S + CO_2 \\
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**Anaerobic Photo**

\[
\begin{align*}
H_2S &\rightarrow H_2 + S_2 \\
\text{Green & Purple Sulfur Bacteria} &\rightarrow H_2 + CO_2 \rightarrow H_2O + CO_2
\end{align*}
\]

Suck down hydrogen sulfide and CO₂ from atmosphere to manufacture sugar. Sequester sulfur and carbon from organic matter in the sediments.

**Aerobic Photo-1**

\[
\begin{align*}
H_2 + O_2 &\rightarrow H_2O \\
\text{Precursor BGA (Blue Green Algae)} &\rightarrow CH_4 + O_2 \rightarrow H_2O + CO_2
\end{align*}
\]

Suck down CO₂ from atmosphere and water from environment to manufacture sugar. Waste oxygen is combined with iron and sequestered as Banded Iron Formation. Organic matter to sediments.

**Aerobic Photo-2**

\[
\begin{align*}
H_2O &\rightarrow H_2 + O_2 \\
\text{Blue Green Algae} &\rightarrow H_2 + CO_2 \rightarrow Sugar
\end{align*}
\]

Suck down CO₂ from atmosphere and water from environment to manufacture sugar. Waste oxygen is released into the atmosphere. Organic matter to sediments.

**Stored in Sediments**

- Suck hydrogen and carbon dioxide out of the atmosphere and put methane into the atmosphere. CO₂ (carbon) is sequestered in sediments as petroleum or natural gas.
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**Stage Two Atmosphere – Archaean**

*Initiation of Biogeochemical Cycling*

- **Methanogens** – Extremophile Archaebacteria
  - Carbon dioxide being sucked down and methane put into atmosphere

- **Anaerobic Photosynthesis** – Green/Purple Sulfur bacteria
  - $\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{sulfur}$
  - $+ \text{CO}_2 \rightarrow \text{sugar}$

- **Fractionation (& sequestering)**
  1. To sediments (petroleum)
  2. To carbonates ($\text{CO}_2$ to $\text{CaCO}_3$)
  3. $\text{CO}_2$ to $\text{CH}_4$

**Archaean Atmosphere**

- $\text{CO}_2$ less
- $\text{CH}_4$ more
- $\text{N}_2$ rising
**Stage Three Atmosphere - Proterozoic**

*The Great Switch*

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<th>Hadean</th>
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<th>Phanerozoic</th>
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Aerobic Photosynthesis - Blue-green Cyanophytes (bacteria)

\[
\text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2
\]

\[
\text{H}_2 + \text{CO}_2 \rightarrow \text{Sugar}
\]

**Proterozoic Atmosphere**

- \( \text{CO}_2 \) less
- \( \text{N}_2 \) rising
- \( \text{O}_2 \) rising
- \( \text{CH}_4 \) reduced
Stage Four Atmosphere - Phanerozoic
Settling in but still Fluctuating

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Relative Nitrogen Pressure

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