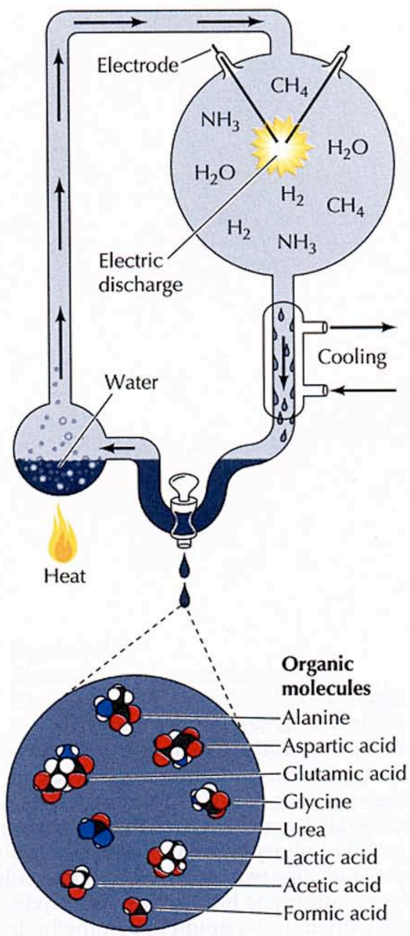
Laboratory Experiments:
Miller-Urey & beyond

Spontaneous formation of organic molecules Water vapor was refluxed through an atmosphere consisting of CH_4, NH_3, and H_2, into which electric sparks were discharged. Analysis of the reaction products revealed the formation of a variety of organic molecules, including the amino acids alanine, aspartic acid, glutamic acid, and glycine.

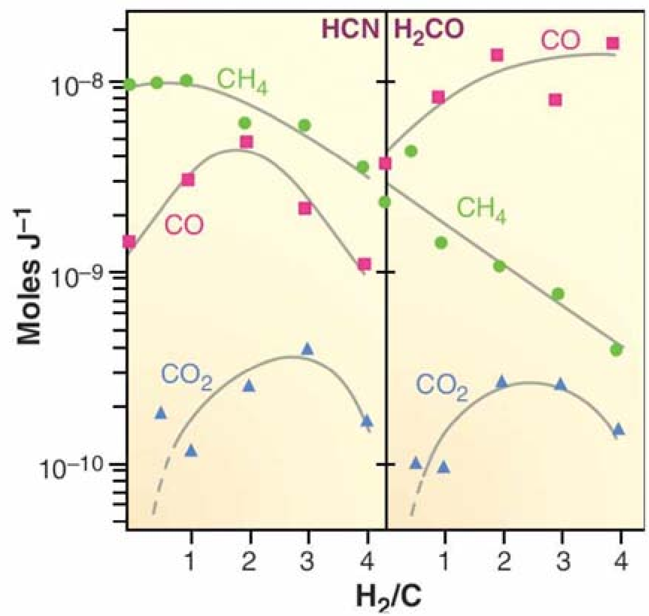


The Miller-Urey experiment

In the 1930s, Oparin and Haldane independently suggested that ultraviolet radiation from the sun or lightning discharges caused the molecules of the primordial atmosphere to react to form simple **organic** (carbon-containing) compounds. This process was replicated in 1953 by Stanley Miller and Harold Urey, who subjected a mixture of H_2O, CH_4, NH_3, and H_2 to an electric discharge for about a week. The resulting solution contained water-soluble organic compounds, including several amino acids (which are components of proteins) and other biochemically significant compounds.

Problem: The assumed atmospheric composition

The experiments only give large yields of interesting organics (amino acids, nucleic acids, sugars) if the gas is **H-rich** (highly reducing). If the early atmosphere was $CO_2 + N_2$ (mildly reducing), as many suspect, the yields are tiny.



Teleological phrasing (implying purpose) is a no-no

Energy sources: no problem

Sufficient energy (see below), but how can a molecular system begin to utilize energy *in order to* maintain its integrity over time? This behavior would be ***metabolism***. Some think first life was a simple metabolic network. This implies a *functional* molecule, but how could you get one before you had a molecule that could utilize energy?

Present-day sources of energy averaged over the Earth.

Source		Energy /J m^{-2} yr^{-1}
total radiation from the Sun		1090000.0
ultraviolet light		1680.0
electric discharges (lightning)	← Miller-Urey	1.68
cosmic rays	← Japanese experiments	0.0006
radioactivity (to 1 km depth)	← hydrothermal vents	0.33
volcanoes		0.05
shock waves (atmospheric entry)		0.46

Atmosphere from volcanic outgassing?

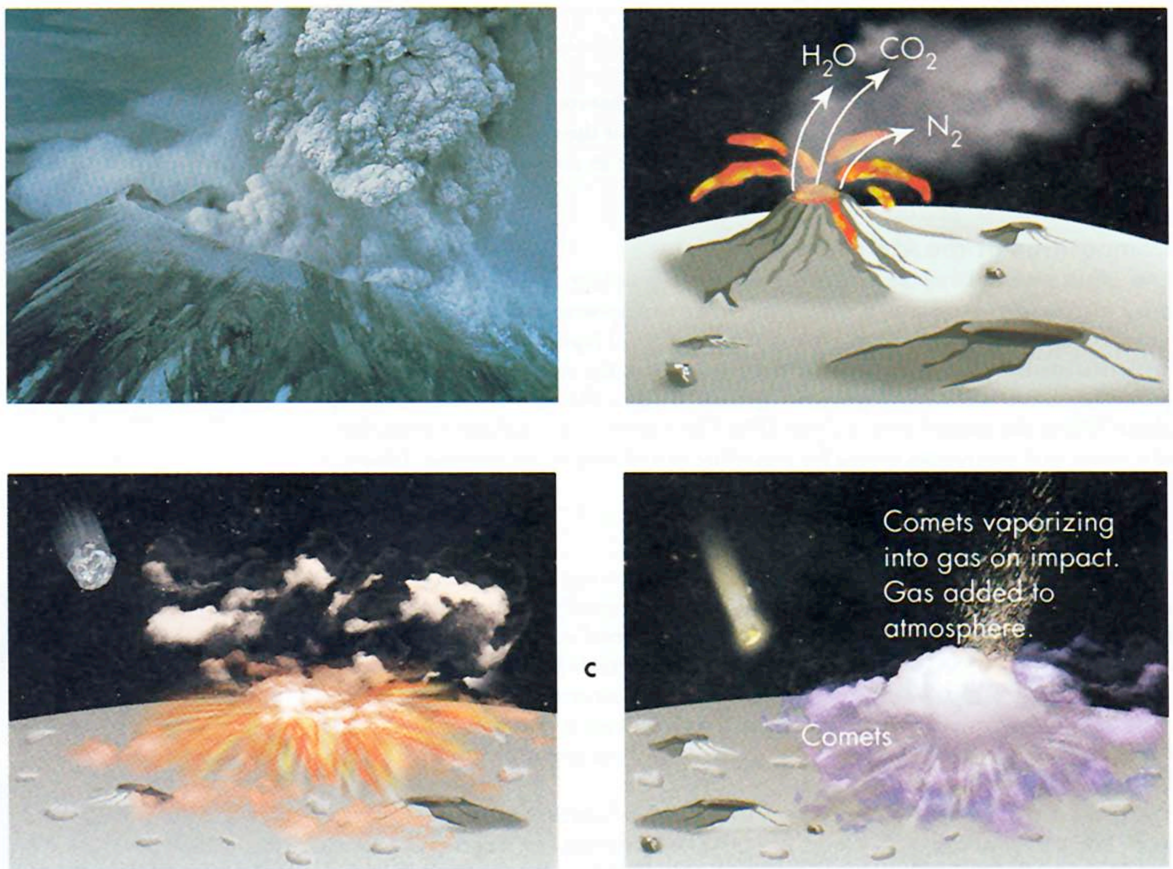
This would give atmosphere rich in CO_2, N_2, and H_2O. *Not* the composition that favors Miller-Urey synthesis.

Could the original atmosphere have been delivered to the Earth from comets, asteroids, …? Perhaps then the composition would be H-rich.

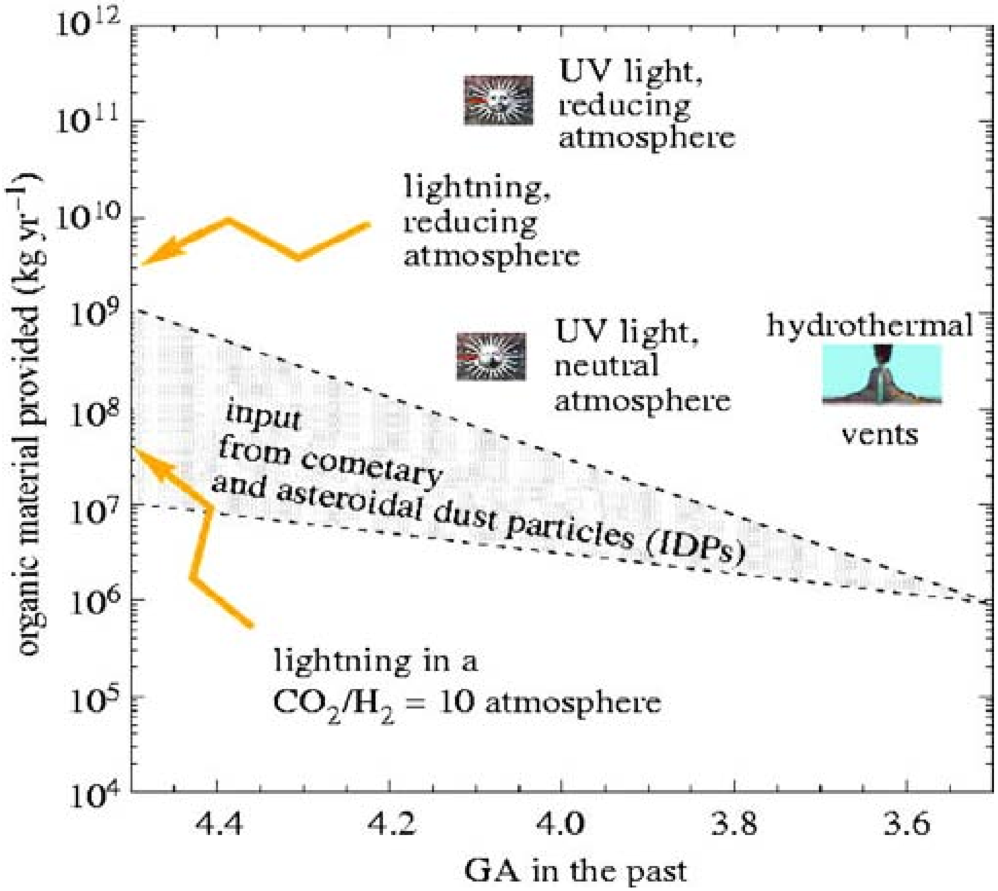
What was the source of the early Earth's atmosphere? Not necessarily "endogenous" (there from the start). Outgassing from the crust due to volcanoes (top two), or planetesimal impact (lower left), or comet vaporization (lower right)? We return to this when we discuss history of the Earth in Sec IV of this course. The point here is that a major alternative is ***exogenous delivery of organics by comets, asteroids, interplanetary dust…***

Endogenous

Exogenous



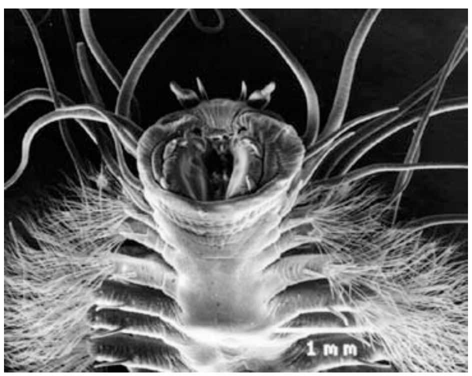
Exogenous Delivery of Organics to Early Earth



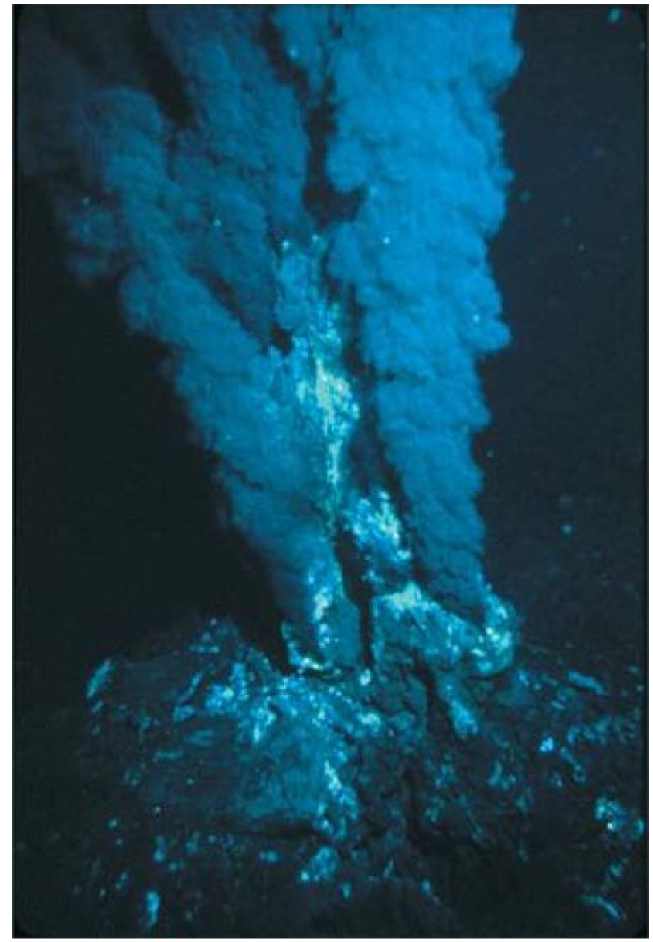
A visual representation summarizing the relative contributions of some major sources of organic molecules, both domestic and imported.

Undersea hydrothermal vents are an attractive alternative environment to some

The assumptions behind the Miller–Urey experiment, principally the composition of the gas used as a starting material, have been challenged by some scientists who have suggested that the first biological molecules were generated in a quite different way: in the dark and under water. Hydrothermal vents in the ocean floor, which emit solutions of metal sulfides at temperatures as high as 400°C, may have provided conditions suitable for the formation of amino acids and other small organic molecules from simple compounds present in seawater.



But biomolecules, especially RNA, are unstable at temperatures like those of vents. So…



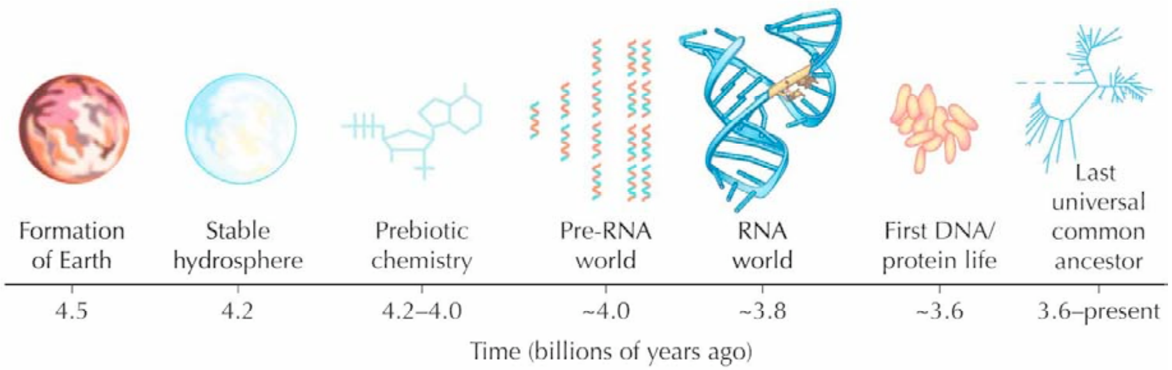
Such ocean-floor formations are known as "black smokers" because the metal sulfides dissolved in the superheated water they emit precipitate on encountering the much cooler ocean water.

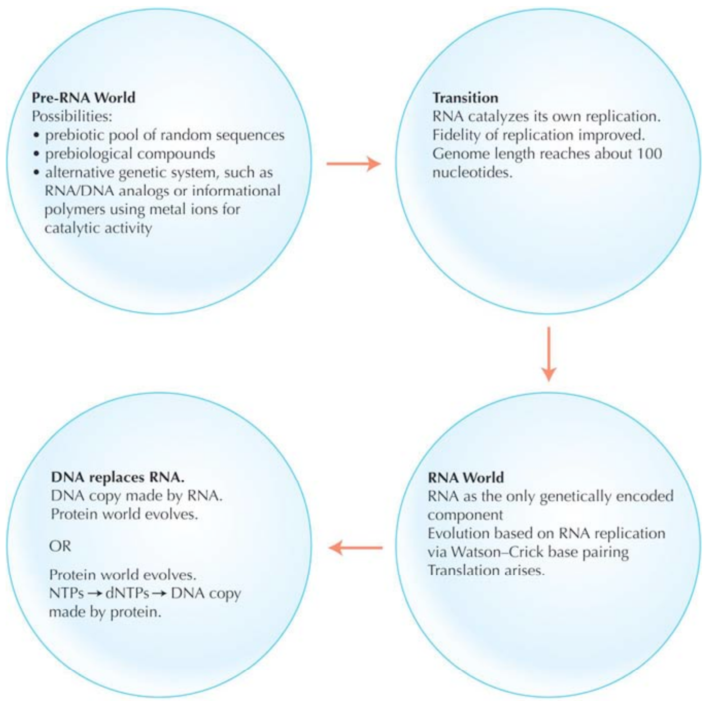
Another alternative: irradiation of ices, either extraterrestrial, or on a cold young Earth

Several groups have produced amino acids and other biologically-interesting molecules by ultraviolet irradiation of ices meant to resemble what we think interstellar ices are like. Munoz Caro et al. (2002) produced 16 amino acids this way. Hudson et al. (2008) et al. recently showed that irradiation of ice with high-energy protons produces amino acids, without any other gases present (I.e. doesn't depend on having hydrogen-rich atmosphere.

The key compound in the ices: Nitriles. In these experiments, it was acetonitrile
You may remember it from the "amino acid-like" molecule discovered in the interstellar medium: CH_3CN. It is also detected in comets and in Titan's atmosphere.

The RNA World: Motivated by discovery of ribozymes (autocatalytic RNA)





A model for the replacement of RNA as the genotype with DNA.

But what preceeded RNA?

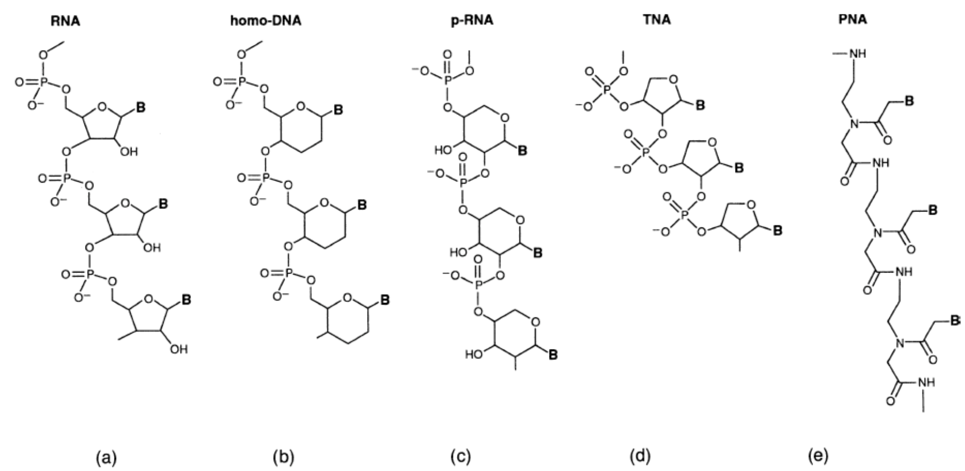
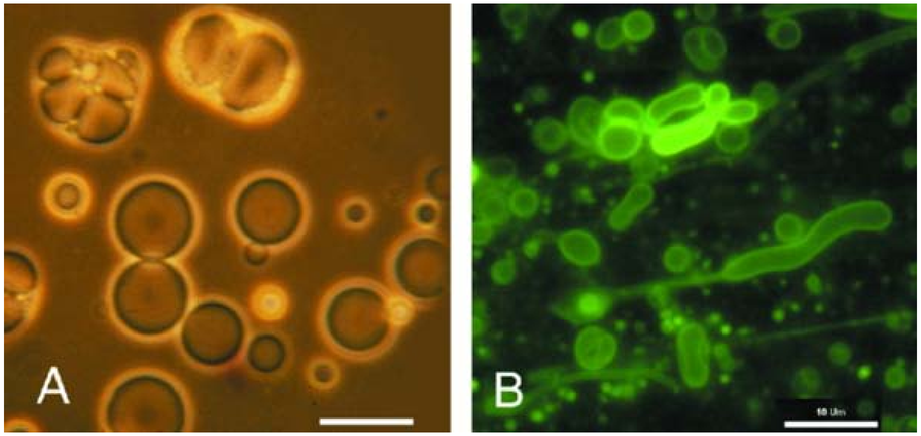


FIG. 9. The structures of single strands of (a) RNA, (b) homo-DNA, (c) p-RNA, (d) TNA, and (e) PNA.

Lessons from cellular nature of life:

1. Nearly all details of cell biology and biochemistry almost certainly reflect evolutionary complexity, *but* it does suggest **encapsulation** may have been early, or even first, step in origin of life ("lipid world")

2. Prokaryotic cells are certainly the most ancient of organisms, with evidence for biological microfossils back to 3 to 3.5 (controversial) Gyr.



Primitive membrane structures visualized by light microscopy. A: Amphiphilic compounds extracted from the Murchison meteorite form membranous vesicles when exposed to dilute aqueous salt solutions at pH > 7.0. The probable components of the vesicles are monocarboxylic acids ranging from 8 to 11 carbons in length together with admixtures of polycyclic aromatic hydrocarbon derivatives. B: Monocarboxylic acids in pure form also self-assemble into membranous vesicles, as shown here for DA:decanol (37 mM:3mM, C10, pH 7.4) stained with rhodamine 6G and observed by epifluorescence microscopy. This dye inserts in the bilayer membranes, which appear green. Bar = 10 m.