12.842 / 12.301 Past and Present Climate
Fall 2008

The Co-evolution of Life, Ocean and Atmospheric Chemistry, and Sedimentary Rocks

12.842 Lecture #3

Fall 2008

The Origin of Life

Theories of the origin of life

“We still have little idea how, when or where life began…. The evidence is circumstantial and can be compared with delving into such records as there are in Massachusetts of the Mayflower, to discern the origins of the English language.”

Nisbet & Sleep (2001) “The habitat and nature of early life” *Nature* Vol. 409: 1083-1091.

Some Milestones in Origin-of-Life Science-1

- 1664: Archbishop Usher announced that his literal reading of the *Bible* indicates that God created humans & higher organisms on Oct. 26, 4004 BC.
- < mid 1800's: Creationism + insects, frogs & other small creatures arise spontaneously from mud & rot.
- mid 1800's:
  - (1) **Pasteur** demonstrated bacteria & other microorganisms arise from parents resembling themselves. Spontaneous generation is dead.
  - (2) **Darwin** proposes natural selection, the theory that environmental pressure results in the perpetuation of certain adaptations. Evolution of complex organisms therefore possible, & all current life forms could have evolved from a single (last) common ancestor.
- Darwin (privately) suggested life could have arisen from chemistry: "in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present."

Adapted from Orgel (1994) *Sci. Am.*, Oct. 1994, 77-83.

Some Milestones in Origin-of-Life Science-2

- 1920s and early 1930s: Oparin (Russia) and Haldane (Britain) independently developed similar theories suggesting how conditions on the early Earth may have been led to the chemical evolution of life. Both presumed a primitive reducing atmosphere in which simple organic compounds were synthesized. They suggested that these organics accumulated in the upper ocean ("primordial soup”) and eventually elementary life forms emerged from this broth.
- 1953: Miller-Urey experiment (U. Chicago) demonstrates that amino acids could be formed with “atmospheric gases” (NH_3, H_2, H_2O, CH_4) + lightning.
- Late 1960s: Woese (U. Illinois), Crick (England), Orgel (Salk Inst., San Diego) concurrently proposed RNA may have preceded proteins & catalyzed all reactions for survival & replication of ‘last common ancestor’. The ‘RNA World’ hypothesis born.
- 1977: Hydrothermal vents on the seafloor discovered teaming with diverse life. Suggests possibility life may not have evolved at the surface.
- 1983: Thomas Cech (U. Colorado) & Sidney Altman (Yale) independently discovered *ribozymes*, enzymes made of RNA. Heritability & reproducibility possible with a single molecule.

The Building Blocks for Biomolecules: The Miller-Urey Experiment (1953)

Image removed due to copyright restrictions.

Orgel (1994) *Sci. Am.*, Oct. 1994, 77-83.

Some Milestones in Origin-of-Life Science-3

- 1988: Günter Wächtershäuser (German patent lawyer!) theorizes that Fe & Ni sulfide *minerals* at hydrothermal vent systems provided the template & catalyst for formation of biological molecules.
- 1998: Jay Brandes (Carnegie Inst.) demonstrates that N_2 is converted to NH_3 in the presence of H_2 & magnetite (Fe_3O_4), at T & P typical of hydrothermal vents (300-800°C). Mineral surfaces and HT vent environments can produce biologically-useful form of N. *Nature 395:265*
- 2000: Cody et al. demonstrate synthesis of pyruvate using mineral catalysis under hydrothermal conditions. Pyruvate is branch point for many extant biosynthetic pathways.

Summary of Origin of Life Theories

•Life may have been well-established by ~3.5 Ga
•How it began will require a lot more work!

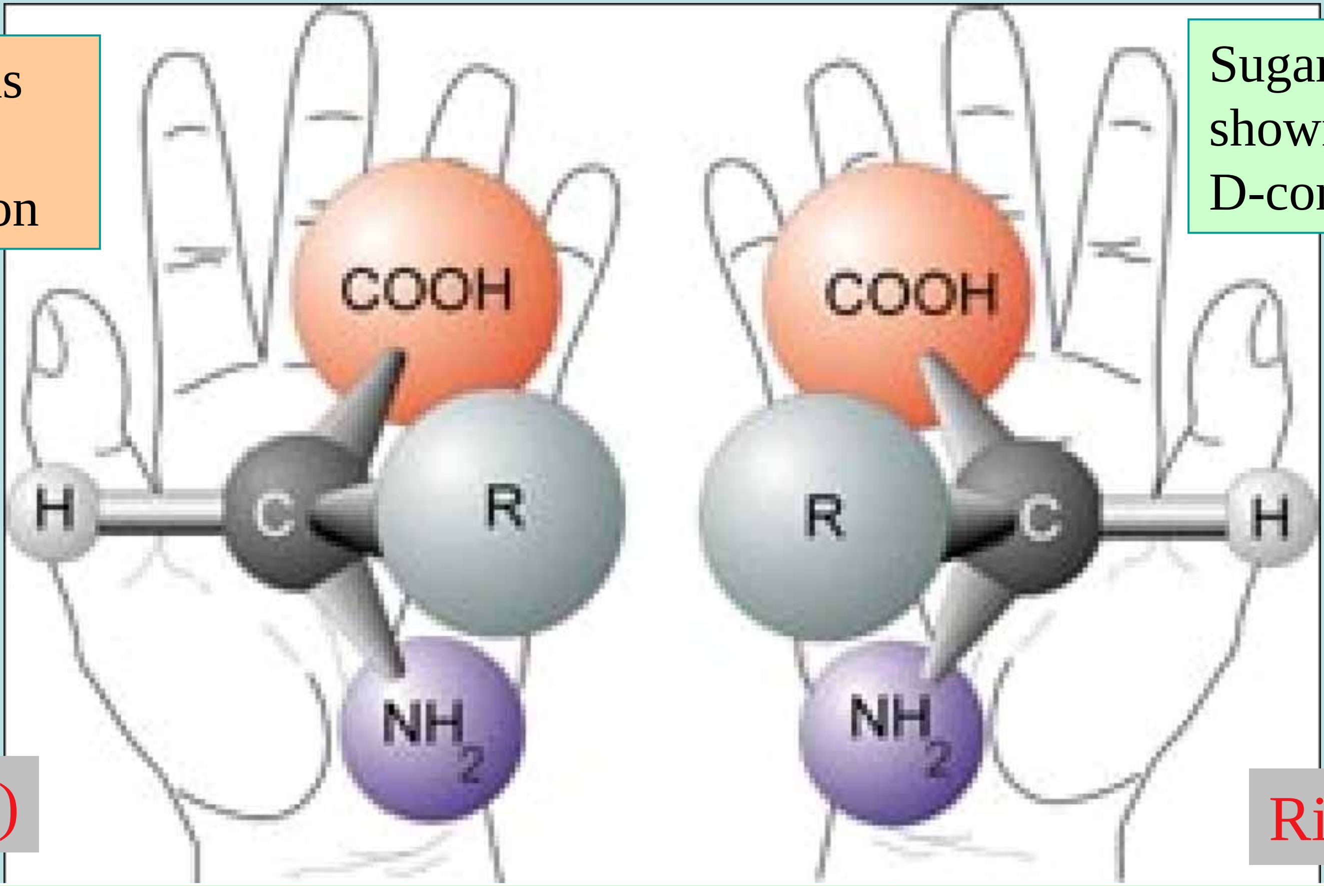
<u>Some promising theories:</u>

•'RNA World'
    -RNA may have preceded proteins
•Hydrothermal Setting / Hyperthermophiles
    -protection from harsh surf. conditions during heavy bombardment
    -metals abundant
    -mineral surfaces for chemical catalysis
•Minerals
    -catalysis, protection, chirality
•Panspermia
    -Mars would have been more hospitable for life 4 Ga
    -Evidence for water and atmospheres conducive to life elsewhere in solar system (e.g., moons of Jupiter and Saturn)

Chirality of Biomolecules

Amino acids have an L-configuration

Sugars (not shown) have a D-configuration



Left (L)

Right (D)

- All amino acids in proteins from living organisms are "left-handed" (L-enantiomers), while sugars are "right-handed". (Chirality was yet another discovery by Louis Pasteur ~150 yr BP!)
- The Miller-Urey experiment, and all similar organic synthetic experiments, produce a 50-50 (racemic) mixture of biomolecules.

http://web99.arc.nasa.gov/~astrochm/aachiral.html

How did chirality of biomolecules arise?

- It may have occurred in the solar nebula during the formation of the solar system.
- Amino acids with a slight L-enantiomeric excess is observed in the Murchison & Murray meteorites
- (Although beware of contamination, since almost all Earthly amino acids begin with L configuration. But note: during natural decomposition processes, protein amino acids revert to a 50-50 (racemic) mixture over time.)
- Crystal faces have surface structures that are mirror-images. Experiments show that crystal faces can select L or D amino acids quite efficiently (40% excess) (Hazen, 2001). While this mechanism can explain the propagation of the L or D configuration, it cannot explain the *origin* of that preference.

A Hyperthermophilic Beginning for Life?

•Given the inhospitable surface environment on Earth < 3.8 Ga, when the intense bombardment likely melted the crust & vaporized the ocean, perhaps repeatedly, it is frequently proposed that life began in a sub-surface environment, perhaps a hydrothermal system where hot water, CO_2 & a variety of metals are readily available.

•The recognition that many of the essential enzymes for life require metals common in hydrothermal settings (Fe, Ni, Mo, Cu, Co, Zn) supports this supposition.

c.f., Nisbet & Sleep (2001) *Nature*, Vol. 409:1083-1091.

rRNA Phylogeny indicates hyper-thermophiles are ancient

Image removed due to copyright restrictions.

A hyperthermophilic Origin?

The rRNA phylogenetic tree has hyperthermophilic organisms clustered near the base of the Archaeal and Bacterial domains

Further evidence for mineral catalysis of simple organic molecules

Image removed due to copyright restrictions.

Hazen (2001) *Sci. Am.*, April 2001: 77-85

$N_2+H_2+Fe_3O_4$(magnetite)
→→**NH_3**

$FeCO_3$ (Siderite) + H_2O →→
hydrocarbons (PAH + alkanes)

- Sealed vessel at 300°C

McCollom (2003) *GCA*, Vol. 67: 311-317.

The ‘RNA World’ Hypothesis

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- Late 1960s: Woese (U. Illinois), Crick (England), Orgel (Salk Inst, San Diego) concurrently proposed RNA may have preceded proteins & catalyzed all reactions for survival & replication of ‘last common ancestor’.
- 1983: Thomas Cech (U. Colorado) & Sidney Altman (Yale) independently discovered *ribozymes*, enzymes made of RNA.
- Previously all biomolecules that catalyzed reactions (enzymes) were thought to be proteins (sequences of amino acids).

Orgel (1994) *Sci. Am.*,
Oct. 1994, 77-83.

Summary of Origin of Life Theories

•Life was probably well-established by ~3.5 Ga
•How it began will seemingly require a lot more work!

Some promising theories:

- ‘RNA World’
  - RNA may have preceded proteins
- Hydrothermal Setting / Hyperthermophiles
  - protection from harsh surf. conditions during heavy bombardment
  - metals abundant
  - mineral surfaces for chemical catalysis
- Minerals
  - catalysis, protection, chirality
- Panspermia
  - Mars would have been more hospitable for life 4 Ga
  - Evidence for water and atmospheres conducive to life elsewhere in solar system (e.g., moons of Jupiter and Saturn)

The Rise of Atmospheric Oxygen

Composition of Earth's Early Atmosphere

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Allegre & Schneider (1994)

Oxidizing the earth's surface: I

- Chemical definitions:

oxidize: remove electrons from an atom or molecule

e.g. metallic $Fe^0 \rightarrow Fe^{3+} + 3e^-$

reduce: add electrons to an atom or molecule

e.g. $Cl^0 + e^- \rightarrow Cl^-$

- Photosynthesis takes two oxidized compounds - carbon dioxide and water - and reduces carbon and oxidizes oxygen:

$C^{+IV}O^{-II}_2 + H_2O \rightarrow C^0H_2O$ (schematic organic matter) $+ O^0_2$

- But if the organic matter is allowed to be degraded by heterotrophic microorganisms, this reaction is reversed:

CH_2O (organic matter) $+ O_2 \rightarrow CO_2 + H_2O$

- Hence, photosynthesis by itself will not oxidize the earth surface - it can do so only if the organic matter is removed from contact with the oxygen (carbon burial).

Oxidizing the earth's surface: II

- Another way to oxidize the earth is to lose hydrogen from the stratosphere:

  ($H_2O + h\nu \rightarrow H + OH$)

  $CH_4 + h\nu \rightarrow 4H + C$

- Hydrogen (and He) gas in the stratosphere has a velocity distribution that overlaps the escape velocity.

- Hence hydrogen loss from the atmosphere to outer space also can oxidize the earth.

The Rise of Atmospheric Oxygen: An Overview

- Photosynthesis by cyanobacteria began > 3.5-2.7 Ga

$$CO_2 + H_2O \text{ ---> } CH_2O + \mathbf{O_2}$$

- No evidence for free O_2 before ~2.4 Ga
- Reduced gases in atmosphere & reduced crust consume O_2 produced during 3.5-2.4 Ga
- Hydrogen escape irreversibly oxidizes atmosphere
- Mantle dynamics & redox evolution reduce O_2 sink over time
- Geologic & geochemical evidence for O_2 :
    - Oxidized Fe & Mn mineral deposits
    - Detrital uraninite & pyrite
    - Paleosols
    - Redbeds
    - Sulfur isotopes
    - Eukaryotes

•**Conclusion: Rapid rise of free O_2 2.4-2.2 Ga**

Geologic Evidence for Atmospheric Oxygen

Detrital Uraninite & Pyrite

Images removed due to copyright restrictions.

- Uraninite: UO_2
- Reduced U(IV)
- Highly radioactive
- Important ore of uranium & radium.

Images removed due to copyright restrictions.

- Pyrite: FeS_2
- Reduced Fe(II)

- \> 2.2 Ga, these ***reduced*** minerals existed as ***detrital*** minerals in Archean sedimentary rocks.
- In other words, they survived weathering process intact & were transported as solid particles. (i.e., not dissolved).
- Preservation of UO_2 and FeS_2 requires ***anoxia***. They are unstable in the presence of free O_2, which oxidizes & dissolves them.

Archean and Proterozoic chemistry timeline

Image removed due to copyright restrictions.
Citation: Canfield (2005) Ann. Rev. Earth Planet. Sci. 33:1-38.

Banded Iron Formations (BIFs)

BHP Iron Ore Mine at Newman, W. Australia

Image removed due to copyright restrictions.

- Hematite ($Fe^{III}_2O_3$) & magnetite ($Fe^{III}_2Fe^{II}O_4$) :

  Fe^{2+} --> Fe^{3+}

  $\mathbf{O_2}$ --> H_2O

- Requires O_2 to oxidize Fe(II)

- Most BIFs > 1.9 Ga; indicates free O_2 existed by then
- Laminated sedimentary rocks
- Alternating layers of magnetite / hematite & chert (SiO_2)

Image removed due to copyright restrictions.

How did BIFs form?

Image removed due to
copyright restrictions.

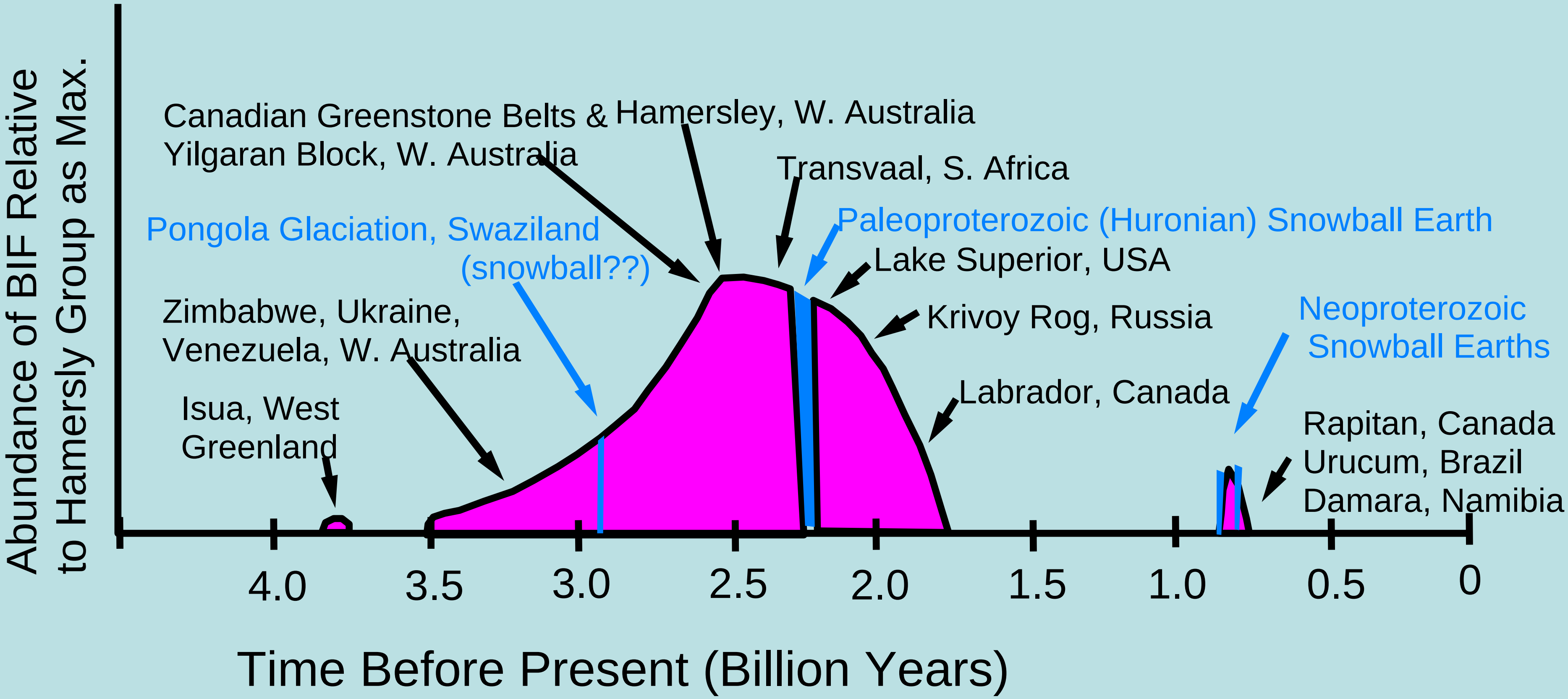
- **A big open question in geology!**

One favored scenario:

- Anoxic deep ocean containing dissolved Fe(II)
- Seasonal upwelling brings Fe(II) to the surface where it is oxidized to Fe(III) by O_2 produced by cyanobacteria/algae.
- Insoluble Fe(III) precipitates out of seawater
- SiO_2 precipitated by algae during non-upwelling season

Precambrian Banded Iron Formations (BIFs)

(Adapted from Klein & Beukes, 1992)



Courtesy of Joe Kirschvink, CalTech. Used with permission.

Abundance of Banded Iron Formations

Image removed due to copyright restrictions.
Citation: Canfield (2005) Ann. Rev. Earth Planet. Sci. 33:1-38.

Courtesy of Joe Kirschvink, CalTech.
Used with permission.

Kalahari Manganese Member, Hotazel Fm., Manatwan Mine, South Africa

$$\mathrm{Mn}^{+2} \rightarrow \mathrm{Mn}^{+4} \text{ insoluble}$$

$$\mathrm{O}_2 \rightarrow \mathrm{H}_2\mathrm{O}$$

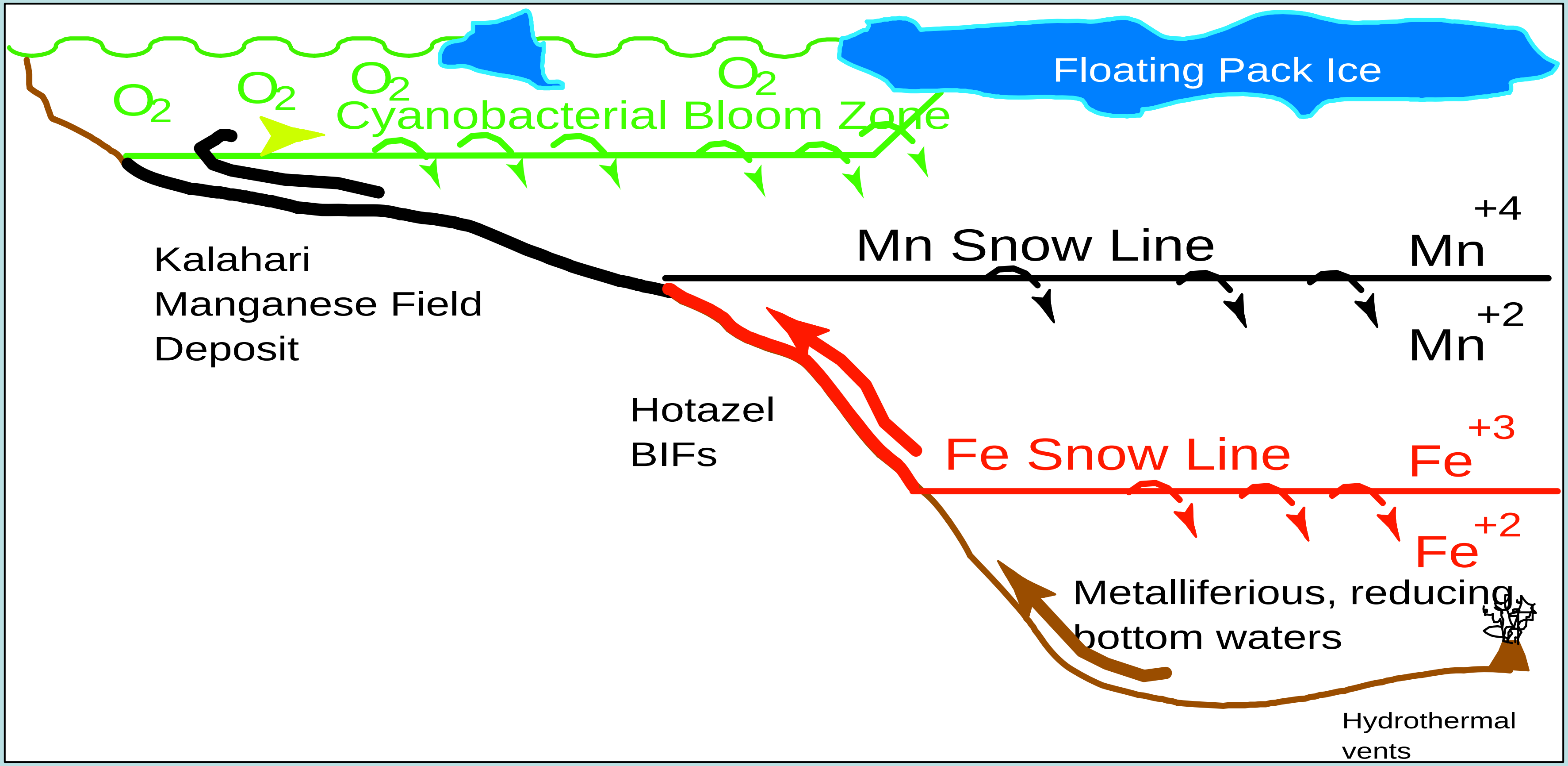
Caryopilite

$(\mathrm{Mn,Mg})_3\mathrm{Si}_2\mathrm{O}_5(\mathrm{OH})$

http://www.mindat.org/min-913.html

At 2400 Ma, oxidized Mn minerals are the oldest constraint on free O_2 in earth history.

Likely Mechanism of Mn & Fe Deposit Formation



Courtesy of Joe Kirschvink, CalTech. Used with permission.

- Cyanobacterial Bloom Yields an Electrochemical Stratification in the Oceans, Depositing Manganese in Upwelling Areas on Continental Shelves.

Separating oxic and reduced zones in the ocean:

- In the surface ocean:

  $CO_2 + H_2O \text{ -> } CH_2O + O_2$

- If organic matter sinks out of the surface ocean, it then can serve as fuel for microbiological transformations such as:

$CH_2O + O_2 \text{ -> } CO_2 + H_2O$ (until O_2 runs out…)

$2CH_2O + MnO_2 \text{ -> } Mn^{2+} + 2HCO_3^- + H_2O$ (until MnO_2 runs out)

Thesr reactions result in chemical stratification in the ocean…

- If deep water (containing soluble Mn^{2+}) upwells to the surface, oxygen can re-oxidize manganese and precipitate solid MnO_2 :

$Mn^{2+} + O_2 \text{ -> } MnO_2$

Red Beds

- Hematite: $Fe^{III}_2O_3$

Fe^{2+} --> Fe^{3+}

O_2 --> H_2O

- Requires free O_2 to oxidize Fe(II)

Courtesy of Kansas Geological Survey. Used with permission.

Courtesy of Kansas Geological Survey. Used with permission.

- Oldest red beds ~ 2.2 Ga
- Sedimentary rock
- Reddish, sandy sediment deposited by rivers and/or windblown dust.

Paleosols

“Ancient Soils”

- > 2.2 Ga: Fe-deficient
- Fe(II) removed by groundwater

Courtesy of Bruce Railsback. Used with permission.

Courtesy of Bruce Railsback. Used with permission.

H. Holland (Harvard)

>2.2 Ga: $O_2 < 0.01$ PAL

<1.9 Ga: $O_2 > 0.15$ PAL

http://www.gly.uga.edu/railsback/FieldImages.html

Biotic Evidence for Atmospheric Oxygen

Archean and Proterozoic chemistry timeline

Image removed due to copyright restrictions.
Citation: Canfield (2005) Ann. Rev. Earth Planet. Sci. 33:1-38.

Rise of Eukaryotes

Image removed due to copyright restrictions.
Citation: Kump et al. (1999).

- Eukaryotes require free O_2 in excess of 1% PAL for respiration
- Need protection from strong UV (e.g., ozone layer, which requires free oxygen in the atmosphere)

Multicellular Algal Fossils--2.1 Ga

Image removed due to copyright restrictions.

Grypania: genus of coiled multicellular eukaryotic algae.
From 2.1 Ga rocks in Michigan.

Stanley (1999)

Archean Molecular Fossils from 2.7 Ga Roy Hill Shale (W. Australia)

Image removed due to copyright restrictions.

J.J. Brocks, G.A. Logan, R. Buick & R.E. Summons *Science*, 285, 1033, 1999

Burgess Shale Fauna

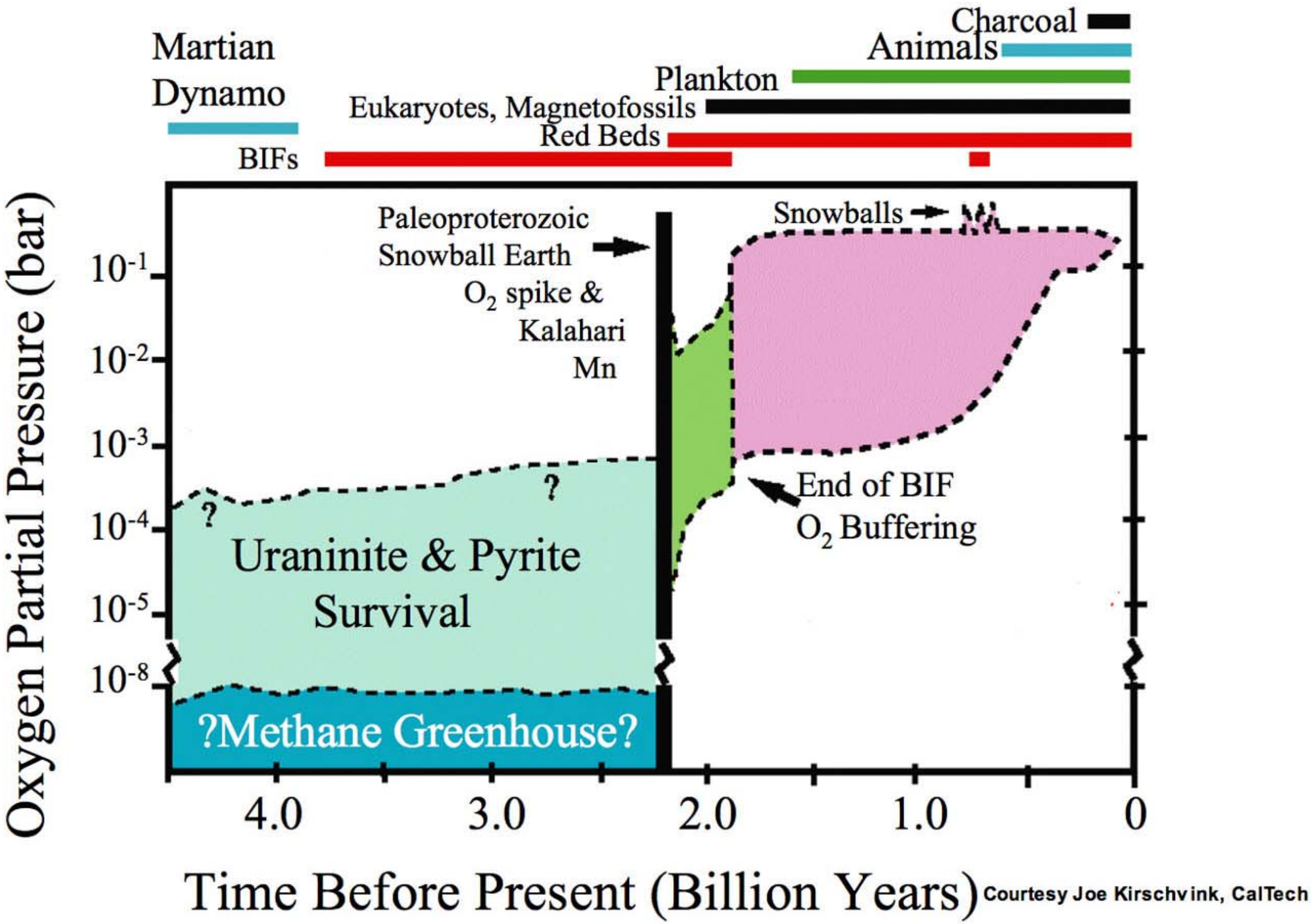
- 545 to 525 Ma :
  extraordinary evolutionary burst

Image removed due to copyright restrictions.

Evolution of atmospheric oxygen

Image removed due to copyright restrictions.
Citation: Canfield (2005) Ann. Rev. Earth Planet. Sci. 33:1-38.

History of Atmospheric Oxygen on Earth



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History of Atmospheric Oxygen

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Kasting (1993)

Evolution of $\Delta^{33}S$ in sulfur-bearing rocks, 0-4 billion years ago

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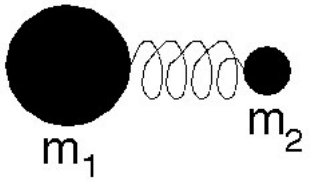
Citation: Canfield (2005) Ann. Rev. Earth Planet. Sci. 33:1-38.

Two geochemical tools:

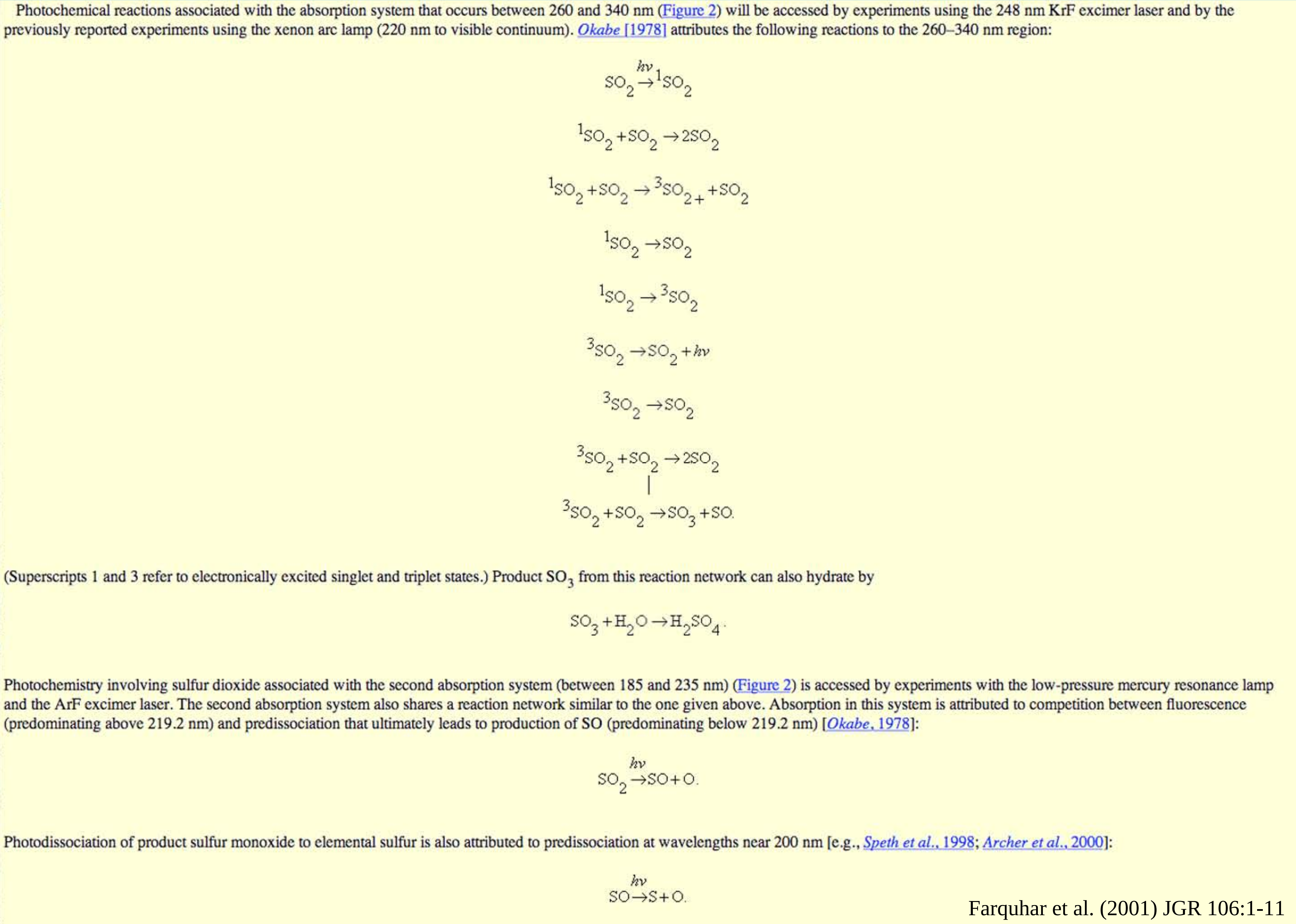
1. Stable isotope ratios:



$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1\right] \times 1000$$

2. Triple stable isotope ratios: $\Delta^{33}S = \delta^{33}S - 0.515\ \delta^{34}S$

detects mass-independent isotope fractionation



Photochemical reactions associated with the absorption system that occurs between 260 and 340 nm (Figure 2) will be accessed by experiments using the 248 nm KrF excimer laser and by the previously reported experiments using the xenon arc lamp (220 nm to visible continuum). *Okabe* [1978] attributes the following reactions to the 260–340 nm region:

$$SO_2 \xrightarrow{h\nu} {}^{1}SO_2$$

$$^{1}SO_2 + SO_2 \rightarrow 2SO_2$$

$$^{1}SO_2 + SO_2 \rightarrow {}^{3}SO_{2+} + SO_2$$

$$^{1}SO_2 \rightarrow SO_2$$

$$^{1}SO_2 \rightarrow {}^{3}SO_2$$

$$^{3}SO_2 \rightarrow SO_2 + h\nu$$

$$^{3}SO_2 \rightarrow SO_2$$

$$\begin{gathered} ^{3}SO_2 + SO_2 \rightarrow 2SO_2 \\ | \\ ^{3}SO_2 + SO_2 \rightarrow SO_3 + SO. \end{gathered}$$

(Superscripts 1 and 3 refer to electronically excited singlet and triplet states.) Product SO_3 from this reaction network can also hydrate by

$$SO_3 + H_2O \rightarrow H_2SO_4.$$

Photochemistry involving sulfur dioxide associated with the second absorption system (between 185 and 235 nm) (Figure 2) is accessed by experiments with the low-pressure mercury resonance lamp and the ArF excimer laser. The second absorption system also shares a reaction network similar to the one given above. Absorption in this system is attributed to competition between fluorescence (predominating above 219.2 nm) and predissociation that ultimately leads to production of SO (predominating below 219.2 nm) [*Okabe*, 1978]:

$$SO_2 \xrightarrow{h\nu} SO + O.$$

Photodissociation of product sulfur monoxide to elemental sulfur is also attributed to predissociation at wavelengths near 200 nm [e.g., *Speth et al.*, 1998; *Archer et al.*, 2000]:

$$SO \xrightarrow{h\nu} S + O.$$

Farquhar et al. (2001) JGR 106:1-11

Molybdenum isotope evidence for mid-Proterozoic ocean anoxia

Image removed due to copyright restrictions.

Arnold, Anbar et al. (2004) Science Vol. 304, Page 88.

If oxygen-producing photosynthesis was occurring by 3.5-2.7 Ga, why doesn’t free O_2 appear until 2.3 Ga, a 1200-400 Myr delay?

What caused the atmosphere to become oxygenated 2.4-2.2 Ga?

Sources

- Photosynthesis
- Hydrogen escape

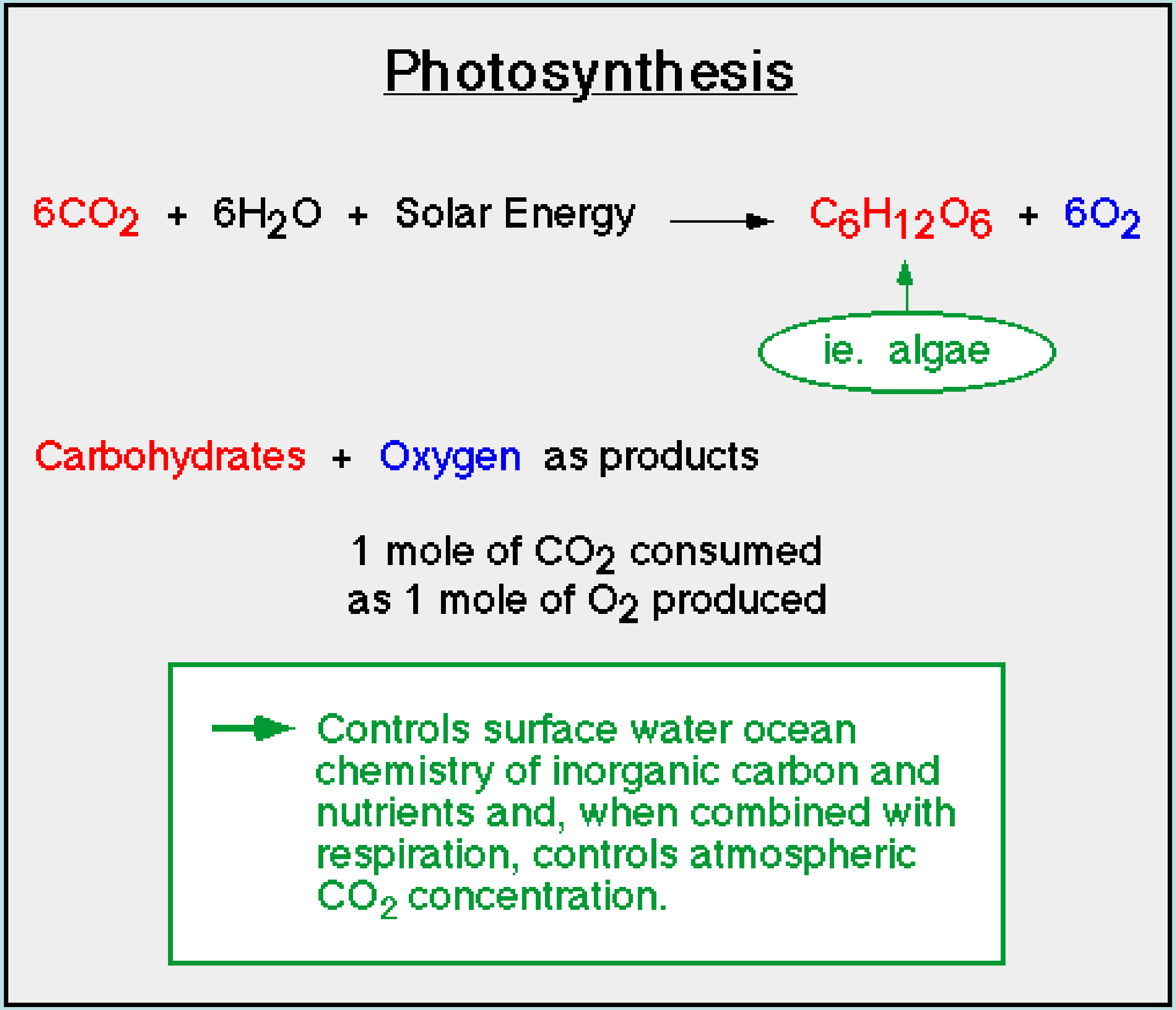
vs.

Sinks

- Respiration
- Reduced minerals in rocks
- Reduced volcanic gases
- Reduced hydrothermal vent fluids

Sources of Oxygen to the Atmosphere

General Photosynthetic Equation



Photosynthesis

$$6CO_2 + 6H_2O + \text{Solar Energy} \longrightarrow C_6H_{12}O_6 + 6O_2$$

ie. algae

Carbohydrates + Oxygen as products

1 mole of CO_2 consumed
as 1 mole of O_2 produced

Controls surface water ocean chemistry of inorganic carbon and nutrients and, when combined with respiration, controls atmospheric CO_2 concentration.

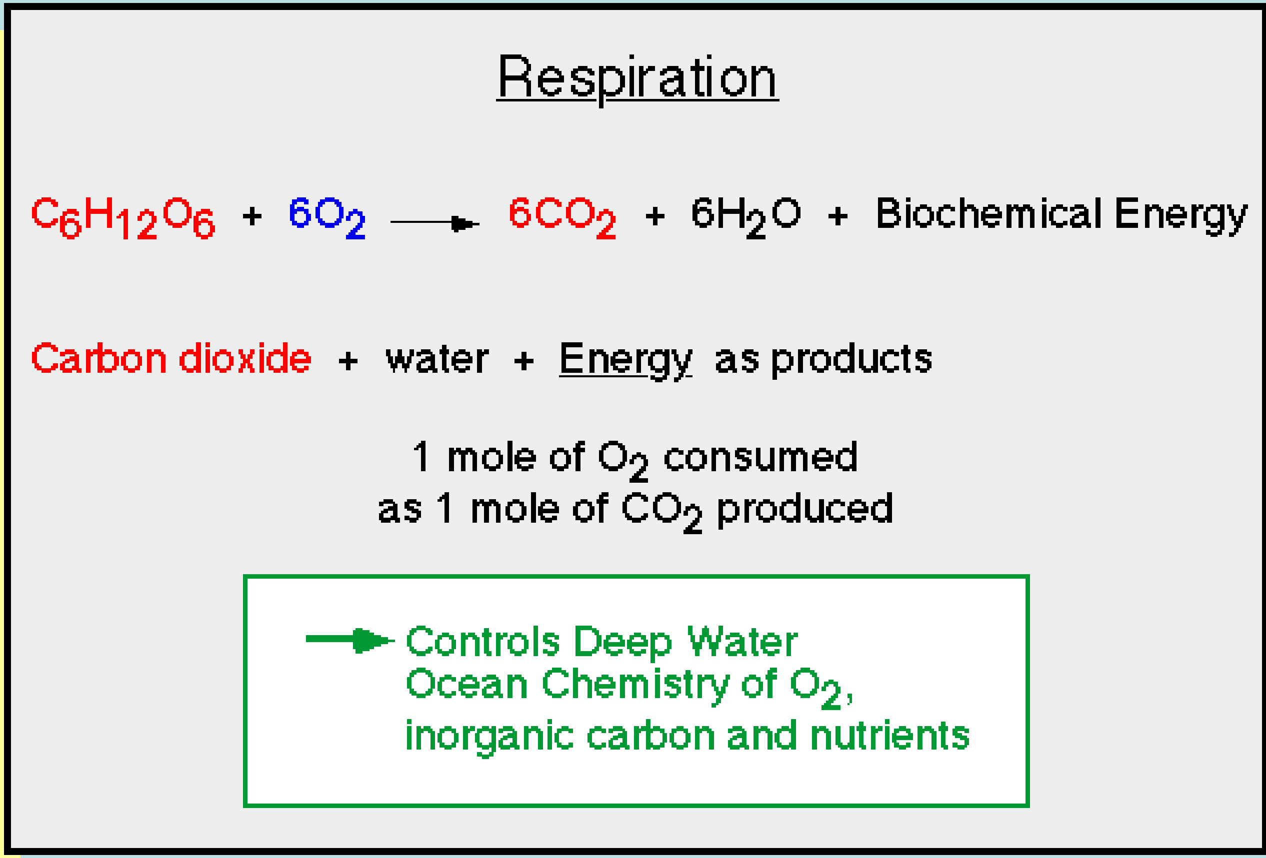
~3.5 Byr of Photosynthesis Based on Carbon Isotope Fractionation

Image removed due to copyright restrictions.

Sinks for Atmospheric Oxygen

Respiration

- Cellular respiration is carried out by all eukaryotes & converts carbon compounds & O_2 into CO_2 & ATP.
- Acting as the counter point to photosynthesis, respiration keeps both autotrophs and heterotrophs alive.
- The trick is to extract high-energy electrons from chemical bonds and then use these electrons to form the high-energy bonds in ATP.
- Bacteria can also break down organic molecules in the absence of O_2 gas (anaerobic respiration).



Respiration

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$ + Biochemical Energy

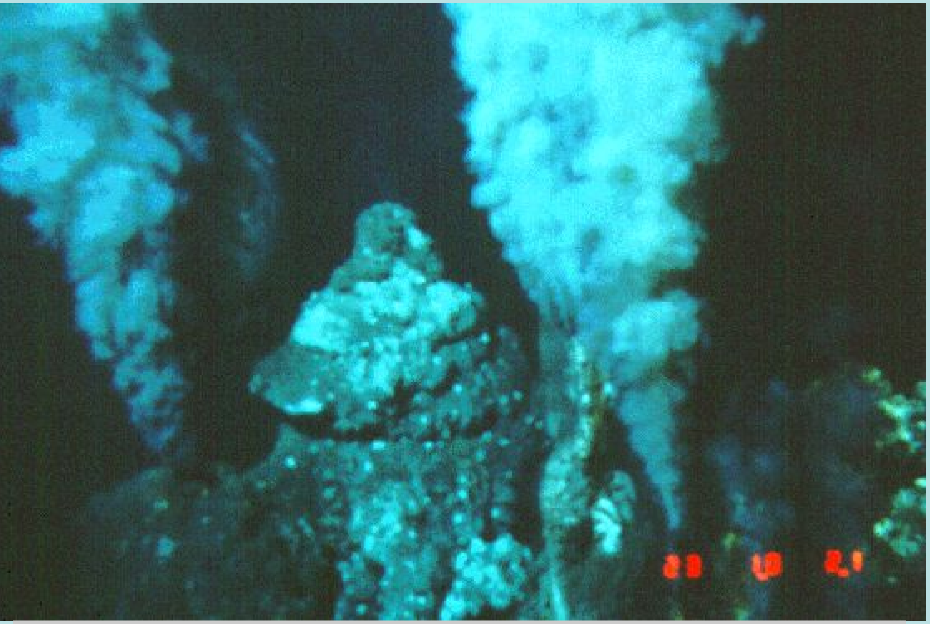
Carbon dioxide + water + Energy as products

1 mole of O_2 consumed
as 1 mole of CO_2 produced

→ Controls Deep Water
Ocean Chemistry of O_2,
inorganic carbon and nutrients

Other Archean O_2 Sinks #1

- Volcanic Outgassing
  H_2, CO, SO_2
- Hydrothermal Vent Fluids
  Fe^{2+}, S^{2-}



Monolith Chimney, Juan de Fuca Ridge

lhttp://www.pmel.noaa.gov/vents/

Mt. Pinatubo, Philippines

http://eos.higp.hawaii.edu/index.html

Oxidative weathering of reduced minerals in rocks (i.e., Fe^{2+}, S^{2-}, CH_2O) removes 75% of O_2 generated by C_{org} burial today (the other ~ 25% sink is volcanic outgassing (~14%) & hydrothermal vents (~10%)).

-Holland (1978) *The Chemistry of the Atmosphere and Oceans*. John Wiley, NY, 351 pp.
-Holland (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, NJ, 582 pp.

Other Archean O_2 Sinks #2

Archean mantle dynamics & redox evolution-1

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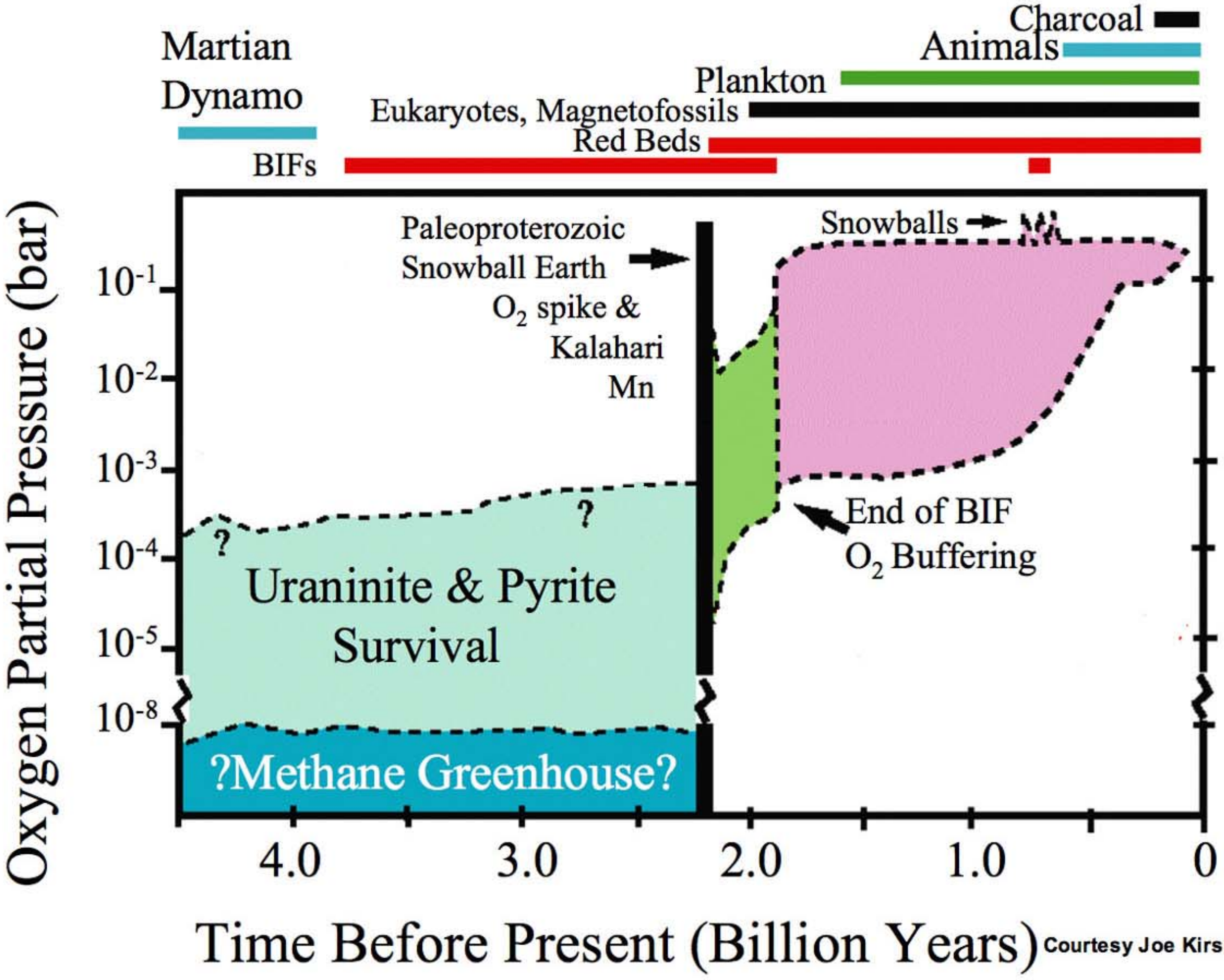
Citation: See Figures 1& 2. Kump et al. (2001)
G3, Vol. 2: 2000GC000114

History of Atmospheric Oxygen on Earth



Courtesy Joe Kirschvink, CalTech

Courtesy of Joe Kirschvink, CalTech. Used with permission.

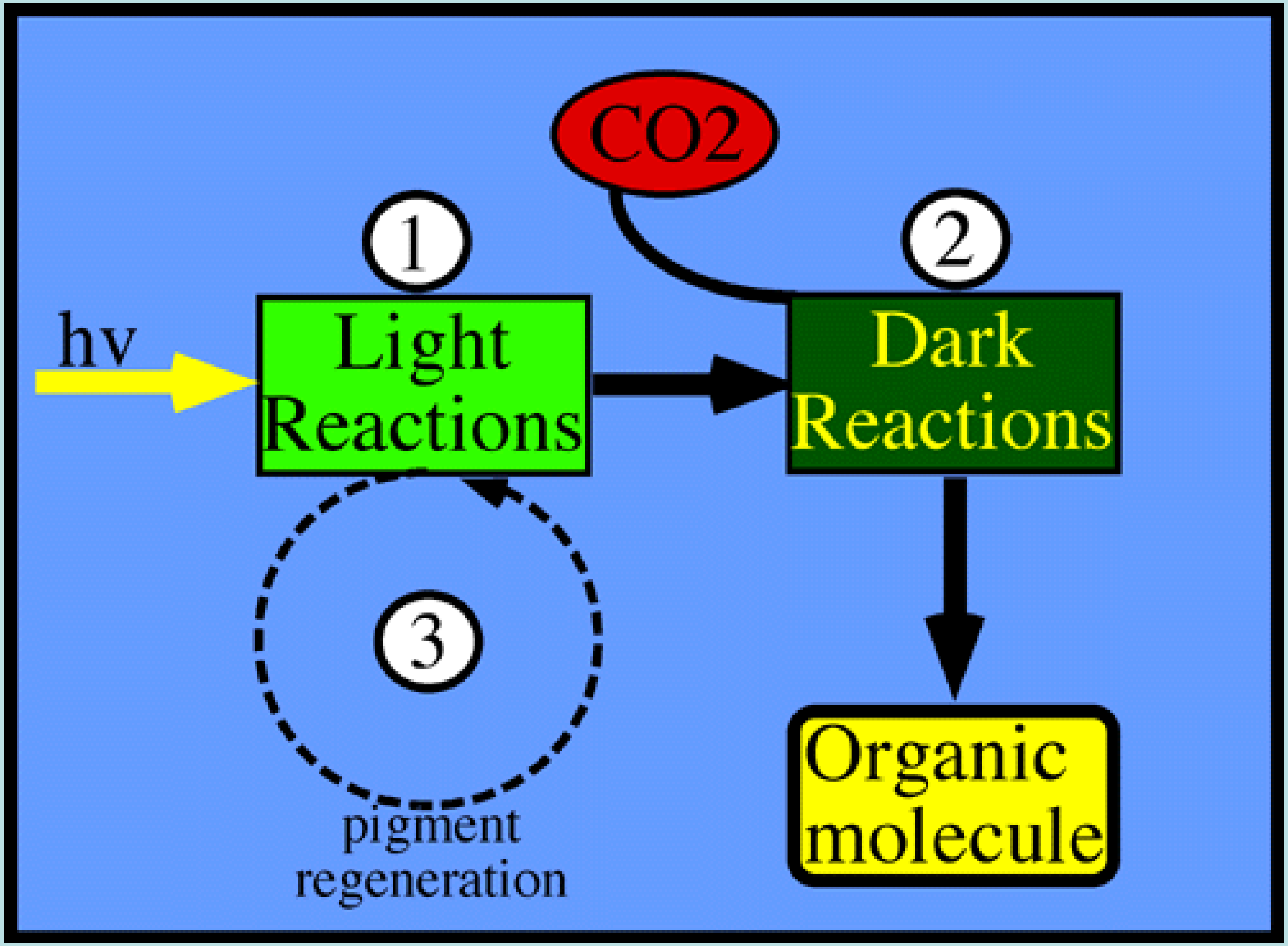
Atmospheric oxygen and the ozone layer

- No oxygen in atmosphere = no ozone layer!
- No ozone layer => intense UV bombardment
- Most life would not be adapted to withstand this UV unless it had some sort of shielding - depth of water, etc.

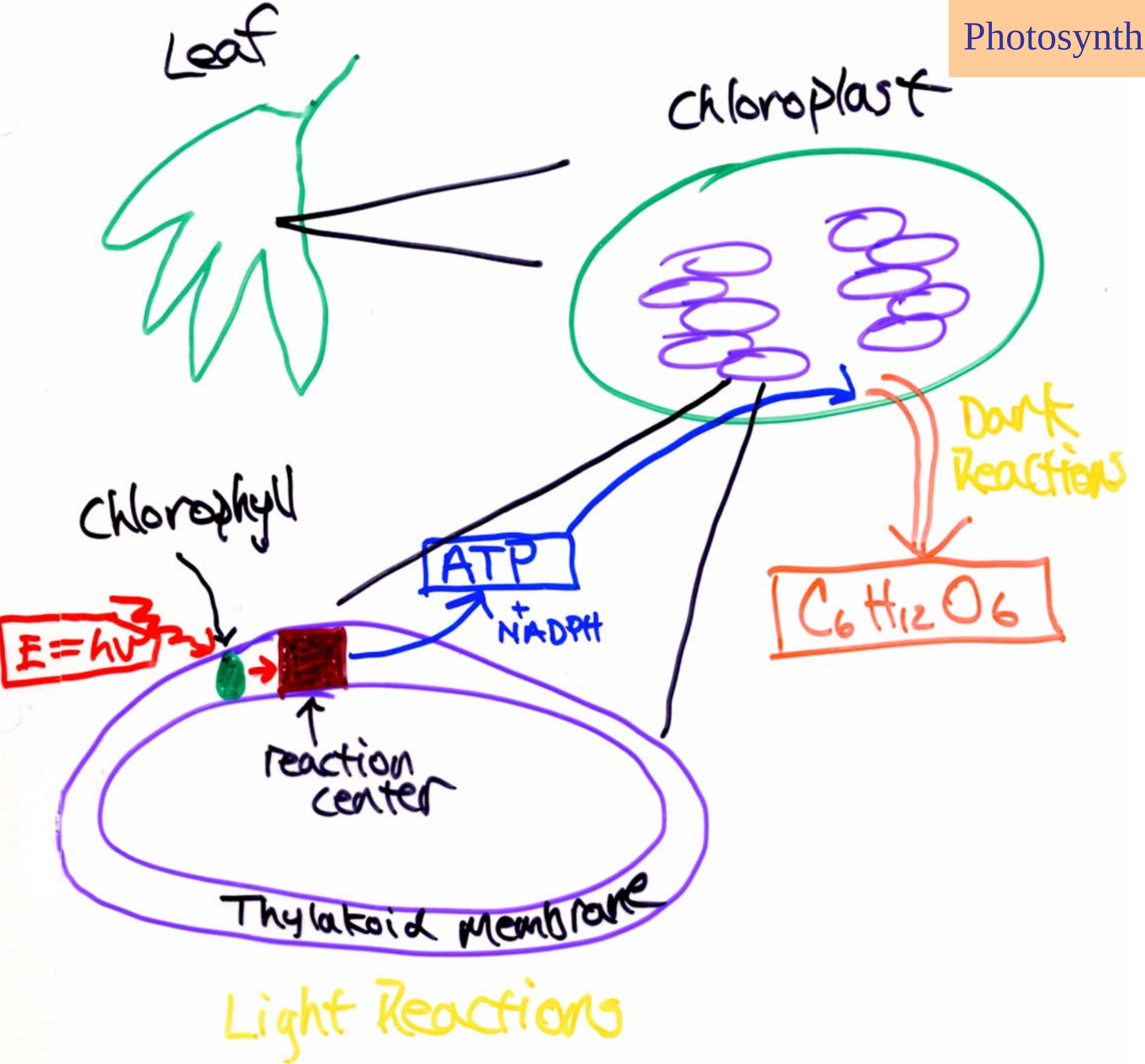
Co-evolution of life and the earth's surface

- The first organisms evolved when oxygen was scarce and reductants were abundant. Micro-organisms made use of the chemical properties that were available at the time. For example, Fe^{2+} was abundant in the ocean, so life did not hesitate to make use of its chemical properties.
- As reductants were exhausted and the chemical balance of the ocean evolved, new organisms evolved from the pathways initiated by early life. Some enzymes etc. were so essential that they were retained despite less favorable conditions. Organisms that were adapted to highly reducing conditions took refuge in isolated environments. New organisms evolved to survive in the less reducing environments.

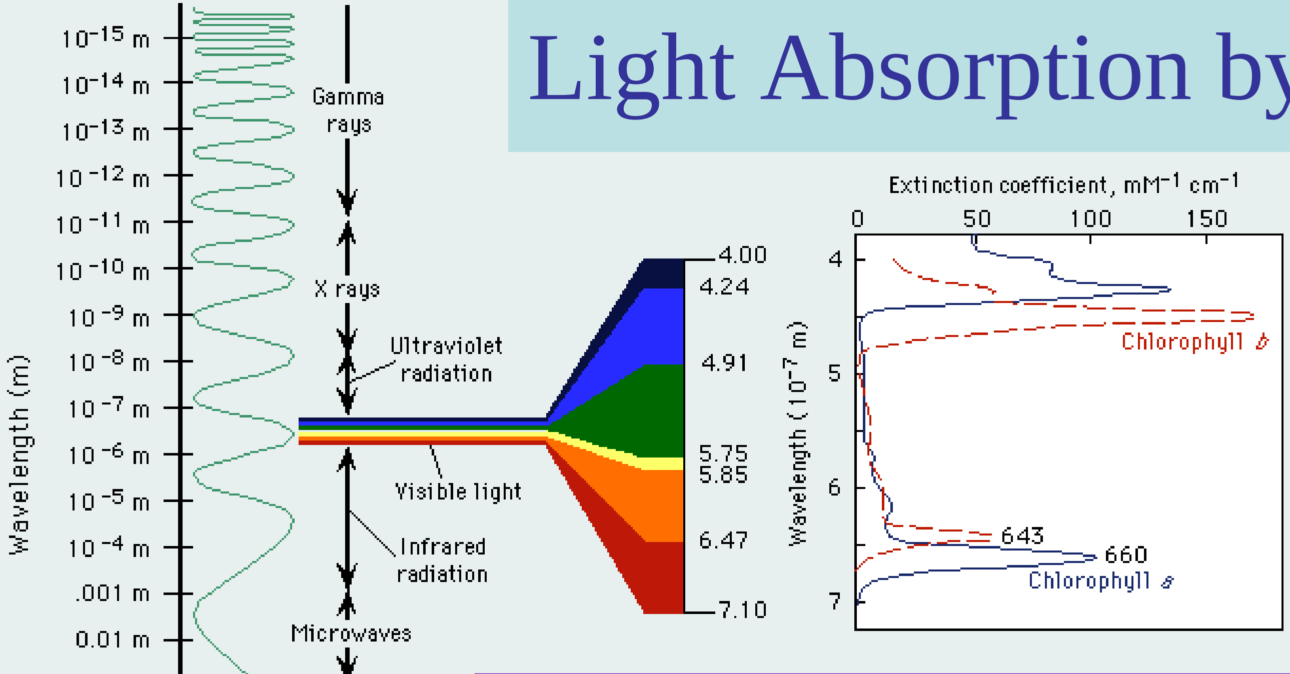
3 Steps of Photosynthesis

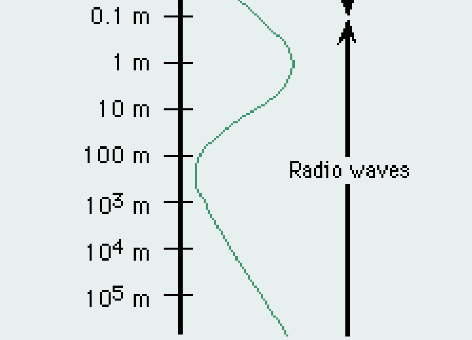


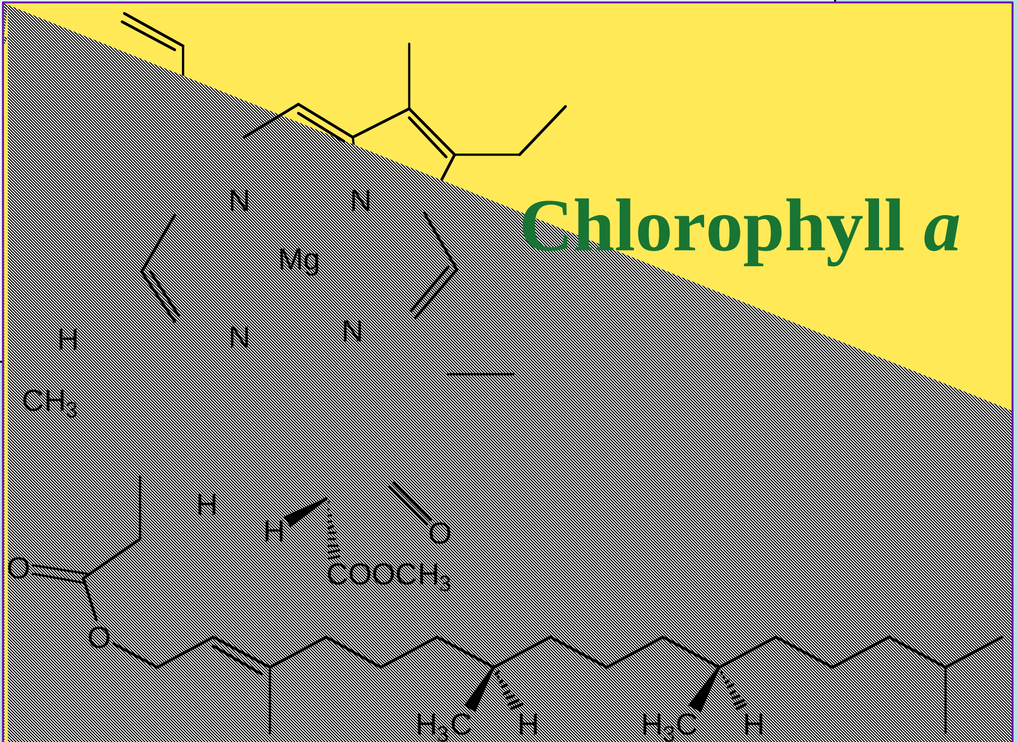
Photosynthesis Schematic



Light Absorption by Chlorophyll







Chlorophyll *a*