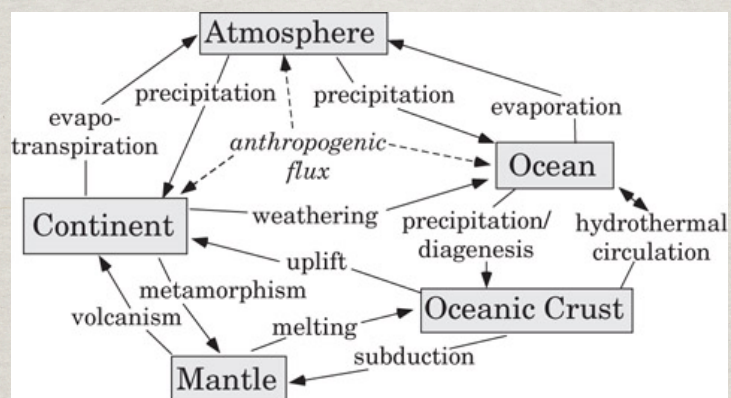


# OCN 401 “ORIGINS...”

- ✿ biologist, geologist, chemist, astrobiologist, oceanographer
- ✿ biogeochemist
- ✿ microbial geochemist
- ✿ microbial ecologist
- ✿ geomicrobiologist

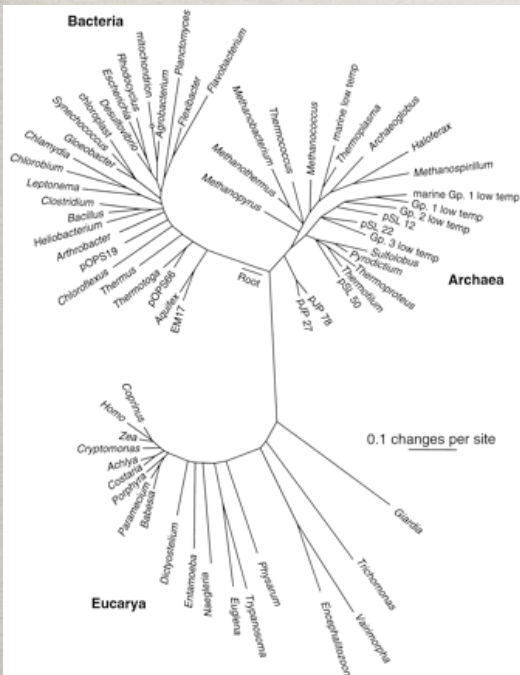
## BIOGEOCHEMISTRY



- ✿ study of chemical, physical, geological, and biological processes and reactions of the natural environment, usually focusing on chemical cycles driven by or impacting biological activity



# MICROBIAL ECOLOGY



☼ study of interrelationships between different microorganisms; among microorganisms, plants, and animals; and between microorganisms and their environment

# MICROBIAL GEOCHEMISTRY

☼ study of microbially influenced geochemical reactions, enzymatically catalyzed or not, and their kinetics, often studied within the context mineral cycles, and emphasis placed on mass transfer and energy flow



# GEOMICROBIOLOGY

- ✿ Winogradsky (1887), discovered *Beggiatoa* could oxidize  $H_2S$  to elemental sulfur
- ✿ “study of the relationship between the history of the Earth and microbial life upon it” - Beerstecher 1954

## THE EARTH AS MICROBIAL HABITAT, AKA, THE “GEOLOGY” PART

- ✿ Earth has been cooling for >4.5 billion years
- ✿ decay of radioactive elements fuels heat & mass transfer
- ✿ heat & mass transfer exchange = energy

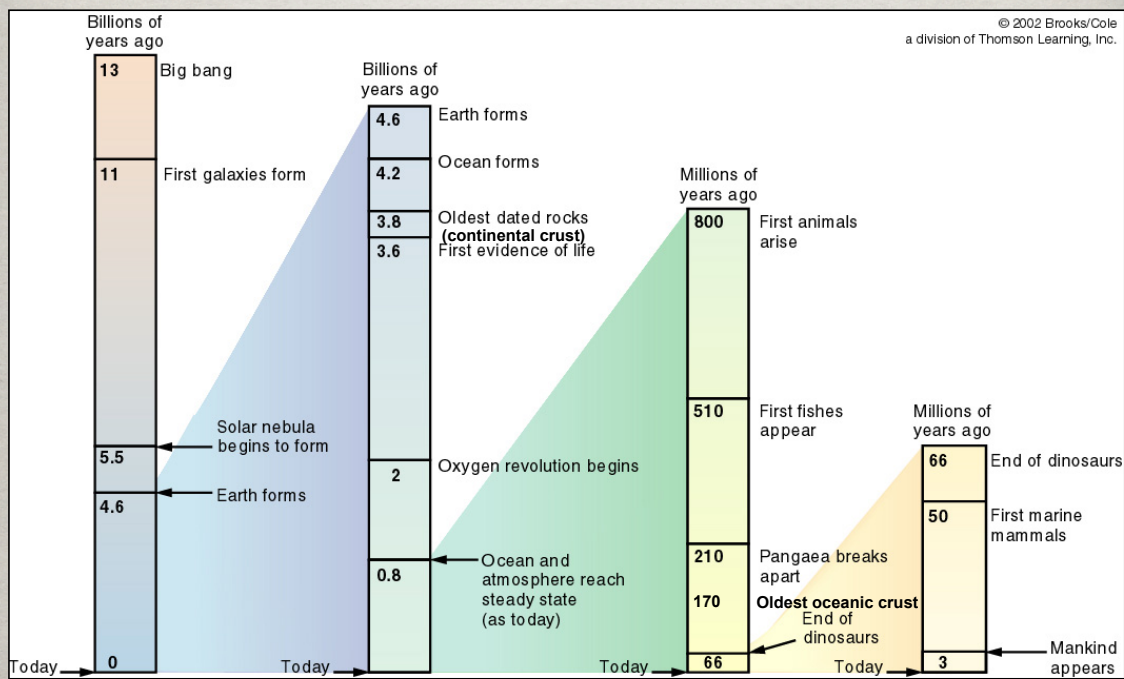


# A FUNDAMENTAL CONCEPT TO THOROUGHLY GRASP AND REMEMBER FOREVER

- ☼ formation of rocks and minerals preserves information about the Earth's history
- ☼ balance between rocks & rock weathering fundamentally controls the chemistry of our aquatic ecosystems (and even the atmosphere)

## History

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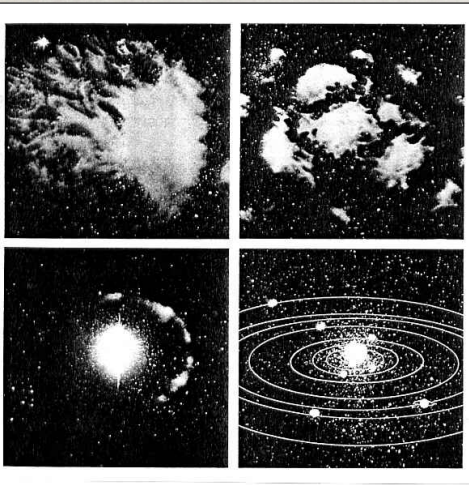




# “BIG BANG” THEORY

- In the beginning - all matter in one place at a single instant
- Big Bang – huge expansion of matter
- Between  $10^{-50}$  and  $10^{-30}$  sec after the Big Bang:  
*Inflation* – rapid expansion of the Universe
- During inflation, universe permeated with radiation and subatomic particles (plasma, dark matter)
- After 100,000 yrs – conditions similar to Sun
- After 300,000 yrs – Temp dropped to  $4500^{\circ}\text{K}$  and gave rise to atomic matter (hydrogen, helium, and deuterium)

# SOLAR NEBULA THEORY



**Figure 2.9 Cameron's theory.** According to the currently accepted solar nebula theory, our solar system had its origins many millions of years ago with the collapse of an interstellar gas cloud (*top left*). Following its collapse, the massive cloud broke into numerous fragments (*top right*), many of which evolved into proto-suns. A. G. W. Cameron has postulated that our sun was one of these proto-suns, a gaseous disk about the size of our present solar system, with its mass concentrated at the center and surrounded by a nebula of gases and dust (*bottom left*). As the central mass continued to shrink and to evolve into a burning sun, the surrounding gases were blown off into space, leaving a few solid bodies formed by the condensation of nonvolatile elements (*bottom right*). These solid forms developed into the planets.

- Collapse of gas cloud is due to internal gravitation attraction of gases
- During collapse, instabilities cause gas cloud to fragment into smaller, separate clouds
- Eventually, some cloud fragments have masses on the order of that of the present Sun
- These fragments can form proto-suns

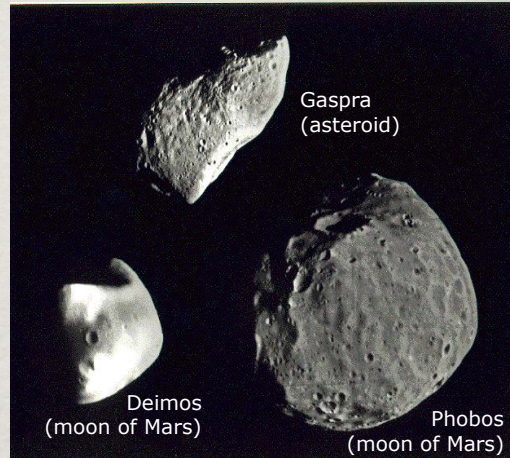






# ACCRETION

- Growth of Earth by accumulation of smaller matter from collisions of planetesimals
- During each collision, kinetic energy is transformed into heat energy
- Heat from radioactive decay increases the Earth's internal temp
- Accumulating outer layers insulate inner material and compress it, also increasing the internal temp
- Earth's inner temp increases to  $>1000^{\circ}\text{C}$
- Loss of volatile elements
- Young Earth - a homogeneous mixture of materials



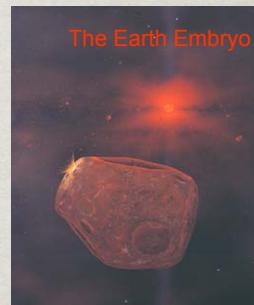
<http://mercury.atmos.albany.edu/geo100/>

# SOLAR ELEMENTAL DIFFERENTIATION

Most of the substance of Earth, its ocean, and all living things, was formed by stars.

However, if all solar matter came from a similar source, how is it that there is a variation in the solar distribution of elements?

During the cooling of the solar disk, the coolest (outer) gases began to interact chemically, producing particles which grew from collisions with other particles.



- The inner planets (Mercury, Venus, Earth, Mars) formed at  $\sim 1200^{\circ}$ 
  - Too hot to capture and retain light, volatile elements
  - Dominated by Fe-rich silicate minerals that condense at intermediate temperatures
- The larger, outer planets captured a greater fraction of the lighter constituents of the initial solar cloud



# COMPARISON OF EARTH VS SOLAR SYSTEM

**TABLE 5-1. The abundances of some elements in the earth and in the solar system**

ATOMIC NUMBER	WHOLE EARTH (ATOMS/10,000 ATOMS Si) (a)	SOLAR SYSTEM (ATOMS/10,000 ATOMS Si) (b)	DEFICIENCY FACTOR [ $\log(b/a)$ ]
H	84	$3.5 \times 10^8$	6.6
He	$3.5 \times 10^{-7}$	$3.5 \times 10^7$	14
C	71	80,000	4.0
N	0.21	160,000	5.9
O	35,000	220,000	0.8
F	2.7	90	1.5
Ne	$1.2 \times 10^{-6}$	50,000	10.6
Na	460	462	0
Mg	8900	8870	0
Al	940	882	0
Si	10,000	10,000	0
P	100	130	0.1
S	1000	3500	0.5
Cl	32	170	0.7
Ar	$5.9 \times 10^{-4}$	1200	6.3
Kr	$6 \times 10^{-6}$	0.87	7.2
Xe	$5 \times 10^{-9}$	0.015	6.5

Inert gases (non-reactive, volatile at low temps)

Refractory elements (volatile at high temps)

From Mason (1958). Copyright 1958 by John Wiley and Sons, Inc., New York. Used by permission of the publisher.

Walker, 1977

## HEATING & DIFFERENTIATION

- Heat retained by early atmosphere – super greenhouse effect
- Was there a magma ocean?

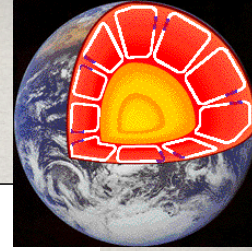


<http://mercury.atmos.albany.edu/geo100/>

- Complete or partial melting of the earth allowed Earth to separate into layers based on density – perhaps aided by *heterogeneous accretion*:
  - Metallic meteorites – similar in composition to core
  - Stony meteorites – similar in composition to crust
- Iron and nickel became concentrated in the core; lighter elements reached the surface, spread and cooled
- Thus, earth became differentiated into a layered system



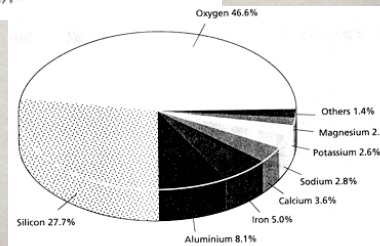
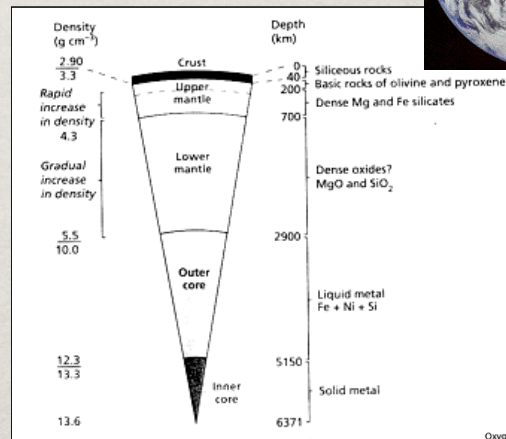
## COOLING



- Earth's structure was largely based on surface cooling of lava 4.5 billion years ago
- Cooling lava formed a hard, rocky crust on the outer layer

**Density stratification** results in an inner and outer core, a mantle and crust:

- **Crust** – less dense silicate rock
- **Mantle** – dense silicate rock
- **Outer Core** – liquid iron nickel; source of Earth's magnetic field
- **Inner Core** – solid iron-nickel



## WATER AND WATER VAPOR

How did water and water vapor form on early Earth?

- The Sun stripped away Earth's first atmosphere
- Gases, including water vapor, released by the process of outgassing, replaced the first atmosphere. Outgassing continues today (evidence: He-3 in oceans).
- Water vapor in the atmosphere condensed into clouds.
- After millions of years, the clouds cooled enough for water droplets to form when  $T < 100^{\circ}\text{C}$ .
- Hot rain fell and boiled back into the clouds.
- Eventually, the surface cooled enough for water to collect in basins.



## THE EARLY ATMOSPHERE

- Similar conc of *di-nitrogen* ( $N_2$ ) as compared to present atmosphere
- More *methane* ( $CH_4$ ) and *carbon dioxide* ( $CO_2$ )
- No *molecular oxygen* ( $O_2$ ) – any free  $O_2$  would have quickly reacted with the reduced metals of the crust

**The result:** The early atmosphere was reducing, different from the oxidizing atmosphere today

## THE GOLDILOCKS THEORY

- Just as Goldilocks found the porridge that was just right, Earth was “just right” for life
- Mars – too far from Sun – too cold, no liquid, thin atmosphere, water frozen in ground
- Venus – too close to Sun – too hot, thick and heavy atmosphere
- Earth – correct distance from Sun – abundant liquid water
  - Hydrated minerals → plate tectonics
  - Atmospheric gases get recycled → maintains appropriate surface temperature





## THE EARLY OCEAN

- The earth's light elements were likely delivered to the earth as constituents of silicate minerals in carbonaceous chondrites
    - These are 0.5 – 3.6% C, 0.01 – 0.28 % N
  - The early ocean contained the anions *bicarbonate* ( $\text{HCO}_3^-$ ), *chloride* ( $\text{Cl}^-$ ) and *sulfate* ( $\text{SO}_4^{2-}$ ) from the dissolution of atmospheric gases:
    - $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$
    - $\text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
    - $\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4$
- These acids were neutralized by interactions with crustal material in weathering reactions, leading to the release of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and other cations
  - $\text{N}_2$  has low solubility in water, so it was likely the dominant atmospheric component
  - The present atmosphere contains <1% of the crustal outgassing – most of the remainder is in the present ocean and various marine sediments

## WHAT IS LIFE? AKA, THE “BIOLOGY” PART

- ☼ How do you know it when you see it?
- ☼ Did life begin on Earth? Once or many times?
- ☼ Are we alone?

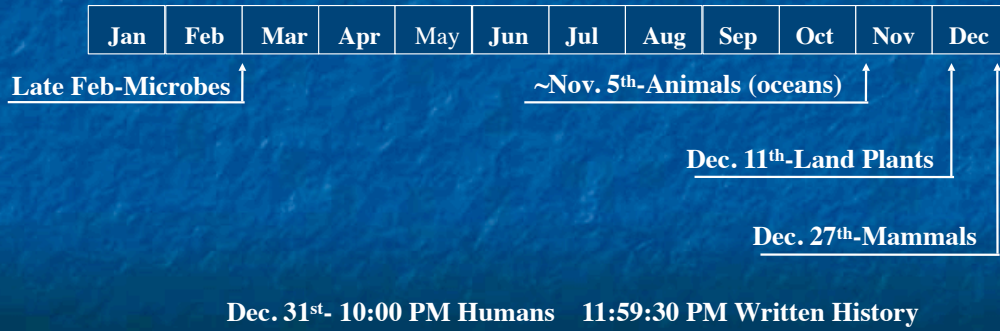


# First, some perspective

- The history of life on earth is overwhelmingly microbial
- The solar system formed 4.5-4.6 billion years ago
  - earth is ~4.5 billion yrs old,
  - microbes arose 3.8 billion years ago (bya)
    - animals-0.7 bya      -- humans-0.001 bya

Jan. 1-Earth Forms

The Microbial Age >3.8 Billion Years



## Characteristics of life

1. Water is essential for active life
2. It is contained in a microenvironment (cell)
3. It is carbon based
  - a. Nucleic acids consisting of 4 nucleotides
  - b. Dual nucleic acid system: RNA and DNA
  - c. Proteins: 20 amino acids
  - d. Lipids with straight chains of methyl branched chains
  - e. Metabolic energetics use phosphate anhydrides, thioesters
  - f. Metabolism uses nucleophile-electrophile reactions with C=O
4. It replicates
5. It evolves (mutation and other mechanisms for acquiring genetic material, and natural selection)



# WHAT ABOUT CHARACTERISTICS OF EARLY LIFE ON EARTH?

- ✿ What was early Earth like?
- ✿ What about before 3.9bya?



# CONNECTIONS BETWEEN EARLY EARTH & ORGANISMS OF TODAY

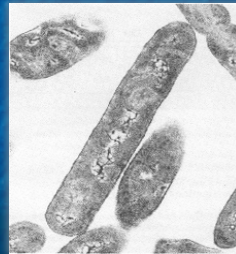
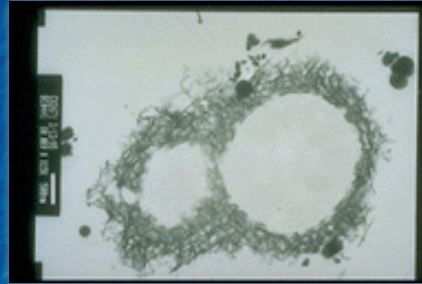


- ✿ Life in extreme environments

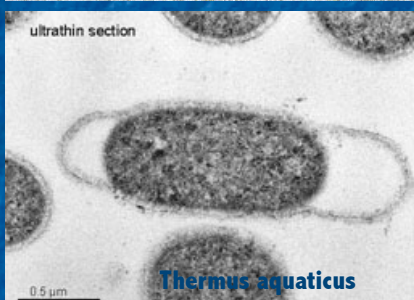


# Barophiles

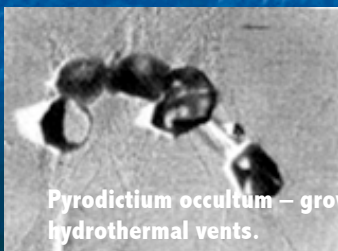
- Deep, dark dwelling bacteria
  - Tolerate high T, P
  - Grow best at P = 500-600 atm
  - Tolerate periods up to 2.5 yr in vacuum
- Habitats
  - Up to 4km depth
  - Barophilic mass > all surface life



Synechococcus  
(Yellowstone)



Thermus aquaticus



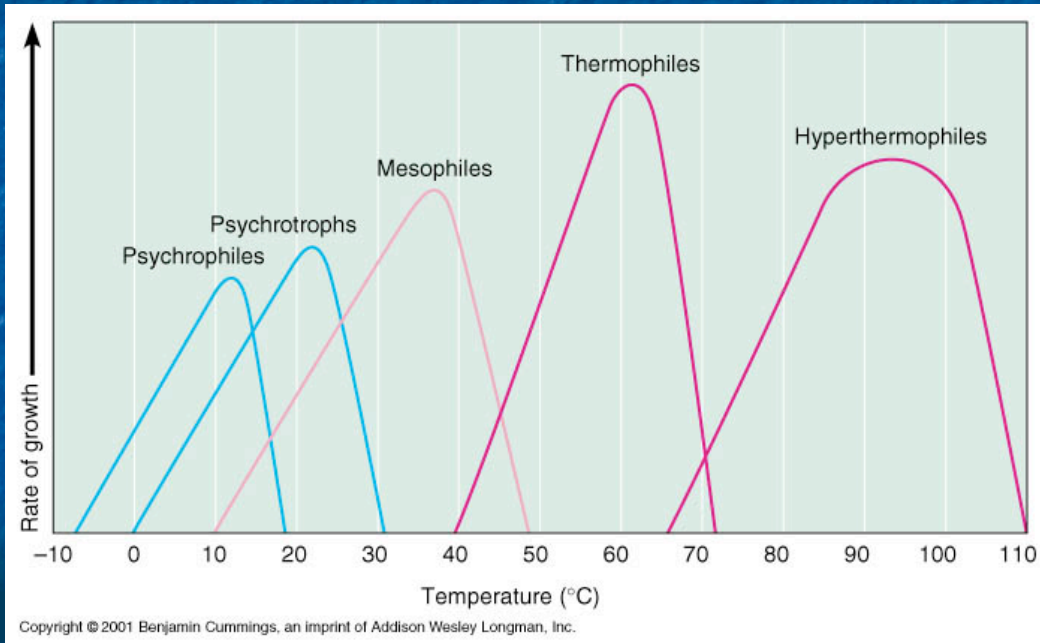
Pyrodictium occultum – grows 105-115°C at hydrothermal vents.

# Thermophiles

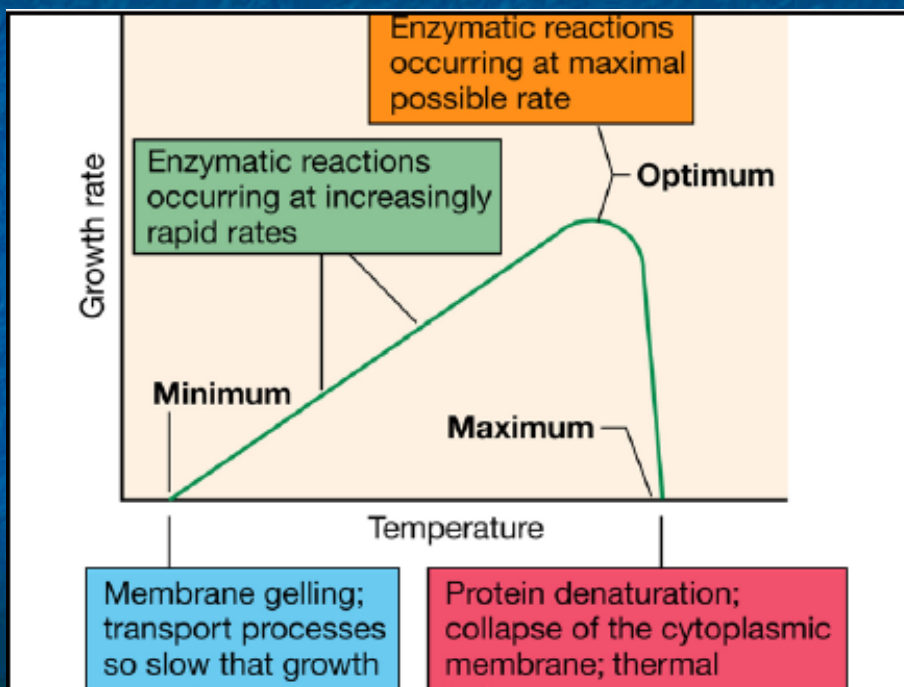
- Prokaryotes
  - Temperatures
    - Low: 45-90°C
    - Optimal 80-110°C
    - High extreme 125°C
  - pH: 1-7.5
  - Can survive high pressure
- Discovered within last 30 yr
- Location (submarine/terrest)
  - Geothermal areas
  - Oil fields, 3 km deep
- Energy:
  - Chemolithautotrophic
  - Inorganic redox for E
  - CO<sub>2</sub> is primary carbon source
  - e<sup>-</sup> donors: H<sub>2</sub>, Fe, reduced S



# Range of Temperatures



# Range of Temperatures





# Psychrophiles



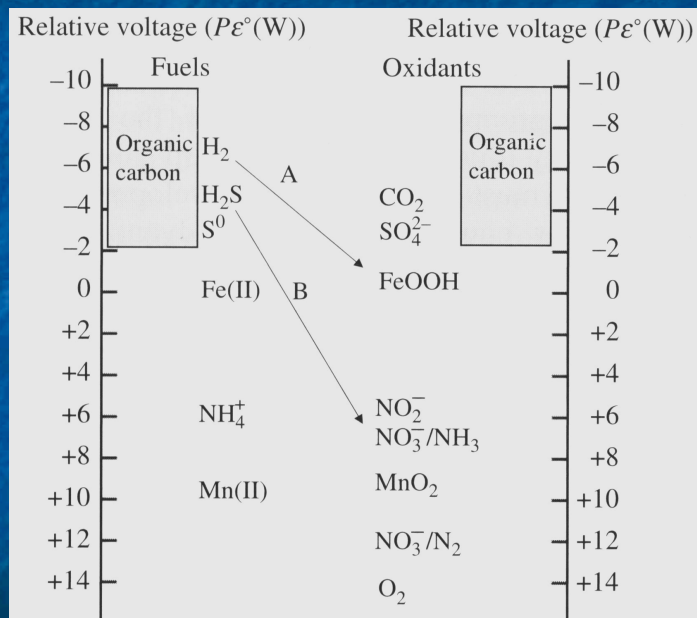
CH<sub>4</sub> worms, Sea of Cortez Ice

- Cold lovers
  - Temps 0-20°C
  - Survive freeze/thaw
  - Reproduce 2°C
- Habitats
  - Soils
  - Deep ocean water
  - Sea ice
- Least studied of extremophiles



# Types of metabolism

- Light is used directly by phototrophs
- Hydrothermal energy is utilized mainly via heat-catalyzed production of reduced inorganics



Nealson and Rye 2004



# SUSTAINING LIFE

We can classify organisms by function -- how they obtain **energy** and **cell-carbon**:

1. Method of **energy** generation (reactions that convert ADP to ATP):

- Photosynthesis -- **Phototroph**  
e.g.: Oxic photosynthesis:  $6 \text{CO}_2 + 6 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 + \text{ATP}$
- Oxidation/reduction of inorganic compounds -- **Lithotroph**  
e.g.: Ammonia oxidation:  $\text{NH}_4^+ + 1\frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2^- + 2 \text{H}^+ + \text{H}_2\text{O} + \text{ATP}$
- Oxidation of organic compounds -- **Organotroph**  
e.g.: Glucose oxidation:  $\text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 \rightarrow 6 \text{CO}_2 + 6 \text{H}_2\text{O} + \text{ATP}$

2. **Carbon** source via chemotrophy:

- Carbon dioxide -- **Autotroph**
- Organic compounds -- **Heterotroph**

## AEROBIC AND ANAEROBIC MODES OF ORGANIC MATTER RESPIRATION

In general: **Reduced organic matter + oxidant** → **CO<sub>2</sub> + reduced oxidant**

Mode of organic matter oxid	Oxidant	Reduced Oxidant	$\Delta G_r^\circ$ (kJ/mole)
<b>Aerobic oxidation</b>	O <sub>2</sub>	H <sub>2</sub> O	-3190
<b>Manganese reduction</b>	MnO <sub>2</sub>	Mn <sup>2+</sup>	-3090
<b>Nitrate reduction</b>	HNO <sub>3</sub>	N <sub>2</sub>	-3030
<b>Iron reduction</b>	Fe <sub>2</sub> O <sub>3</sub> FeOOH	Fe <sup>+2</sup> Fe <sup>+2</sup>	-1410 -1330
<b>Sulfate reduction</b>	SO <sub>4</sub> <sup>2-</sup>	S <sub>2</sub> <sup>-</sup>	-380
<b>Methanogenesis</b>	CO <sub>2</sub>	CH <sub>4</sub>	-350

More on evolution of metabolic pathways later...



# PREBIOTIC CHEMISTRY

☼ “A laboratory earth was created. It did not in the least resemble the pristine earth of two or three billion years ago; for it was made of glass...” --Stanley L. Miller, 1953

# PREBIOTIC CHEMISTRY



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Physics of Life Reviews 2 (2005) 47–64

PHYSICS of LIFE  
reviews

[www.elsevier.com/locate/plrev](http://www.elsevier.com/locate/plrev)

## Prebiological evolution and the physics of the origin of life

Luis Delaye, Antonio Lazcano\*

*Facultad de Ciencias, UNAM, Apdo. Postal 70-407, Cd. Universitaria, 04510 Mexico, Mexico*

Orig Life Evol Biosph (2008) 38:469–488  
DOI 10.1007/s11084-008-9150-5

PREBIOTIC CHEMISTRY

### Which Amino Acids Should Be Used in Prebiotic Chemistry Studies?

Dimas A. M. Zaia • Cássia Thaís B. V. Zaia •  
Henrique De Santana



# How could life originally arise from non-living matter?

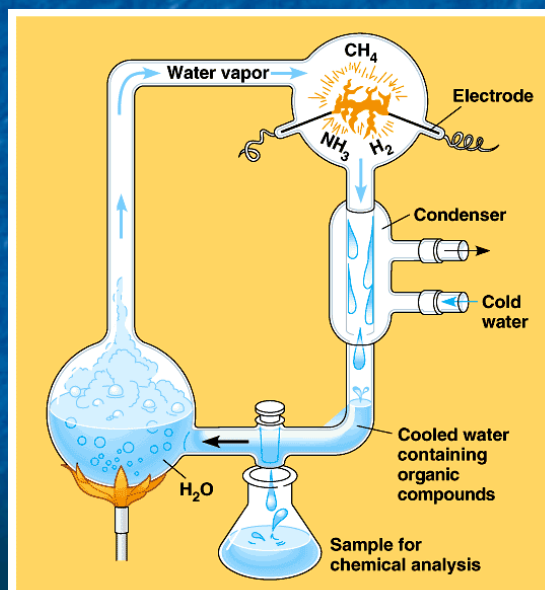
A four-stage hypothesis has been proposed:

1. **Abiotic synthesis of small organic molecules like amino acids and nucleotides**
  - ❖ Plenty of energy available
2. **Abiotic joining of small molecules into polymers**
  - ❖ Proteins and nucleic acids
3. **Self-replicating molecules arise**
  - ❖ Basis for inheritance
4. **Packaging into “protobionts”**
  - ❖ Remember that lipids self-assemble into bilayers in an aqueous environment

## The Miller-Urey experiment: Abiotic synthesis of organics

Figure 26.10

- **Simulated early Earth**
  - Reducing atmosphere
    - $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$
  - Simple inorganic molecules
  - Electric sparks (lightning)
- **Produced amino acids and other organic molecules**
- **Couldn't happen under modern conditions**
  - Oxidizing atmosphere attacks organic bonds
- **Or: possibly Earth was contaminated with organics from space**







## Abiotic synthesis of polymers

- For life to arise, polymers must be able to form without enzymes or cells
- Monomers splashed onto hot rock/clay/sand lose water and polymerize
  - Polypeptides can be made this way
- Imagine waves/rain on lava or deep-sea vents



# Abiotic replication of molecules

- RNA was probably the 1st hereditary material
- RNA molecules can be synthesized abiotically
- RNA can also have catalytic activity (ribozymes)
- In solution with ribonucleotides, a new strand is formed using base-pairing rules; “early-heredity”

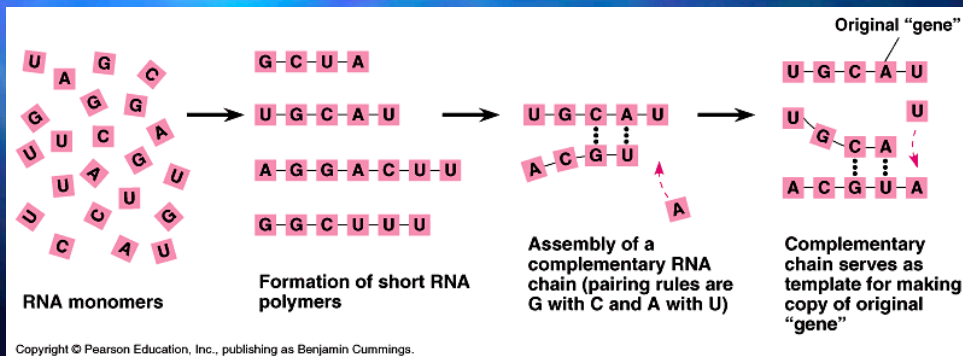


Fig. 26.11

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# Self-assembly of protobionts

- Protobiont = aggregate of abiotically produced molecules that maintain a different internal environment
  - Liposomes = lipids that self-organize into a bilayer
    - Can contain organic molecules
    - Semi-permeable, absorb substrates, release products
    - Shrink & swell osmotically
    - Can have membrane potential (charge)
    - Can fuse and split (“grow” & “reproduce”)
  - Exhibit metabolism and excitability
  - No precise reproduction
  - Not “alive” but exhibit some hallmarks of life



Liposomes can “grow” by engulfing smaller liposomes or “reproduce” by splitting off

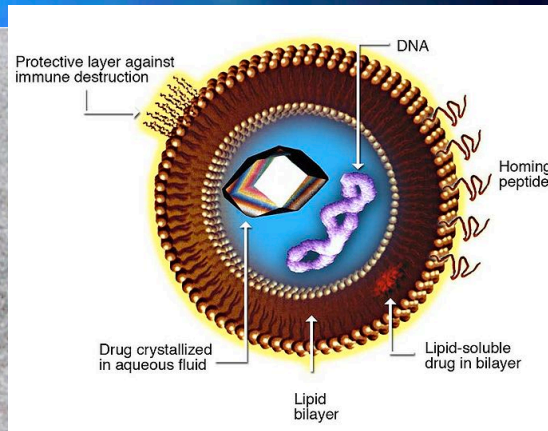
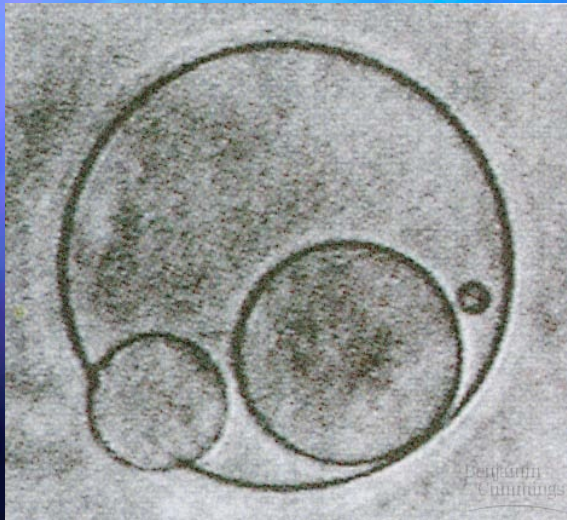


Fig. 26.12a

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Enzymes can be incorporated into protobionts

- The protobionts can then absorb substrates from their surroundings and release the products of the reactions catalyzed by the enzymes
- Containing substrates, active molecules (enzymes) and energy within a membrane is critical to life

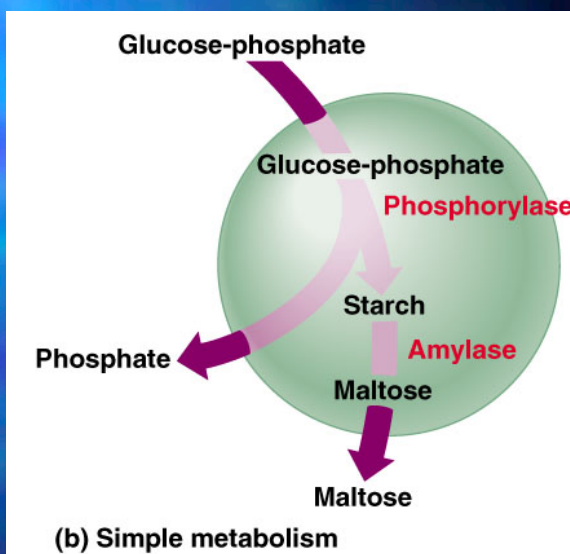


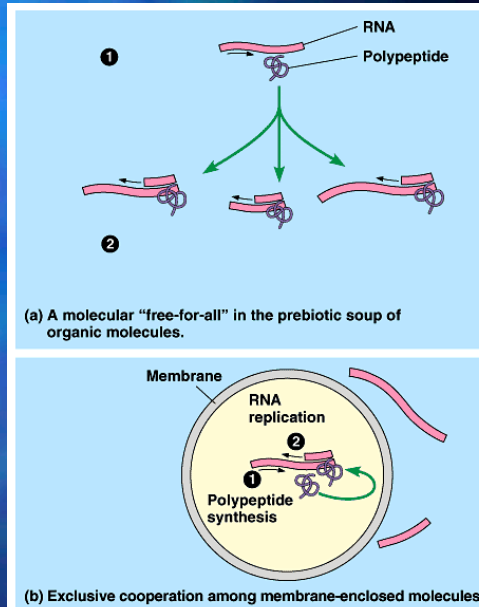
Fig. 26.12b

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## Natural selection of protobionts containing hereditary information, polypeptides, other organics eventually becomes life

- Once primitive RNA genes and their polypeptide products were packaged within a membrane, protobionts could have evolved as discrete units.
- Molecular cooperation could be refined because components & energy were concentrated together, rather than spread throughout the surroundings.



(a) A molecular "free-for-all" in the prebiotic soup of organic molecules.

(b) Exclusive cooperation among membrane-enclosed molecules.

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Fig. 26.13

## A FUNDAMENTAL CONCEPT TO THOROUGHLY GRASP AND REMEMBER FOREVER

- ☼ natural selection is the process by which inheritable traits make it more likely for survival over successive generations
- ☼ always remember to consider the selective pressures at hand



# What is “life” anyway?

- There are really no “biological” reactions that can’t take place abiotically under correct conditions
- Organisms, however, catalyze many reactions that wouldn’t normally occur due to energy required, probability of encounter, accumulation of product, etc.
- Life is the compartmentalization, orchestration, and choreography of chemistry
  - Not all reactions can or should occur at same time
  - Ordering and containing reactants and reactions is key to life
  - Capturing and containing energy is key to life

MAKING THE  
CONNECTION BETWEEN  
‘PREBIOTIC CHEMISTRY’  
AND ‘EXTREME  
LIFE’ ...AKA DEBATING  
THE ORIGIN(S)...



# ORIGIN OF LIFE ON EARTH

**Primordial soup - heterotrophic origin** (*Oparin, 1936*)

Dissipated Structures “*Order Out of Chaos*” (*Prigogine 1980*)

**Submarine Hydrothermal Vents** (*Corliss et al., 1981*)

Mineral World (*Cairns-Smith, 1982*)

**RNA World** (*Gilbert, 1986*)

Thioester World (*De Duve, 1981*)

**Pyrite World - Metabolism first** (*Wächterhäuser, 1988*)

Self-organization and complexity theory (*Kauffman, 1993*)

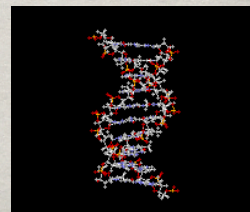
Fe/S membrane, redox/pH front at vents (*Russell, 1994; 1997*)

**Deep, hot biosphere** (*Gold, 1992*)

- *elsewhere out there???*

# ECOLOGY WITHOUT CULTIVATION

- Use molecular biology techniques to:
  - Identify microbial “species” & describe distributions
  - Predict metabolic capacities from genetic information
  - Link microbial “species” with system function; assign functional roles





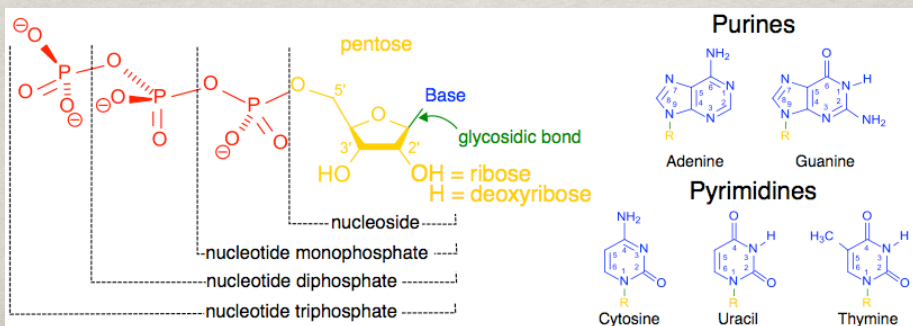
A FUNDAMENTAL CONCEPT TO THOROUGHLY  
GRASP AND REMEMBER FOREVER

## CENTRAL DOGMA OF MOLECULAR GENETICS

DNA----->RNA----->Protein

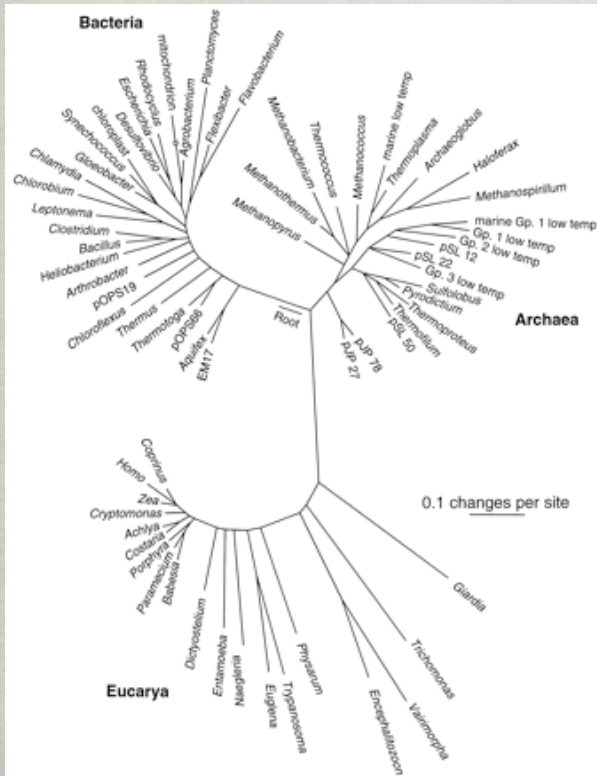
## WHY CLASSIFY USING DNA?

- Present in all known organisms. DNA stores information in genes.
- Genes are discrete sequences of nucleotides. The 4 nucleotides in DNA are adenine (A), thymine (T), guanine (G), and cytosine (C) [AGCT]
- Information in genes is transcribed (written) into ribonucleic acids (RNA). These contain uracil (U) instead of thymine (T) [AGCU]
- The 'message' in the RNA is read (translated) and proteins synthesized in *ribosomes*





# “KNOW THYSELF”



☼ IF there is life out there somewhere else, our best shot at recognizing it and understanding it is to understand as much about the fundamentals of life here on Earth, both present and past.

☼ who? how many?  
where? what? how?  
how fast?

## PHYLOGENETIC TREES

- In a perfect world, we would manipulate and compare whole genomes to determine relationships among microbes
- Not yet feasible
- Must substitute a phylogenetic marker: a gene whose sequence is used to infer phylogenetic relationships among microbes
- MAJOR ASSUMPTION: gene phylogeny more or less reflects the evolutionary history of the microbes possessing the gene of interest