Chemical Evolution Theory of Life's Origins

1. the synthesis and accumulation of small organic molecules, or monomers, such as amino acids and nucleotides.
   - Production of glycine (an amino acid)
     $3\ \mathrm{HCN} + 2\ \mathrm{H_2O} \stackrel{\mathrm{energy}}{\longrightarrow} \mathrm{C_2H_5O_2N} + \mathrm{CN_2H_2}.$
   - Production of adenine (a base):
     $5\ \mathrm{HCN} \rightarrow \mathrm{C_5H_5N_5},$
   - Production of ribose (a sugar):
     $5\ \mathrm{H_2CO} \rightarrow \mathrm{C_5H_{10}O_5}.$
2. the joining of these monomers into polymers, including proteins and nucleic acids. Bernal showed that clay-like materials could serve as sites for polymerization.
3. the concentration of these molecules into droplets, called protobionts, that had chemical characteristics different from their surroundings. This relies heavily on the formation of a semi-permeable membrane, one that allows only certain materials to flow one way or the other through it. Droplet formation requires a liquid with a large surface tension, such as water. Membrane formation naturally occurs if phospholipids are present.
4. The origin of heredity, or a means of relatively error-free reproduction. It is widely, but not universally, believed that RNA-like molecules were the first self-replicators — the RNA world hypothesis. They may have been preceded by inorganic self-replicators.

Acquisition of Organic Material and Water

- In the standard model of the formatio of the solar system, volatile materials are concentrated in the outer solar system. Although there is as much carbon as nearly all other heavy elements combined in the Sun and the bulk of the solar nebula, the high temperatures in the inner solar system have lead to fractional amounts of C of 10^{-3} of the average.
- Ices are similarly much more abundant in the outer solar system.
- Meteorite and comet impacts could deliver much of the Earth's volatile material, especially C and H_2O. At present-day rates, a billion years is needed to deliver the C in Earth's biosphere, but 4 billion years ago, the delivery rate was much larger.
- Some simple organic materials would have been included in this delivered material, as indicated by their presence in the Murchison meteorite.
- A reducing atmosphere on the early Earth would generate more organics.

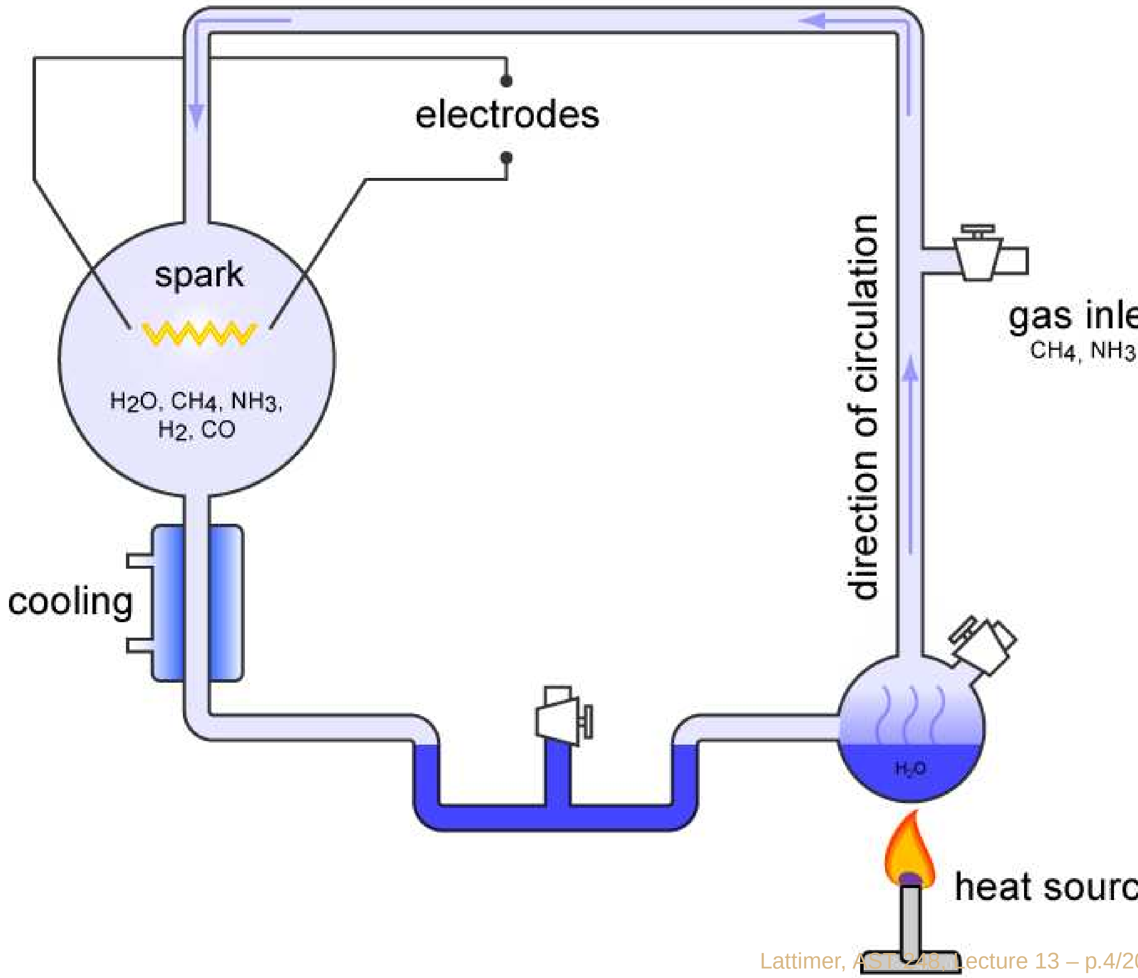
	Role	Life	Murchison meteorite
water	solvent	yes	yes
lipids (hydrocarbons and acids)	membranes, energy storage	yes	yes
sugars (monosaccharides)	support, energy storage	yes	yes
polysaccharides (polymerized sugars)		yes	no
amino acids	many (support, enzymes, etc.)	yes	yes
proteins (polymerized amino acids)		yes	no
phosphate	genetic information	yes	yes
nitrogenous bases		yes	yes
nucleic acids (polymerized sugars, phosphates and nitrogenous bases)		yes	no

Abiogenesis

- Self-organization leads to more complex structure
  Big Bang → atoms → stars → galaxies
- Crucial questions which did not have experimental answers up until now, but new evidence has become evident:
  - Synthesis of nucleotides
  - Polymerization of nucleotides
  - Incorporation of a self-copying gene into single cells upon which natural selection could act
    - "Gene-first" mechanism
    - "Metabolism-first" mechanism
      Primitive metabolism provides environment for later emergence of RNA replication. Example: Wächtershäuser's iron-sulfur world theory, De Duve thioester theory. But can't explain the high specificity of chemical reactions. Thermosynthesis world, involving thermal cycling, suggests an ATP-like enzyme that promotes peptide bonds: the "First Protein".
  - Origin of homochirality
  - Genesis of the protein translation mechanism
- Pieces are now coming together to support plausibility of spontaneous generation
- Minimal number of genes seems to be about 206 in theory, in experiment there seem to be 387 essential genes
- Evidence suggests that this complexity has evolved, step by step, from very simple beginnings

Monomer Production:

- Step 1 is possible in the early Earth's atmosphere if it was was highly **reducing** as opposed to **oxidizing** (*cf.* Miller & Urey experiment).
  Later research cast doubt on the existence of a reducing atmosphere and pointed to a neutral atmosphere dominated by CO_2. More recent evidence is that H escaped very slowly on early Earth and its abundance wasn't negligible after all. Supported by evidence from chondritic meteorites which were Earth's building blocks. Discovery of highly reducing conditions near hydrothermal vents and in volcanos may make this debate irrelevant.
- Energy sources to drive initial chemical reactions available from UV solar radiation, radioactivity, electrical discharges (lightning), cosmic rays and solar wind (Earth's magnetic field not yet formed). Volcanic and vent energy available near hydrothermal vents.

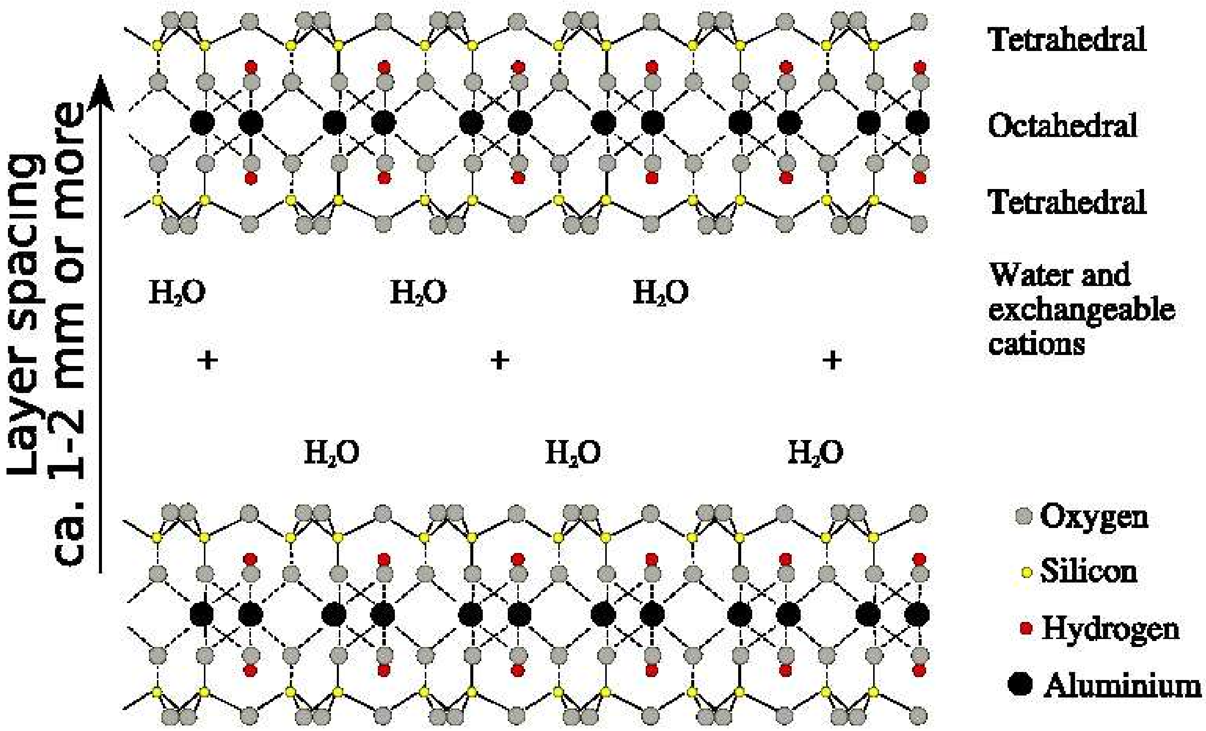


The Role of Minerals

Four key roles minerals could have played:

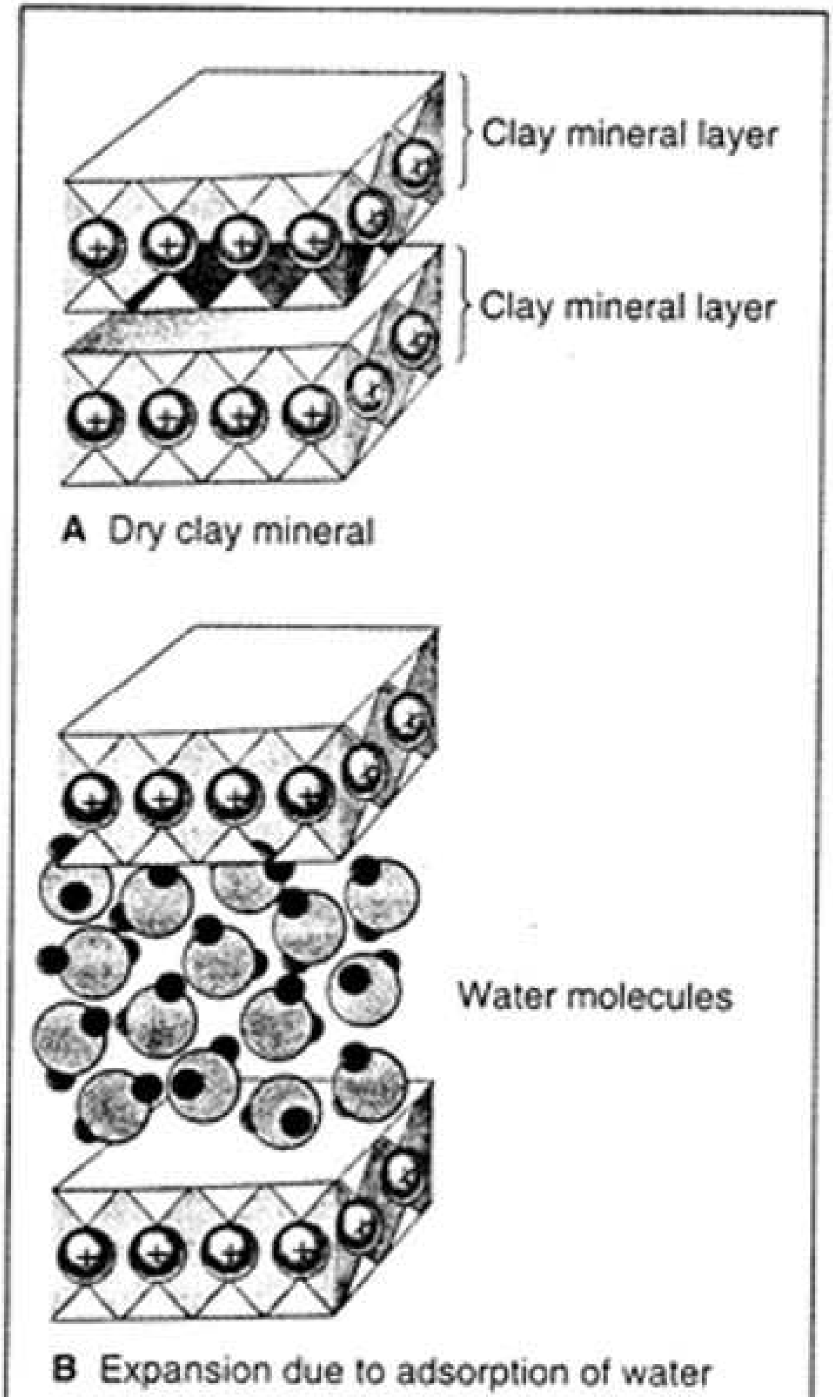
- Protection and concentration
  Minerals acted as hosts, protecting them from dispersal and destruction. Example: volcanic rock containing many small air pockets formed from expanding gases; common minerals developing microscopic pits from weathering.
- Support
  Surfaces act as support structures aiding accumulation and interaction. Example: clays.
- Selection
  Many minerals have crystal faces that are mirror images. Calcite bonds strongly with amino acids, and left- and right-handed amino acids bond to different crystal faces.
- Catalysis
  Nitrogen is important, but most of it is in the atmosphere as nonreactive N_2. N_2 and H_2 passed over metal surfaces can bind and generate NH_3, ammonia, a valuable source of nitrogen for biological reactions. Could have occurred near hydrothermal vents where iron oxide and iron sulfide surfaces are abundant.

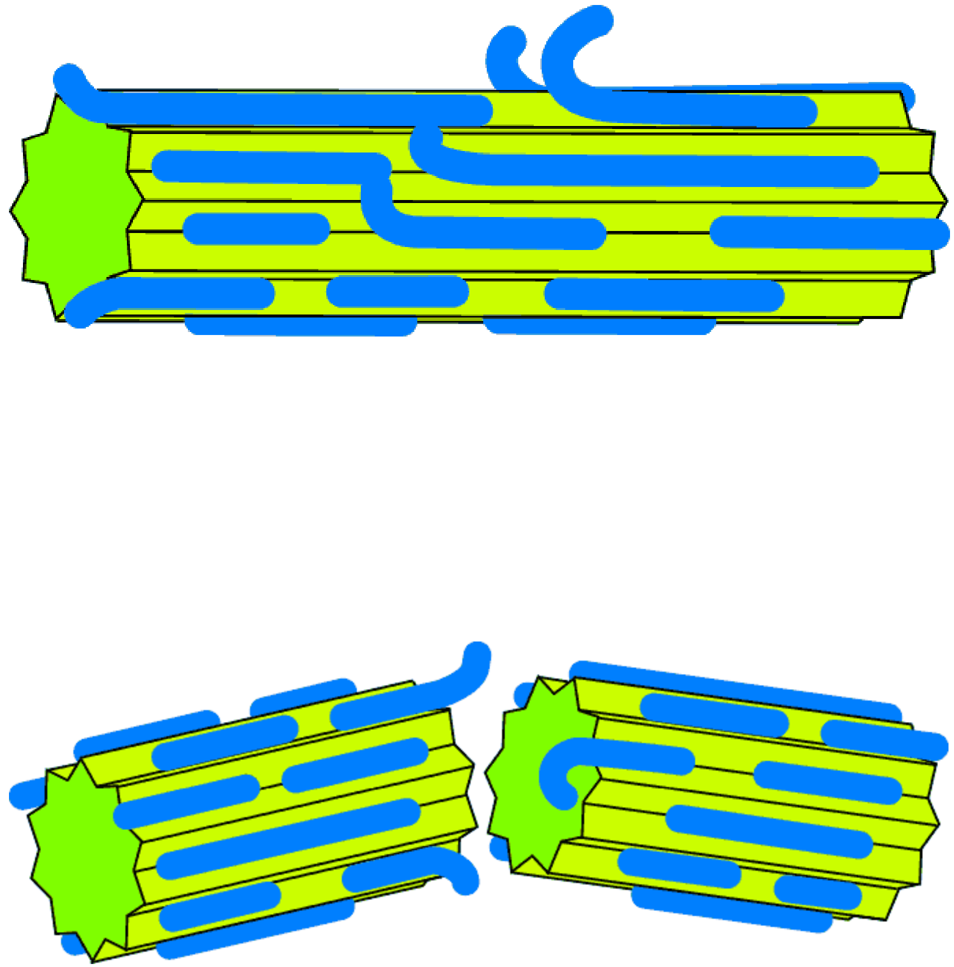
Clays and Polymerization



Andreas Trepte, translated by User:Itub; Wikipedia

- Clay structure is that of alternating negatively charged sheets of Si O_4 and Al O_4 tetrahedra separated by positive cations (Ca, Na, Fe, or Mg).
- Clays are extremely common on the Earth and Mars.
- Charged layers and cations provide multitudinous sites for monomers to stick.
- Water can easily flow through the structure as the layers are separted by 1 mm or more, enabling dehydration.
- A cubic centimeter (thumb-tip) of clay has the net surface area of a football field.
- Many peptide bonds are catalyzed by clays; RNA strands up to 100 bases in length have been produced in laboratories; lipids can be polymerized into pre-cells, sometimes containing short RNA strands.


Clay mineral layer
Clay mineral layer
A Dry clay mineral
Water molecules
B Expansion due to adsorption of water

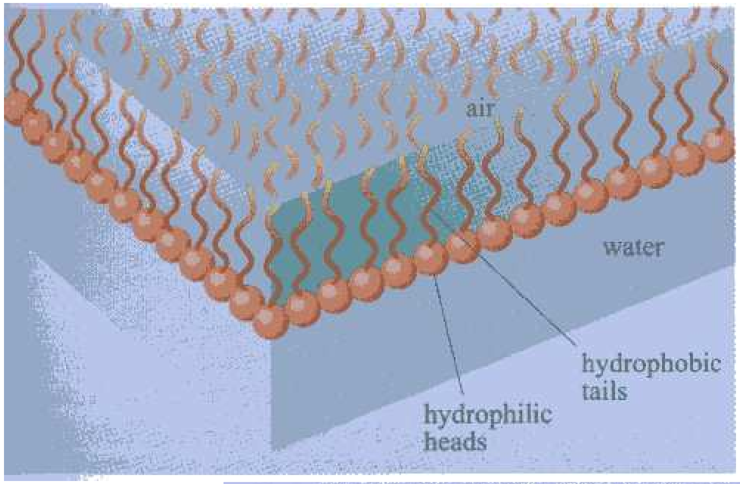


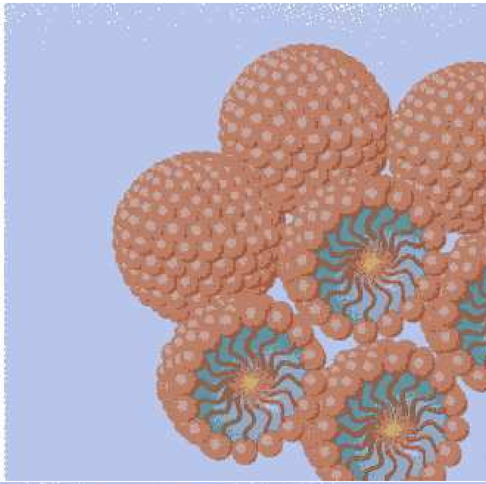
Droplets and Boundary Layers

How does self-assembly occur?

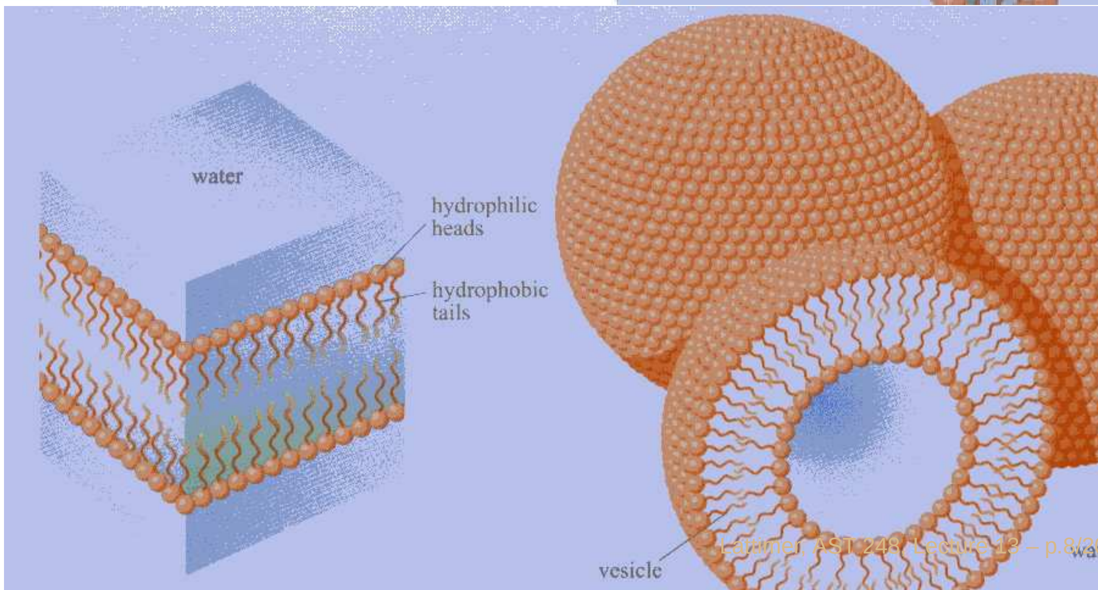
- Certain materials are ambiphilic: they have a polar hydrophilic head and a hydrophobic tail. Hydrophilic materials can be dissolved in water.
- Ambiphilic molecules added to water tend to stay on the surface with hydrophilic heads in the water, creating a single (or mono-) layer, i.e., a membrane.

Formation of spheres, or micells, permits surface area and free energy reduction.





In sufficient concentrations, ambiphilic molecules will form a double-layer structure, or bilayer. Spheres, or bilayer vesicles, will form.

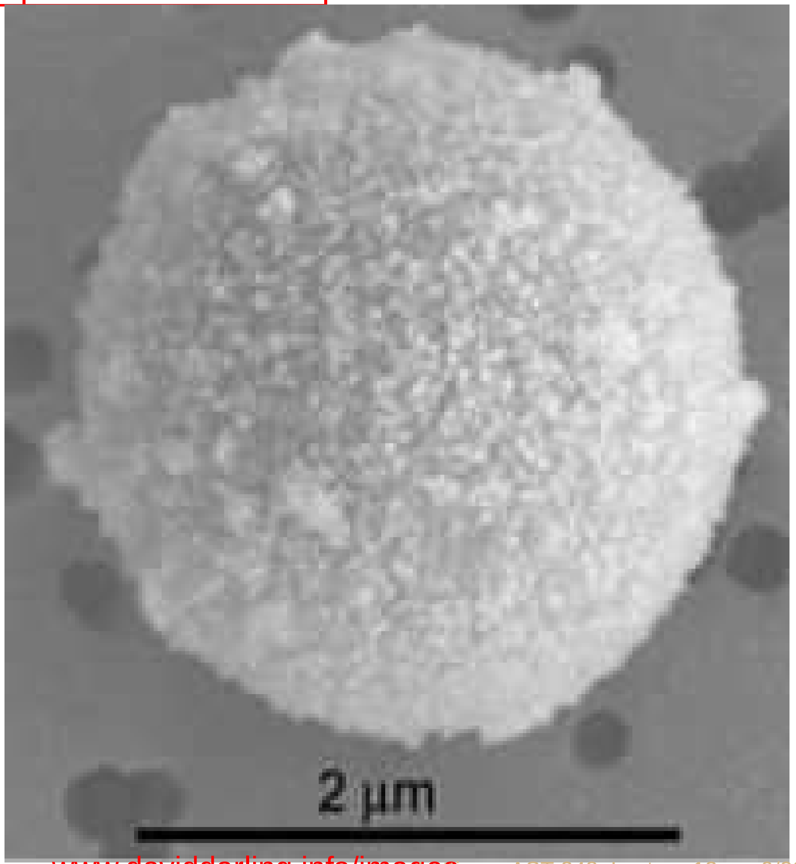


Droplet Formation

- High surface tension of water leads to large drops, not individual molecules

Properties	8 small drops	1 large drop
radius (mm)	1	2
volume per drop (mm^3)	$(4\pi/3) \cdot 1^3$	$(4\pi/3) \cdot 2^3$
total volume (mm^3)	$32\pi/3$	$32\pi/3$
surface area per drop (mm^2)	$4\pi \cdot 1^2$	$4\pi \cdot 2^2$
total surface area (mm^2)	32π	16π

- Polymeric clumps (coacervates) observed
- Phospholipids self-assemble into films forming semi-permeable membranes
- Concentration of polymers
- Existence of enzymes for growth
- Fission forms daughter drops
- Limited raw material, growth enzyme
- Random inheritance of important enzymes
- Keys: Autocatalytic polymers, systematic inheritance



www.daviddarling.info/images

Droplet Formation

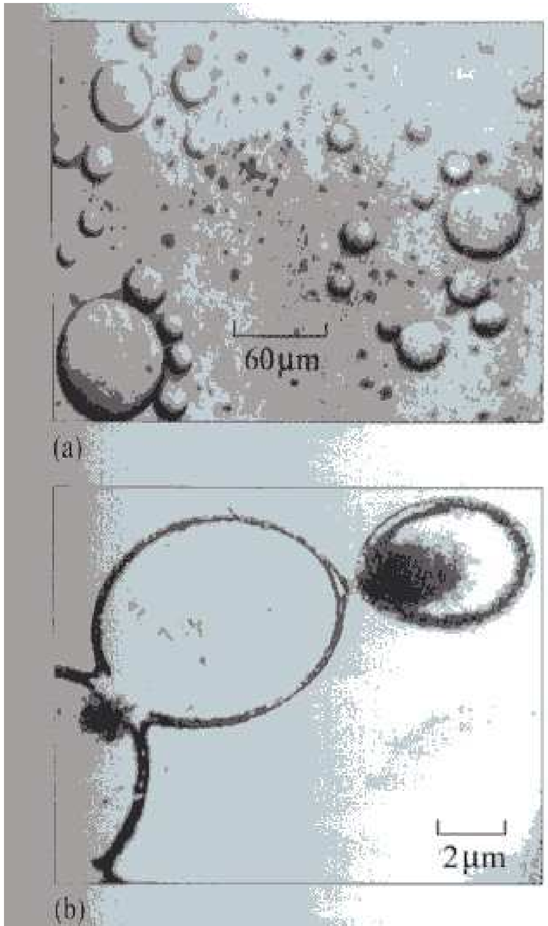


Figure 1.30 (a) Coacervates and (b) proteinoid microspheres. ((a) sourced from www.angelfire.com; (b) sourced from University of Hamburg website)

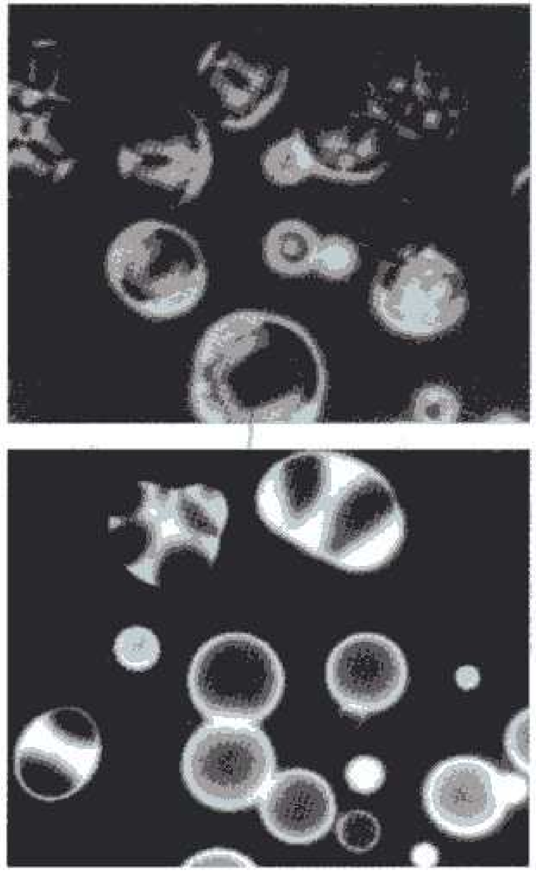
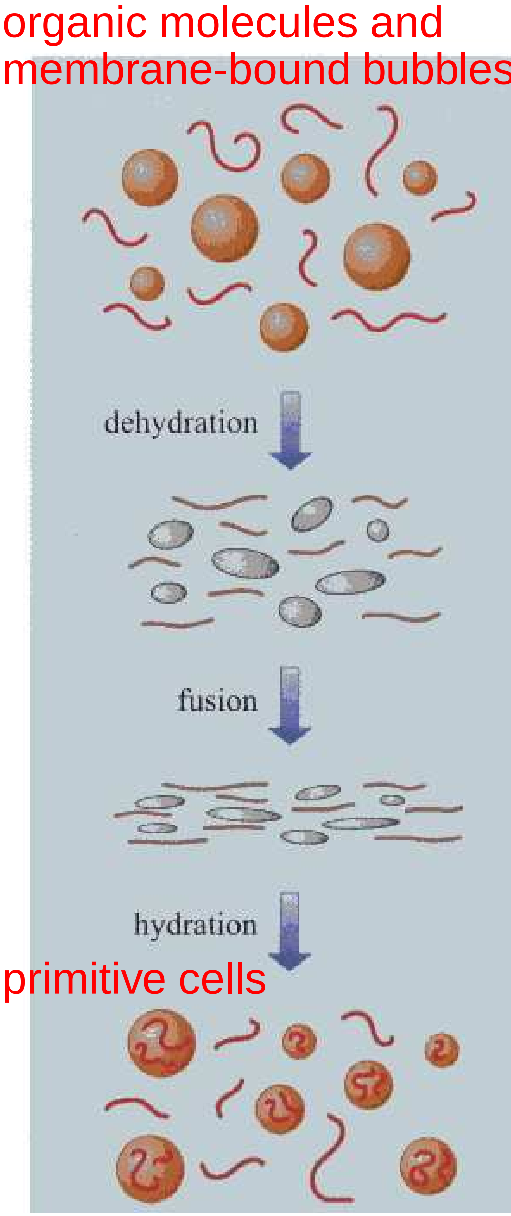
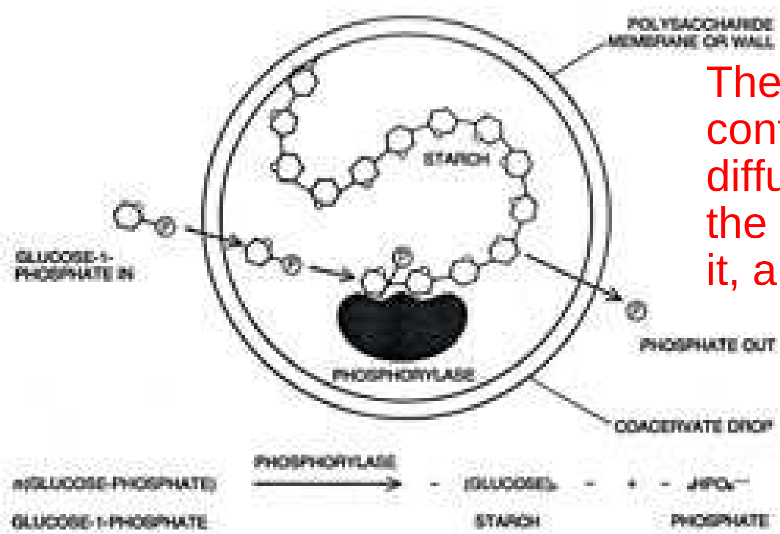


Figure 1.31 Bilayers generated from the Murchison meteorite organic matter. (Dr. David Deamer)

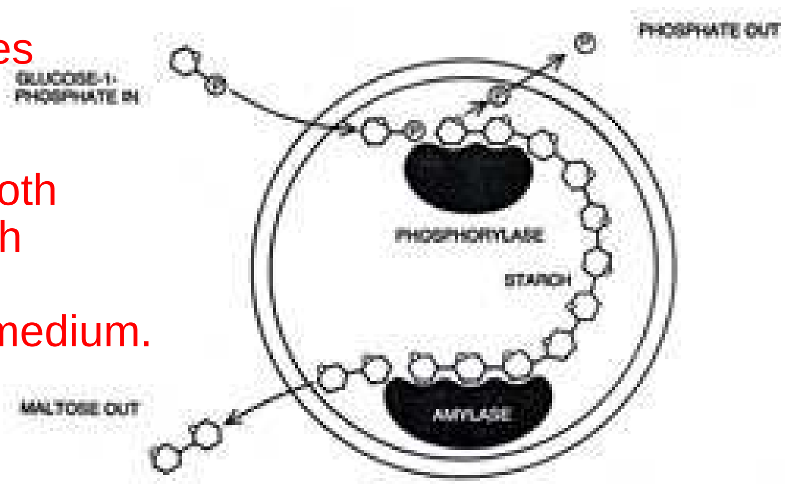


Droplet Growth



The droplet, consisting of protein and polysaccharide, contains the enzyme phosphorylase. Glucose-1-phosphat diffuses into the droplet and is polymerized to starch by the enzyme. The starch migrates to the wall, thickens it, and increases volume of droplet.

The enzyme, phosphorylase, polymerizes glucose-1-phosphate to starch. A second enzyme, amylase, degrades the starch to maltose. Droplets containing both enzymes do not grow because the starch disappears as fast as it is made. Maltose diffuses back into surrounding medium.



instruct1.cit.cornell.edu/courses/biog105/pages/demos/106/unit04/3a.protobionts.html

Why RNA Might Have Been First

- RNA nucleotides are more easily synthesized than DNA nucleotides;
- DNA's greater stability argues it took over some of RNA's roles;
- RNA probably evolved before most proteins because no plausible scenario exists where proteins can replicate without RNA or DNA.
- The molecule ATP is closely related to a monomer of RNA.

This suggests a simpler RNA world existed once, in which RNA replicated and evolved without specialized proteins.

Eventually, RNA became capable of transcribing DNA which is more efficient.

RNA can create DNA, as is illustrated by the example of retroviruses.

Natural selection led to the DNA + protein world which outcompeted the RNA world.

Are retroviruses a dark legacy of our ancestors that can still wreak havoc in the modern world?

RNA World Hypothesis

Prebiotic life has an RNA forerunner if it could:

- replicate without proteins
- catalyze all steps of protein synthesis

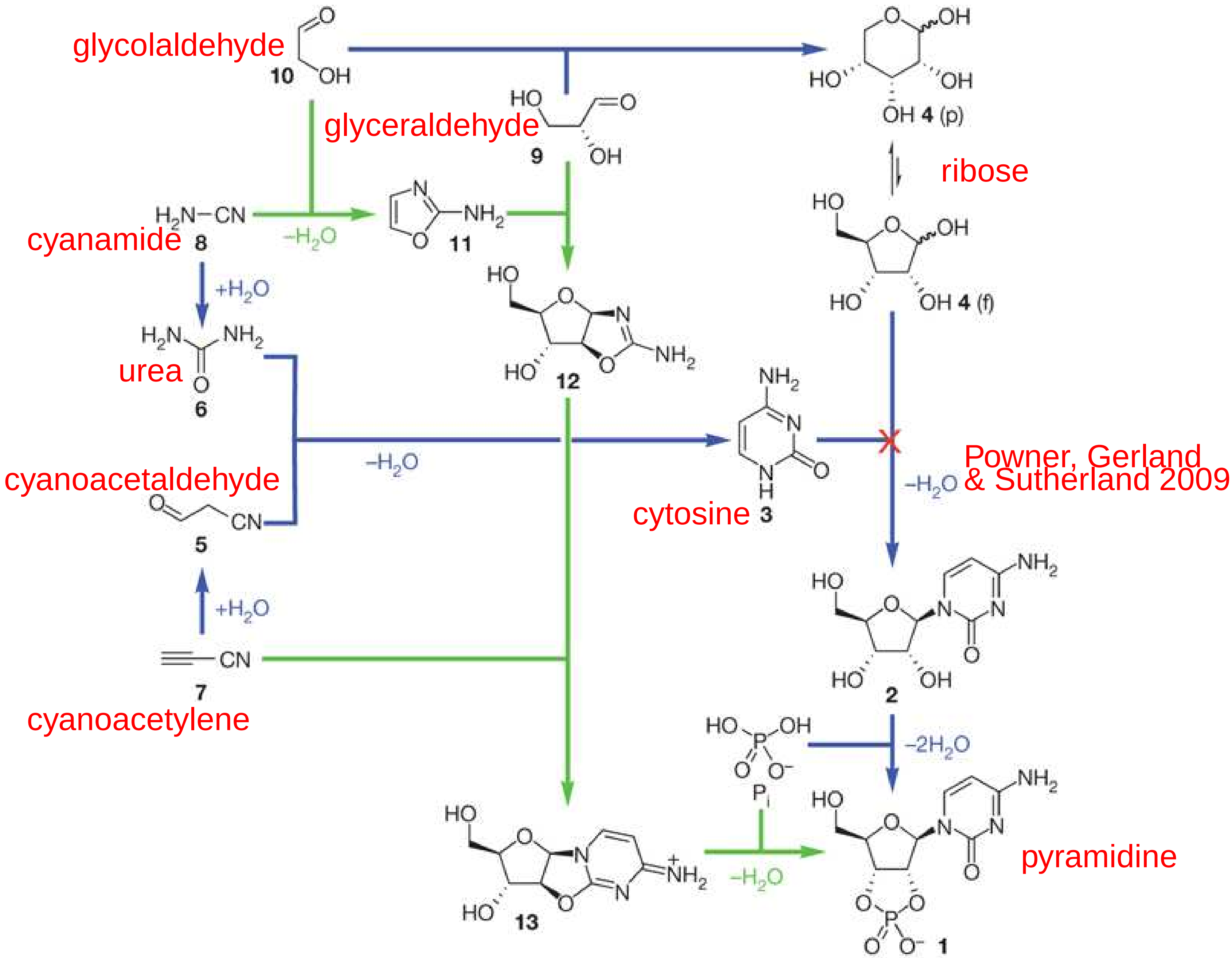
RNA today does not have these properties. However

- Proteins were not first, they can't be catalyzed without gene information
- DNA gene information without catalysis, provided by proteins, necessary for life's functions, is useless

Evidence for the "RNA World Hypothesis":

- New pathways recently found for nucleotide self-assembly
- RNA, not protein, enzymes called ribozymes play a central role in protein synthesis, although proteins also speed up the process.
- RNA is also an important catalyst for the synthesis of new RNA.
- Primitive RNA sequences can evolve under abiotic conditions.
- Unlike double-stranded DNA, single-stranded RNA can take a variety of shapes specified by their nucleotide sequences.
- RNA thus have both a genotype (sequence) and phenotype (shape) that interacts with surrounding molecules.
- Protein transcription in Archaea and Bacteria have different forms implying they independently formed DNA genomes and methods of transcribing DNA into RNA.

Abiotic Nucleotide Synthesis

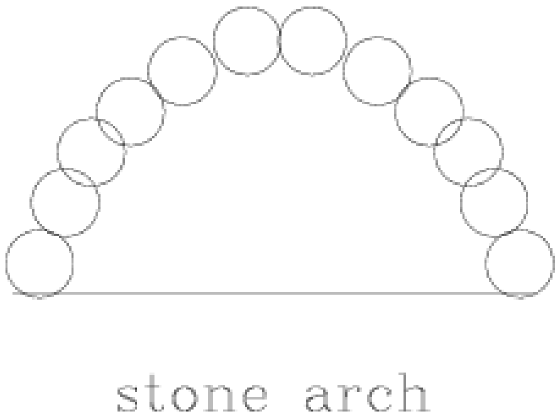


What would happen:

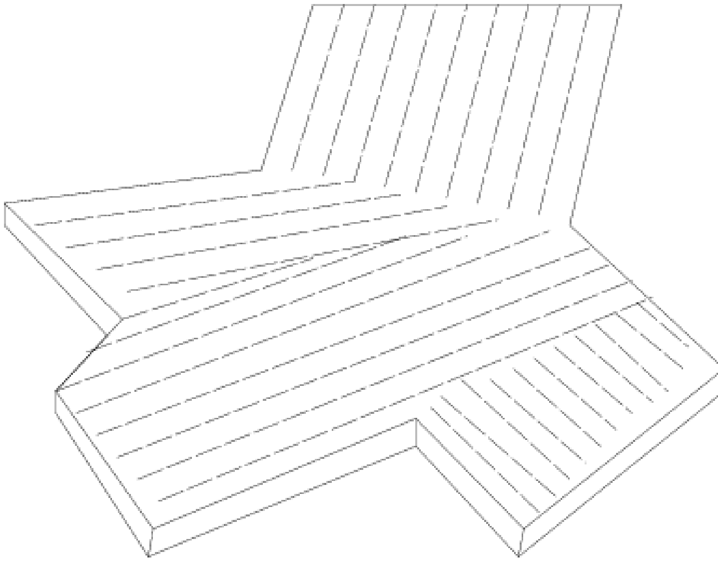
- Reactive nucleotides made random polymers, and the first RNA molecules could have been short, virus-like sequences.
- Inside protobionts, some amino acid polymers could have had rudimentary catalytic properties, aiding in RNA replication.
- Under certain conditions, some RNA sequences are more stable and replicate faster and with fewer errors than other sequences.
- RNA-directed protein synthesis may have begun as a weak binding of specific amino acids to bases along RNA molecules which served as templates holding a few amino acids together long enough for them to link (rRNA does this today).
- Some RNA molecules may have produced short amino acid chains that were enzymes for RNA replication.
- Other RNA sequences may have enabled the use of high-energy molecules like H_2S to provide energy.
- A protobiont with self-replicating, catalytic RNA would dominate the population of molecules.
- The first protobiont would have only limited genetic information, but because thier properties were heritable, they could be acted on by natural selection.
- Mutation (occasional copying errors) and natural selection leads to more stable and faster replicating varieties.
- Natural refinement to replace RNA by DNA as the repository of genetic information; being double-stranded it is more stable and accurately reproduced.

Genetic Takeover Hypothesis

- RNA, nucleotides too complex, evolved from simpler systems
- Interdependency evolved by means of scaffolding



- First organism contained information only; material and machinery for replication provided by environment
- Organic molecules too varied, reversible bonds too weak, to be simple and self-assembling
- Simple inorganic self-assemblers with strong reversible bonds exist: soap bubbles, clay crystals
- Growth naturally controlled by supersaturation
- Life is information: crystal defects



- Information: control of environment (supersaturation, raw materials?)
- Evolution (natural selection) by direct genetic action
- Advantage gained by going to indirect genetic action
- Organic polymers have advantage of efficiency, flexibility, size
- Possible links:
  - Photosynthesis can control supersaturation
  - Amino acids control concentration of metal ions (Al, Mg)
  - Polysaccharides control consistency of solutions
- Gradually, structure & genetic information transferred to organic polymers
- Organic polymers take over. Efficiency and self-assembly work against inorganics

Panspermia or Exogenesis

- Once an outlandish idea, presence of organic material in meteorites and comets implies organic material forms and survives in harsh interplanetary space.
- Discovery of endospores, which might remain dormant for hundreds of millions of years, points to possible long-term survivability.
- Rocks can be ejected into space as a result of an impact's explosion.
- Earth, Moon, Mars and Venus have been exchanging material for billions of years. Over 3 dozen known meteorites believed to have originated on Mars; even more believed to have originated on the Moon.
- Original blast, fiery passage through atmosphere, and exposure to solar wind and cosmic rays in between melts or destroys a relatively thin layer on a meteorite; sensitive, volatile material within is protected.
- Vast majority of projectiles from Venus or Mars will orbit millions of years before landing again on a planet, but 1/10,000 of them will land within a decade.
- Migration from other stellar systems is extremely unlikely, both in terms of number of such meteorites (no known extra-solar meteorites) and in terms of travel times.
- If life is extremely difficult to form, then perhaps it got here by migration. But this just moves the problem of origin to another place. Furthermore, no other location known where formation might have been easier.
- If life is easy to form, life would originate where suitable conditions arose first, and migrate from there. Mars had suitable conditions before Earth.
- If it is possible for Earth life to survive on another planet like Venus or Mars, then it might well be there already because of migration. This means if life is discovered on Mars we have to carefully consider whether it is indigenous or not.

Circumstantial Evidence for Panspermia†

- A relatively narrow time window exists for geogenesis, between LBH 3.9 Gyr ago and the earliest evidence for life on the Earth, 3.5-3.85 Gyr ago. On the other hand, the age of the Universe is about 13.7 Gyr, and abundant C, N and O have been present for 12.7 Gyr. This window for exogenesis is thus about 9 Gyr.
- Existence of extremophiles and ability for dormancy up to millions of years.
- Many potential habitats for life exist outside of Earth within our Solar System (Mars, Europa, Enceladus, Triton, Titan) and, by inference, outside our Solar System.
- Exchange of material within inner Solar System well-documented.
- Disputed evidence for extraterrestrial life, including
  - Red Rain of Kerala: Analyses (2003-6) of dust yielded spores claimed to be extraterrestrial, which “reproduce plentifully” even in “water up to 300°C”.
  - Meteorite ALH84001 from Mars was shown (1996) to contain microscopic structures resembling terrestrial microfossils, but thought by many to be too small to sustain life. Furthermore, abiotic origin is very possible. Recent research into nanobes makes this find interesting again.
  - Several studies (2000-2003) claim to obtain microorganisms from high altitudes (up to 40 km) that are common terrestrial organisms: not inconsistent with panspermia.
  - Claims of bacteria inside meteorites (2001) with non-terrestrial DNA.
  - Lingering suspicions by some Viking lander researchers that positive results in the life experiments were not false-positives.

†Source: Wikipedia

Counterevidence Against Panspermia

- Space is a damaging environment (cosmic rays, extreme cold).
- Studies of ice core bacteria indicate a half-life for dormant DNA of 1.1 million years in a radiation-free environment.
- Occam's Razor says when developing an hypothesis, avoid making unsupported assumptions. On this basis, geogenesis is supported as the simpler hypothesis: life originates as a matter of probability as opposed to being a singular event, or Earth does not meet proper conditions.

Directed Panspermia

- Crick and Orgel proposed life is deliberately spread throughout universe by intelligent civilizations. Cost-effective strategy for seeding life is to randomly send small grains containing DNA. Motivation: avoid catastropic annihilation or to terraform planets for later colonization. Crick later removed his support in favor of the RNA world hypothesis for life's origin.
- Abundant science fiction rationalizations, including the explanation for the improbable tendency for fictional extraterrestrials to be humanoid and living on similar (*i.e.,* class M) planets (a result of genetic codes spread through the Universe by the "Ancient humanoids".