

# Origin of Life: I

## Monomers to Polymers

# Synthesis of Monomers

Life arose early on Earth

## Conditions

1. Liquid Water
2. Reducing or Neutral Atmosphere
3. Energy Sources

## 2. Reducing atmosphere

$\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$

1953: Miller-Urey Experiment

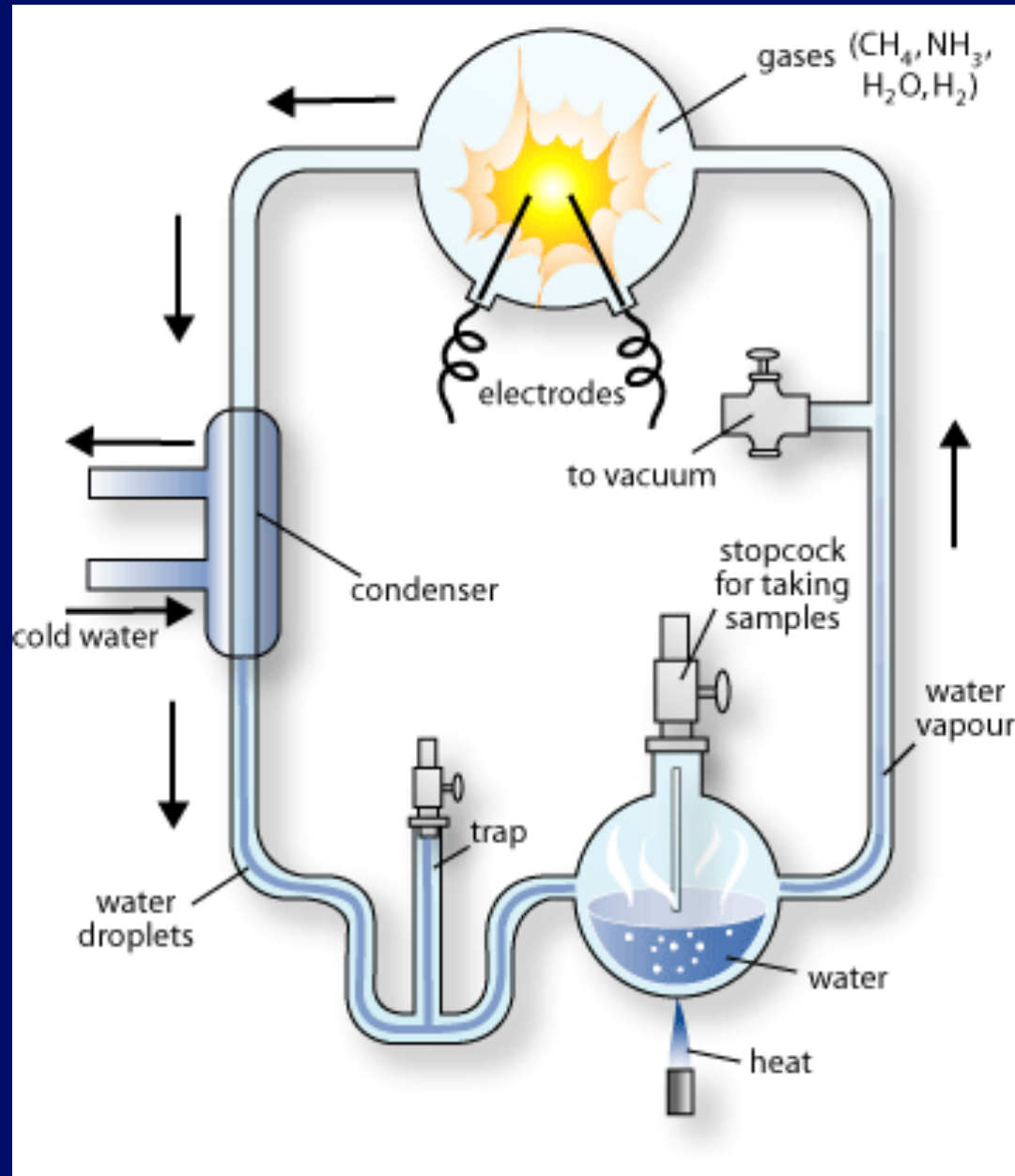
## 3. Energy Sources

Ultraviolet Light (No Ozone)

Lightning

Geothermal (Lava, Hot Springs, Vents, ...)

# Miller-Urey Experiment



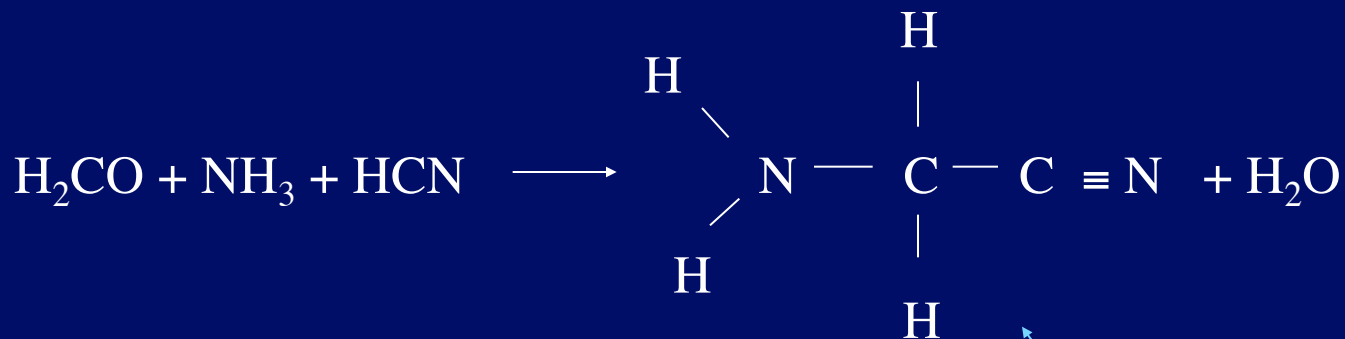
<u>COMPOUND</u>	<u>Relative Yield</u>
<b>Glycine</b>	270
Sarcosine	21
<b>Alanine</b>	145
N-methylalanine	4
Beta-alanine	64
Alpha-amino-n-butyric acid	21
Alpha-aminoisobutyric acid	0.4
<b>Aspartic acid</b>	2
<b>Glutamic acid</b>	2
Iminodiacetic acid	66
Iminoacetic-propionic acid	6
Lactic acid	133
Formic acid	1000
Acetic acid	64
Propionic acid	56
Alpha-hydroxybutyric acid	21
Succinic acid	17
Urea	8
N-methyl urea	6

# How did Amino Acids form in Miller-Urey Experiment?

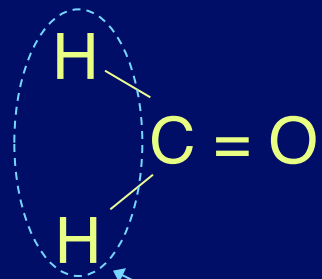
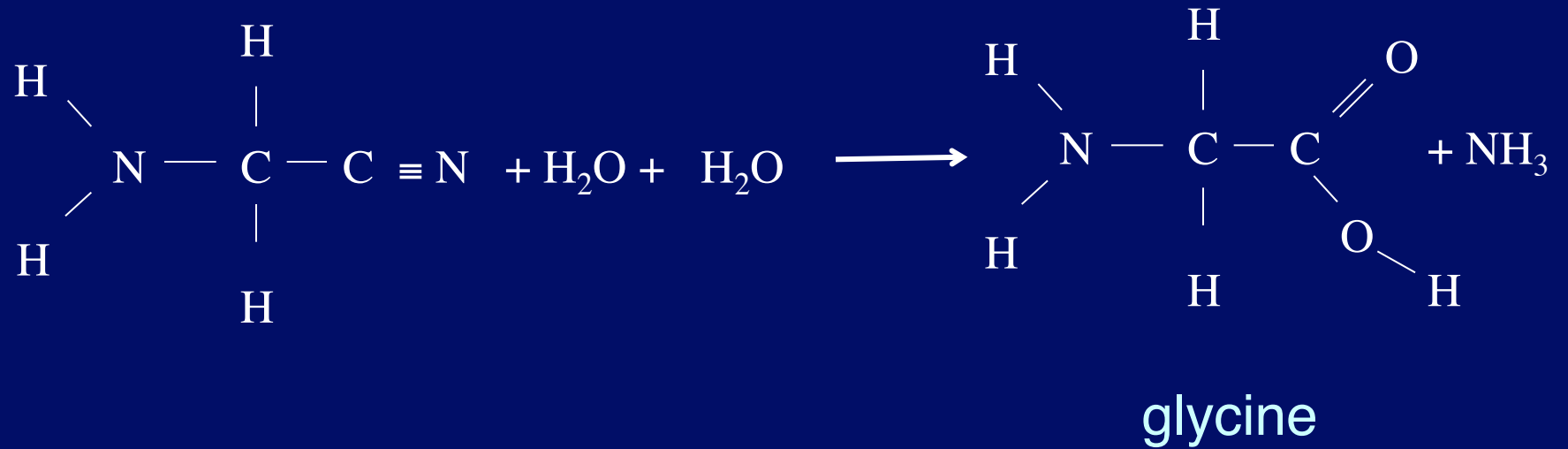
## Strecker Synthesis e.g. Glycine Synthesis



Reactive



Aminoacetonitrile



form Aldehyde

Replace with more complex group  
 Get other aldehydes  
 They can form more complex amino acids

# Building Blocks of Nucleic Acids

Not formed in Miller-Urey, but some intermediates were

## 1. Ribose Sugar:



## 2. Bases



### b) Pyrimidines





### 3. Phosphate

Rock Erosion

Origin of building blocks of nucleic acids is less understood than amino acids

# Problems with Miller-Urey

Atmosphere was  $N_2$ ,  $CO_2$ ,  $H_2O$

$NH_3$ ,  $CH_4$  would react to make  $N_2$ ,  $CO_2$

Try  $N_2$ ,  $CO_2$ ,  $H_2O$  in Miller-Urey simulation

Only get trace amounts of glycine

Need  $CH_4$  to get more complex amino acids

Need  $H_2/CO_2 > 2$  to get much of any amino acid

# Alternative Sites

## Locally reducing environments

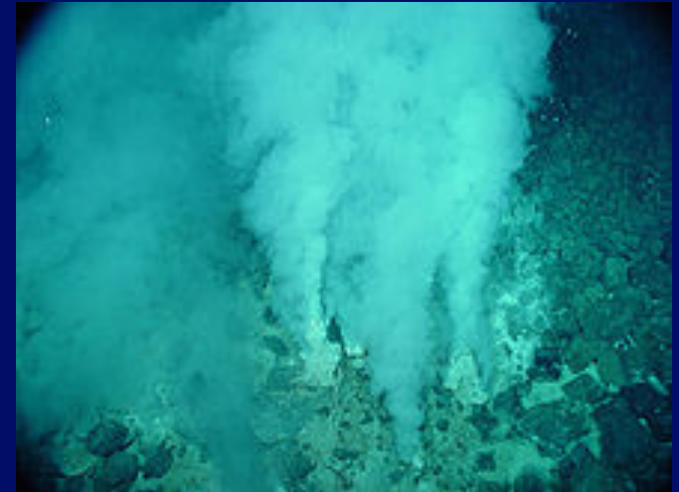
### 1. Ocean vents

Sources of  $\text{CH}_4$  and  $\text{H}_2\text{S}$

Current Vents have ecosystems based on energy from chemicals - not photosynthesis

$\text{H}_2\text{S} \rightarrow$  Bacteria  $\rightarrow$  Clams, Tube Worms

Pre-biotic amino acid synthesis?



# Alternative Delivery

2. Molecular clouds - strongly reducing, contain many molecules used in Miller-Urey ( $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ) and intermediates ( $\text{HCN}$ ,  $\text{H}_2\text{CO}$ ,  $\text{HC}_3\text{N}$ ) and aminoacetonitrile (glycine precursor)

Problem: These would not have survived in part of disk where Earth formed

But interstellar ices can get incorporated into comets and some asteroids.

Evidence from similar molecules  
(e.g.  $\text{C}_2\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{HNC}$ , ...)

Cratering record on moon, ...

⇒ heavy bombardment early in history

Comets, asteroids, and their debris could have brought large amounts of “organic” matter to Earth

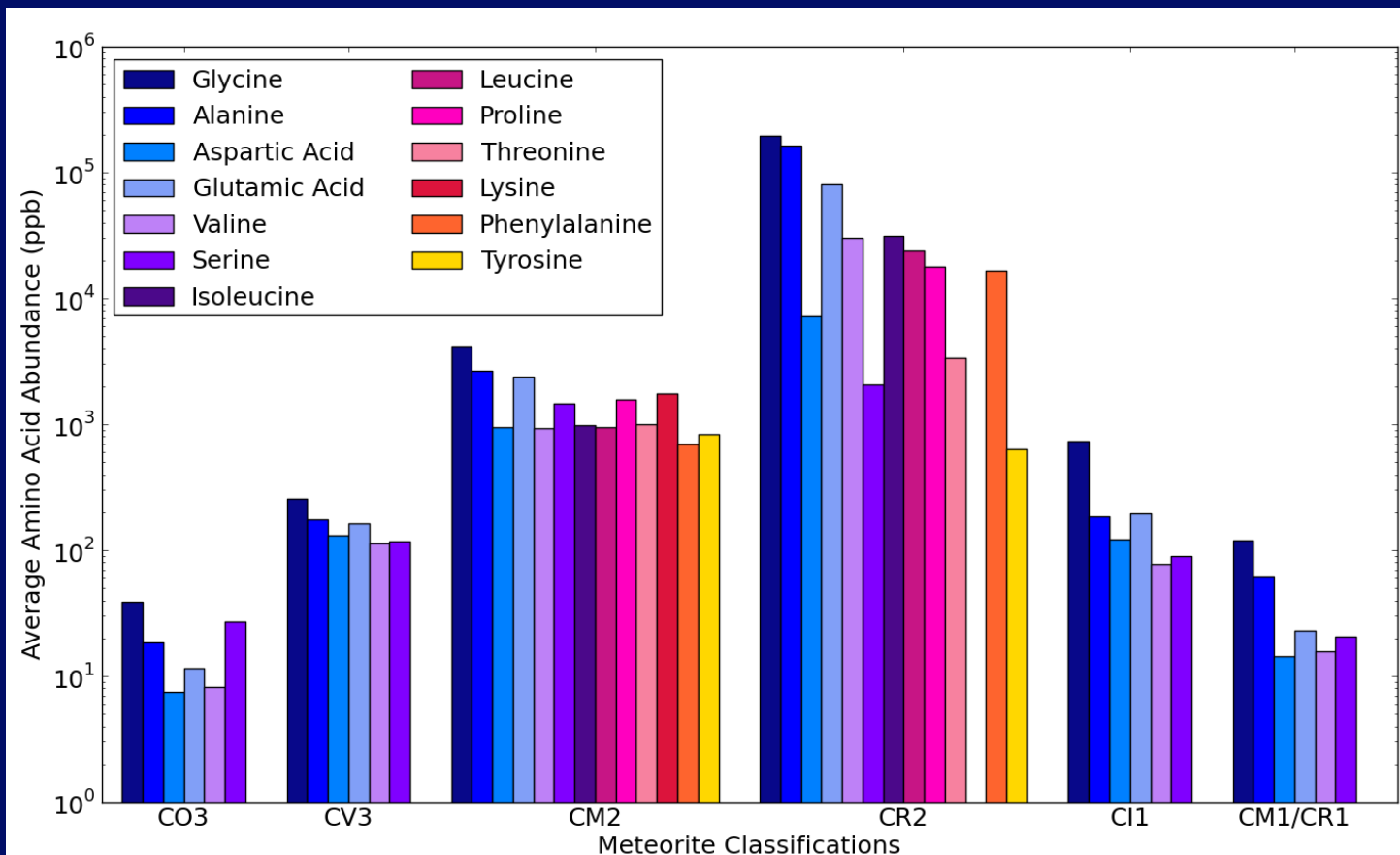
(and probably the oceans)

Some evidence for non-biological amino acids in layer deposited after asteroid impact 65 million years ago

# Amino Acids in Meteorites

- Amino acids are found in some classes of meteorites (carbon-rich ones)
- Recent analysis of some carbon-rich meteorites found in Antarctica
  - Richest source of amino acids so far
  - Up to 250 parts per million
  - Very clearly extraterrestrial (not contamination)
    - Type of amino acids
    - $^{13}\text{C}$  is enhanced (opposite of what life does)

# Amino Acids in Meteorites



Cobb and Pudritz 2014

# Sources of Organic Molecules

Quantitative comparison by Chyba & Sagan, Nature  
1992, Vol. 355, p. 125

Currently, Earth accretes  $\sim 3.2 \times 10^6 \text{ kg y}^{-1}$  from  
interplanetary dust particles (IDP)

$\sim 10\%$  organic carbon  $\Rightarrow 3.2 \times 10^5 \text{ kg y}^{-1}$

$\sim 10^3 \text{ kg y}^{-1}$  comets

$\sim 10 \text{ kg y}^{-1}$  meteorites

$\sim 10^3 \times$  more at  $4.5 \times 10^9 \text{ yr ago}$  (?)

(cratering record)

UV + reducing atmosphere  $2 \times 10^{11} \text{ kg y}^{-1}$

But if  $\text{H}_2/\text{CO} \lesssim 0.1$  IDP's dominant source



So if atmosphere very neutral, IDP's may have been important

Most of mass in IDP's in range of size  $\sim 100 \mu\text{m}$   
mass  $\sim 10^{-5} \text{ g}$

Complex structure - composites of smaller grains, some carbon rich

Enhanced deuterium implies low T

**Deuterium enhancement also found in interstellar molecules**

May imply connection back to interstellar chemistry

2 kinds  
(mass ranges)  
can supply  
organic matter

1. Interplanetary  
dust particles  
( $m \lesssim 10^{-5}$  g)

2. Smaller  
meteorites  
( $m \lesssim 10^8$  g)

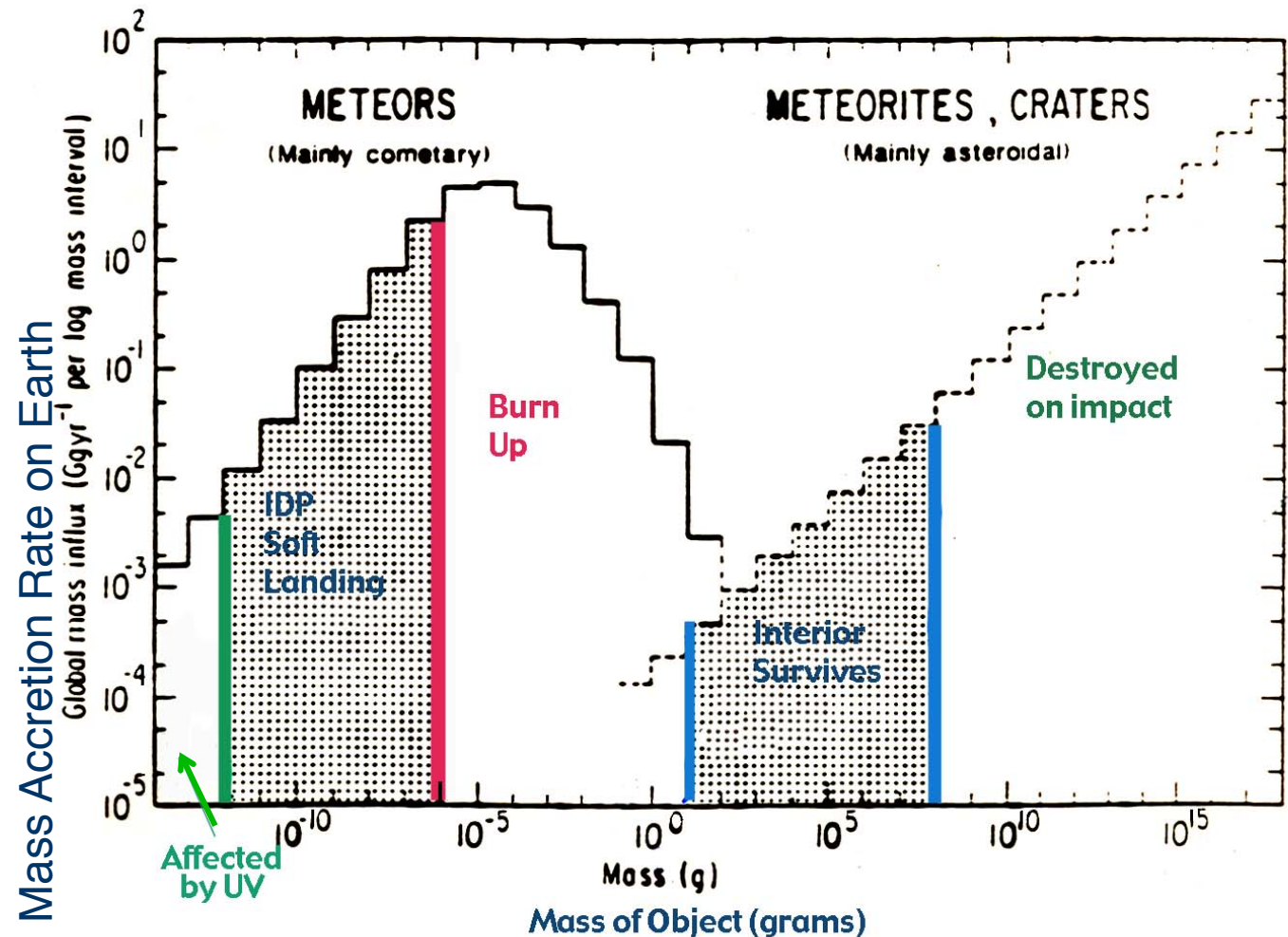


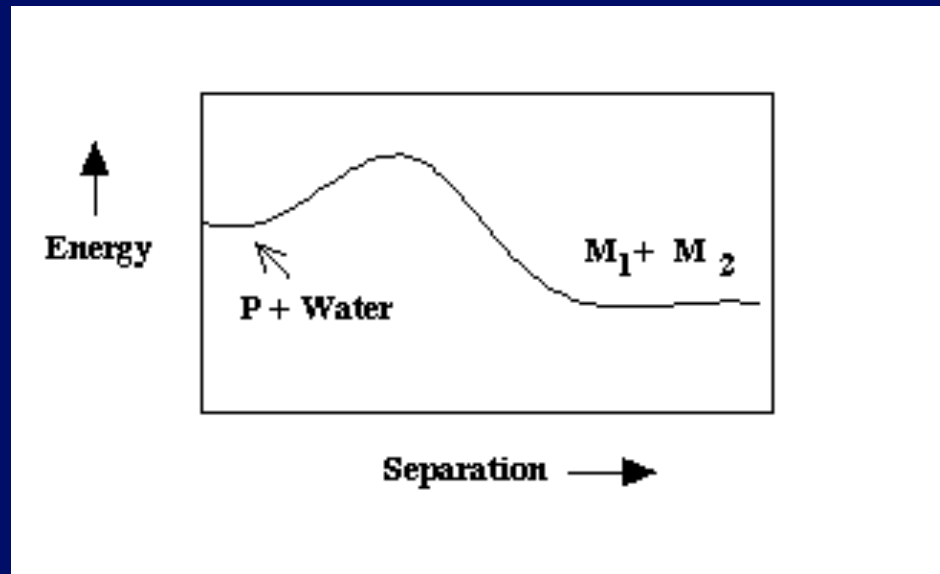
FIG. 1 Infall rate of meteoritic matter on Earth (adapted from ref. 5). Intervals where organic matter can survive passage through atmosphere are shaded. The curve on the right is based on the relation<sup>5</sup>  $N=0.54 r^{-2.1}$  ( $N$ =number of impacts per Myr,  $r$ =radius in km), for an assumed density of  $3 \text{ g cm}^{-3}$ . The corresponding mass accretion rate ( $\text{Gg yr}^{-1}$ ) between  $r_1$  and  $r_2$  is  $15.83 (r_2^{0.9} - r_1^{0.9})$ .

E. Anders (1989) Nature, 342, 255

# Synthesis of Polymers



← more likely in liquid  $H_2O$



**Solutions:**

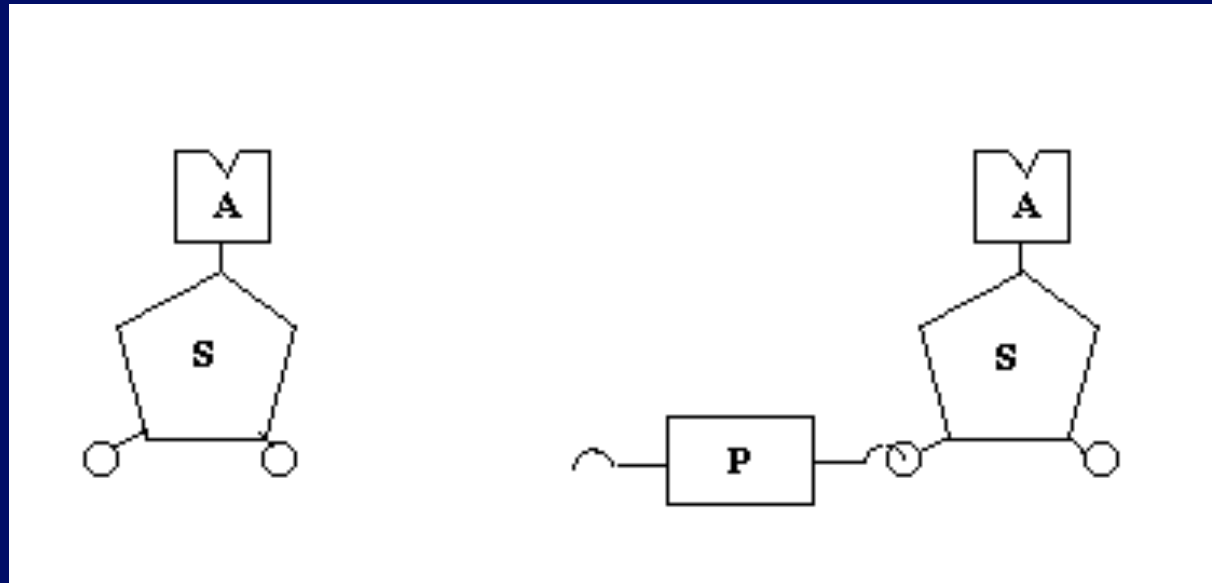
Remove  $H_2O$  (Drying, Heat)

Sydney Fox  $\longrightarrow$  Proteinoids

Energy Releasing Reactions ( $H_2NCN$  or  $HC_3N$ )

Catalysts: Clays

Problem is worse for Nucleic acids because more complex



nucleoside

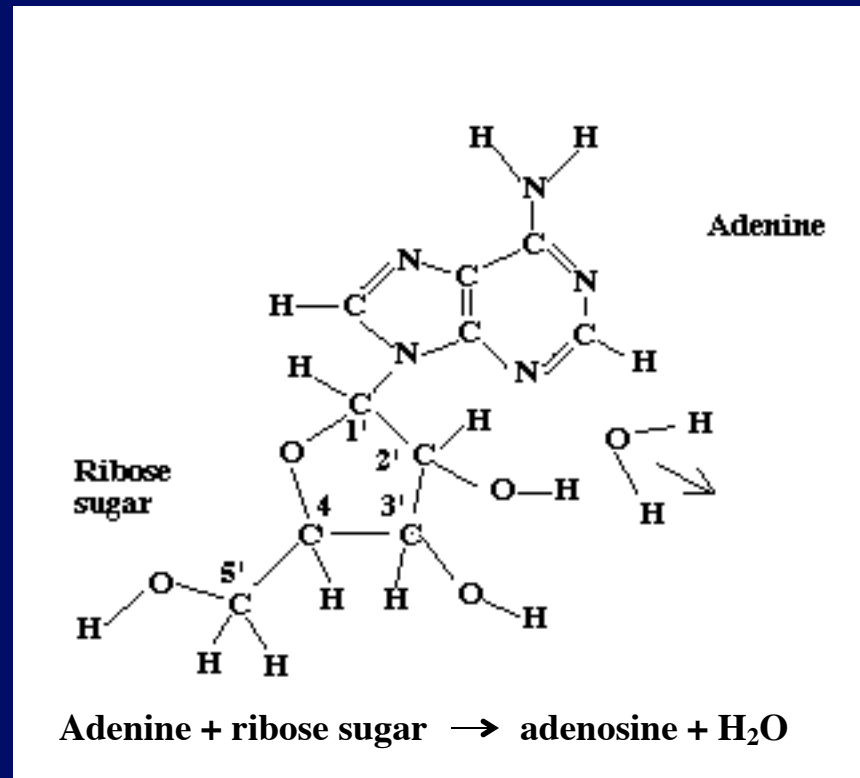
nucleotide



Monomers of nucleic acids

# Synthesis of Adenosine

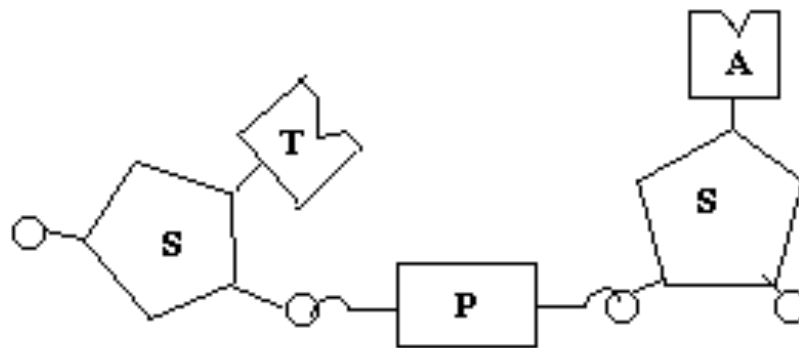
Base on 1' Carbon (Why?)



Also phosphates

3' & 5' carbons

Otherwise, you are likely to get  
Misalignment



# New Approach

- Progress from a group in England
  - Mix HCN, H<sub>2</sub>CO, ... and phosphate
  - Energy led to nucleotides without making sugars, bases. Different route.
  - Linkages not all correct
  - But exposure to ultraviolet destroyed incorrect ones.
  - Clay soils can catalyze polymerization into nucleic acids.

# The Odds

- We need to get an “interesting” polymer
  - Enzyme
  - Self replicator
- Properties of polymer depend on
  - Order in which monomers combine
- If we combine monomers at random,
  - How likely to get something interesting?



# Statistics of an unlikely event

Random reactions in primordial soup?

Unlikely event versus many trials

Probability Primer: Consider tossing 10 coins

Probability of all heads = product of prob.

$$P = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(\frac{1}{2}\right) \dots \left(\frac{1}{2}\right)^{10} = \frac{1}{1024}$$

Probability of getting 10 amino acids → protein

Chosen from 20 in a particular order

$$\left(\frac{1}{20}\right)^{10} = \frac{1}{1 \times 10^{13}}$$

Based on discussion by  
R. Shapiro

But if you try many times, the chance of success is higher

$$P(r) = \frac{n!}{r! (n-r)!} p^r (1-p)^{n-r}$$

$r$  = # of successes     $p$  = prob. of success on each trial

$n$  = # of trials

$n! = n (n-1) (n-2) \dots 1$

e.g. make  $n = \frac{1}{p}$  (flip all 10 coins 1024 times)

$$P(1) = \frac{n!}{1! (n-1)!} \binom{1}{n} \left(1 - \frac{1}{n}\right)^{n-1} = 0.37$$

Chance of one or more successes = 0.63

For reasonable chance need  $n \sim \frac{1}{p}$

# How many do we have to get right?

## 1. How many atoms?

Lipids	$10^2 - 10^3$
Enzymes, RNA	$10^3 - 10^5$
Bacterial DNA	$10^8 - 10^9$
Bacterium	$10^{11} - 10^{12}$
Human Being	$10^{27} - 10^{28}$

If we choose from H,C, N, O (ignore S,P)

probability of right choice 1/4

So for enzyme:  $(\frac{1}{4})^{10^3} \sim 10^{-600}$

# of trials: R. Shapiro computes

$N = 2.5 \times 10^{51}$  (surely an overestimate)

$n \ll \frac{1}{p}$  for simple enzyme

2. What if we start with amino acids?

Need  $\sim 10^{13}$  trials to get 10 amino acid protein

To get 200 amino acids in right order

$$\left(\frac{1}{20}\right)^{200} = 10^{-260} \quad \text{Hopeless!}$$

Need something besides random combinations

Selection (Natural?)

# Improving the Odds

Many proteins composed of interchangeable segments (Domains)

10 to 250 amino acids

One domain found in ~ 70 different proteins

Intermediate building blocks?

If so, may only need to get enough amino acids in right order for a domain

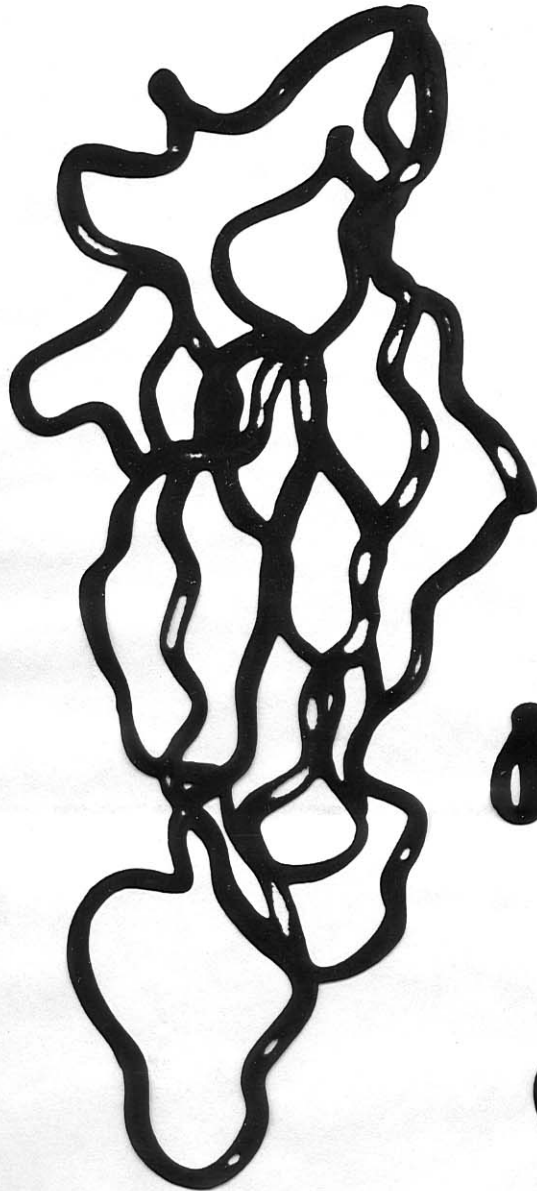
e.g. 18 amino acid domain

$$P = \left(\frac{1}{20}\right)^{18} = 10^{-23}$$

Also, many variations in amino acids don't  
destroy function

and many different sequences may be  
interesting

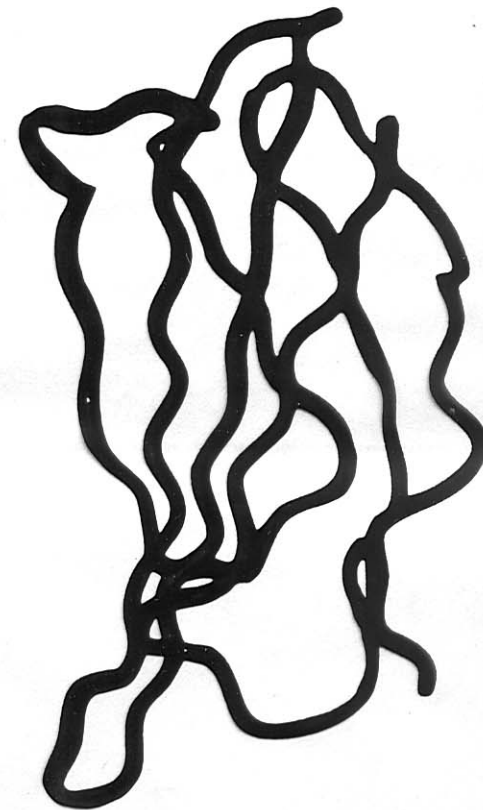
**GENETICALLY MOBILE MODULES** have been found in many proteins. Two types of these modules, or domains, are shown here. The Fn3 and the GHR domains are examples of fibronectin type III modules. The PapD and CD2 domains are immunoglobulin domains. These modules are linear sequences of amino acids that can fold themselves into consistent, recognizable structures with specific biochemical properties. During evolution, these domains can move as discrete units from one protein to another, which helps new types of proteins to appear.



**PapD DOMAIN 1**



**GHR DOMAIN 1**



**Fn3 (10TH DOMAIN)**

# Summary

- Reactions in atmosphere (Miller-Urey) or sea vents or delivery from space can provide some monomers
- Formation of monomers of proteins easier than for nucleic acids
- Making polymers easier for proteins
- New route for synthesis of nucleotides is promising
- Have to get selection started before polymers get too complex