Photosynthesis and the Rise of Atmospheric Oxygen

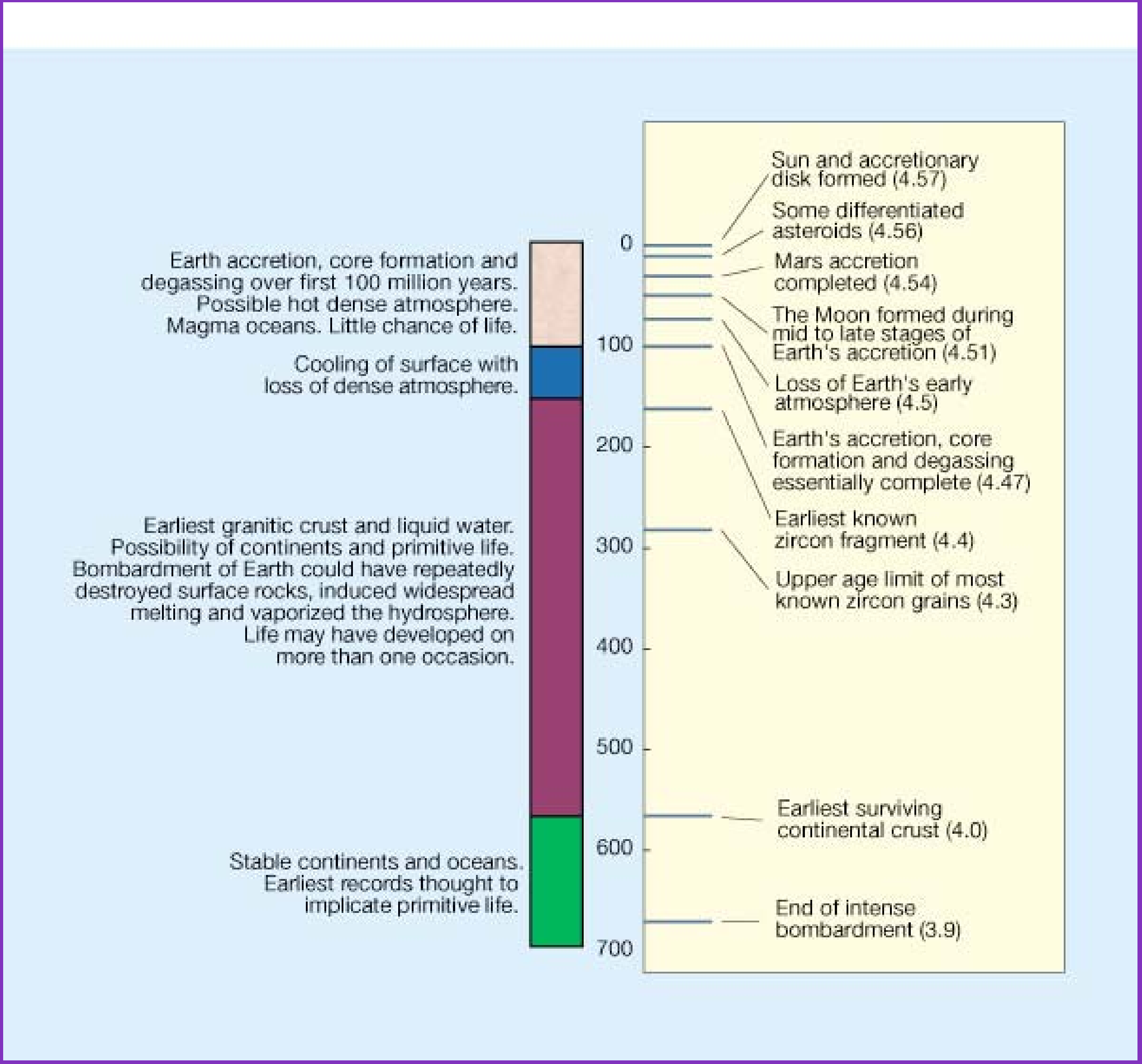
Assigned Reading

- Stanley: pp. 257-269, 323-325
- Catling D. C., Zahnle K. J., and McKay C. P. (2001) Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. *Science* **293**, 839-843.
- Holland, H.D. (1999) When did the Earth's atmosphere become oxic? A Reply. *Geochem. News*, **100**(July), 20-22.
- Kasting, J.F. (1993) Earth's Early Atmosphere. *Science*, **259**, 920-926.
- Kasting, J.F. (2001) The rise of atmospheric oxygen. *Science*, **293**, 819-820.

Suggested Reading:

- Kasting, J.F., Eggler, D.H. & Raeburn, S.P. (1993) Mantle redox evolution and the oxidation state of the Archean atmosphere. *J. Geol.*, **101**, 245-257.
- Kump, L.R. & Holland, H.D. (1992) Iron in Precambrian rocks: Implications for the global oxygen budget of the ancient Earth. *Geochim. Cosmochim. Acta*, **56**, 3217-3223.

Early Earth History



The Rise of Atmospheric Oxygen

- Photosynthesis by cyanobacteria began > 3.5-2.7 Ga

  $CO_2 + H_2O \text{ ---> } CH_2O +$ **O_2**
- No evidence for free O_2 before ~2.4 Ga
- Reduced gases in atmosphere & reduced crust consume O_2 produced during 1200-400 Myr
- 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

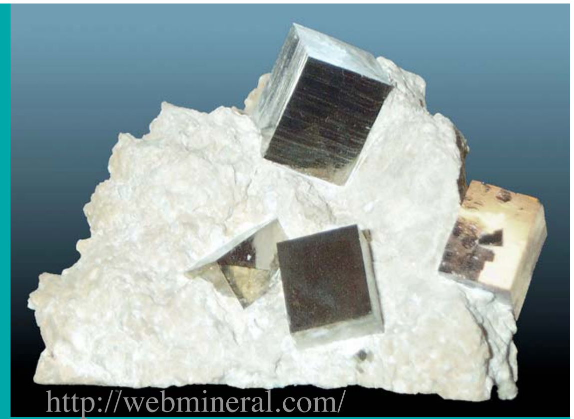
  Redbeds

  Sulfur isotopes

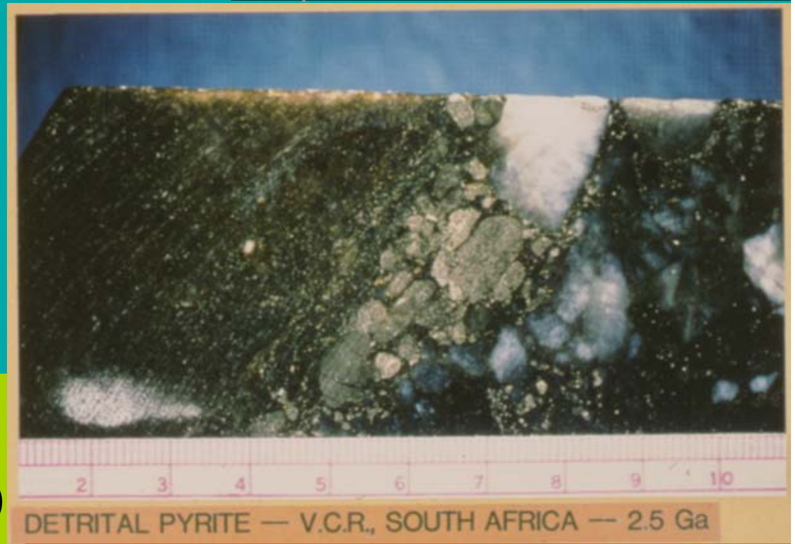
  Eukaryotes
- **Conclusion: Rapid rise of free O_2 2.4-2.2 Ga**

Geologic Evidence for Rise of Atmospheric Oxygen

Detrital Uraninite & Pyrite



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



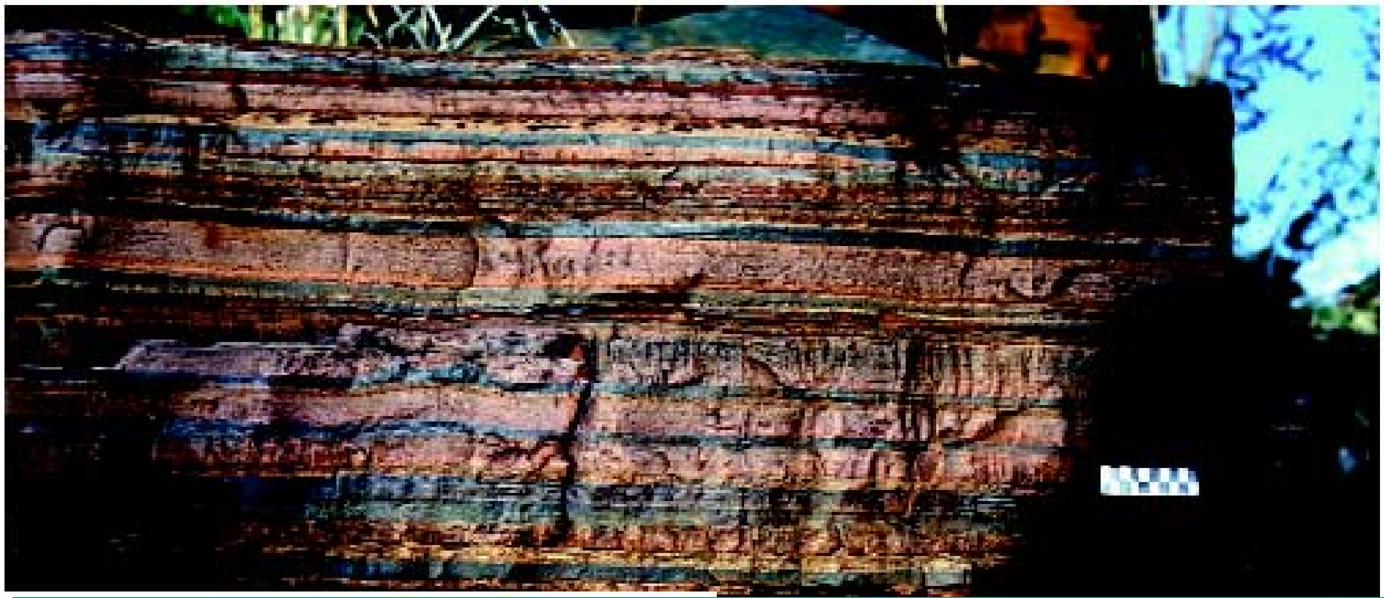
- Pyrite: FeS_2
- Reduced Fe(II)

- > 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.

Banded Iron Formations (BIFs)

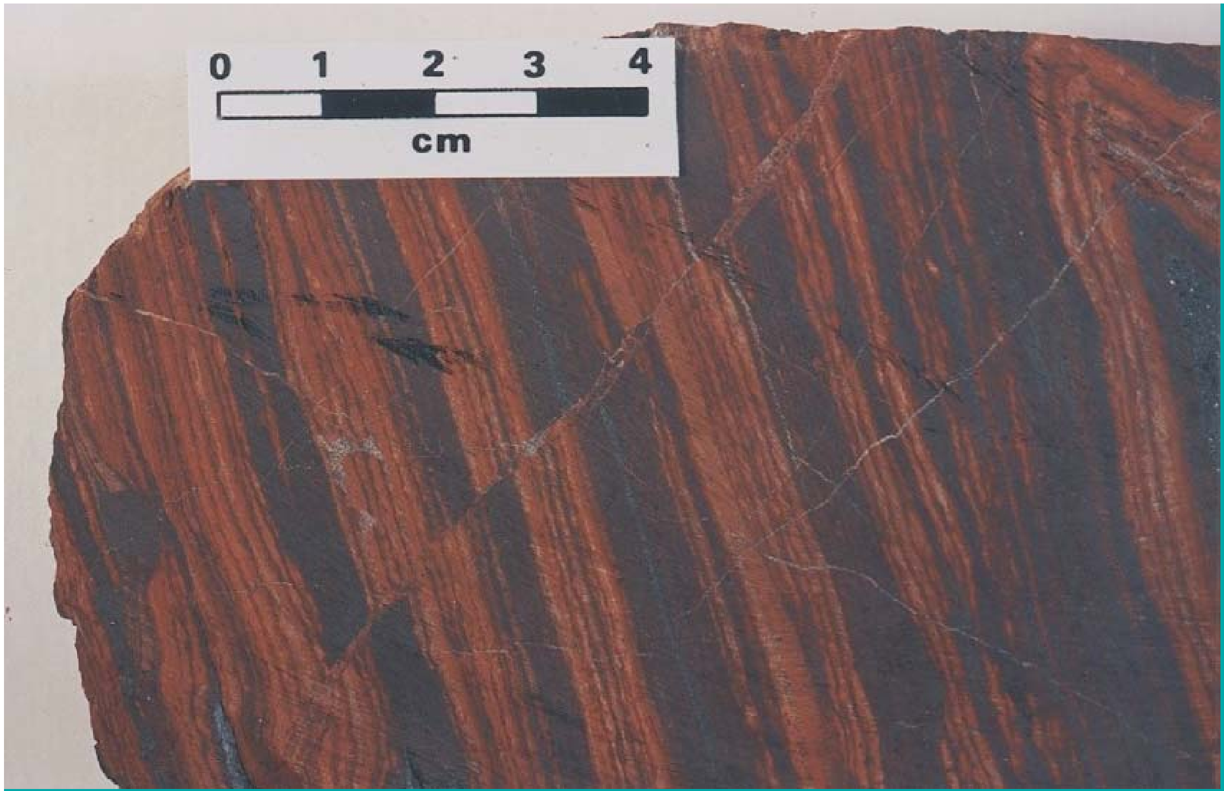
- Hematite (Fe_2O_3) & magnetite (Fe_3O_4) :
  - Fe^{2+} --> Fe^{3+}
  - O_2 --> H_2O
- Requires free O_2 to oxidize Fe(II)

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



A Typical Banded Iron Stone


Black
Chert
vein



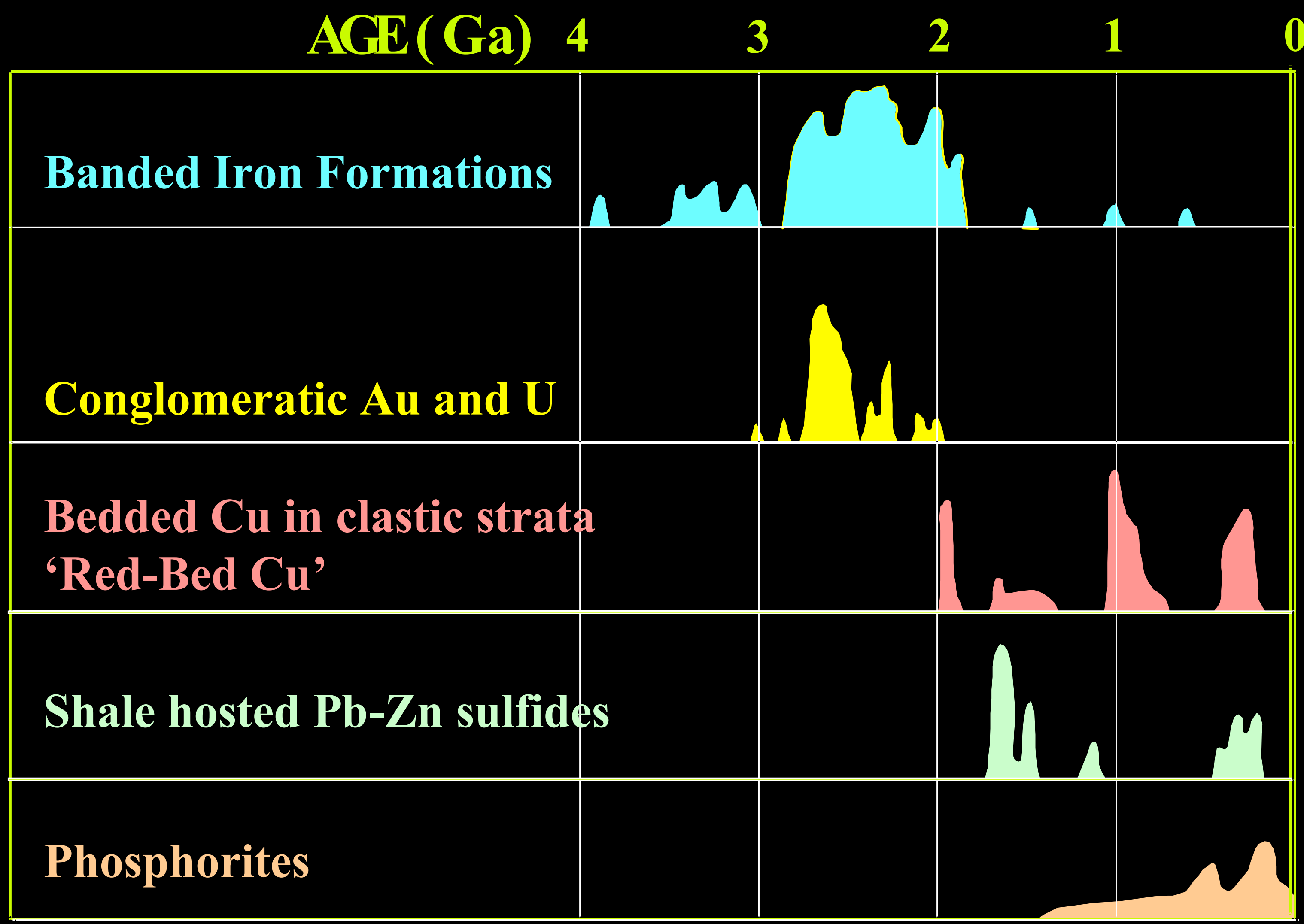
How did BIFs form?

•A big open question in geology!

<u>One favored scenario</u>:

- 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

Mineralization Through Geologic Time



(adapted from Lambert & Groves, 1981)

Sulfur Isotopic Evidence for O_2-#1

See the figure by J. Farquhar, H. Bao, M. Thiemens. *Science* **289 (20000**: 756-758.

- Earth's S cycle > 2.3 Ga controlled by *mass-independent fractionation* of S
- Gas-phase photochemical reactions--e.g., photolysis of SO_2 in atmosphere
- Requires very low O_2 in atmosphere

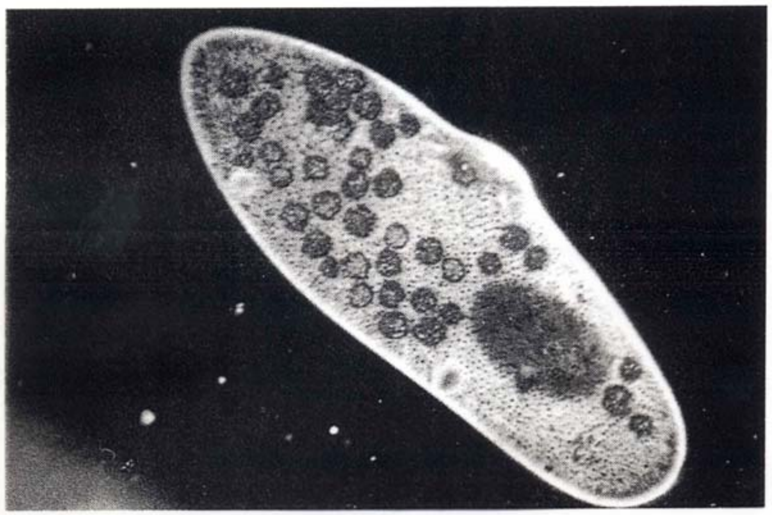
Biotic Evidence for Atmospheric Oxygen

Rise of Eukaryotes

- Eukaryotes require free O_2 in excess of 1% PAL for respiration

Prokaryote

(a)



(b)

Eukaryote

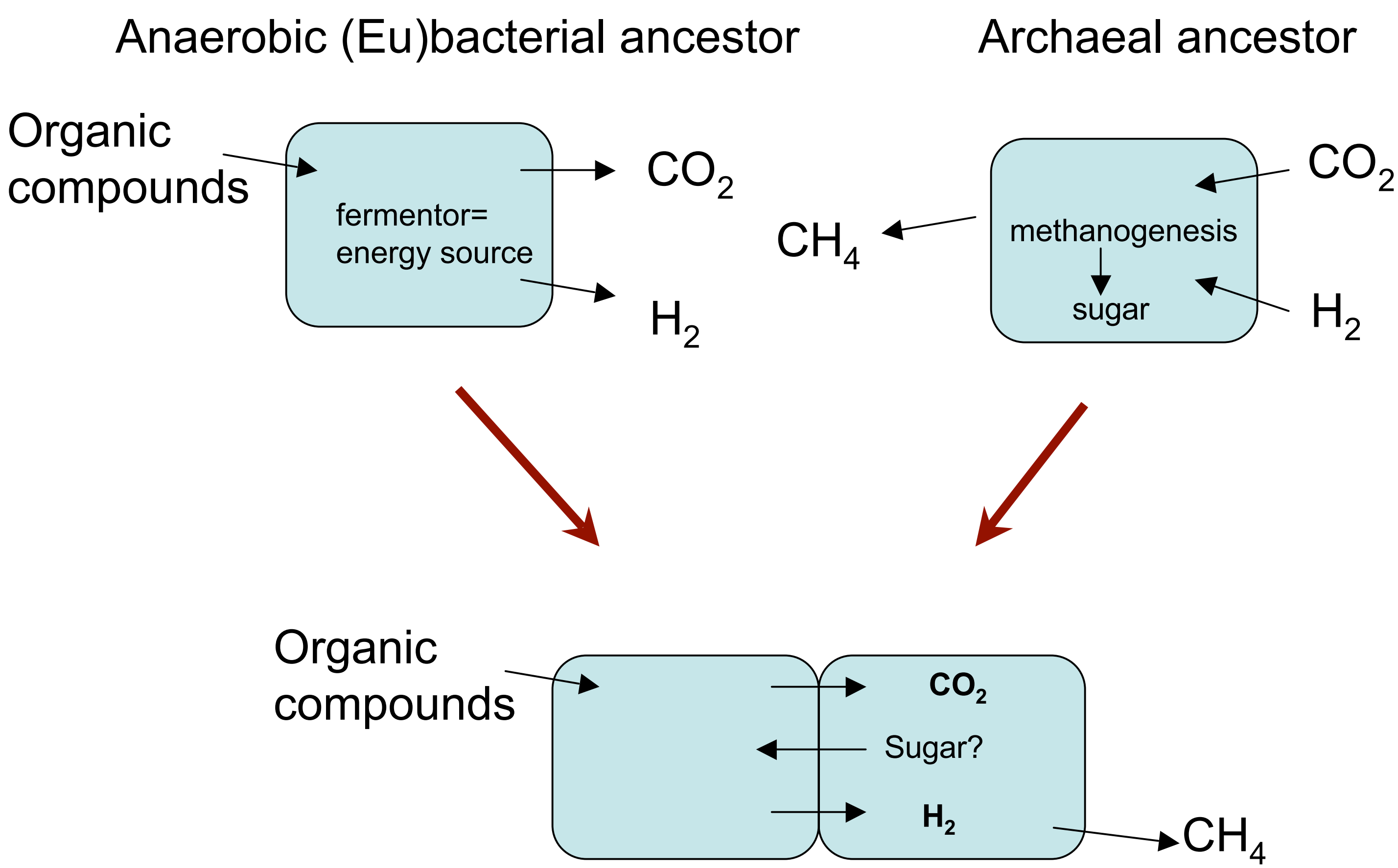
Nucleus contains genetic material

≥ 0.001 PAL O_2 Required

Likely sequence of critical evolutionary events leading tp multicellular forms

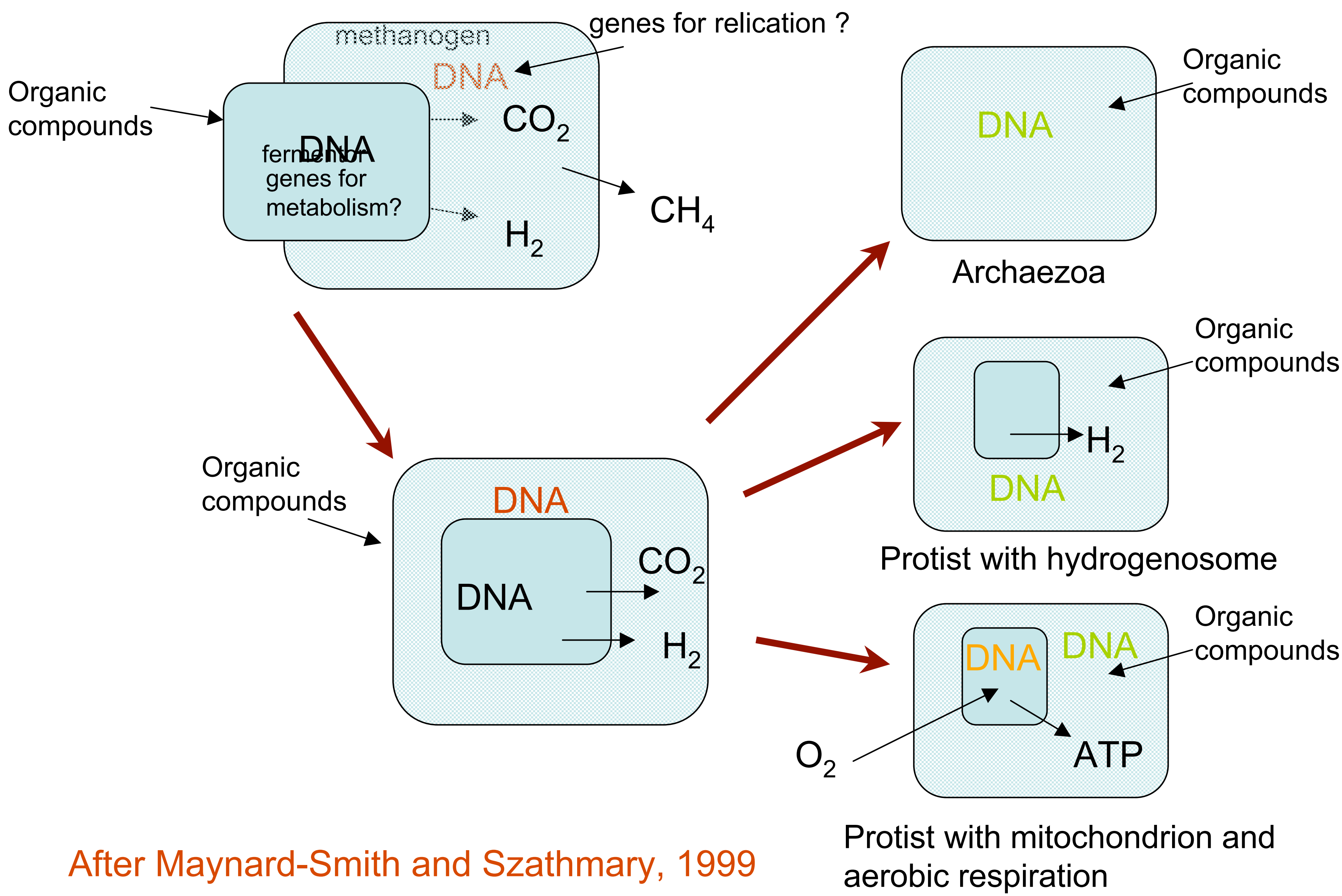
- Eukaryotes likely arose from union of two prokaryotic cells.
- Internalized cell became mitochondrion (where E from food derived by respiration).
- DNA & RNA in mitochondrion is different than in surrounding cells.
- Protozoan consumed & retained cyanobacterium that became chloroplast.
- Chloroplasts contain own DNA & RNA (like mitochonrdrion) and are remarkably similar to cyanobacteria.

Symbiosis leading to proto-eukaryote



After Maynard-Smith and Szathmary, 1999

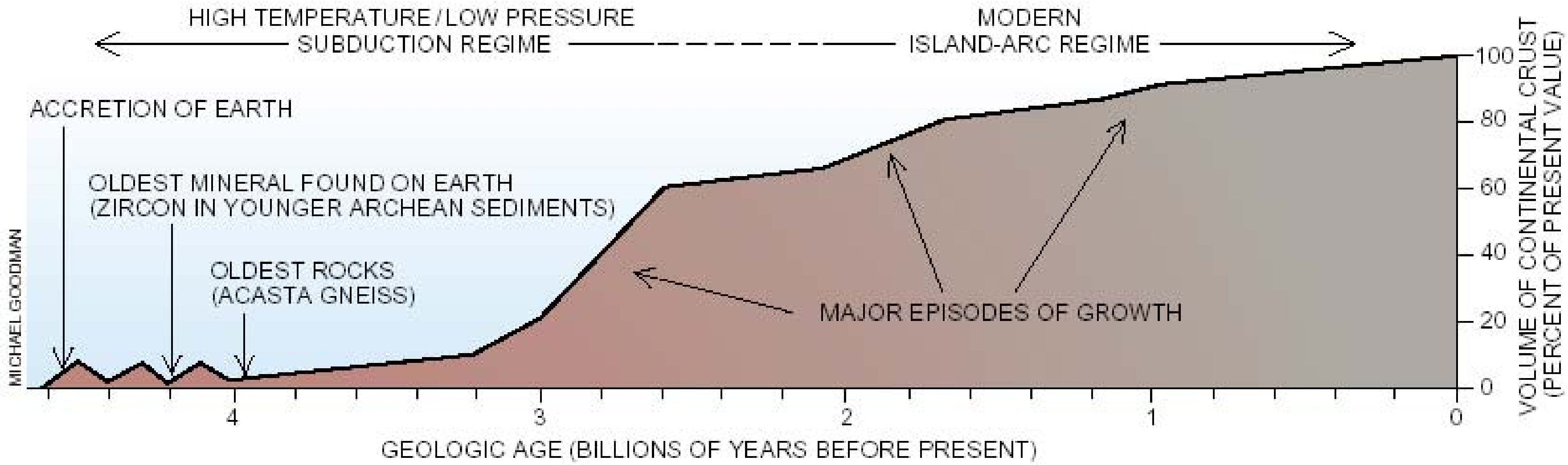
Symbioses leading to Eukaryotes



After Maynard-Smith and Szathmary, 1999

Origin and Early Evolution of Life

- The lost record of the origin of Life? Few crustal rocks from >3 Ga and half life of sediments 100-200Ma so most destroyed



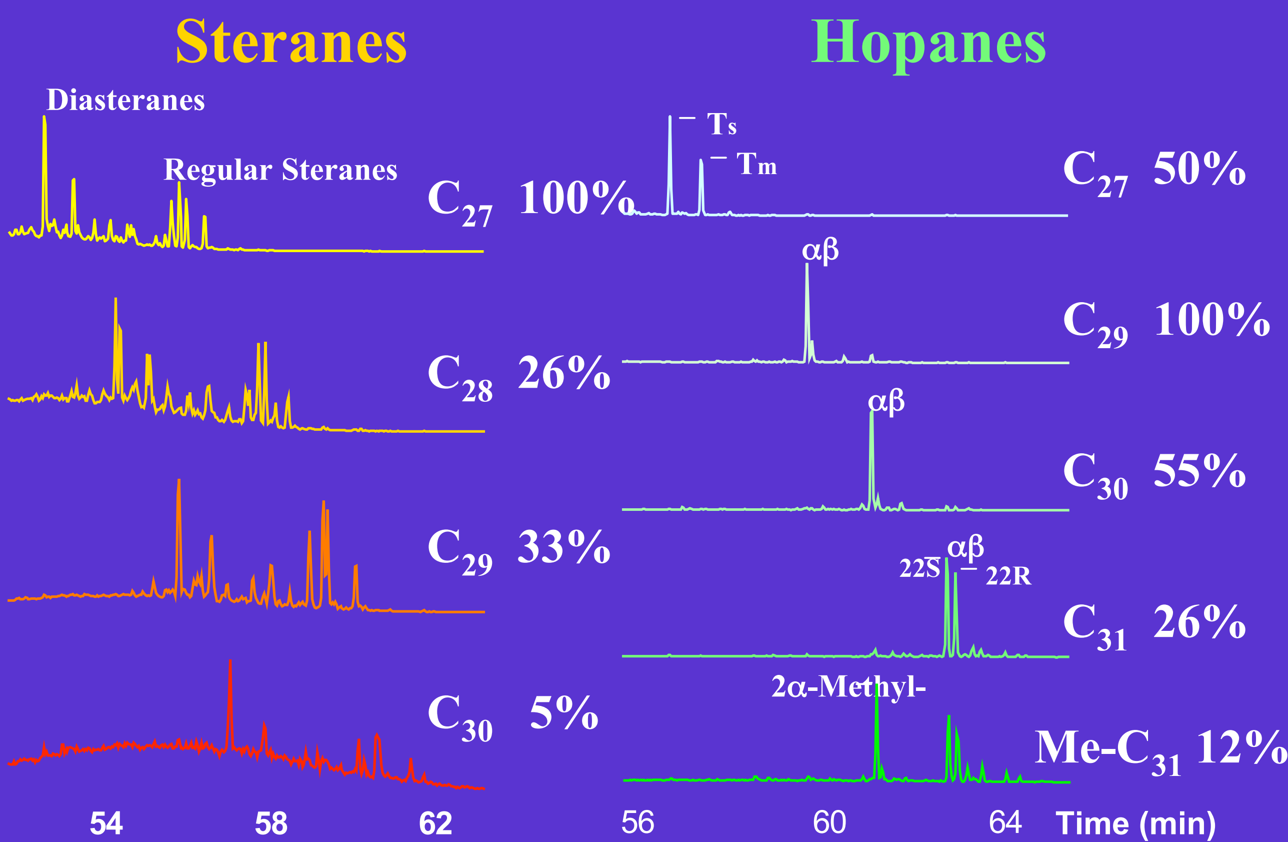
CRUSTAL GROWTH has proceeded in episodic fashion for billions of years. An important growth spurt lasted from about 3.0 to 2.5 billion years ago, the transition between the Archean and Proterozoic eons. Widespread melting at this time formed the granite bodies that now constitute much of the upper layer of the continental crust.

The majority view seems to be that stromatolites are the first good evidence for life, placing its origin in the vicinity of 3.5 Ga.

By 3.47 Ga there is additional evidence for microbial life in the form of isotopically-depleted sulfur minerals….

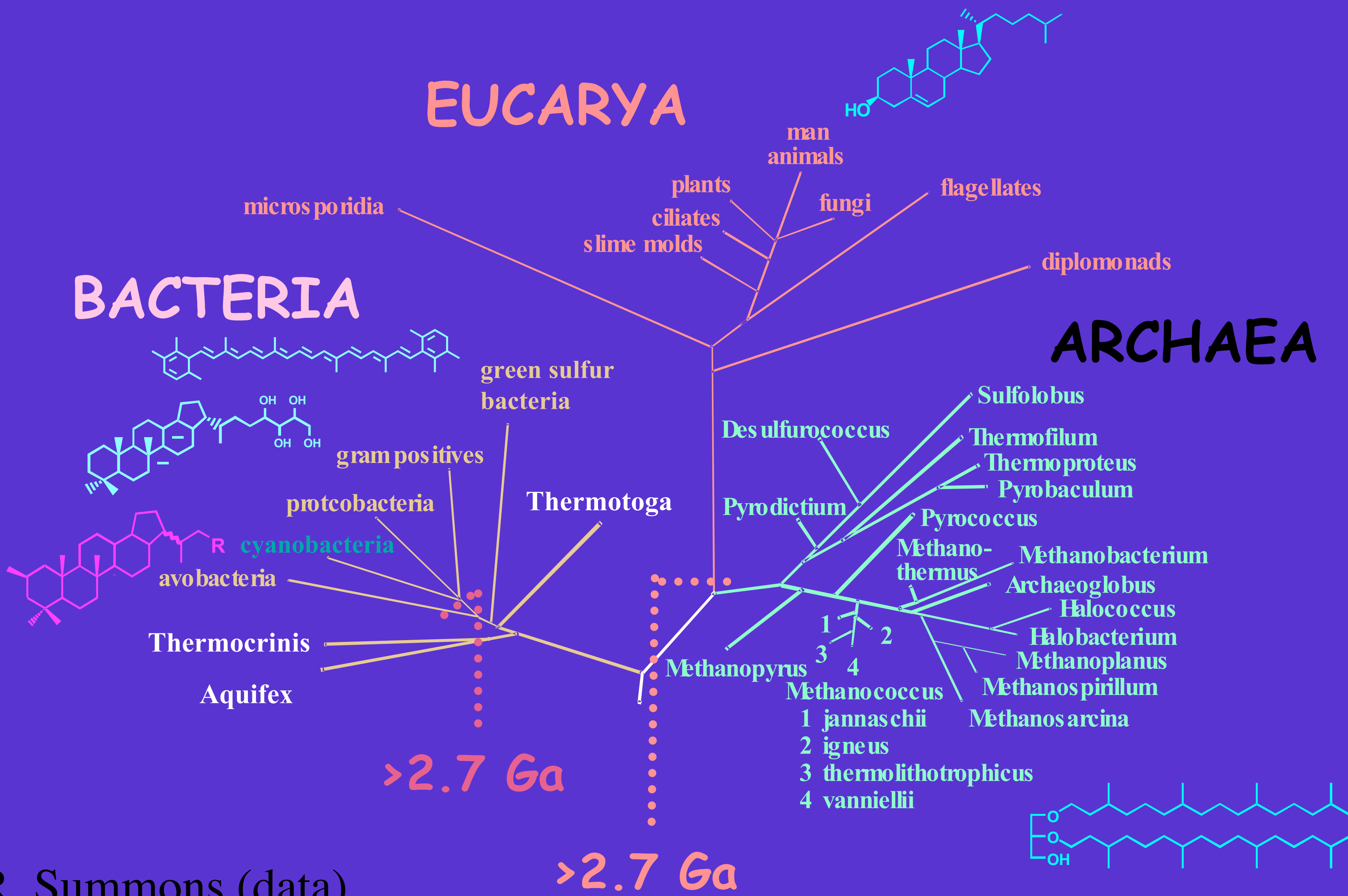
By 2.7 Ga there is excellent evidence for both microbial life, eukaryotes & oxygenic photosynthesis from *molecular fossils.*

Eukaryote & Prokaryote Biomarkers by 2.7 Ga



Summons, Brocks, et al.

Parallel Molecular Signatures



R. Summons (data)

Conundrum: 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

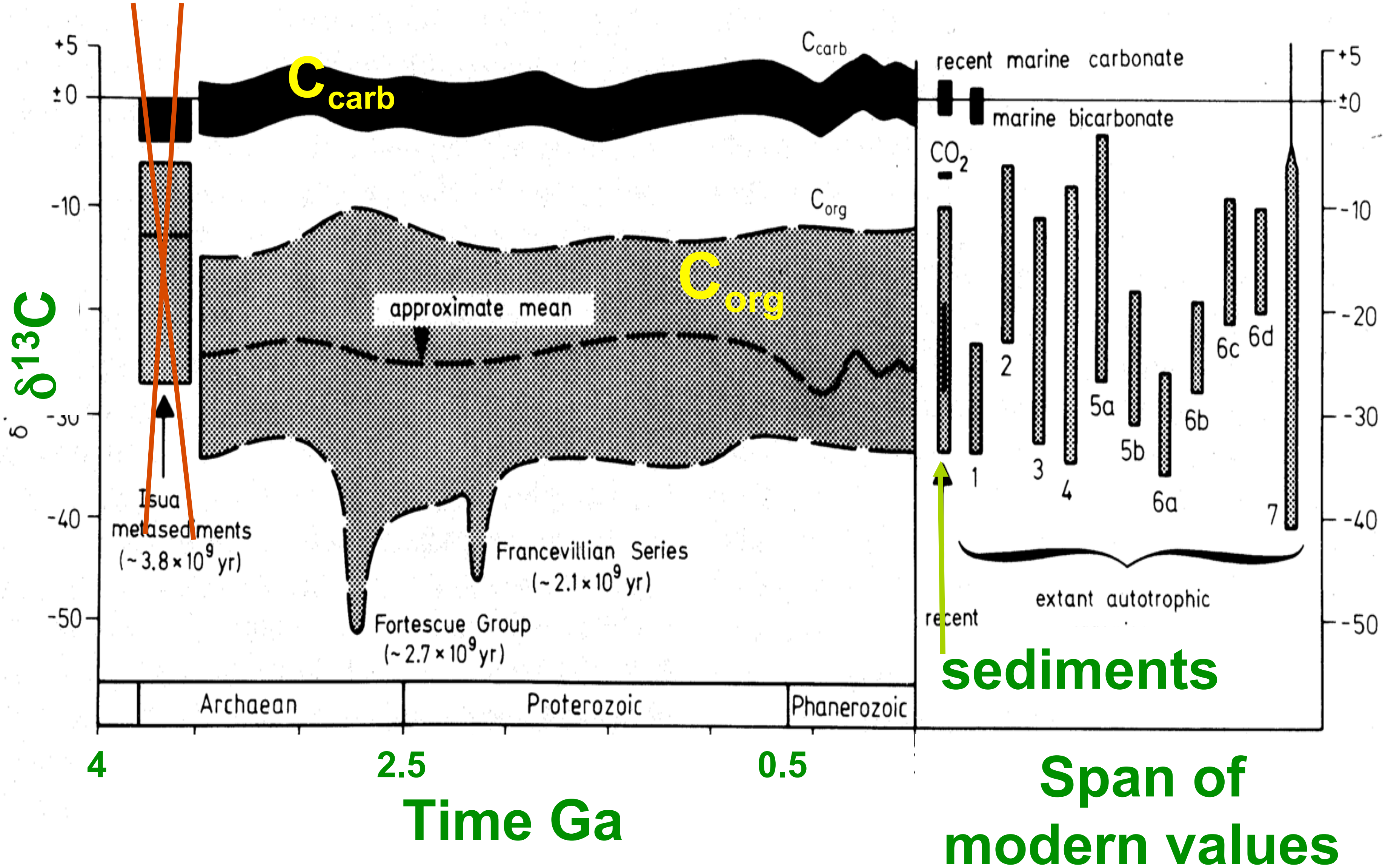
•Reduced hydrothermal vent fluids

Sources of Oxygen to the Atmosphere

Oxygenic Photosynthesis

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$

Revised C Isotope Evidence for Life's Antiquity



EVIDENCE FOR AUTOTROPY & OXYGENIC PHOTOSYNTHESIS

~3.8 Ga **Isua ^{13}C-depleted graphites**

~3.5 Ga **Warrawoona stromatolite; Apex microbiota**

~2.8 Ga **- 45 to - 50 ‰ PDB kerogens**

~2.7 Ga **Fortescue microbiota:**
stromatolites, putative cyanobacteria

~2.5 Ga **peak of BIF's**

~2.2 Ga **paleosols**

~2.1 Ga **Gunflint microbiota:**
Cb, acritarchs, Grypania

~2.7 Ga oldest steroids

4.0 3.0 2.0 1.0 0.0

What is Photosynthesis?

APhotosynthesis.

#The transfer of energy from solar radiant energy to a molecule. (physics to chemistry).
#the fixation of 120 billion metric tons of carbon a year.
#the primary process by which energy enters the biosphere.

It was the evolution of oxygen evolving photosynthetic bacteria some 3x109 ya that ultimately created an atmosphere of 21% O2 and set the stage for the evolution of all complex life forms, including ourselves!

General photosynthetic equation: (Fig. 1).

$$6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$$

There are three basic steps in photosynthesis: (Fig. 2).

#Light reactions - energy capture: chemiosmosis generation of ATP from harvested sunlight.
#Dark reactions - fixation of carbon: enzyme catalyzed reactions using the energy of ATP formed in the light reactions to fix atmospherically derived carbon (CO2) into sugars (CH2O).
#Pigment regeneration - electron replacement from the splitting of H2O in oxygenic photosynthesis.

The Transfer of Energy from Solar Radiant Energy to a Molecule (physics to chemistry)

Typically the frequencies at which electrons in bonds oscillate back and forth between various nuclei fall in the range 1014 - 1015 cycles/sec. These frequencies correspond to those of light with wavelengths in the range of 200-700 nanometers, the visible and ultraviolet regions of the solar spectrum. It is light of these wavelengths that are involved in photosynthesis. Shorter wavelengths are disruptive to molecules, causing photo-dissociation, the breaking of bonds between atoms. We saw this happen in the atmosphere with the photo-dissociation of oxygen and ozone by ultraviolet light. Light with wave lengths longer than 700 micrometers is absorbed by water, which makes up the bulk of living creatures. This absorption heats the water but does not effect electron energies. As we learned in week one, wavelengths between 200 and 700 micrometers is where the bulk of the sun's output is.

How does a light wave excite (increase the energy) of an electron? Imagine a light wave passing a stationary molecule. The wave causes electrical and magnetic disturbances in the region of space through which it travels. It turns out that the magnetic force on the electron is very weak compared to the electrical force so we can ignore it and think only of the electrical force. As the light wave passes, the electrons of the molecule experience an electrical disturbance caused by the repulsive and attractive forces of the light wave's undulating electric field. At any given point in the electron cloud, the electric field strength due to the light wave will vary as a function of time i.e., it may start at a value of zero, build up to an (attractive) maximum, decrease to a value of zero, and then begin to produce a field opposite to the previous one, build to a (repulsive) maximum, decrease to a value of zero, then start the cycle all over again. The degree to which interaction between the light wave and the electron cloud of a molecule occurs depends on the relation between the resonant frequency of the electron cloud and the frequency of the light wave. This is similar to the situation of a platoon of marching soldiers reaching a bridge. The platoon leader, if he has been well trained, will have his men fall out of step as they cross the bridge. This will avoid the unfortunate possibility of the platoon knocking the bridge down if the frequency of the soldiers marching is similar to the natural resonant frequency of the bridge. Another example is female opera singers who can sing at frequencies similar to wine glasses. They have been known to impress the guests at gala events by holding this critical note and breaking the (empty) wine glasses.

In the classical model of light absorption, the maximum rate of energy absorption from a light wave occurs at resonance. The frequency of the light wave is similar to the frequency of the electron cloud. Thus light absorption by a molecule is an all or nothing proposition. The net result of absorption is to create an oscillatory motion in the electron cloud. This motion contains energy that can be released or stored. This energy is available to move electrons in chemical reactions.

General Photosynthetic Equation

Photosynthesis

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

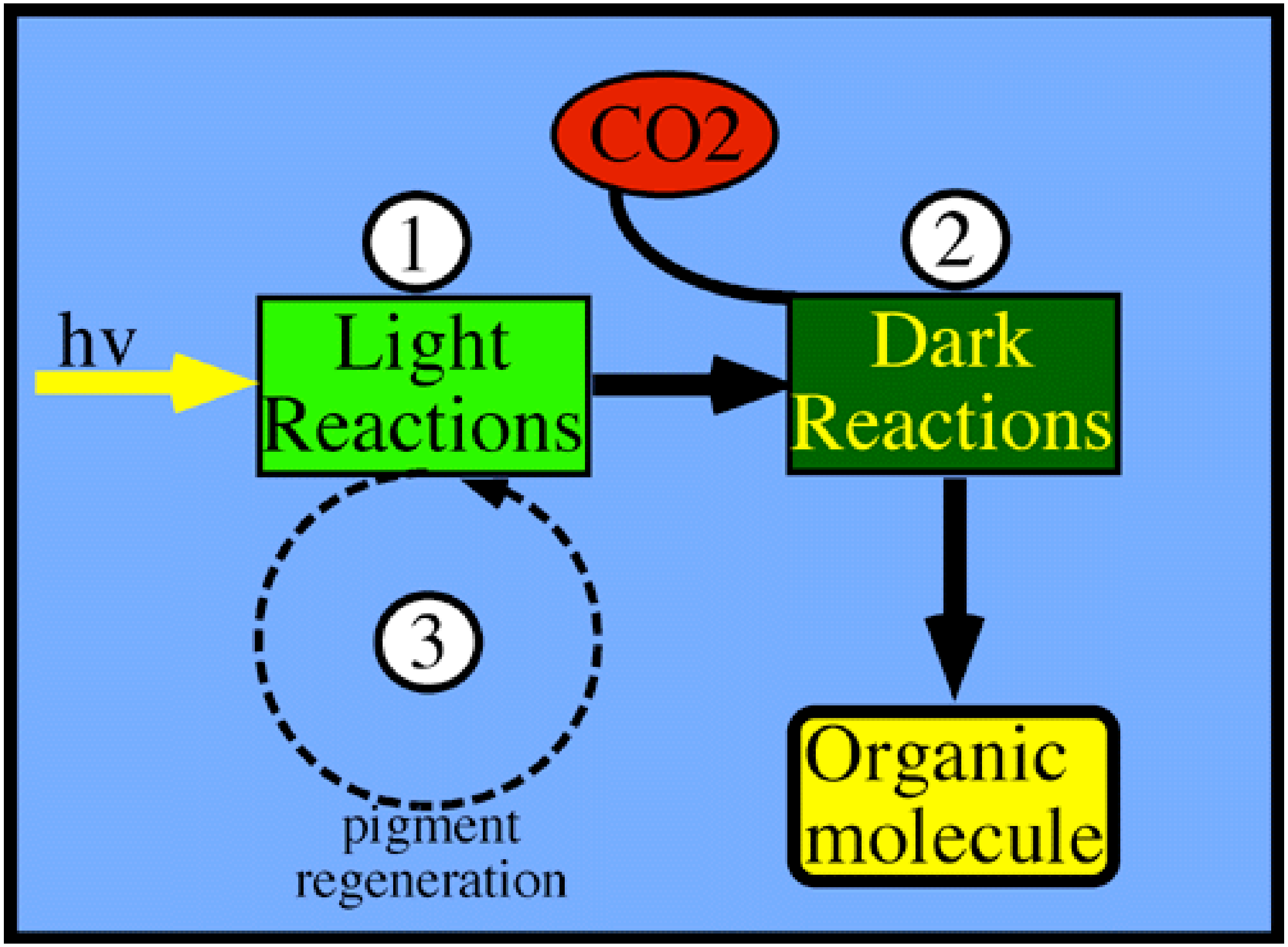
ie. algae

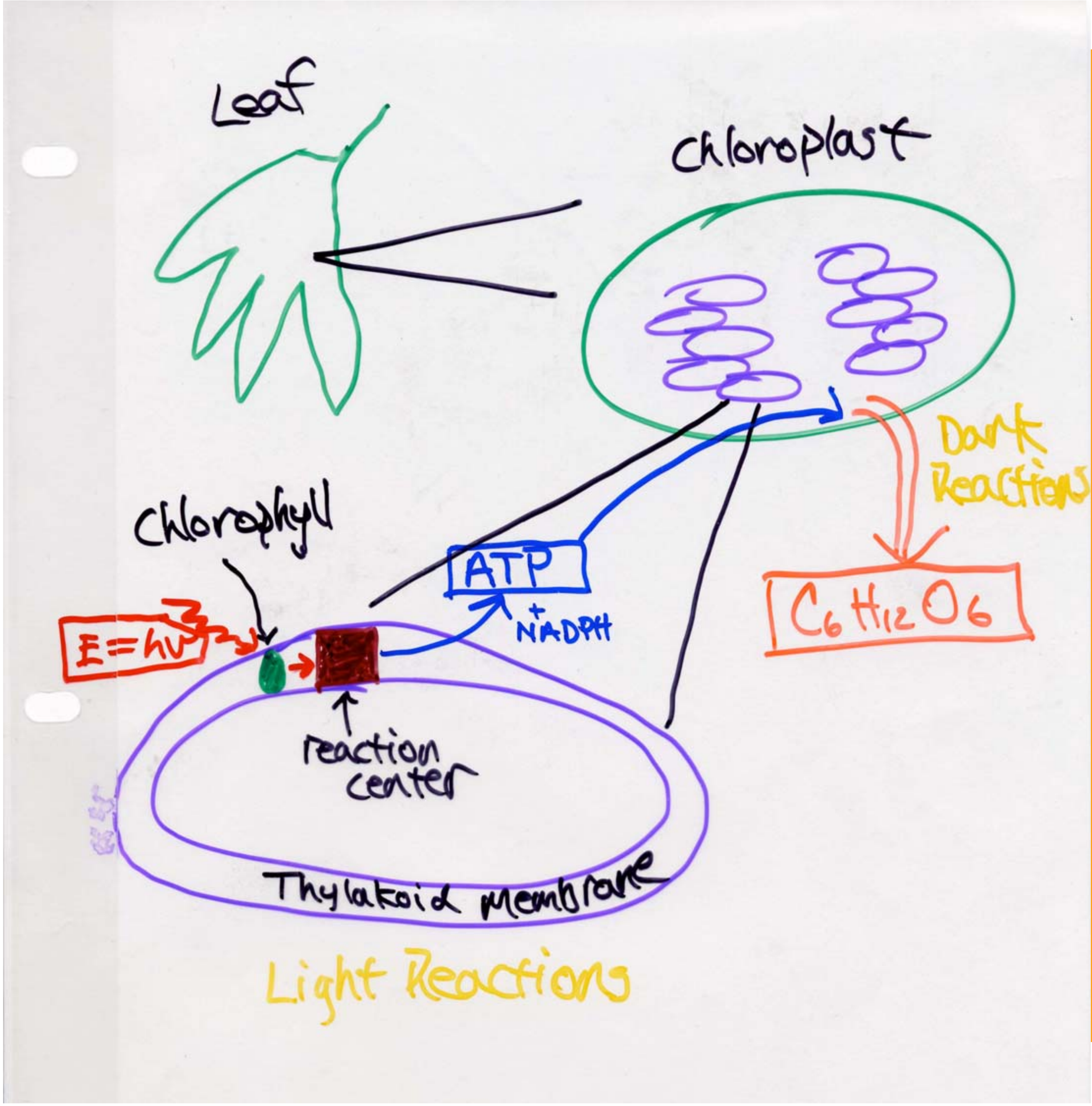
Carbohydrates + Oxygen as products

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 Steps of Photosynthesis





Photosynthesis Schematic

Steps in Photosynthesis #1: The Light Reactions

•The Light Reactions: absorbing light energy

• Photosynthesis requires the input of energy in the form of light (photons). The light energy that reaches the surface of the Earth is made up of a continuous spectrum of various wavelengths and photons known as the electromagnetic spectrum, the energy in each being inversely proportional to its wavelength.

• A very specific energy is required for photochemistry since only photons of a certain critical wavelength can dislodge electrons from an object. Photosynthetic pigments are used to absorb light of precisely the right energy to facilitate electron transfer via the photoelectric effect. Photosynthetic active radiation (PAR) is adsorbed by chlorophylls, pigments that absorb in the red and blue spectra and reflect green.

• When the energy absorbed by the chlorphylls is released, some goes into the formation of chemical bonds (ATP, NADPH).

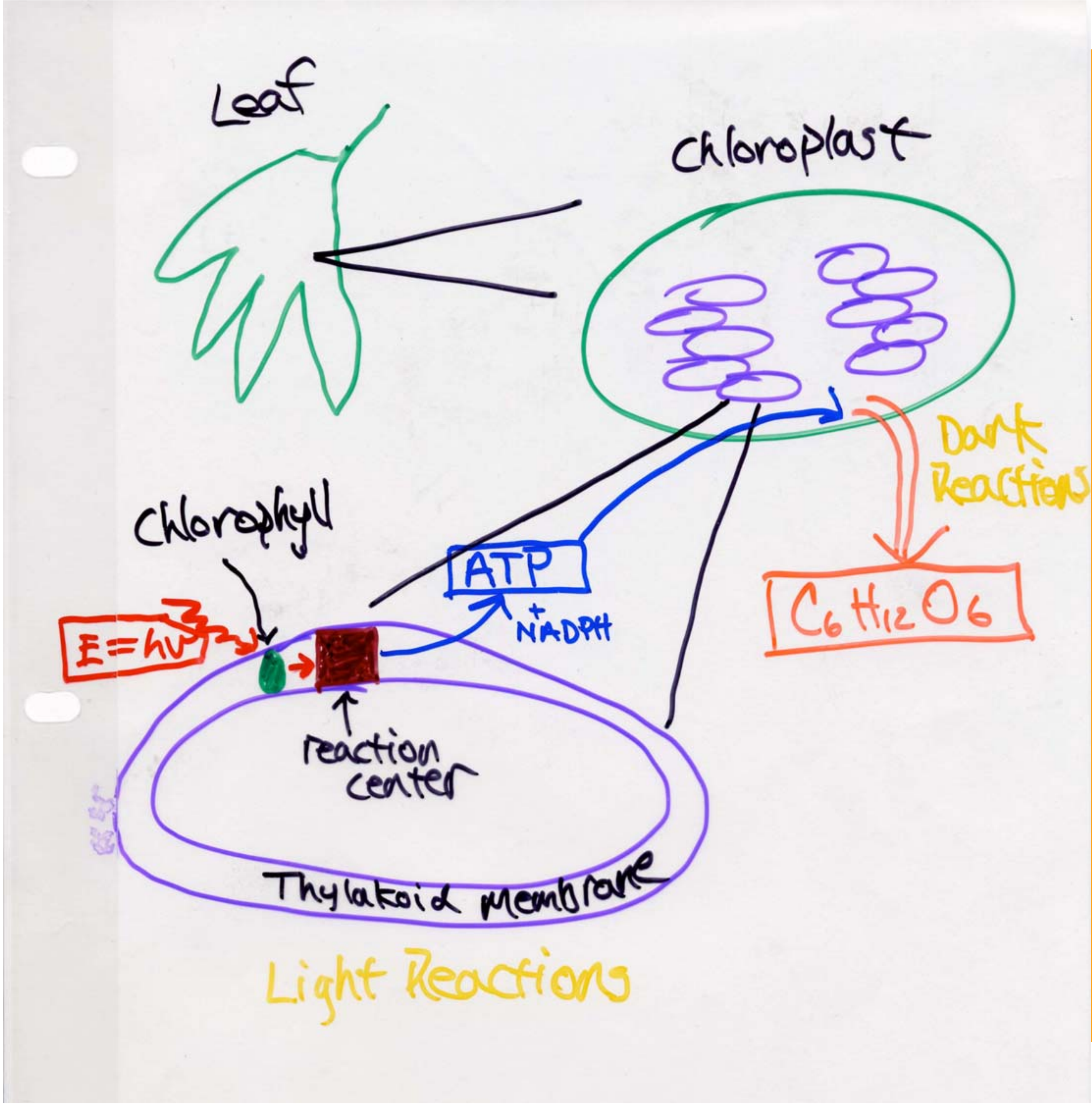
Steps in Photosynthesis #2: The Dark Reactions

•<u>Dark Reactions: carbon fixation</u>

The cellular energy source gained from the light reactions (ATP and NADPH), is subsequently used to build organic (carbon based) molecules. The steps that comprise the enzymatic fixation of carbon are known as the dark reactions since they can readily proceed in the absence of light, however don't be confused, these processes can just as easily proceed (and commonly do) in the light.

•<u>Pigment Regeneration: water splitting</u>

Light energy was adsorbed by chlorophyll, and an electron was sent to a higher energy state, as this electron decayed, it transferred its energy to form ATP which was then used make sugars. In order to obey the conservation of mass and energy, the transferred electron has to be replaced. This replacement comes from water, which is split releasing oxygen!



Photosynthesis Schematic

ATP (Adenosine triphosphate)

- ATP ATP is a nucleotide that performs many essential roles in the cell.
  - It is the major energy currency of the cell, providing the energy for most of the energy-consuming activities of the cell.
  - It is one of the monomers used in the synthesis of RNA and, after conversion to deoxyATP (dATP), DNA.
  - It regulates many biochemical pathways.

- Energy

  When the third phosphate group of ATP is removed by hydrolysis, a substantial amount of free energy is released.
  The exact amount depends on the conditions, but we shall use a value of 7.3 kcal per mole.

  $$ATP + H_2O \rightarrow ADP + P_i$$

  ADP is adenosine diphosphate. Pi is inorganic phosphate.

- Synthesis of ATP
  - $ADP + P_i \rightarrow ATP + H_2O$
  - requires energy: 7.3 kcal/mole
  - occurs in the cytosol by glycolysis
  - occurs in mitochondria by cellular respiration
  - occurs in chloroplasts by photosynthesis

- Consumption of ATP
  - Most anabolic reactions in the cell are powered by ATP.
  - Examples:
    - assembly of amino acids into proteins
    - assembly of nucleotides into DNA and RNA
    - synthesis of polysaccharides
    - synthesis of fats
    - active transport of molecules and ions
    - beating of cilia and flagella

NADP

•Nicotinamide adenine dinucleotide (NAD) & its relative nicotinamide adenine dinucleotide phosphate (NADP) are two of the most important coenzymes in the cell. NADP is simply NAD with a third phosphate group attached as shown at the bottom
of the figure.

•Because of the positive charge on the nitrogen atom in the nicotinamide ring (upper right), the oxidized forms of these important redox reagents are often depicted as NAD+ and NADP+ respectively.

•In cells, most oxidations are accomplished by the removal of hydrogen atoms. Both of these coenzymes play crucial roles in this. Each molecule of NAD+ (or NADP+) can acquire two electrons; that is, be reduced by two electrons. However, only one proton
accompanies the reduction. The other proton produced as two hydrogen atoms are removed from the molecule being oxidized is liberated into the surrounding medium.

•For NAD, the reaction is thus:

NAD+ + 2H -> NADH + H+

•NAD participates in many redox reactions in cells, including those
in glycolysis and most of those
I n the citric acid cycle of cellular respiration.

•NADP is the reducing agent
produced by the light reactions of photosynthesis
consumed in the Calvin cycle of photosynthesis and
used in many other anabolic reactions in both plants and animals.

•Under the conditions existing in a normal cell, the hydrogen atoms shown in red are dissociated from these acidic substances.

Steps in Photosynthesis #3: Pigment Regeneration & Water-Splitting

Pigment Regeneration: water splitting

Light energy was adsorbed by chlorophyll, and an electron was sent to a higher energy state, as this electron decayed, it transferred its energy to form ATP which was then used make sugars. In order to obey the conservation of mass and energy, the transferred electron has to be replaced. This replacement comes from water, which is split releasing oxygen!

Nutrients

•Plants need more than C,O and H to make all of the organic compounds they need to live. This is why we fertilize our house and cultivated plants.

•Aquatic habitats, particularly the open ocean can be strongly nutrient limited. Nitrogen (N) is essential in the structure of all proteins and nucleic acids, Sulfur (S) is essential in the structure of most proteins and Phosphorus (P) is essential in the structure of nucleic acids and molecules involved in energy transfer (ATP).

•While nitrogen is always abundant as N_2 gas, most plants can only use "fixed" nitrogen (e.g. NO^{3-}, NH^{4+}). Only some micro-organisms are able to convert N_2 gas to a fixed (useable) form.

•In the ocean, there is always plenty of CO_2 and water, so plant growth is usually limited by N & P, and sometimes Iron (Fe), a trace nutrient important for photosynthesis.

•Nutrients are carried into the deep ocean with sinking biological debris.

•Respiration in the deep ocean releases the nutrients back into the water along with the carbon.

Elemental Abundance in Continental Crust		Elemental Abundance in the Atmosphere		Elements of Life
Element	General Abundance weight %	Element	Abundance wt. %	Elements
O	Both greater than 20%	N_2	78	C
Si		O_2	20	O
Al		Ar	01	H
Fe		CO_2	0.035	N
Ca	Greater than 1 but less than 10 %	H_2O	variable	P
Na				
K				
Mg				
H				
Ti	Between 0.1 and 0.9 %			
Cl				
P				

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

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

Carbon dioxide + water + Energy as products

1 mole of O_2 consumed
as 1 mole of CO_2 produced

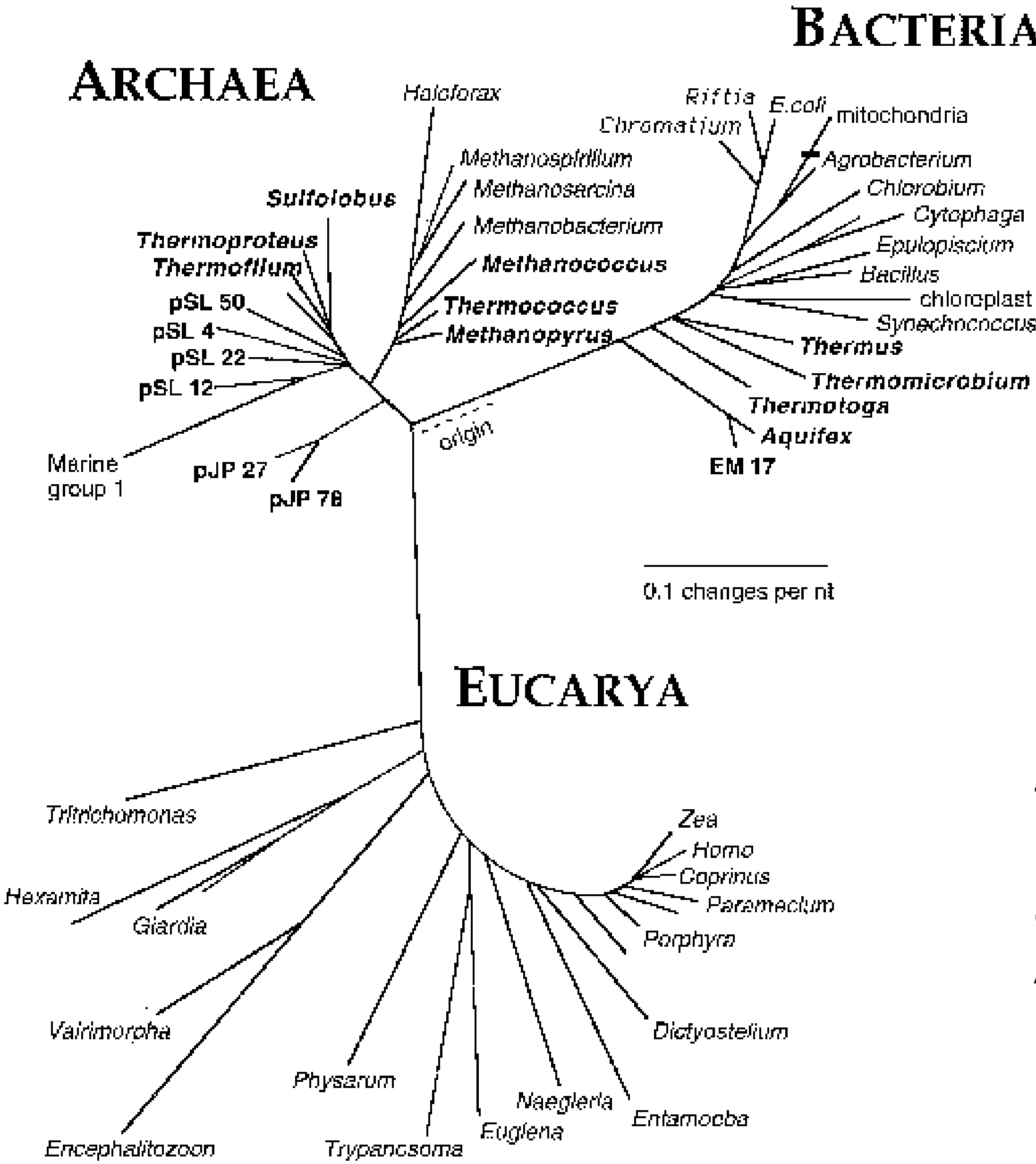
→ Controls Deep Water Ocean Chemistry of O_2, inorganic carbon and nutrients

Other Archean O_2 Sinks #2

Archean mantle dynamics & redox evolution-2

- Ferrous iron in basalts erupted at mid-ocean ridges & on land

  $Fe(II) + H_2O \rightarrow H_2 + Fe(III)$
- H_2 escapes atmosphere or consumed by biota
- Oxidized (Fe(III))oceanic lithosphere subducted
- Accumulates in ‘graveyard’ near core-mantle boundary
- Transfer of oxidized material to base of mantle caused “upside-down Earth,” with upper mantle reduced & lower mantle oxidized
- *Reduced* volcanic gases emitted from upper mantle continue to be large sink for atm. O_2
- Timing of O_2 Rise: Huge magmatic plume 2.47-2.45 Ga (Large Igneous Province (LIP)) brought some oxidized lower mantle to surface, resulting in decreased O_2 sink.



A hyperthermophilic Origin?

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

Complexity of Extant Life

Species	**Type**	**Approx. Gene Number**
Prokaryotes		
E. Coli	typical bacterium	4,000
Protists		
O. Similis	protozoan	12,000-15,000
S. Cerevisiae	yeast	7,000
Distyostelium discoideum	slime mould	12,500
Metazoan		
C. Elegans	Nematode	17,800
D. melanogaster	Insect	12,000-16,000
S. Purpuratas	Echinoderm	<25,000
Fugu rubripes	Fish	50,000-10,0000
Mus musculus	Mammal	80,000
Homo sapiens	mammal	60,000-80,000

After Maynard-Smith and Szathmary, 1999

Major Transitions in Origin/Evolution of Life

replicating molecules	populations of molecules in protocells
independent replicators	chromosomes
RNA as a gene and enzyme	DNA genes, protein enzymes
prokaryotic cells	Cells with nuclei & organelles ie eukaryotes
asexual clones	sexual populations
single bodied organisms	fungi, metazoans and metaphytes
solitary individuals	colonies with non-reproductive castes
primate societies	human societies with language

After Maynard-Smith and Szathmary, 1999

Parallel Molecular Signatures