

The origin of biology on habitable planets

So a rocky planet survives migration and settles down in an orbit in which the temperature will level off in the liquid-water range, and stay there for billions of years.

- ...either because it is in the habitable zone, or because it is tidally heated in a resonant orbit.
- It won't level off at that happy temperature for a while, as it is born molten and takes hundreds of millions of years to cool off to a solid, silicate-rock surface.
- □ While it's molten it retains very few of the **prebiotic** or **volatile** molecules that went into its building, except for heavier gases in the atmosphere (e.g.N₂, CO₂).
- Good thing there are still smaller bodies around, which had never completely melted, and included volatiles.

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The Solar system's smaller bodies



The best-known nearby collection of small bodies is the Asteroid Belt between the orbits of Mars and Jupiter. The total mass in the main belt is thought to be about 0.04% of Earth's mass. There are about 200,000 asteroids larger than 1 km in diameter. Typically they lie about 0.07 AU apart.

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The Solar system's smaller bodies (continued)



Outside Neptune's orbit is the Kuiper Belt, best known as the source of short-period comets, and as the family to which Pluto belongs. Kuiper-belt objects (KBOs) are small and cold, and therefore faint; it'll take another 10-20 years to complete their census. But there used to be lots more, <u>as we saw</u>.

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The Solar system's smaller bodies (continued)

Further out, at about 10,000 AU, we find the Oort cloud, best known as the reservoir of long-period comets.

□ Only one candidate Oort-cloud object known (Sedna). When Uranus and Neptune switched orbits due to perturbations by Jupiter and Saturn, around 600-800 Myr after the Sun formed, something like 99% of the small bodies of the Solar system were violently displaced.

□ Lots were ejected and formed the Oort cloud.

Lots were driven to the inner Solar system, where the episode, known as the Late Heavy Bombardment, is evident in the cratering records of the Moon, Mars, and Mercury.

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Sweeping up the small bodies

Like all the planets, Earth constantly sweeps up smaller bodies. The rate is always much larger than the rate at which Earth loses mass (hydrogen, helium, satellites,...)

□ Seems to vary by quite a bit: 10⁷-10⁹ kg per year.

- □ Much of mass in rather large bodies, most of which come from the asteroid belt. Since these are relatively infrequent they are responsible for the variation.
- □ Substantial mass, though, in small bodies and interplanetary dust particles (IDPs), nearly all of which come from comets.
- □ All originate beyond the snow line.
- □ 4 Gyr ago, the rate was about 1000 times the present rate.

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Sweeping up the small bodies (continued)

METEOR

So these small bodies have been decorating the surface of Earth with ices and organics. Much burns up, which of course needn't destroy

small molecules like water. 90% of Earth's oceans were probably delivered by asteroids, the rest by comets.



METEORITES , CRATERS

12%

17-60 ppm

>35 ppm

3319 ppm

>100 ppm

>315 ppm

1.3 ppm

11 ppm

68 ppm

2 ppm

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But not all burn up: IDPs make a soft landing with their molecules intact, and moderate-size meteorites land with their interiors intact. Molecules preserved therein since the beginning are released.

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Sweeping up the small bodies (continued)

Of particular interest are hydrocarbon	molecule
molecules, since Earth's surface is so poor	Water
in carbon.	Amino acids
□ IDPs are rich in organic molecules	Ordinary hydrocarbons
(10% by mass). They account for most of the 3.2×10^5 kg per year of carbon the	Aromatic hydrocarbons (PAHs)
01 5	

- of the 3.2×10⁵ kg per year of carbon the Earth currently sweeps up (<u>Chyba and</u> <u>Sagan 1992</u>). Fulrenes D But large parcels arrive too, like the Pyrimidines
- But large parcels arrive too, like the Murchison meteorite (1969, Australia), containing treasure troves of biomolecules (table from <u>Machalek</u> <u>2007</u>).

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Alcohols

Sulphonic acids

Phosphonic acids

Is delivery necessary? Formation of prebiotic molecules *in situ*

It was long assumed that any prebiotic molecule would need to be formed *in situ* (in place, on Earth) from simpler, inorganic chemicals.

- □ In the 1920s and 1930s, Oparin (USSR) and Haldane (UK) proposed that the early Earth would have had no prebiotic molecules, and a **reducing** atmosphere similar to the giant planets would give rise to them.
 - Reducing = components of gas give up electrons easily. Examples: hydrogen, ammonia, methane.
- □ Miller and Urey (USA) reasoned that lightning and solar UV would provide the energy necessary for the neutralneutral reactions, and simulated these conditions in the lab.

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The original Miller-Urey experiment

A classic of molecular biology.

ultraviolet light as well.

□ Ingredients: H₂, NH₃, CH₄ gas in 5-l flask, connected by condenser to "ocean," water in the 500 cc flask.

A high-voltage discharge (a continuous



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□ Ran like that for a week, repeated several times with new glassware and electrodes.

Result: after a week, 10-15% of the carbon had become incorporated into a wide variety of prebiotic molecules including several amino acids, sugars, lipids and other organic acids.

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The original Miller-Urey experiment

- □ Lots of H₂CO, HCN, HC₃N and NH₂CONH₂ (urea) formed in the gas, and condensed into the "ocean."
- Note that all these are seen in Alpha-aminoisob ISM and/or meteorites.
- □ The other molecules formed in the water with "wet chemical" reactions among the H₂CO, HCN, HC₃N and NH₂CONH₂. Good example is the "Strecker synthesis" of the amino acids.

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Compound	Ticiu
Glycine	270
Sarcosine	21
Alanine	145
N-methylalanine	4
Beta-alanine	64
Alpha-amino-n-butyric acid	21
Alpha-aminoisobutyric acid	0.4
Aspartic acid	2
Glutamic acid	2
Iminodiacetic acid	66
Iminoacetic-propionic acid	6
Lactic acid	133
Formic acid	1000
Acetic acid	64
Propionic acid	56
Alpha-hydroxybutyric acid	21
Succinic acid	17
Urea	8
N-methyl urea	6
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Modern Miller-Urey results

Alas, it's not so simple: it seems impossible that Earth's early atmosphere was this reducing.

- Gravity insufficient to hold much hydrogen.
- Volcanism, heat and solar UV light seem sure to have made the atmosphere oxidizing (opposite of reducing), producing lots of CO2 and N2, and vaporizing water. The atmosphere would have been more like that of Saturn's moon Titan.
- □ And H₂CO, HCN, HC₃N and NH₂CONH₂ aren't produced by reactions in a $CO_2/N_2/H_2O$ atmosphere.
- This has moved attention to volcanic vents, which can produce locally high concentrations of reducing gases like CH4 and NH3.

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Modern Miller-Urey results (continued)

As long as the precursor molecules H2CO, HCN, HC3N and NH₂CONH₂ are supplied, though, interesting molecules get formed in the "ocean":

- HCN and ammonia have been shown to react in water to produce adenine, one of the nucleobase components of DNA and RNA (Oro 1961).
- Two more nucleobases, cytosine and uracil, are made in water by reacting HC₃N and NH₂CONH₂ (Robertson and Miller 1995; yes, that Miller).
- □ The sugar ribose can be formed in high concentrations of formaldehyde: five H₂COs make one ribose. (Better in soil or clay than in water, though.)

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Summary: synthesis of prebiotic molecules

Either by slight reducing properties of the early atmosphere, or by the reducing atmosphere near volcanic vents, or by delivery via IDPs and meteorites of molecules formed in the reducing atmosphere of the ISM, it seems that the early Earth had supplies of H₂CO, HCN, HC₃N and NH₂CONH₂.

- □ And with the liquid water supplied by the meteorites serving as the solvent, the primary prebiotic molecules: the amino acids and the nucleoside bases can be made without much trouble or imagination.
- □ The next step is the polymerization of these monomers: the generation of long, much more complex molecules that can encode information.

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1st Mid-lecture Break.



Wet chemistry of amino acids

In water, important modifications are made to amino acids and nucleoside bases, owing to the propensity of water to grab positive charges.

□ When any acid dissolves in water, loosely-bound hydrogen nuclei attach themselves to water and leave their electrons behind. Example of hydrochloric acid:

 $HCl + H_2O \rightarrow Cl^- + H_3O^+$ (in liquid water)

This would happen just as well in liquid ammonia, which shares this propensity with water:

 $HCl + NH_3 \rightarrow Cl^- + NH_4^+$ (in liquid ammonia)

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Wet chemistry of amino acids (continued)

Amino acids express these tendencies on both of their ends: "amino" refers to the NH_2 group they all have at one end, and the H in the COOH organic-acid group they have at the other end is the one that comes off in solution.

□ Example: the simplest amino acid, glycine:





□ In aqueous solution the H in the COOH group is swiped by a water molecule...



Wet chemistry of amino acids (continued)

This is a general and key property of amino acids in solution: there is a positive electrical charge localized on one end (the amino group), and a negative charge on the other end, with the molecule overall being electrically neutral.



Glycine in solution

Glycine

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□ Such molecules are called zwitterions by biochemists. All amino acids are zwitterions when dissolved in water.

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Wet chemistry of amino acids (continued)

That the electrical charges are localized on these groups, rather than shared among the atoms of the molecule as, for example, the electrons among a benzene ring, means that the amino ends of amino acids will be electrically attracted to the acid ends of other molecules. It's as if each amino acid has hook and eyelet connectors on opposite ends.

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Wet chemistry of amino acids (continued)

The electrostatic attraction between hook and eyelet can lead to chemical bonds, creating a longer zwitterion and a spare water molecule. Example of two glycines:



Wet chemistry of amino acids (continued)

Or, using our hook and eyelet shorthand, and noting that a spare water molecule is generated every time a hook and eyelet connect:



Obviously this can be repeated *ad nauseam*, and it doesn't need to be the same amino acid every time. A long-chain **polymer** has been created from amino-acid **monomers**.

Amino	 Amino	 Amino	\square	Amino	<
acid 11	acid 12	acid 13		acid 14	

A polymer of amino acids is generally called a protein.

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Other monomers: wet chemistry of ribose

Ribose $(C_5H_{10}O_5)$ is a sugar that is made in the "ocean" or even better on dry land by the formaldehyde either delivered or made by Miller-Urey means.



Other monomers: phosphoric acid

Phosphoric acid (H_2PO_4) can also be made in electrical discharges in a reducing atmosphere, if there is any phosphorous around. (There's never much.)

□ Its two dangling OH groups turn out to be good at making bonds with the "eyelet" groups on sugars, in much the same way that the "hook" groups do in amino acids. H₂PO₄ hook plus sugar eyelet lead to a bond that, like a peptide bond, releases a water molecule.



Other monomers: wet chemistry of nucleobases

Another interesting family of molecules made in the Miller-Urey ocean are the **nucleobases**, which divide into two categories, **purines** and **pyrimidines**. Five of these are of particular importance.

 \Box Purines: adenine (C₅H₅N₅) and guanine (C₅H₅N₅O), planar molecules each containing two CN rings.



- □ These two purines are essential in all Earth life forms. (Another purine, caffeine, is essential to my life form.)
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Wet chemistry of nucleobases (continued)

□ Pyrimidines: cytosine (C₄H₅N₃O), thymine (C₅H₆N₂O₂), and uracil (C₄H₄N₂O₂), also planar molecules. Their structure, in order (C-T-U):



- □ These are also essential to Earthly life forms: thymine in DNA, uracil in RNA, cytosine in both.
- The sizes of these five molecules match each other in a special way that promote hydrogen bonding.

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Wet chemistry of nucleobases (continued)

□ Hydrogen bonds are weaker than the usual (covalent) chemical bonds: they are the manifestation of the attraction of an atom (like O and N) that's good at stealing hydrogen, for the hydrogen atoms bound covalently to other atoms. Social analogies are not hard to find.

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□ The essential purines and pyrimidines match up in pairs with particularly strong hydroger bonds: adenine with thymine or uracil...



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- □ Each nucleobase has an NH group that is good at combining with a dangling OH group on ribose, making a bond rather like a peptide bond and releasing yet another water molecule. The combination is called a **nucleoside**.
- □ Hang a phosphate group on the sugar (releasing a water molecule, of course), produces an interesting monomer called a **nucleotide**. Note that they can be chained together, hook to eyelet, making a sugar-phosphate backbone with nucleobases sticking out.

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Nucleotide polymers

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By now you probably see where this is heading: nucleotides can polymerize into long chains, like amino acids can polymerize into proteins.

□ Owing to the use of ribose and nucleobases, and the hookand-eyelet ends, this particular kind of polymer is called a ribonucleic acid (RNA).



2 nd Mid-le	ecture Break.	
❑ That was a lot you deserve another break	the second	Crick,
	Alexander Rich, Les Orgel and James Wa 1955 (MIT)	lie tson in
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Nature "makes" choices

There are several chemically equivalent ways to polymerize amino acids and nucleotides but only one each prevailed in Earthly life.

- □ Why? Leading explanation is that those were the ones easiest to replicate, and natural selection favored them: they were made consistently, and thus outnumbered the ones that were made randomly.
- □ How? That's debated but several experiments and theories provide explanations, as we'll see.

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Nuances of polymerization: amino acids

Optical isomerization (except glycine): identical chemical contents look like not-identical mirror images.

- □ The name comes from the way solutions transmit linearlypolarized light: one of the forms rotates the polarization clockwise as seen from behind (D), one counterclockwise (L, as shown)
- Discovered by Biot, who also discovered that meteorites fell from the sky.





Nuances of polymerization: nucleotides



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Nuances of polymerization: nucleotides (continued)

- Geometry of the nucleobase pairs: bonds to the sugars are made by NH groups on opposite sides of the hydrogen-bonding sites.
- □ In adenine-thymine or guaninecytosine pairs, these sugarbonding groups are precisely 1.09 nm apart.
- □ The five essential nucleobases are the only ones in this size. Can't substitute others, or DNA and RNA wouldn't work.

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