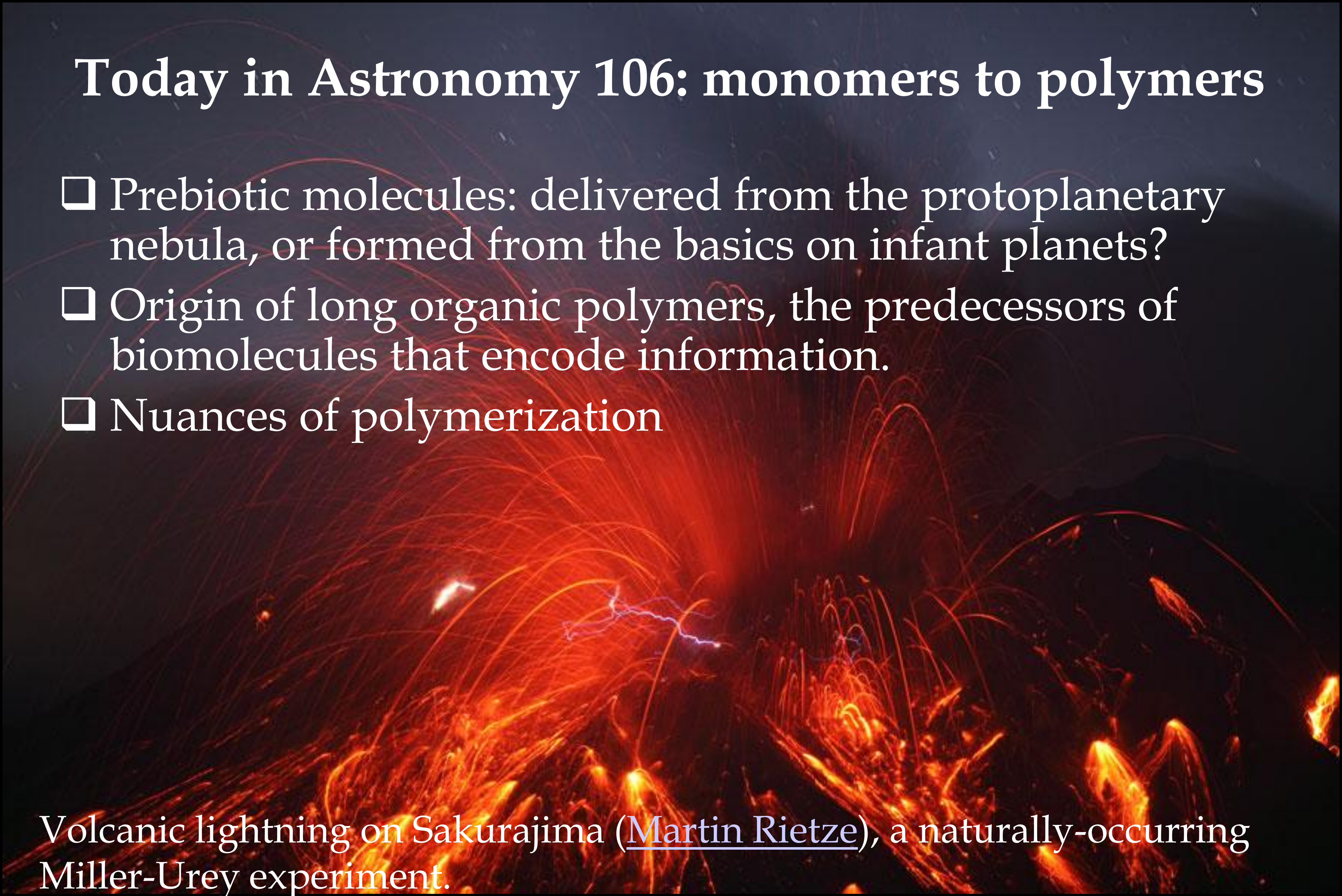
# Today in Astronomy 106: monomers to polymers



☐ Prebiotic molecules: delivered from the protoplanetary nebula, or formed from the basics on infant planets?

☐ Origin of long organic polymers, the predecessors of biomolecules that encode information.

☐ Nuances of polymerization

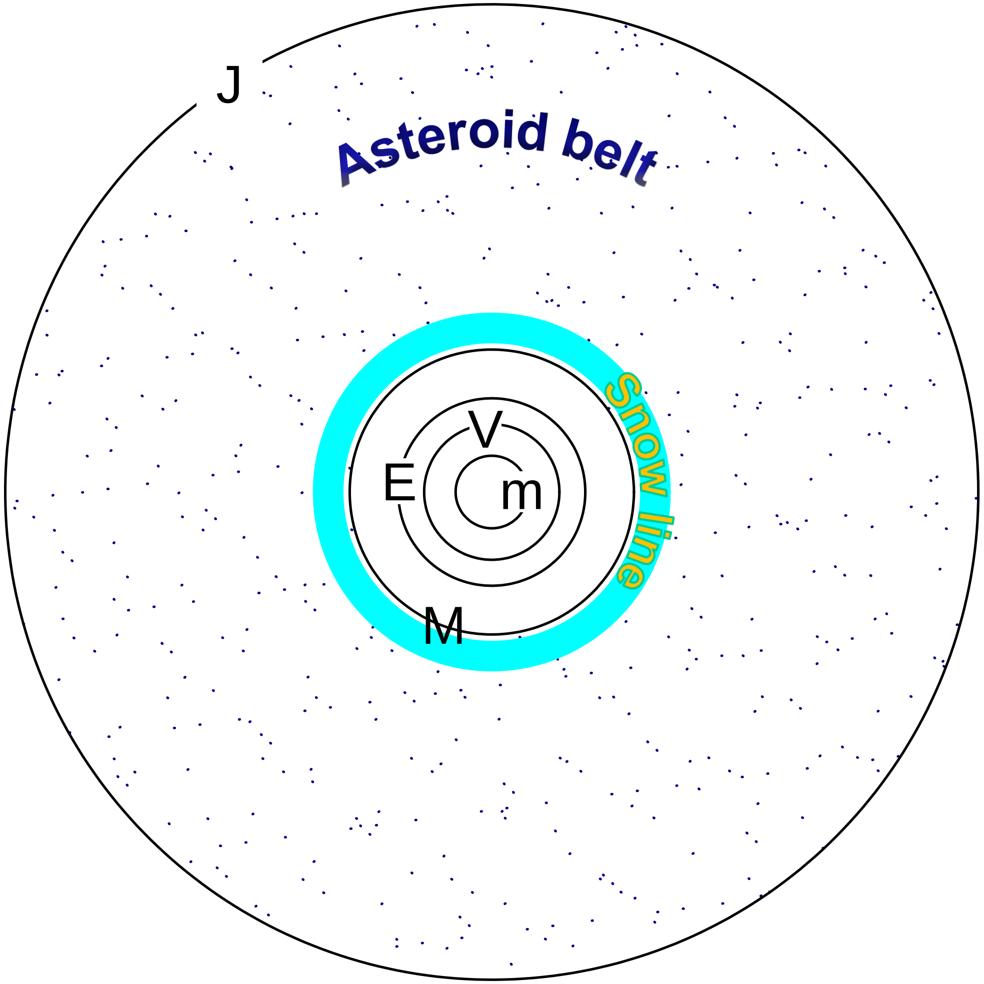
Volcanic lightning on Sakurajima (Martin Rietze), a naturally-occurring Miller-Urey experiment.

# 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.$N_2$, $CO_2$).
- ☐ Good thing there are still smaller bodies around, which had never completely melted, and included volatiles.

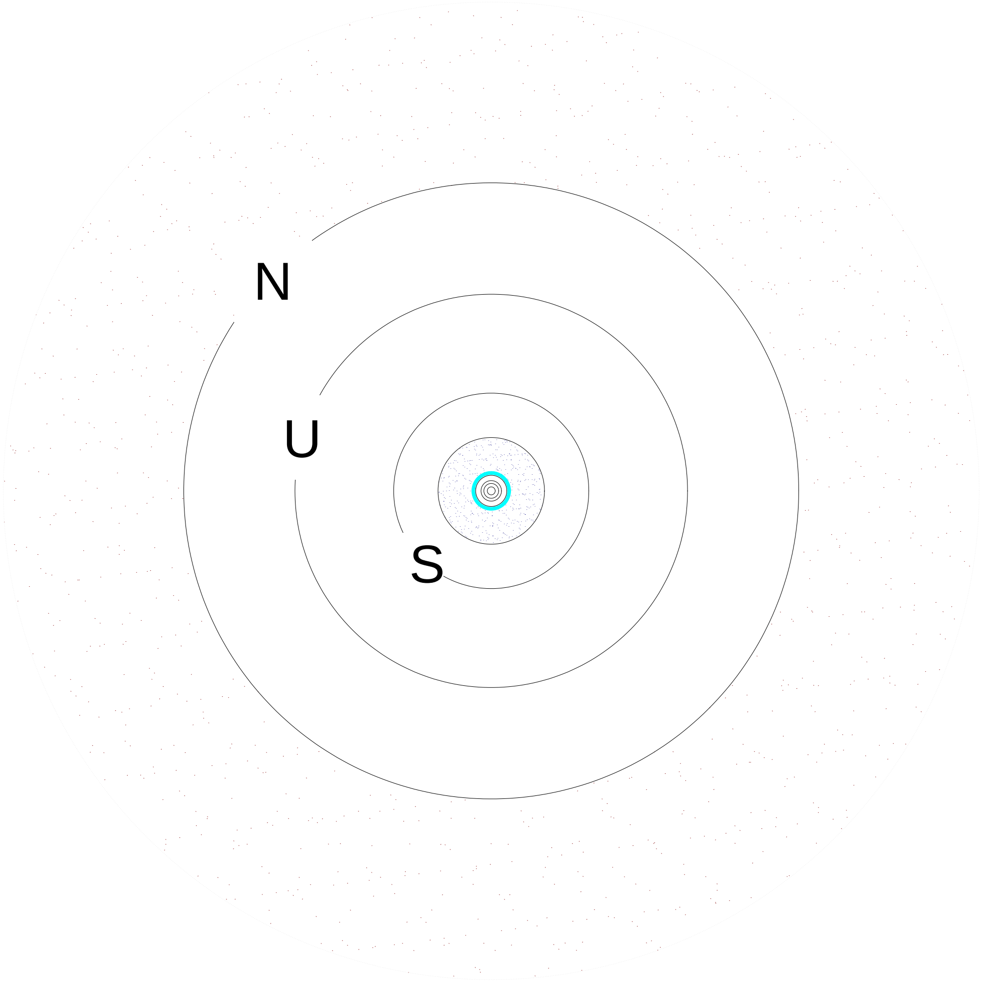
# The Solar system's smaller bodies



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.

# 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, as we saw.

# 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.

# Sweeping up the small bodies

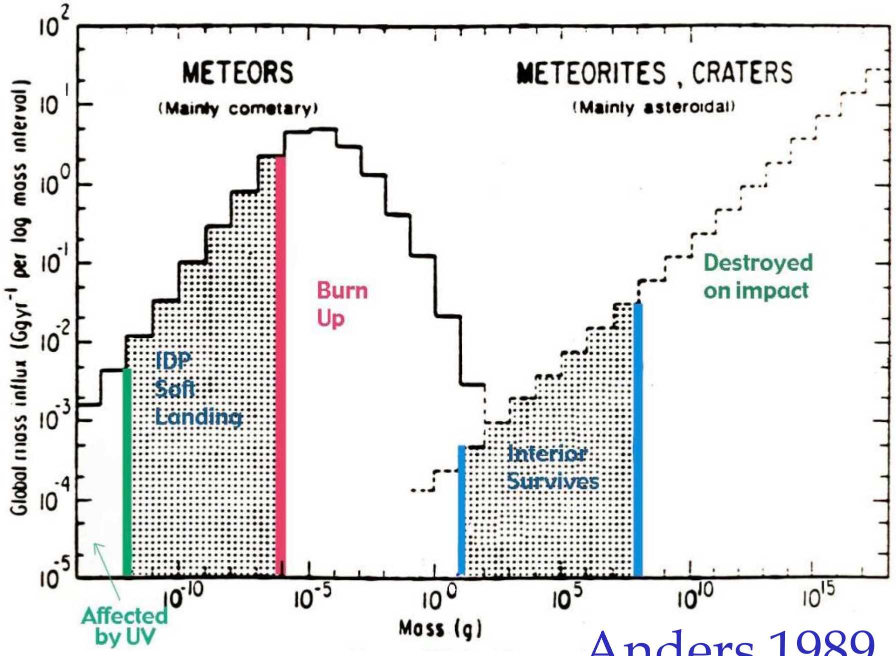
Like all the planets, Earth constantly sweeps up smaller bodies. The rate is always much larger than the rate at which Earth loses mass (hydrogen, helium, satellites,…)

- Seems to vary by quite a bit: $10^7$-$10^9$ 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.

# Sweeping up the small bodies (continued)

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.



Anders 1989

- 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.

# Sweeping up the small bodies (continued)

Of particular interest are hydrocarbon molecules, since Earth's surface is so poor in carbon.

- ☐ IDPs are rich in organic molecules (10% by mass). They account for most of the $3.2\times10^5$ kg per year of carbon the Earth currently sweeps up (Chyba and Sagan 1992).
- ☐ But large parcels arrive too, like the Murchison meteorite (1969, Australia), containing treasure troves of biomolecules (table from Machalek 2007).

| Prebiotic molecule | Concentration by mass |
|---|---|
| Water | 12% |
| Amino acids | 17-60 ppm |
| Ordinary hydrocarbons | >35 ppm |
| Aromatic hydrocarbons (PAHs) | 3319 ppm |
| Fullerenes | >100 ppm |
| Organic acids | >315 ppm |
| Purines and Pyrimidines | 1.3 ppm |
| Alcohols | 11 ppm |
| Sulphonic acids | 68 ppm |
| Phosphonic acids | 2 ppm |

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

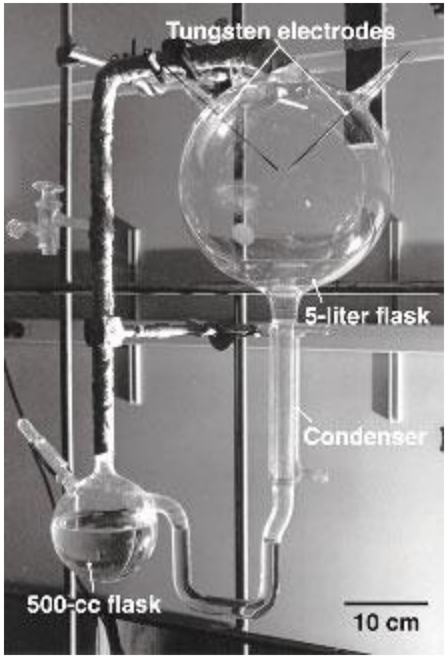
It was long assumed that any prebiotic molecule would need to be formed *in situ* (in place, on Earth) from simpler, inorganic chemicals.

- ☐ 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 neutral-neutral reactions, and simulated these conditions in the lab.

# The original Miller-Urey experiment

A classic of molecular biology.

- ☐ Ingredients: $H_2$, $NH_3$, $CH_4$ gas in 5-l flask, connected by condenser to “ocean,” water in the 500 cc flask.
- ☐ A high-voltage discharge (a continuous spark) simulated lightning, and provided ultraviolet light as well.
- ☐ 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.

# The original Miller-Urey experiment

- ☐ Lots of $H_2CO$, HCN, $HC_3N$ and $NH_2CONH_2$ (urea) formed in the gas, and condensed into the “ocean.”
- ☐ Note that all these are seen in ISM and/or meteorites.
- ☐ The other molecules formed in the water with “wet chemical” reactions among the $H_2CO$, HCN, $HC_3N$ and $NH_2CONH_2$. Good example is the “Strecker synthesis” of the amino acids.

| Compound | Yield |
|---|---:|
| 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 |

# 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 $CO_2$ and $N_2$, and vaporizing water. The atmosphere would have been more like that of Saturn's moon Titan.
- ☐ And $H_2CO$, HCN, $HC_3N$ and $NH_2CONH_2$ 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 $CH_4$ and $NH_3$.

# Modern Miller-Urey results (continued)

As long as the precursor molecules $H_2CO$, HCN, $HC_3N$ and $NH_2CONH_2$ 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 $HC_3N$ and $NH_2CONH_2$ (Robertson and Miller 1995; yes, *that* Miller).
- ☐ The sugar ribose can be formed in high concentrations of formaldehyde: five $H_2CO$s make one ribose. (Better in soil or clay than in water, though.)

# 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 $H_2CO$, HCN, $HC_3N$ and $NH_2CONH_2$.

- ❑ 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.

# 1st Mid-lecture Break.

- ☐ As we are covering a lot of material there will be 2 short breaks today in lieu of the one long break.
- ☐ Recitation Today, 12:30 PM, B&L 315
- ☐ Homework #3 will be available tomorrow and is due the Thursday 9 June 2011 by midnight.

UCSD Prof.
Stanley
Miller
(1930-2007)

UCSD Prof.
Harold
Urey
(1893-1981)

# 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:

$$\mathrm{HCl} + \mathrm{H_2O} \rightarrow \mathrm{Cl^-} + \mathrm{H_3O^+} \quad \text{(in liquid water)}$$

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

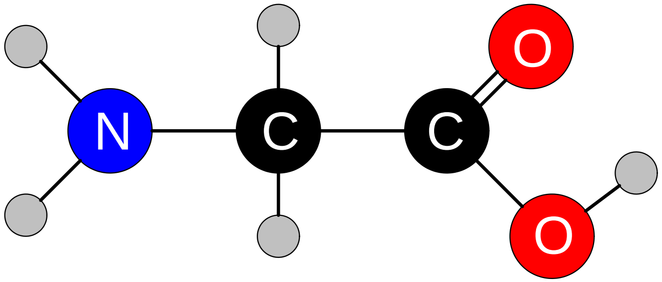
$$\mathrm{HCl} + \mathrm{NH_3} \rightarrow \mathrm{Cl^-} + \mathrm{NH_4^+} \quad \text{(in liquid ammonia)}$$

# 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:

$NH_2CH_2COOH$



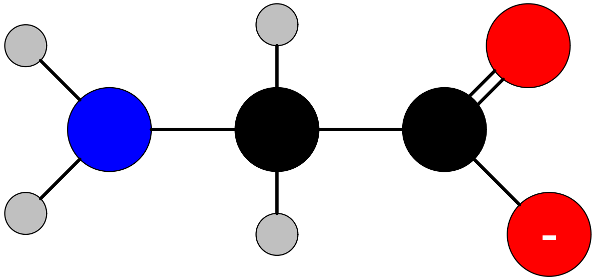
Note the color code, which we will use henceforth.

The cool thing about them is that **the $NH_2$ group on the end has the same propensity to grab positive ions as ammonia does in liquid**.

# Wet chemistry of amino acids (continued)

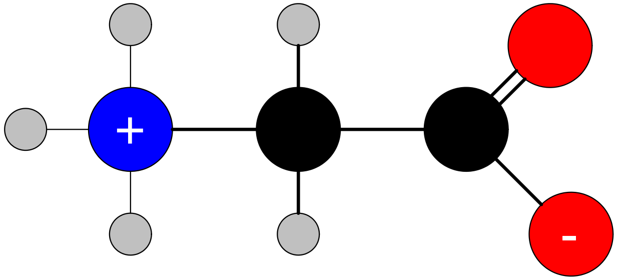
- ☐ In aqueous solution the H in the COOH group is swiped by a water molecule…

$$NH_2CH_2COOH + H_2O \rightarrow$$
$$NH_2CH_2COO^- + H_3O^+$$



- ☐ and the amino group acquires an $H^+$ from a $H_3O^+$ (hydronium) ion:

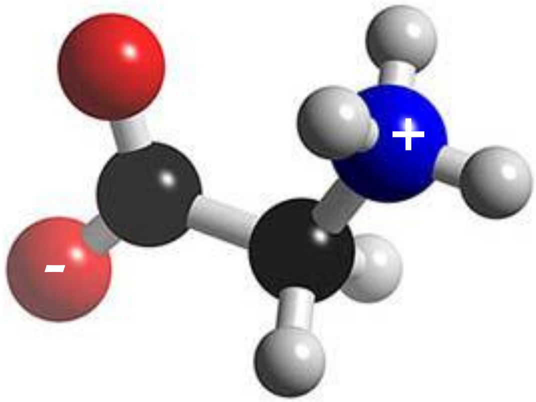
$$NH_2CH_2COO^- + H_3O^+ \rightarrow$$
$$(NH_3)^+ CH_2COO^- + H_2O$$



# 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.

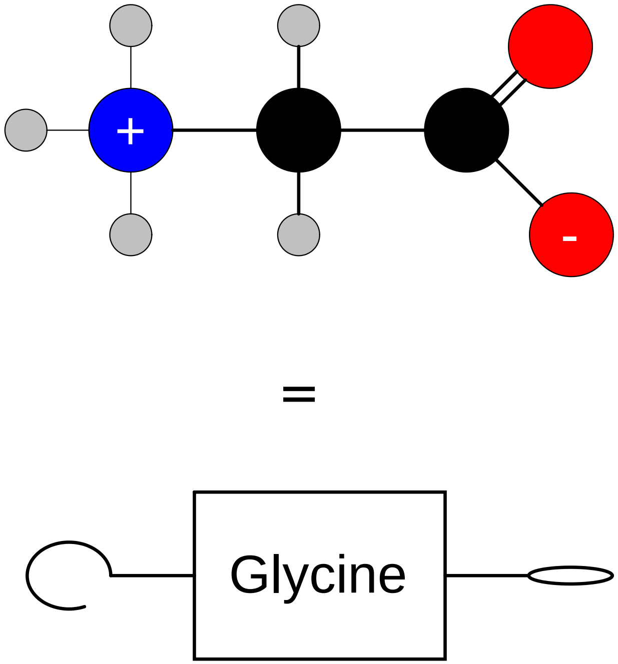
- ❑ Such molecules are called **zwitterions** by biochemists. All amino acids are zwitterions when dissolved in water.



Glycine in solution

# Wet chemistry of amino acids (continued)

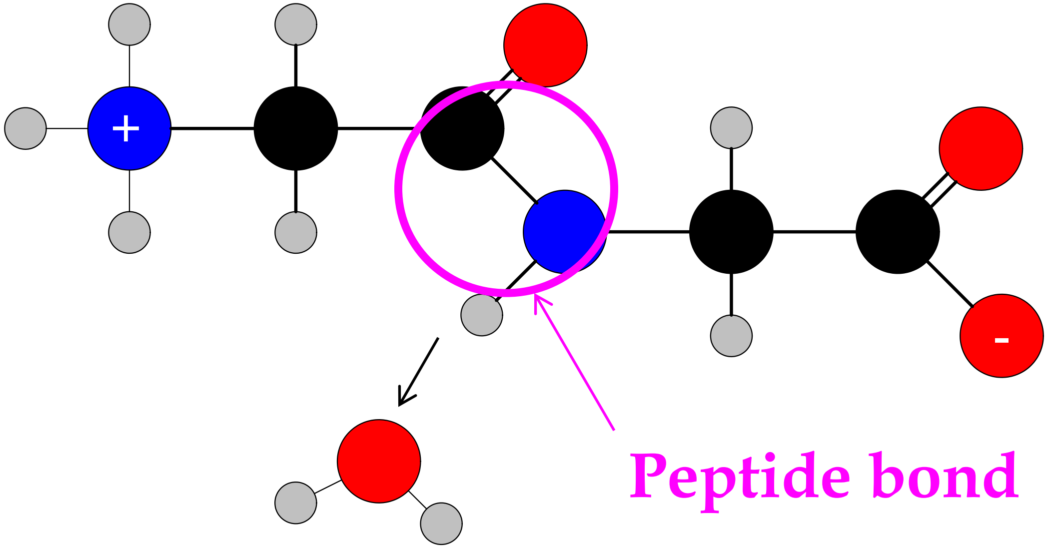
That the electrical charges are localized on these groups, rather than shared among the atoms of the molecule as, for example, the electrons among a benzene ring, means that the amino ends of amino acids will be electrically attracted to the acid ends of other molecules. It's as if each amino acid has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



# 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:

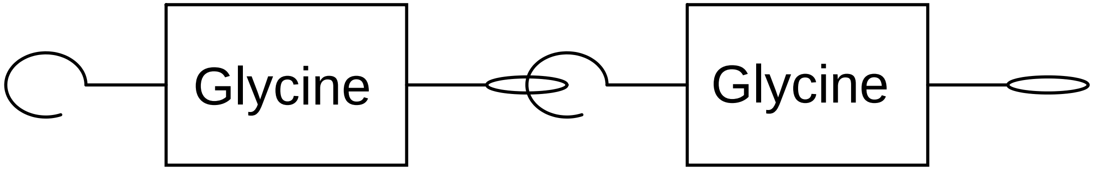
$$2\left[\left(\mathrm{NH_3}\right)^+\mathrm{CH_2COO^-}\right]\rightarrow\left(\mathrm{NH_3}\right)^+\mathrm{CH_2CONHCH_2COO^-}+\mathrm{H_2O}$$



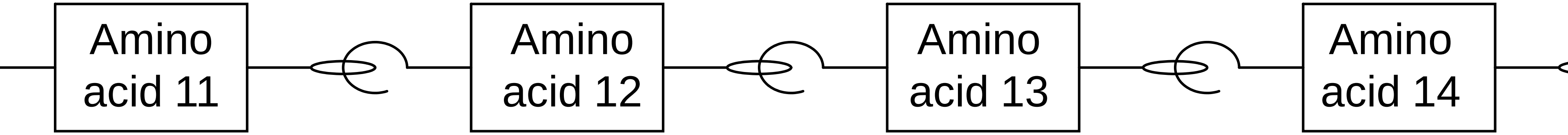
**Peptide bond**

# 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**.

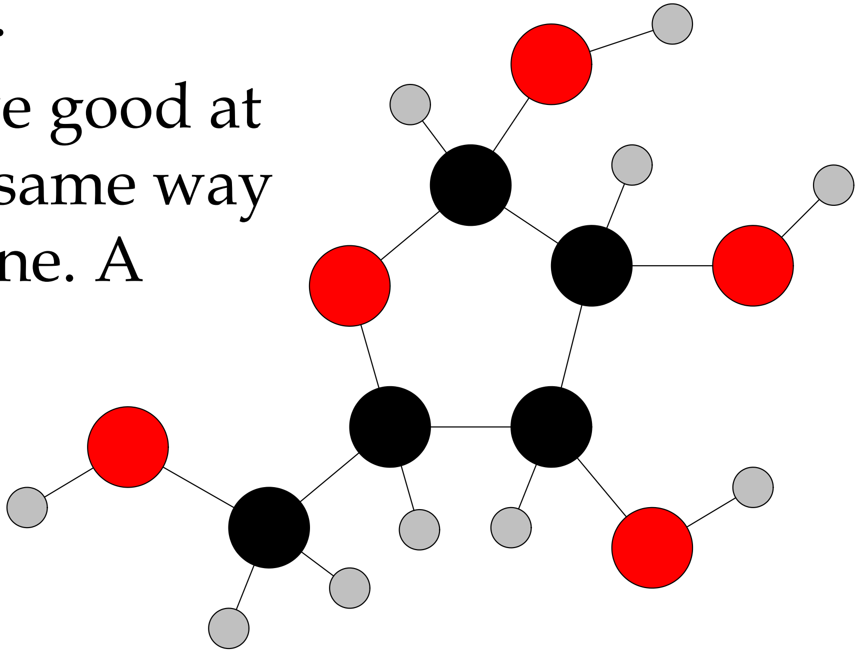


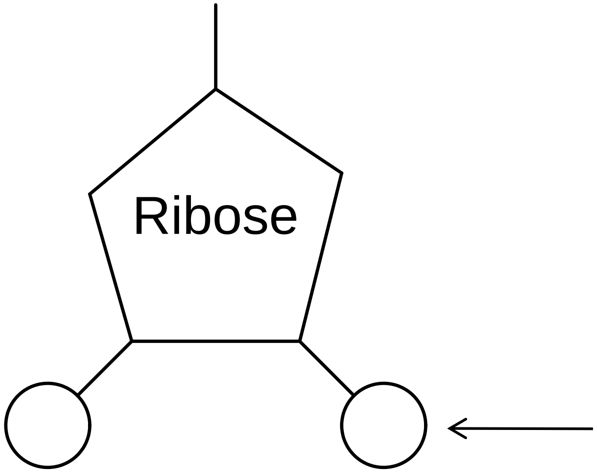
A polymer of amino acids is generally called a **protein**.

# 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.

- The dangling OH groups are good at making bonds in much the same way as the dangling OH in glycine. A shorthand schematic:



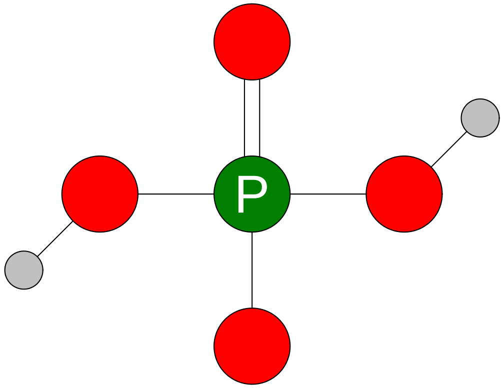


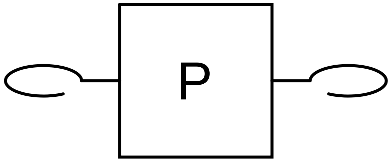
Glycine-like "eyelets"

# 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. $H_2PO_4$ hook plus sugar eyelet lead to a bond that, like a peptide bond, releases a water molecule.



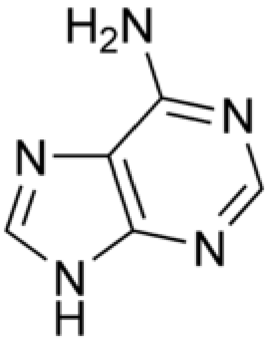


# Other monomers: wet chemistry of nucleobases

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.

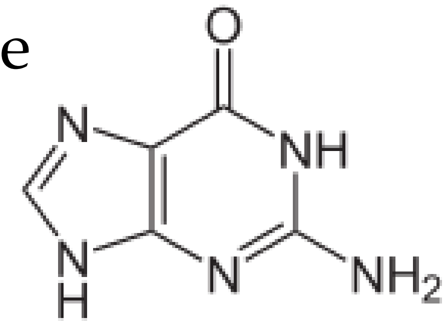
- Purines: **adenine** ($C_5H_5N_5$) and **guanine** ($C_5H_5N_5O$), planar molecules each containing two CN rings.

Adenine



Images from Wikimedia Commons.

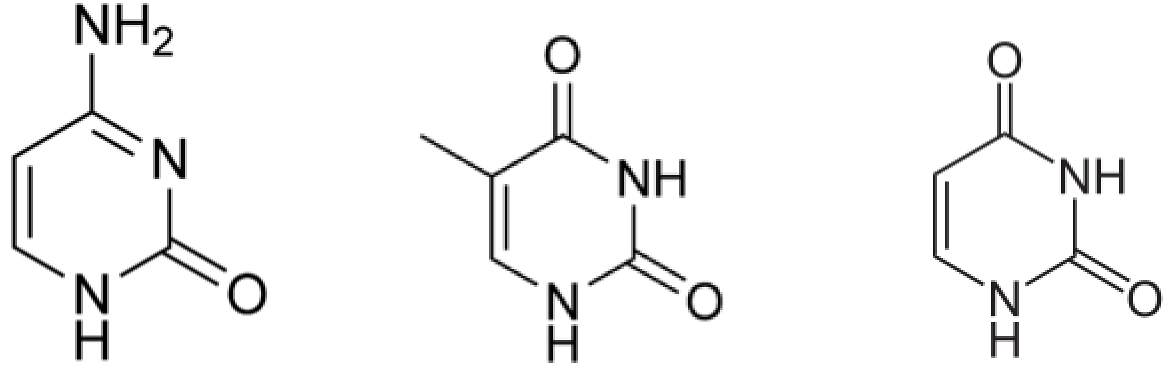
Guanine



- These two purines are essential in all Earth life forms. (Another purine, caffeine, is essential to my life form.)

# Wet chemistry of nucleobases (continued)

- Pyrimidines: **cytosine** ($C_4H_5N_3O$), **thymine** ($C_5H_6N_2O_2$), and **uracil** ($C_4H_4N_2O_2$), also planar molecules. Their structure, in order (C-T-U):

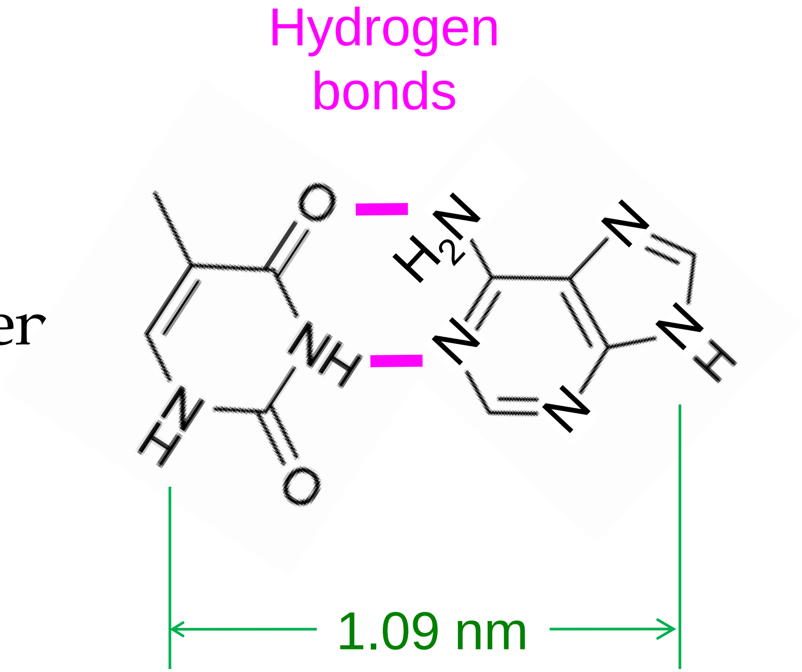


Images from Wikimedia Commons.

- 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**.

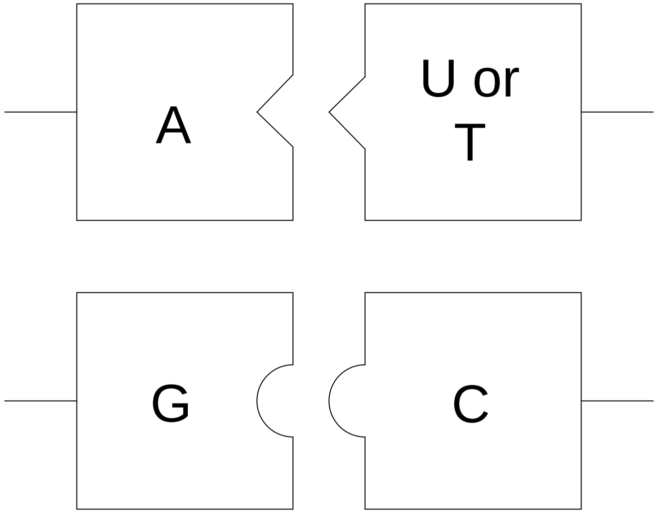
# Wet chemistry of nucleobases (continued)

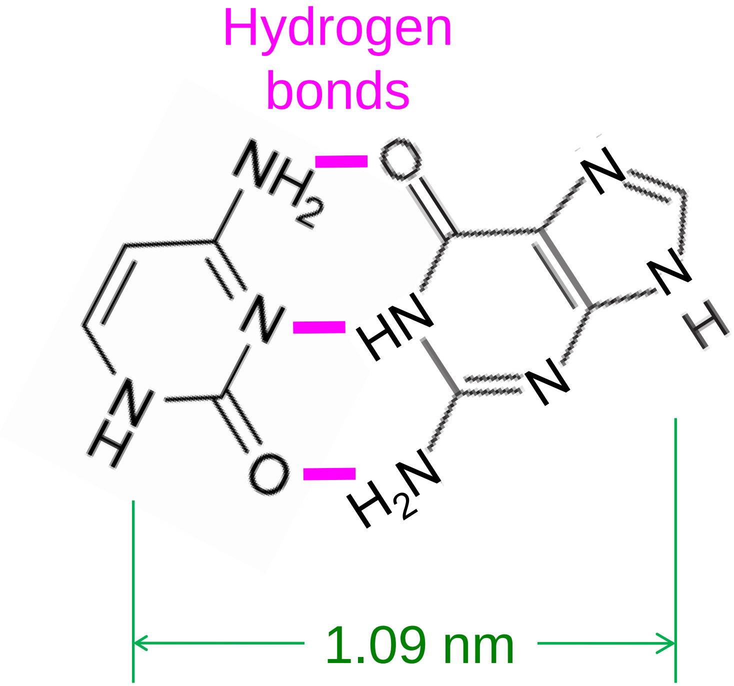
- Hydrogen bonds are weaker than the usual (covalent) chemical bonds: they are the manifestation of the attraction of an atom (like O and N) that's good at stealing hydrogen, for the hydrogen atoms bound covalently to other atoms. Social analogies are not hard to find.
- The essential purines and pyrimidines match up in pairs with particularly strong hydrogen bonds: adenine with thymine or uracil…



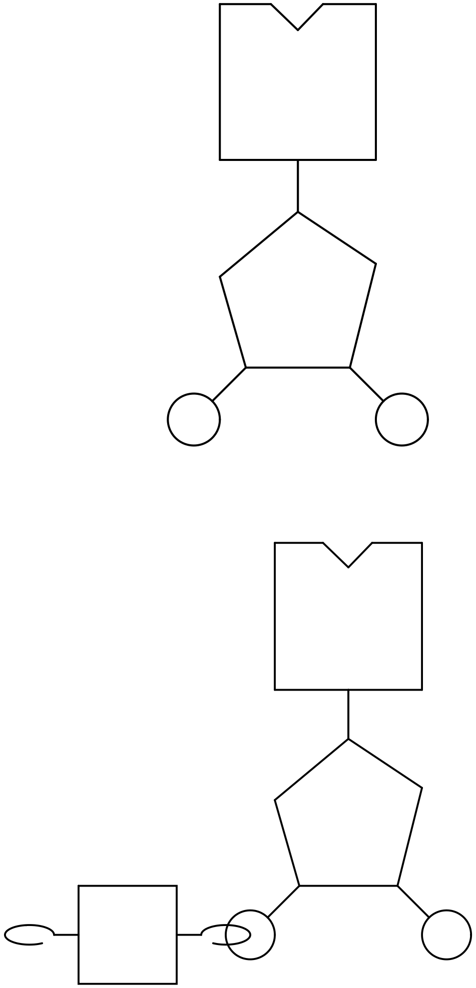
# Wet chemistry of nucleobases (continued)

- …and guanine with cytosine.
- It will be useful to have a schematic shorthand for these monomers too, to reflect their key-like ability to bond with each other:





# Wet chemistry of nucleobases (continued)

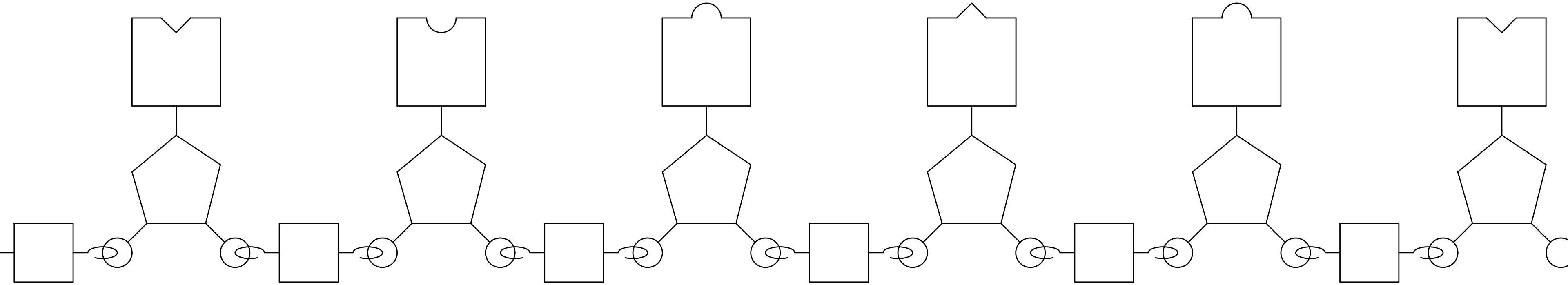


- Each nucleobase has an NH group that is good at combining with a dangling OH group on ribose, making a bond rather like a peptide bond and releasing yet another water molecule. The combination is called a **nucleoside**.
- Hang a phosphate group on the sugar (releasing a water molecule, of course), 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.

# Nucleotide polymers

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 hook-and-eyelet ends, this particular kind of polymer is called a **ribonucleic acid (RNA)**.



# $2^{nd}$ Mid-lecture Break.

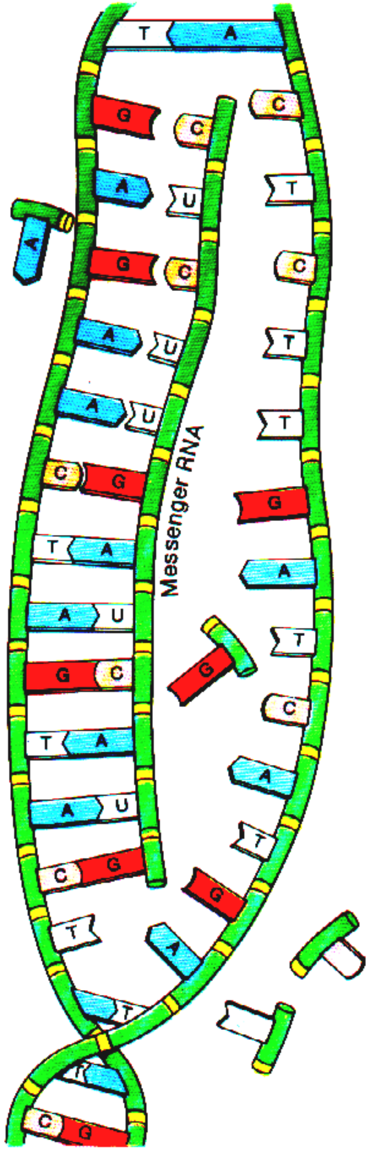
- ☐ That was a lot…
  you deserve another break.

Left to right: Francis Crick, Alexander Rich, Leslie Orgel and James Watson in 1955 (MIT).

# Nature “makes” choices

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

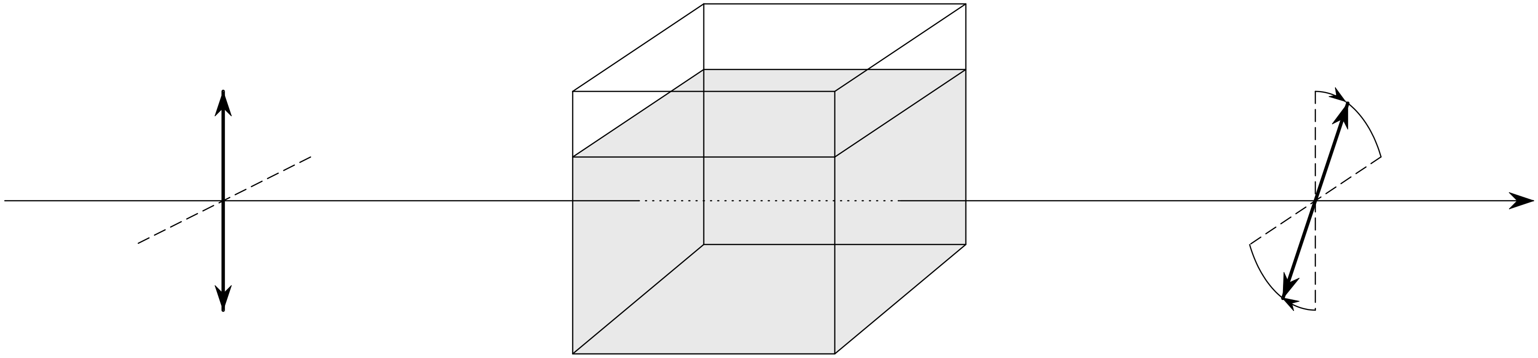
- **Why**? Leading explanation is that those were the ones easiest to replicate, and natural selection favored them: they were made consistently, and thus outnumbered the ones that were made randomly.
- **How**? That’s debated but several experiments and theories provide explanations, as we’ll see.



# Nuances of polymerization: amino acids

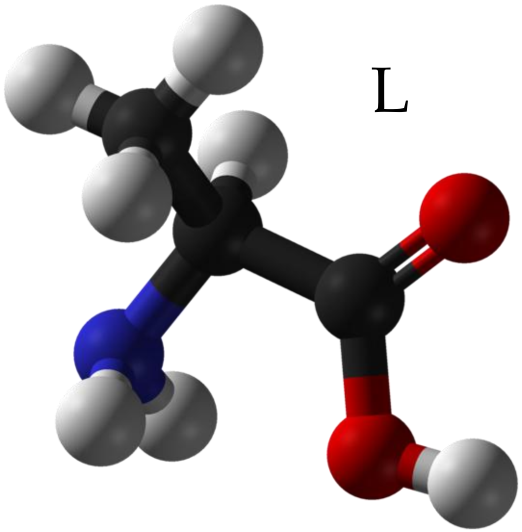
**Optical isomerization** (except glycine): identical chemical contents look like not-identical mirror images.

- ❑ The name comes from the way solutions transmit linearly-polarized 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.

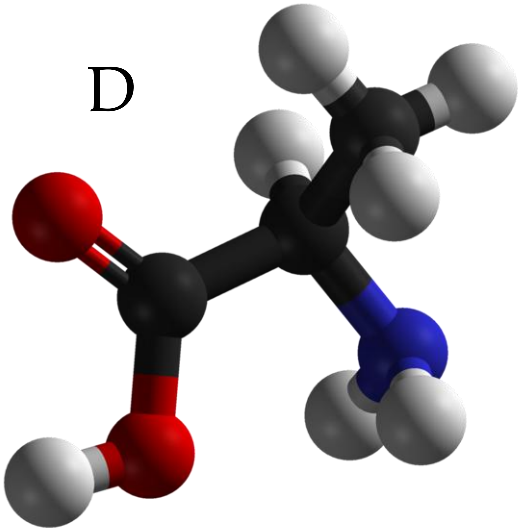


# Nuances of polymerization: amino acids (continued)

- **All amino acids in Earthly life are of the L type**. We don’t know why.
- Polymers of L will of course wrap around differently from polymers of D.
- But Miller-Urey produces equal amounts of L and D (called a **racemic** mixture). Probably the ISM does too. Amino acids found in meteorites are racemic too. And pure L and D convert to racemic if left around long enough (millions of years).



Alanine (dry)

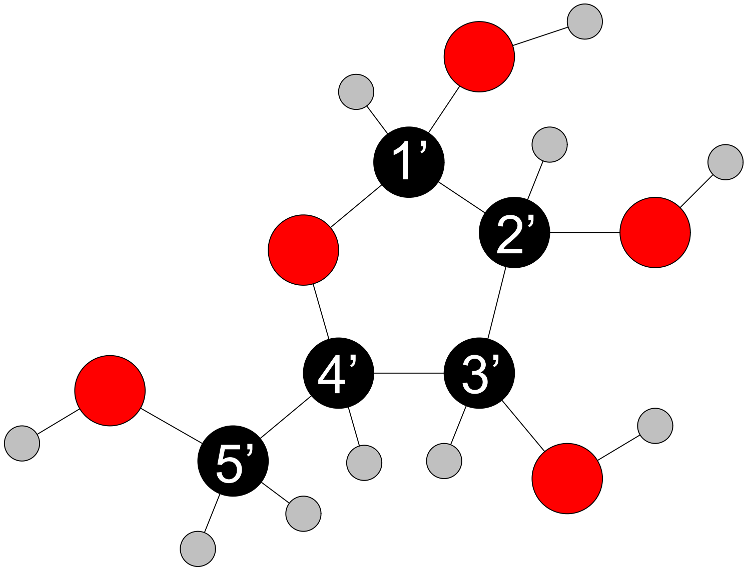


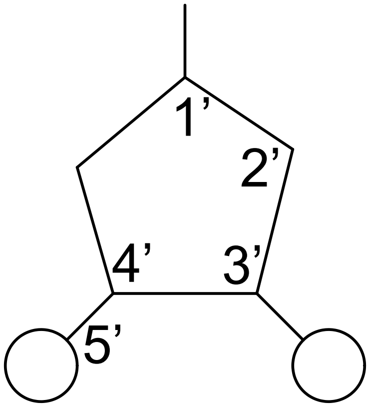
Images from Wikimedia Commons.

# Nuances of polymerization: nucleotides

Four **nuances**, to be precise:

- ☐ **Bonding to ribose**: Carbons 1′, 2′, 3′, and 5′ look identical, but long straight polymer chain only possible if nucleobase bonds to 1′ and phosphates to 3′ and 5′.
- ☐ Not sure how originally effected, but it was found by Leslie Orgel that double-oxidation-state ions like Zn$^{++}$ in solution catalyze polymerization of long chains (as long as 50) in the correct alignment.

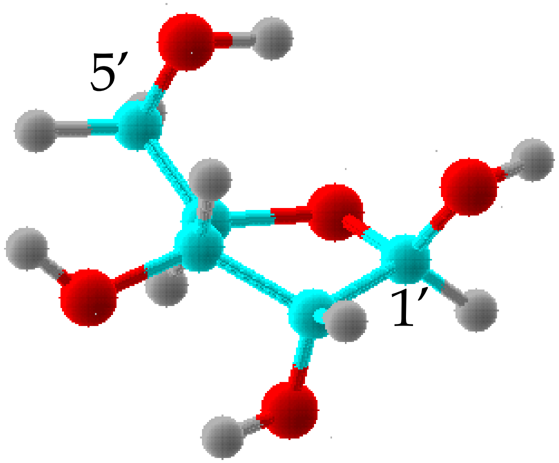




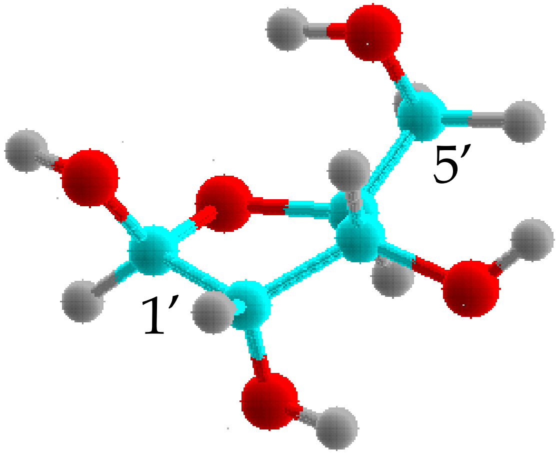
# Nuances of polymerization: nucleotides (continued)

- **Optical isomerization**: the five important nucleobases and phosphoric acid do not exhibit optical isomerization but sugars do.
- Sugars used in Earthly life are all D-type: not just the ribose that forms the backbone of RNA, but also the other sugars like glucose that play roles in energy and metabolism of organisms.

At right: D- and L-ribose.



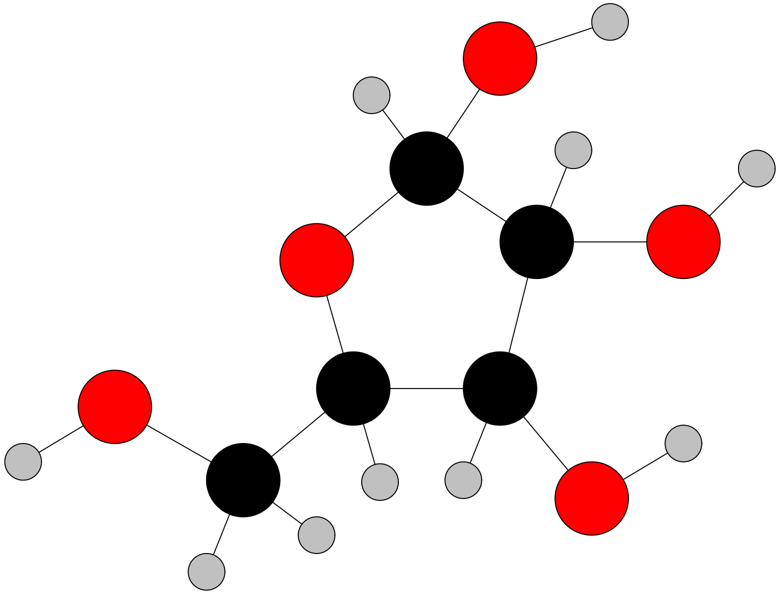
D



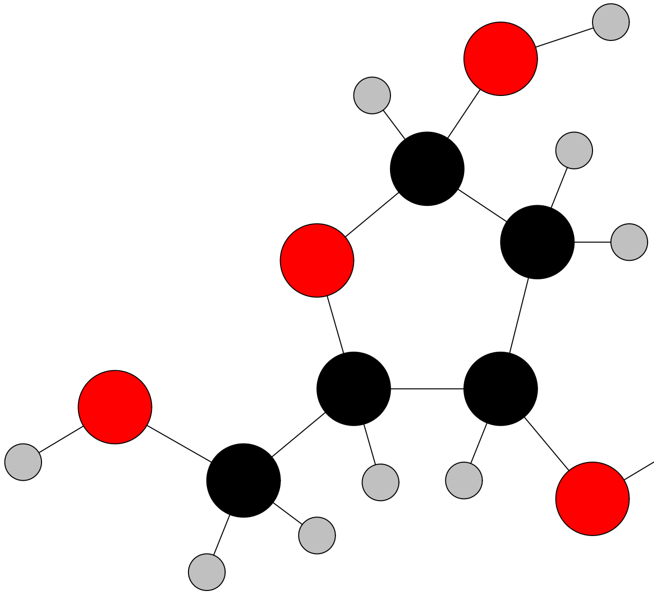
L

# Nuances of polymerization: nucleotides (continued)

- **Nucleotide polymerization** just as easy with **deoxyribose** instead of ribose: this lacks an OH on the 2′ carbon, and has a mere hydrogen in its place.



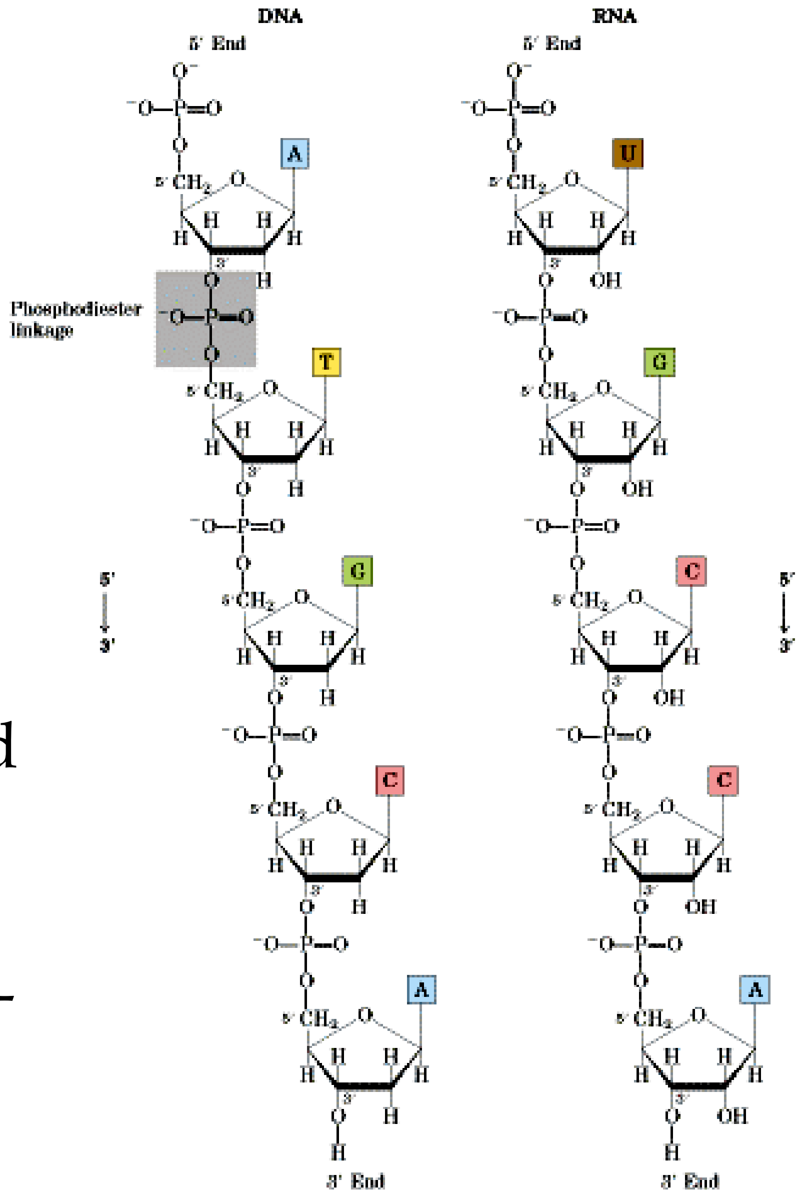
Ribose



Deoxyribose

# Nuances of polymerization: nucleotides (continued)

- When deoxyribose is the sugar, thymine is substituted for uracil; otherwise the same bases are used.
- The polymer that uses deoxyribose is of course called a **deoxyribonucleic acid (DNA)**.
- DNA, famously, has a double-helical, ladder-like structure.



From Neal Evans's [AST 390L lecture notes]().

# 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 guanine-cytosine pairs, these sugar-bonding 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.