

Chemical Evolution of Life on the Early Earth

All organisms on Earth today use the same four bases in the same genetic code and the same 20 amino acids (out of the hundreds possible). Furthermore they all use the same basic mechanism of DNA-protein conversion (transcription and translation). Even more surprising is that the genes that specify certain functions in vastly different creatures are very similar in their sequence of bases (“homologous”). For example, the genes that determine the formation of the insect compound eye and the eyes of mammals are not that different—they code for the formation of a light-sensitive organ, with structural details filled out in a species-specific manner. The presence of a large number of homologous genes in organisms from the simplest bacterium to the fruit fly to humans, along with the other similarities noted above, suggests that all life originated from a common ancestor long ago. This ancestor may have been much more simple or primitive than even the simplest contemporary bacterium, and probably did not even have the full apparatus (cells, DNA-RNA-protein machinery, ATP energy, ...) of current life. In order to discuss some of the ideas, and problems, about the origin of life, it is crucial to understand what the conditions were like on Earth when the first life appeared, which is believed to be about 3.5 or so billion years ago (see below). First we discuss the Earth’s early atmosphere.

Origin of the Earth's atmosphere

→ Sun surrounded by gas & dusty debris in disk; mostly hydrogen

→ accretion of debris into planets: Earth forms. Hydrogen in atomic or molecular form too light for gravity to hold onto, so most escaped.

→ heating of surface by impact of leftover planetesimals, meteorites & comets

Note: this probably occurred until at least 4 billion years ago (from lunar cratering record), and would probably have wiped out any life trying to form up to that time, although there are “refugia” like the deep ocean or subsurface rock.

Despite this picture of a molten early Earth, there is fairly strong (recent) evidence that the Earth had liquid water at least 4 (and maybe 4.4) billion years ago (from zircon crystals).

→ heating due to radioactive decay---inner parts become molten, get geological activity (e.g. volcanoes)

When did all this occur?

Oldest Earth rock (only lower limit to age of Earth) → 3.8 billion yr. (Isua, Greenland; now evidence for an older, 4.0 Gyr old rock). [Note: rock ages are times since solidification, so lower limits to Earth age.] There are single crystals (zircons) with ages of 4.2 to 4.6 billion yr.

Oldest moon rocks, meteorites → 4.6 billion yr.

[These ages come from radioactive dating. I will go over this technique in detail in the next part of the course, but for now you may just tentatively accept my statement that getting the ages of rocks from radioactive dating is extremely well-founded and there is virtually no way the ages could be wrong by more than, say, five percent and probably much better.]

When did life begin?

Just as it is extremely difficult to find very old rocks because of geological burial, it is even more difficult to find evidence for life in such rocks: such rocks are “metamorphic” and any older than 3.5 to 3.6 billion years (Gyr) old would have been deformed so much that direct evidence for microfossil imprints should have been lost. Microorganisms *do* leave fossilized imprints that can be recognized from their similarity to organisms alive today, and strong direct evidence from such microfossils goes back to at least 2 to 2.5 billion years (Gyr) ago.

There are several less convincing cases for older microfossils. The most famous (now infamous?) case is the evidence for 3.5 Gyr old microfossils presented by Schopf around 1990. Schopf claimed that the imprints in the rocks resembled modern cyanobacteria, which would be amazing because these are complex, photosynthetic organisms; this conclusion was generally accepted until M. Brasier’s group reanalyzed these rocks in 2001 and found that when you “zoom out” on the image of the “microfossil” it appears to be just a segment of a crack in the rock. This and other evidence strongly argues against cyanobacteria at these early times, although the rocks could still have contained life, based mostly on the negative $\delta^{13}\text{C}$ values (see below).

However the conclusion about photosynthesis has been revitalized by researchers who have found 3.5 Gyr rock formations that strongly resemble “**stromatolites**,” which are mats of microorganisms (sometimes called biofilms). Present-day stromatolites are all photosynthetic bacteria, and there is now good evidence that the mats layered in these 3.5 Gyr old rocks were photosynthetic also (but NOT using oxygen—this is called “anaerobic photosynthesis”). Your textbook has some good photos of current and fossil stromatolites.

There is another, widely-used way to test for biological activity, called the $\delta^{13}\text{C}$ test. It is based on the fact that biological activity, in particular the production of organic matter by autotrophic organisms (look it up), preferentially uses ^{12}C over the isotope ^{13}C . The quantity $\delta^{13}\text{C}$ is the measured difference (in percent) in the ratio $^{13}\text{C}/^{12}\text{C}$ between a given sample and the average non-biological value. There is a large range in this ratio for different organisms (graph shown in class), but generally they are between -10 and -40% , with even smaller values occurring for the “methanogen” bacteria.

Analyses of the 3.85 Gyr old rocks from Isua, Greenland, have shown negative values for $\delta^{13}\text{C}$, although the value is small enough that it is arguable. More recent analyses of carbon inclusions in single grains of the mineral apatite from these rocks give $\delta^{13}\text{C}$ between -20% and -40% , which falls well within the biological range. Although it has been argued that there are non-biological chemical processes that could produce small $\delta^{13}\text{C}$ values, nobody has shown that values this small could be produced without biology.

A very recent analysis of lava from a region in South Africa by H. Furnes et al. (2004) claims direct evidence for marine microbial activity at 3.5 Gyr ago in these subaqueous volcanic rocks, based on the presence of certain structures found in the rocks.

So even though Schopf’s claim of 3.5 Gyr photosynthetic cyanobacteria cannot be supported, there is now fairly good evidence for life between 3.5 and 3.8 Gyr ago. Considering that the Earth was supposedly undergoing heavy bombardment until about 3.8 Gyr ago, this means that life took remarkably little time to get going, maybe 0.1 to 0.5 Gyr. Since this evidence probably refers to relatively complex life that underwent the kind of metabolism that can affect $\delta^{13}\text{C}$ and produce characteristic structures, the origin of life may have occurred even earlier.

What was the temperature on the early Earth?

It has always been expected that the Earth was extremely hot during the era of heavy planetesimal bombardment, until at least 4.0, and maybe 3.8, billion years ago. In addition to bombardment, heating of the Earth by radioactive decay must have been about five times higher at that time, contributing to the heating. However there are several reasons for thinking that the Earth was instead cool during this period.

1. The Sun was 30% fainter when it was very young, and the reduced amount of light on the Earth should have resulted in freezing temperatures. This is

considered a major problem because it is hard to see how to get life going without *liquid* water, but it is also hard to see how to unfreeze the early Earth. There has been a lot of work on what kind of greenhouse gases could have kept the temperature above the liquid water limit. Carbon dioxide seemed like a good candidate, since we think there was so much of it (see below), but it turns out that other mineralogical evidence rules out a carbon dioxide pressure large enough to warm the Earth enough. Another popular candidate is methane CH₄, although it is difficult to get enough of it unless there were already methane-producing bacteria (methanogens, still around today) already existing at that time.

2. The existence and morphology of very old (older than 4 Gyr, and probably 4.4 Gyr, see Wilde et al. 2004 Nature) detrital zircon crystals from Western Australia indicate that there was probably liquid oceans in place at that time. In addition, these zircons suggest that some continental crust formed as early as 4.4 Gyr ago, so the Earth's surface certainly wasn't all molten. Finally, studies of oxygen isotope ratios (which are commonly used as temperature proxies) in these zircons suggest that the Earth's surface temperatures didn't change much between 4.4 and 2.6 Gyr ago (Valley et al. 2002), again implying a cool early Earth.

3. Although less direct, it is recognized that it is very difficult to obtain polymerization in liquid water. Some recent work has shown that polymerization of RNA molecules is accelerated if the prebiological organics are within an ice matrix. This ice-scenario also gives some "containment" to the molecules so they can react faster (instead of dispersing off in a liquid). Very recent work even shows that the RNA can self-catalyze its own activities (see below—this was a fundamental discovery that led to the idea of the "RNA world" model for early life) faster in a frozen environment!

So the weight of the evidence seems to point to an Earth that must have cooled very rapidly in order to maintain early oceans, and might have even been frozen.

What was composition of Earth's original atmosphere? (Crucial for Miller—Urey-type experiments)

Clues: 1. Oldest rocks (3.8 billion yr) show no evidence for H-rich atmosphere.
2. He, Ar, Xe, Ne rare in Earth's atmosphere compared to Sun. [Only He light enough to escape.]

→ Earth did not collect much atmosphere from gas in solar nebula. Suspect it was blown away (with the rest of the solar nebula) by strong solar wind. So no "primary" atmosphere!

Two general kinds of ideas about the origin of the Earth's earliest atmosphere.

A. The gases of the early atmosphere were originally trapped within the solid crust of the Earth, and then released ("outgassed") either by **volcanoes** or by violent **planetesimal impacts**. Another alternative is **hydrothermal vents** on the ocean floor, which today cook up a lot of organic molecules.

B. The early atmosphere was delivered by **comets**. Comets are ices + frozen gases and when they strike the Earth the ices melt and the frozen gases vaporize (become gaseous). We know comets impact planets today (Comet Shoemaker-Levy 9 collision with Jupiter in 1994), and rate was almost certainly enormously larger billions of years ago.

Both types of processes can yield enough gas to account for our atmosphere (probably much more), and give a similar result, which is notably different from today's atmosphere. Let's look at the first process in more detail.

Outgassing (volcanos & heated rocks)---

trapped ice → gas. Studies of today's volcanoes show the emissions to be H₂O, CO₂, H₂S, N₂. But *not* (or at least very little) NH₃ or CH₄ and *no* O₂. "Mildly reducing"

➡ H₂O: oceans and some H₂O + solar UV → H + H + O →

O₂ (~1%) + small amount of ozone O₃ (but not enough for UV protection)

➡ CO₂ dissolved in oceans, then incorporated in rocks. This means original atmosphere was probably much more massive than today's.

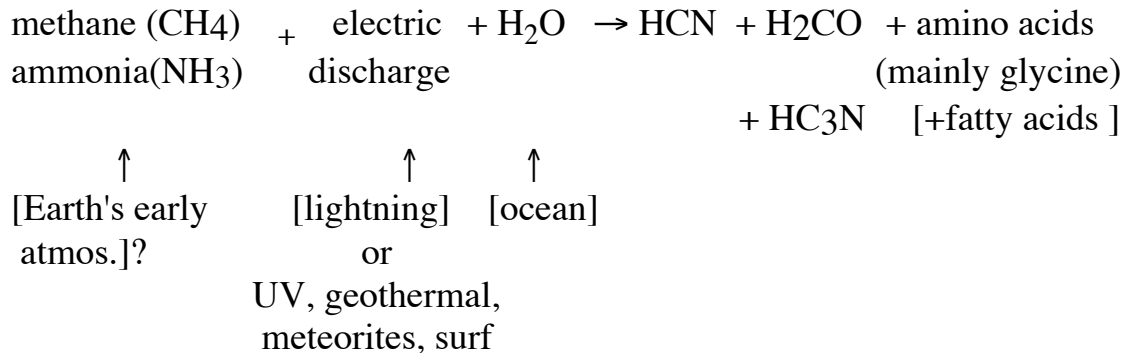
➡ N₂: unreactive; eventually dominated. (Today's creatures use the energy of the N₂ bonds, but then return N₂ to the atmosphere, through a complex and interesting process called the "nitrogen cycle.")

Most of present-day O₂ (21%) *probably* came from primitive plants converting CO₂ → O₂ thru photosynthesis → No substantial free oxygen until life existed. *Then* got significant ozone, which made the land and upper ocean habitable. (See graph shown in lecture.)

Support for this idea:

1. Minerals *older* than 2.5 billion yr. are oxygen-poor
 2. Stromatolites---colonies of blue-green algae; appear at 2.0--2.3 billion yr. ago, not before. Current blue-green algae use oxygen. (Note: there is evidence for NON-oxygenic photosynthesis at earlier times from fossil stromatolites.)
- Production of monomers** = {sugars, phosphates, bases}, and amino acids

Miller--Urey experiment [don't need to know any detailed chemical reactions]



This looked good: Besides getting amino acids (building blocks of proteins), also can get 5 H₂CO + heat --> ribose sugar, and 5 HCN (hydrogen cyanide) ---> adenine (a base of nucleic acids).

There have been hundreds of such “gas-discharge” experiments since then. They have produced not only many of the amino acids used by life, but also the four bases (A, C, G, U) used by RNA and sugars (including ribose, although in small amounts).

The problem is that nearly everyone agrees that there is no evidence that the early earth had such a “reducing” (rich in hydrogen compounds, esp. ammonia and methane) atmosphere. Volcanoes today emit mostly carbon dioxide (CO₂), nitrogen (N₂), and water vapor, but no ammonia or methane. With no hydrogen to react with, CO₂ and N₂ cannot make HCN, which is crucial for the production of the most interesting prebiological molecules. If a little H₂ is added (volcanoes do emit a small amount of hydrogen), some amino acids are produced in spark-discharge experiments, but with greatly reduced yields. So for chemical synthesis a la Miller-Urey to produce the monomers of life, the Earth’s atmosphere would have had to be highly reducing (H-rich), and there is no evidence for this. You *could* get some methane from hydrothermal vents on the ocean floor, and from comets. Ammonia + nitrogen react to give HCN and hydrogen, and this could have resulted in a little methane. So there are ways to get a *mildly* reducing early Earth atmosphere, but not as reducing as assumed in Miller-Urey-type experiments that give large yields of amino acids and bases.

But we know it can't be *too* difficult to get amino acids and nitrogenous bases, because these have been found in meteorites, and the bases of RNA and DNA have been observed in the tails of comets.

This suggests another way to get the simpler organic molecules into the early Earth atmosphere: they were (and are) delivered to the Earth by **comets**. This is called "exogenous delivery." Organic molecules have been known to exist in comets for a long time, but no one calculated the rate of delivery to the earth until fairly recently (~1990). It has even been suggested that comets (which are mostly H₂O) were the source of Earth's oceans! Other scientists prefer other icy planetesimals early in the evolution of the solar system (But rates of early impact delivery are very uncertain.)

But a problem here is that large bodies (say 100km—these would be asteroids, planetesimals) hit the ground at high speed, leading to very high temperature on impact; so organic molecules couldn't survive. At somewhat smaller sizes (like smaller cometary meteors) they burn up during their descent before hitting ground. However smallest interplanetary dust particles (IDPs), with sizes around 1-100 microns (tiny) can make a "soft landing." IDPs have been found to have large organic content, and their number, extrapolated to 4 billion years ago, seems sufficient to build up earth's biomass in a short time. But the production rates are not much more than you'd get from "endogenous" (Miller-Urey-type, or maybe hydrothermal vents...see later) synthesis in a mildly reducing environment, at least according to some.

But big problems for Miller-Urey (and similar) scenarios:

1. Earth's early atmosphere probably wasn't strongly reducing. (This isn't such a problem if comets deliver the organics.) Some people have suggested seafloor vents + geothermal heat ("**geothermal vents**" or "deep sea fissures"), since these vents emit reduced gases, and strange micro-organisms live there. Sulfur chemistry would then also be important. In this model organics are produced deep in the ocean, not in the atmosphere. But decomposition of *monomers* at these high temperatures is a problem.

2. How to produce polymers (proteins, nucleic acids)?
The gas-discharge experiments only produce monomers (if conditions are right), but none produce the long chain molecules that are the ultimate basis for life on

Earth. This is a problem with all ideas for the origin of life, whether energized gas from volcanoes and comets, or hydrothermal vents.

We want $M_1 + M_2 \rightarrow \text{polymer} + \text{H}_2\text{O}$. But the *reverse* is more likely in the ocean (look at the reaction in reverse). So must get rid of liquid water *and* need energy source.

Possibilities:

1. Hot tidepools (e.g. on side of volcano) \rightarrow “proteinoids” = long polymers of amino acids; self-ordering? \rightarrow “microspheres”? (Sydney Fox)
OR tidepools \rightarrow nucleosides (base+sugar) \rightarrow RNA?

This is usually called the “RNA World” model

2. Something analogous to, but simpler than, ATP energy (complex energy-producer in present-day organisms), e.g. HC_3N (see above) \rightarrow energy-rich triple bonds; i.e. metabolism before reproduction; could get metabolism first (“hypercycles”), before replication--“genetic takeover” occurs later.
3. Clays---layered silicate rocks, water between layers. Experiments show certain clays promote polymerization into chains of more than 50 amino acids. Cairn-Smith's “living clay” (to be discussed in more detail below); again get organic, genetic takeover later. Most people agree that polymerization into *short* polymers (called “oligomers”) is greatly facilitated on silicate surfaces.
4. Hydrothermal vents—some of the most ancient microorganisms thrive there, and it has the reducing environment lacking in the Earth’s atmosphere, but the bases of RNA, DNA are very unstable at high temperatures, and should break down. This is a big problem for this model.

Now we’ll go into more detail.

Now consider the question of the transition to “life”.

The major problems:

1. How could very long sequences arise by chance?

It is unimaginably improbable to get the long RNAs that exist today by chance.

Consider: 10 coins. What is probability of all heads? Product of individual probabilities, $p=(1/2)(1/2)(1/2)\dots = (1/2)^{10} = 1/1024$.

Now think of same problem for getting the correct sequence (i.e. a particular order-it doesn't matter which) of 10 amino acids to code for a protein, where the

amino acids are chosen from the 20 amino acids. This probability is $(1/20)^{10} = 10^{-13}$. That's a small number, but if there were enough molecules and enough time for 10^{13} tries, it could occur. But proteins contain many more amino acids than this. To get 200 amino acids in the right order the probability is $(1/20)^{200} = 10^{-120} \Rightarrow$ hopeless!

The situation is even worse when you consider nucleic acids. What if we want a particular sequence of bases (i.e. a gene) that is “only” 1000 bases long? If each position in the polymer can be occupied by one of the four different nucleotides, the probability is $4^{-1000} = 10^{-602}$!

So you need *something* to improve the odds. Solutions include

- a. An original genetic code that had only, say, two bases, and coded for very short proteins;
- b. Some kind of “emergent self-organization” process as theorized for other (simpler) complex systems;
- c. Having intermediate levels of structure, like the protein domains. In this case, would only need to get enough amino acids in right order for a domain (say 18 to 250 amino acids).
- d. A catalyst enzyme (a “replicase” -but these are long proteins, so how could they have arisen?);
or (favorite candidate)
- e. Natural selection acting on mutations at the molecular level. We'll see below that this has been demonstrated in the laboratory.
- f. Something to speed up the reactions, like cellular enclosures coming first.

2. The 2nd major problem is: how did the gene-protein linkup occur?

In today's organisms, you don't get replication without proteins, but proteins serve no function without the genes that code for their formation. Apparently this is too complex a setup to be a candidate for the earliest life. In that case, which came first? You should appreciate this first “chicken and the egg” conundrum.

1. “Naked gene” or “random replicator” theories.
1st need nucleosides (= base+ sugar)

RNA world? Recall the huge difficulties in getting to the RNA stage (chance problem, polymerization, error catastrophes, nucleoside formation,...). Also, ribose and other sugars are very unstable.

Doubt also arises because it seems too unlikely to get a *self-replicating ribozyme* without evolution by natural selection, but there can't be any evolution without replication: another chicken-and-egg conundrum.

(Recall that in the 1960s Orgel got a replicator without using an enzyme, but

then the “copy” couldn't make another “copy.”)

The major problem: gene-protein linkup---which came first?

Also: why 20 amino acids? Why chirality? Why “junk DNA” (introns)?

1. “Naked gene” or “random replicator” theories.

1st need nucleosides (= base+ sugar)

→heat sugar + bases + salts → suggests drying tidepools

But then must polymerize the nucleosides. Tough!

Spiegelmann: Q β virus + enzyme + free nucleotides → “Spiegelman monster”

(w/long RNA)

This was an extremely important experiment because, even though it didn't show how life could begin (it already used a virus), it *did* demonstrate evolution occurring at the molecular level, something which has been used to evolve special-purpose bacteria, etc. in the laboratory ever since.

Eigen: enzyme + free nucleotides + salts → short RNA random replicator. Eigen called this proto-life a “quasi-species” but also showed that it could not grow longer than about 100 nucleotides because of an “error catastrophe” associated with the mutation rate. (Eigen won Nobel prize for this and related work.)

But both S. & E. started with proteins.

Orgel: RNA can form a double helix without any protein. But then stopped.

Cech *et al.*: self-catalytic RNA--RNA can cut up different RNAs, acting as an enzyme. It can also join short RNAs into longer chains. (Extremely influential result; gave rise to term “RNA World”--see dense 1993 proceedings by that title, ed. Gesteland and Atkins, for activity in field.)

1994: Joyce *et al.* made synthetic RNA that can copy itself (given the right proteins).

1997: Two studies in Jan.21 Proc.Nat.Acad.Sci. claim experimental evidence related to enzymes that convert between RNA and DNA.

2001 (Johnstone *et al.*): RNA shown to catalyze its own replication without enzymes. It only replicates *part* of itself, but still, it is very suggestive.

Gilbert: first wrote about the likelihood of an “RNA world” and how it might evolve---self-catalytic RNA forms, eventually synthesizes (“discovers”) proteins as better enzymes. This is illustrated in your book.

Eigen’s version:

1. Random replicator RNA forms by change in “soup”
2. RNA learns to control proteins → primitive genetic code
3. “Hypercycles”---cooperative interactions between RNAs & proteins.
4. Random mutations & competition among hypercycles leads to prototypes of modern cells.

Problems with gene-first theories (now often called “RNA world” theories):

1. How does 1st RNA form by chance encounter between ~100 nucleotides?
 2. Water opposes polymerization reaction.
 3. Error rate too large for short base length. But to get longer, need enzyme. (“error catastrophe”) How to make enzyme from short RNA?
- Neisser---computer experiments discovered 3 more “catastrophes”

Pre-RNA candidates

a. PNA (peptide nucleic acid) – This nucleic acid, designed and synthesized by P. Nielsen (1993), has a peptide backbone instead of one made of ribose+phosphates. It is a polymer of a molecule called AEG. Nelson, Levy, & Miller (2000) showed experimentally that the *components* of PNA are synthesized under spark discharge and other possibly relevant prebiotic conditions. But the yield is only $\sim 10^{-5}$ using spark discharge in a gas of CH_4 , NH_3 , N_2 and H_2O . Also produced amino acid glycine as a product (as usual for this type of Miller-Urey setup). They suggest even larger yields of AEG on primitive Earth because it is known that yields of ED (ethylenediamin – part of AEG) under UV acting on $\text{CH}_4 + \text{NH}_3 + \text{water}$ is very large ($\sim 33\%$!).

Notice that one argument against $\text{CH}_4 + \text{NH}_3$ is that they are easily broken up by UV, and the H would escape (e.g. Sagan & Chyba 1997). But it is just this property that may have been the dominant source of ED and AEG.

Still, have to show how to polymerize the resulting components, a problem for any early genetic system. They cite preliminary results that AEG polymerizes into AEG short polymers efficiently. But there is still the problems of the instability of ribose (if that was used – see below) and the decomposition of nucleosides at high temperatures around 100°C (*if* life was exposed to high temperatures).

And, still have to account for PNA replication! So even if PNA *was* synthesized efficiently on early Earth, the problem is far from solved!

b. pRNA=pyranosyl-RNA. A. Eschemoser designed this molecule. He used a sugar that is slightly different from ribose sugar, 5C + 1 O rather than 4C + 1 O. The RNA-like strands containing this component (called pRNA) can base-pair just like regular nucleotides. Eschemoser has apparently shown that it can copy parts of itself (I'm unclear on this).

c. Another idea is that the first genetic code was different from the present one. It is generally thought that the present code evolved in such a way as to reduce mutations and translation errors in cells, although there are several theories (see DiGiulio 1997, *J. Theor. Biol.*) In fact many people think that the first code may have only had 2 or 3 bases instead of 4. Levy & Miller (1998) showed that G and C are very unstable at high temperatures (think: hydrothermal vents, tidepools on sides of volcanoes) and suggested that the first genetic system was a two-letter code like A and U, A and T, or A and I (inosine). (This idea goes back at least to

Crick 1968 and Orgel 1968). This also helps with the “chance problem”. But there is still the difficulty of forming pyrimidine nucleosides, at least in the laboratory. So maybe different bases in kind, and not just number.

A number of alternative base pairs have been proposed (see Levy & Miller 1998 for references). An example is urazole – a 5-membered ring substitute for the 6-membered pyrimidine base uracil. Miller's group has found that this base can be easily linked to ribose to form nucleosides. An interesting property of urazole (and guanazole, another proposed substitute base) is that it is transparent in the ultraviolet region of the spectrum where the RNA/DNA bases are most susceptible to damage and degradation. There would have been a strong selective advantage for such nucleic acids on the early Earth because of the absence of an ozone layer. So they would have offered protection.

There are other pre-RNA world candidates, like energy-driving substitutes for the phosphates (“PPi”); another RNA substitute called TNA; sulfur-containing derivatives of simple organic acids called “thioesters” (see books by Christian de Duve). This last “thioester world” idea is becoming a rich area for research chemists. If organic acids were converted into thioesters in sulfide-rich regions near volcanoes (a process that has been seen in laboratory experiments), the thioesters could trigger the formation of “multimers” (something like polymers, but not necessarily regular chains). “It seems that sulfur, belching out of the vents and volcanoes of the early Earth and transformed into many highly reactive compounds, played a significant role in the origin of life.”

2. Try to make proteins first

Early work: Oparin made "coacervate droplets", but the seed polymers were from living things.

More recently: Sidney Fox: Proteinoid microspheres

Fox heated (dry) amino acids (maybe in deserts, volcano rims)

→ proteinoids (or "thermal proteins")

dissolve proteinoids in warm water, cool slowly → microspheres (protocells?)

Pro: sizes and appearance like single-celled organisms (your book has an photo of a proteinoid microsphere)

catalyze chemical reactions

surfaces like cell membranes

can produce electrical responses "like nerve cells"

sensitive to light

can "proliferate" (fission & form buds) & evolve by natural selection

Con: Many tiny inorganic particles have these traits

main problem → They don't grow, **reproduce**, and evolve in the same way as living things (by copying their own internal organization)

Also: Many are biased against the "protein-first" idea simply because they work on nucleic acids! See Sidney Fox, *The Emergence of Life: Darwinian Evolution from the Inside* (1988, Basic Books).

Dual origin theories (Shapiro, Dyson): Note: these violate the "Central Dogma of Molecular Biology."

More recently: Oil molecules. Some of these (e.g. mayonnaise oil) form, in the presence of water, cell-like "vesicles" or "bubbles". The bubble membrane separates it from environment, allows chemicals to "brew". Some people see this as the first step in the origin of life, not a later development.

A relevant experimental result: Keefe et al. (Feb.23 1995 Nature; this is S. Miller's group) synthesized pantethine in a setting like evaporating bodies of water besides beaches and lagoons. Pantethine is part of a larger molecule, "coenzyme A", which helps link amino acids together. The reaction could occur at temperatures as low as 40 degrees C.

3. Clays as the first life (Cairnes-Smith)

silicate rocks: $\text{SiO}_2 + 4\text{O} (\text{SiO}_4)^- + \text{Mg, Al, Ca, ...}$

clay minerals: layered silicates (e.g. mica, kaolinite)

They grow by stacking "sheets" or "pages."

Imperfections are copied → replication of a pattern of imperfection, i.e. information storage

Sometimes errors in replication → mutation, natural selection

→ Don't need special atoms, soup, or energy. No great leap in organization.

Mineral communities; use "apparatus"; eventually experiment with organic construction materials. Then dual clay-organic genetic systems, then organic takeover.

See Cairns-Smith, *Genetic Takeover and the Mineral Origin of Life* (1982), and *Seven Clues to the Origin of Life* (1985).

Even people who don't like the "non-organic life" idea now admit that mineral surfaces may have been crucial in forming polymers long enough for self-replication (without the copying error catastrophes). e.g. Experiments by Ferris et al. May 2, 1996 Nature: produced long "oligomers" by pouring solutions of amino acids and nucleotides over a clay and two other minerals, then evaporating; repeat many times.

In models like this, "polymers of life were more likely to have been baked like prebiotic crepes than cooked in a prebiotic soup."

Also: Recent work by lawyer/chemist Wachterhauser on iron pyrite (fool's gold) as basis for "metabolism-first" model of origin of life. But actually, if you read about this model, you'll see that although it does use a mineral as its basis, it is far less radical than the Cairns-Smith silicate rock idea. The electric charge at the surface of the mineral is used to energize the chemical reactions and polymerization.

4. Hydrothermal vents and the origin of life—discuss in class.

An Infected World?

~1850: Pasteur

Panspermia (Arrhenius ~1900)

propelled by stellar radiation pressure?

suspended animation?

protection against UV and cosmic rays?

Directed panspermia (purposeful seeding: Crick & Orgel)

motivation: would greatly increase number of planets with life!

Continued influence (Hoyle and Wickramasinghe)

Bacteria, viruses carried in comets, interstellar clouds (Hoyle's SF "novel", *The Black Cloud*)

Controls evolution? Epidemics?

Main argument:

Uniformities in Earth life:

→ same nucleic acid, genetic code, set of amino acids, handedness of amino acids, sugars.

Which of the following is the more plausible explanation?

Common ancestor drove *all* others to *complete* extinction?

or

Uniformity indicates only one plan ever available? (Panspermia)

Unfortunately the evidence that Hoyle et al. (now the Cardiff Center for Astrobiology) tried to use for this was poor, and led to the idea's disrepute.

Today: It is established that transplanetary transport of rocks does occur (e.g. the "Martian meteorites," whether or not they have traces of Martian life—we'll discuss this in the next section of the course), and that some prebiotics, and maybe biological molecules, were comet-delivered. So not so "quacky" any more, although restricted to our solar system.

A major problem for this theory: relative abundances of trace elements is about the same in living things as in Earth's oceans. But of course if Earth's oceans were delivered here by comets...