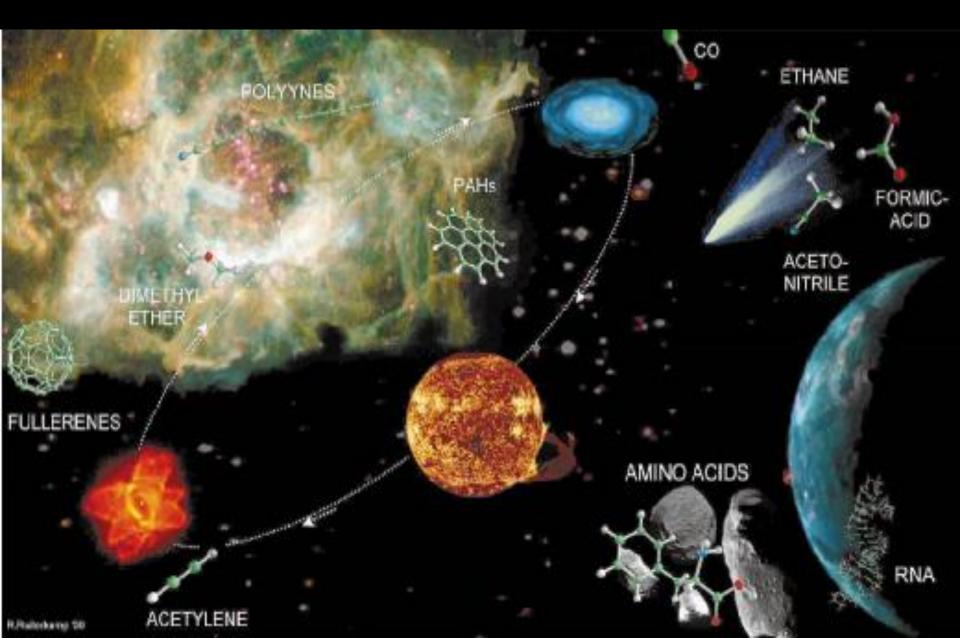
ASTROCHEMISTRY & ASTROBIOLOGY



FOLLOW THE LIFE

- Solvent
- → Biogenic elements
 - Source of Free Energy

searches for life within our solar system commonly retreat from a search for life to a search for "life as we know it," meaning life based on liquid water, a suite of so-called "biogenic" elements (most famously carbon), and a usable source of free energy.

(Chyba & Hand, 2005, p. 34)

SIGA A VIDA

- Siga a água (Follow the water)
- → Siga o carbono
 - Siga o nitrogênio
 - Siga o fósforo
 - Siga a energia
 - Siga a entropia
 - Siga a informação
 - Siga o significado

Universo Orgânico!

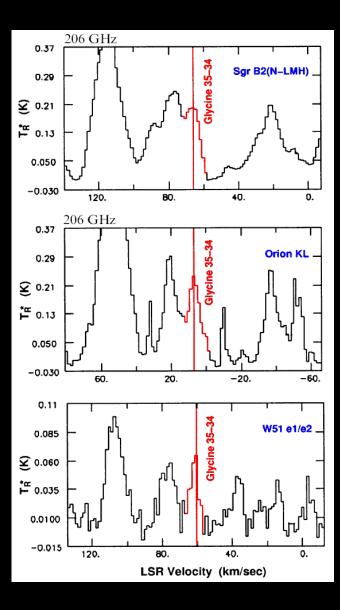
- 0.5 % da matéria bariônica "visível" está na forma molecular. (Fraser, McCoustra & Willians, 2002, A&G, 43, 2.11).
- ~170 Moléculas detectadas no espaço (~50% orgânicas: CHON).

Como são encontradas as biomoléculas ?



Radiotelescopes (rotational lines)





Onde são encontradas as biomoléculas?

Gaseous Pillars – Eagle Nebula

Key hole Nebula



Titan

Hale-Bopp

Murchinson

2 atoms	H_2	AlF	AlCl	C_2	CH	CH^+
	CN	CO	CO^+	CP	SiC	HCI
	KCl	NH	NO	NS	NaCl	OH
	PN	SO	SO^+	SiN	SiO	SiS
	CS	HF	HD	FeO (?)	O_2	CF^+
	SiH (?)	PO	AlO	OH^+	CN-	SH^+
	LiH	SH	N_2	S_2^{\dagger}	N_{2}^{+} †	CN^+
3 atoms	C_3	C_2H	C_2O	C_2S	CH_2	HCN
	HCO	HCO^+	HCS^+	HOC^+	H_2O	H_2S
	HNC	HNO	MgCN	MgNC	N_2H^+	N_2O
	NaCN	OCS	SO_2	$c - SiC_2$	CO_2	NH_2
	H_{3}^{+}	H_2D^+	HD_2^+	SiCN	AINC	SiNC
	HCP	CCP	AlOH	H_2O^+	H_2Cl^+	KCN
	FeCN	OCN^-	CO_2^+	H_2S^+	CN_2	HDO
	CS_2^{\dagger}					
4 atoms	$c - C_3 H$	$l - C_3 H$	C_3N	C_3O	C_3S	C_2H_2
	NH_3	HCCN	$HCNH^+$	HNCO	HNCS	$HOCO^+$
	H_2CO	H_2CN	H_2CS	H_3O^+	$c - SiC_3$	CH_3
	C_3N^-	$PH_{3}(?)$	HCNO	HOCN	HSCN	H_2O_2
	C_4 (??)					
5 atoms	C_5	C_4H	C_4Si	$l - C_3H_2$	$c - C_{3}H_{2}$	H_2CCN
	CH_4	HC_3N	HC_2NC	HCOOH	H_2CNH	H_2C_2O
	H_2NCN	HNC_3	SiH_4	H_2COH^+	C_4H^-	HC(O)CN
6 atoms	C_5H	$l - H_2C_4$	C_2H_4	CH_3CN	CH_3NC	CH_3OH
	CH_3SH	HC_3NH^+	HC_2CHO	NH_2CHO	$C_{5}N$	$l - HC_4H$
	$l - HC_4N$	$c - H_2C_3O$	$H_2CCNH(?)$	C_5N-		
7 atoms	C_6H	CH_2CHCN	CH_3C_2H	$HC_{5}N$	$CH_{3}CHO$	CH_3NH_2
	$c - C_2 H_4 O$	H_2CCHOH	C_6H-			
8 atoms	CH_3C_3N	$HC(O)OCH_3$	$CH_{3}COOH$	C_7H	H_2C_6	CH ₂ OHCHO
	$l - HC_6H$	$CH_2CHCHO(?)$	CH_2CCHCN	H_2NCH_2CN	$C_{2}H_{6}^{\dagger}$	$(NH_2)_2CO(??)$
9 atoms	CH_3C_4H	CH_3CH_2CN	$(CH_3)_2O$	CH_3CH_2OH	HC_7N	C_8H
	$CH_3C(O)NH_2$	C_8H^-	C_3H_6			
10 atoms	CH_3C_5N	$(CH_3)_2CO$	$(CH_2OH)_2$	CH_3CH_2CHO	$NH_2CH_2COOH(??)^{\dagger}$	
11 atoms	HC_9N	CH_3C_6H	C ₂ H ₅ OCHO		- **	
12 atoms	C_6H_6	$C_2H_5OCH_3?$	$n - C_3H_7CN$	$CO(CH_2OH)_2(??)$		
> 12 atoms	$HC_{11}N$	$C_{10}H_{8}^{+}$	$C_{14}H^+_{10}(??)$	C24(??)	C_{60}	C_{70}
		-				

Molecules in Space

338 Molecules

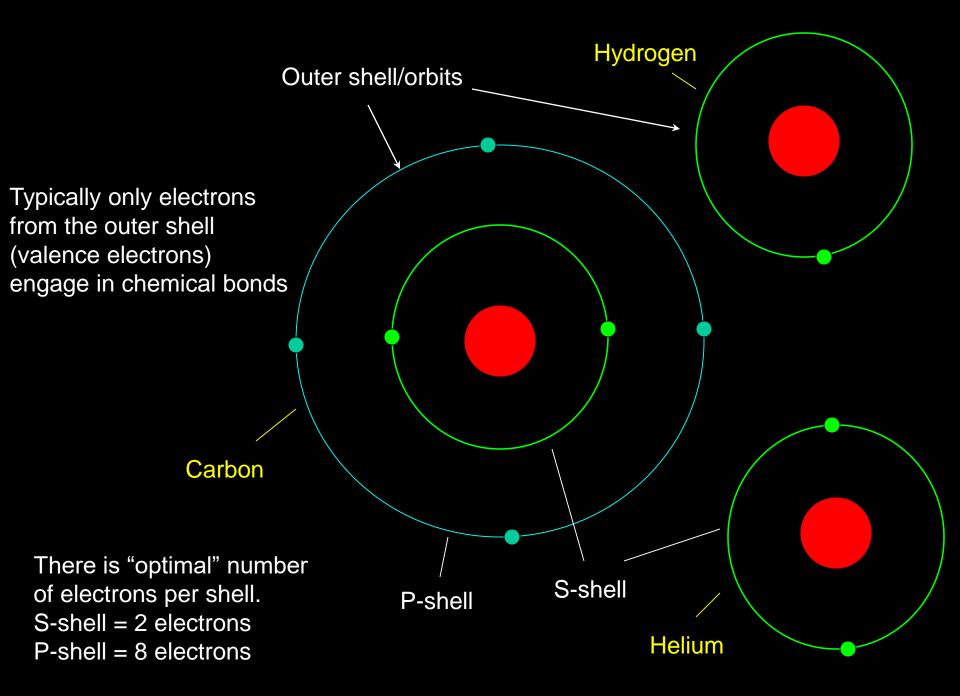
as if May 2024

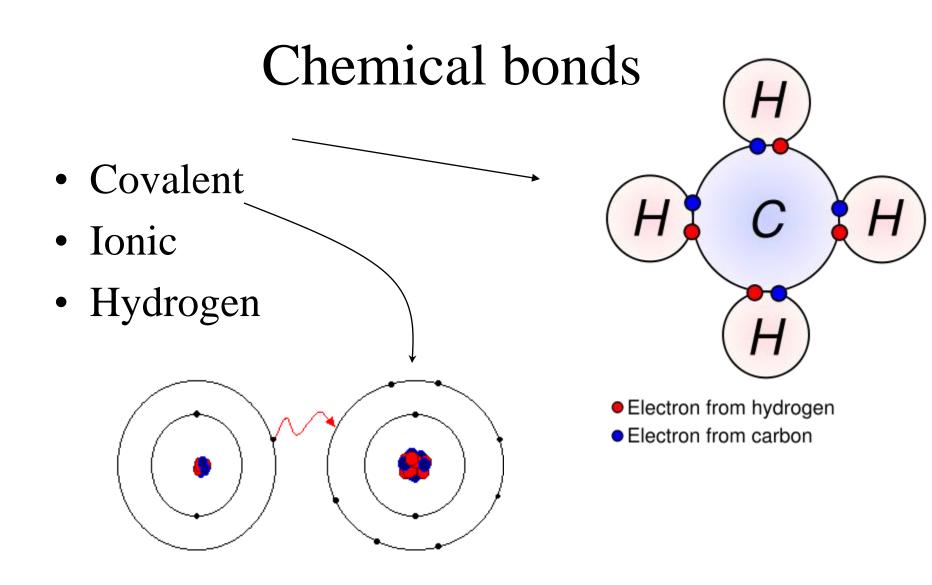
Abundâncias relativas dos elementos químicos

The abundances are in numb Sources: Lehninger 2000 (hu		; Asplund, Grevesse & Sauval 2004 (C, N, and O are neteoritic values)
Human Body	Earth Crust	Cosmic
H 247	O 100	H 21 900
O 100	Si 59.6	O 100
C 37.3	AI 16.8	C 53.7
N 5.49	Fe 9.6	N 13.2
Ca 1.22	Ca 7.5	Mg 7.41
P 0.86	Na 5.3	Si 7.10
CI 0.31	K 5.3	Fe 6.17
K 0.24	Mg 4.7	S 3.16
S 0.20	Ti 1.1	AI 0.58
Na 0.12	H 0.4	Ca 0.43
Mg 0.04	C 0.4	Na 0.41

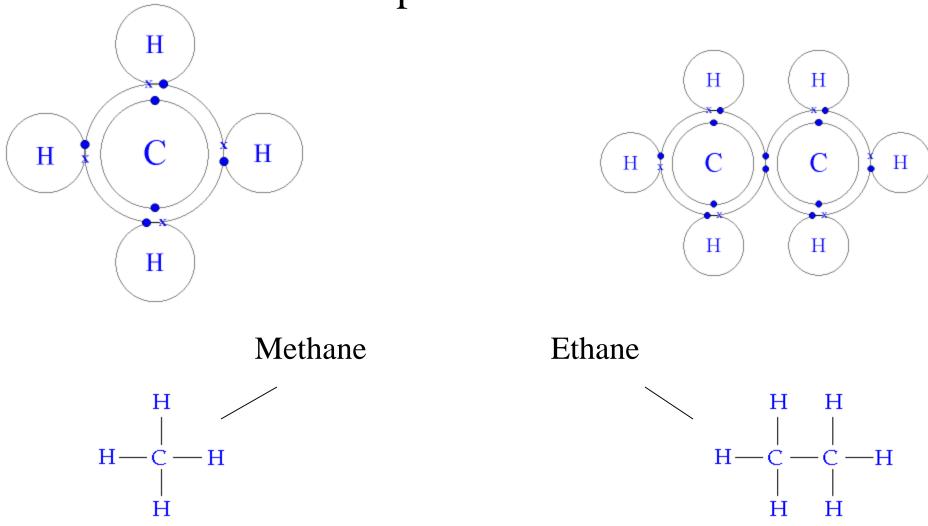
Why Carbon?

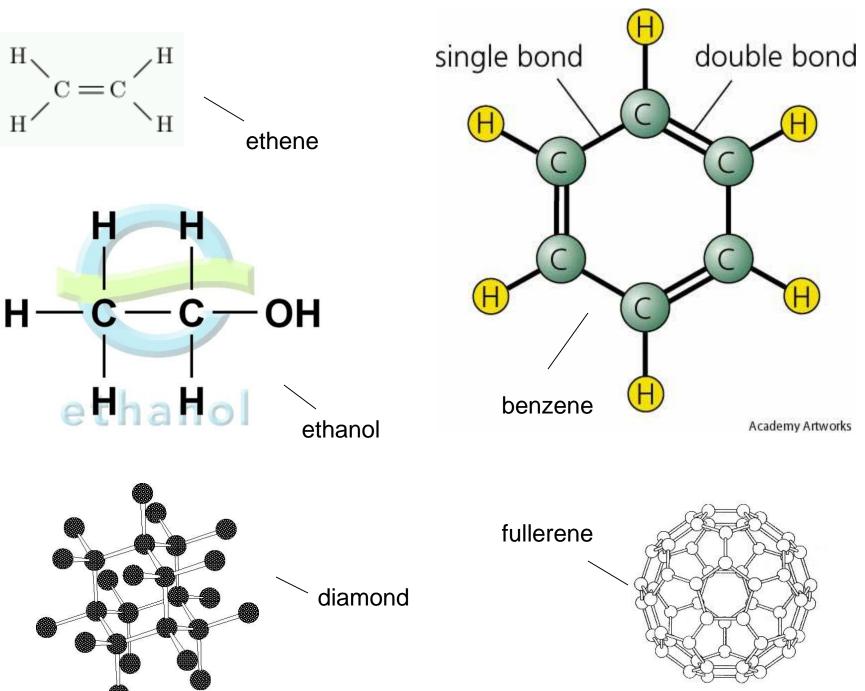
- Carbon atom can form up to 4 chemical bonds with many other atoms – can form long and complex molecules
- Carbon can form compounds that readily dissolve in water.





Carbon has 4 valence electrons – can form up to 4 bonds





5.34b

Polymerization

• A **polymer** is a substance composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds. Well known examples of polymers include plastics and DNA. radical addition $\xrightarrow{\text{polymerization}} \cdots \xrightarrow{\begin{array}{c}H_2\\C\\C\\H_2\end{array}} \xrightarrow{\begin{array}{c}H_2\\C\\C\\H_2\end{array}} \xrightarrow{\begin{array}{c}H_2\\C\\C\\H_2\end{array}} \xrightarrow{\begin{array}{c}H_2\\C\\H_2\end{array}} \xrightarrow{\begin{array}{c}H_2\\C\\H_2\end{array}} \cdots$

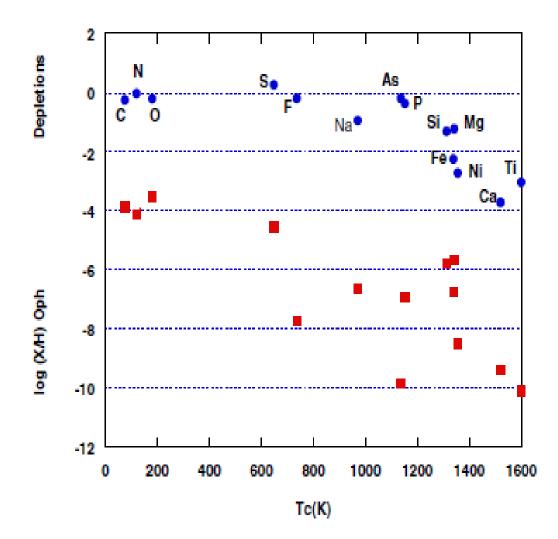
Fig 1: The polymerisation of ethene in to poly(ethene)

Silicon life?

- Si is abundant and also can form four bonds at once (like C). But!
- Si bonds are much weaker complex molecules based on Si will be fragile
- Si does not form double bonds less variety







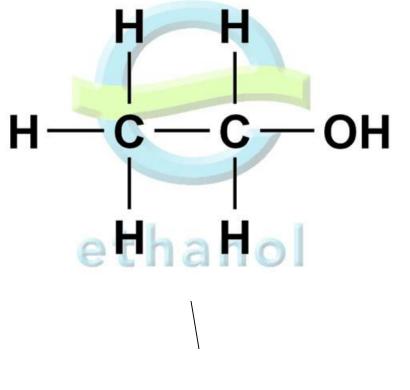
Organic and Inorganic Carbon

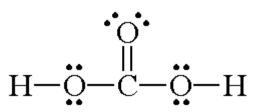
C can be in <u>reduced</u> or <u>oxidized</u> forms.

Organic carbon (reduced) Inorganic carbon (oxidized)

'CH₂O'

Example: Glucose -- C₆H₁₂O₆ CO_2 carbon dioxide H_2CO_3 carbonic acid HCO_3^- bicarbonate ion CO_3^{2-} carbonate ion



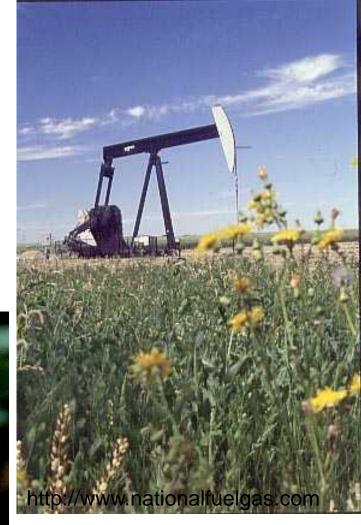


carbonic acid

Inorganic carbon (C-O bonds only)

Organic carbon (has C-H and C-C bonds)





Oil



Organic carbon

Inorganic carbon

Seashells





Coral



Four types of organic macromolecules in living systems.

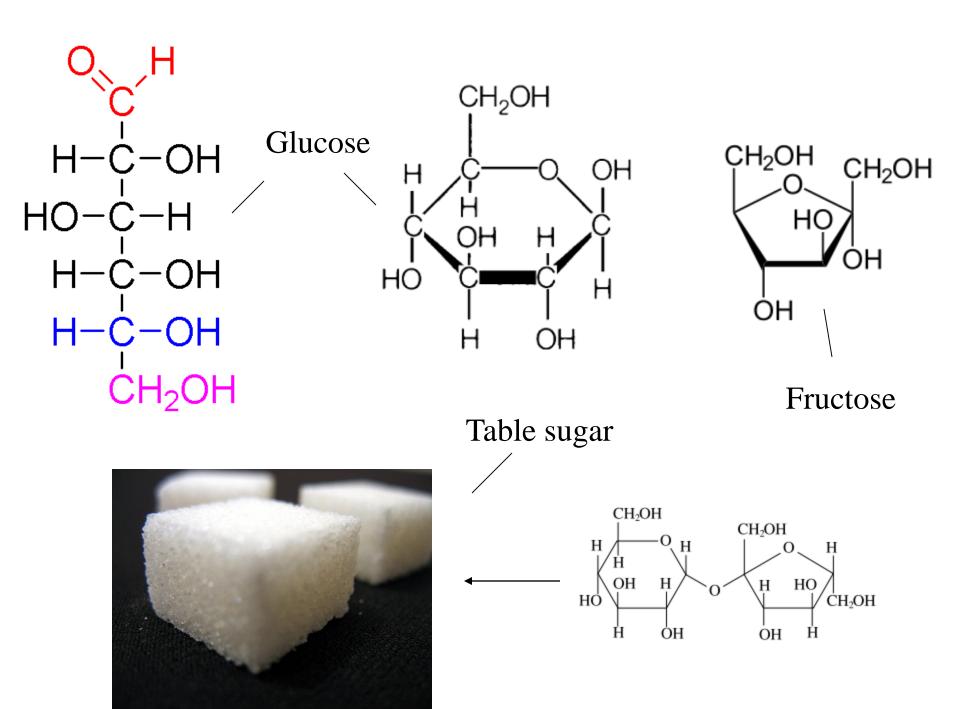
Most of the molecules in the living systems are water (H_2O) and large organic macromolecules:

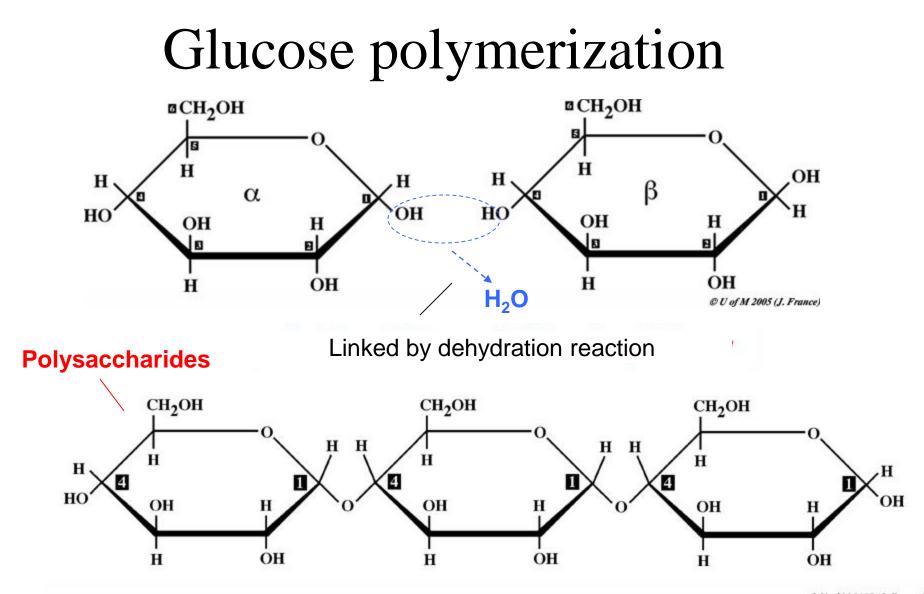
- Carbohydrates
- Lipids
- Proteins
- Nucleic Acids

Carbohydrates (sugars, starches)

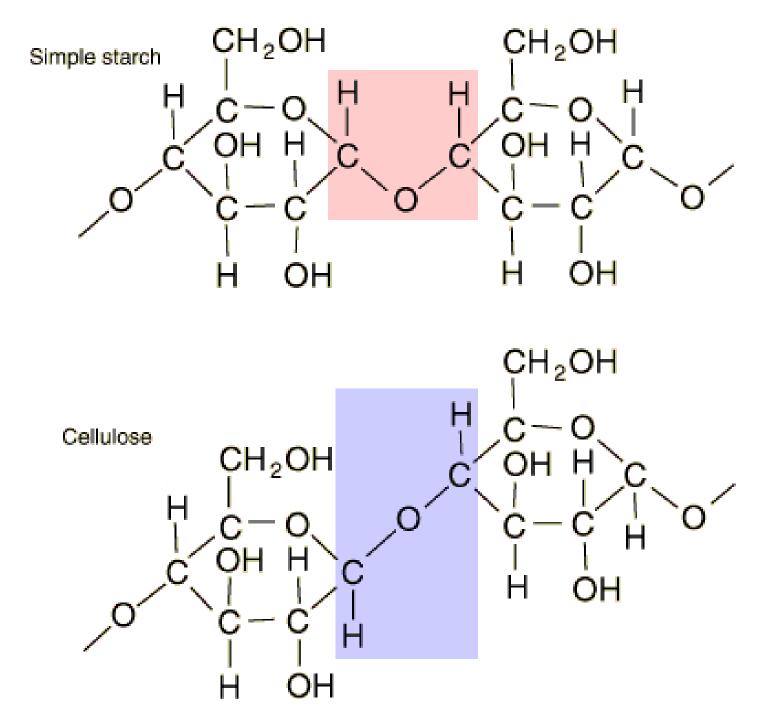
- Representatives: Glucose, Fructose
- Many hydroxyl groups (-OH)
- Soluble in water
- Form Polysaccharides
- Good energy source
- Structural support for organisms (cellulose
- the main constituent of wood)







In starch molecule (potato) there can be 100s thousands of glucose units



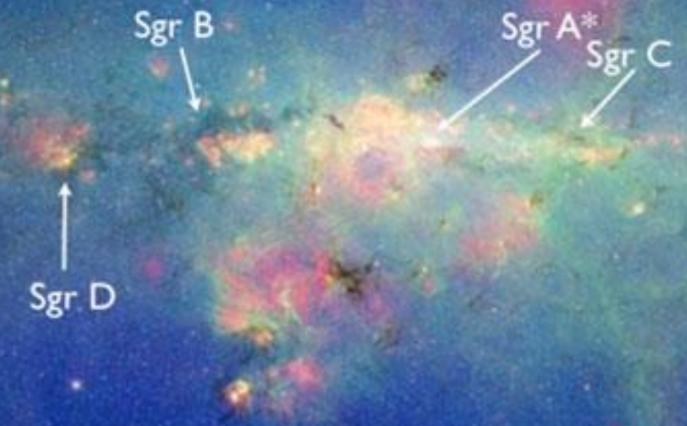
Carbohydrates are important as a source of energy for life

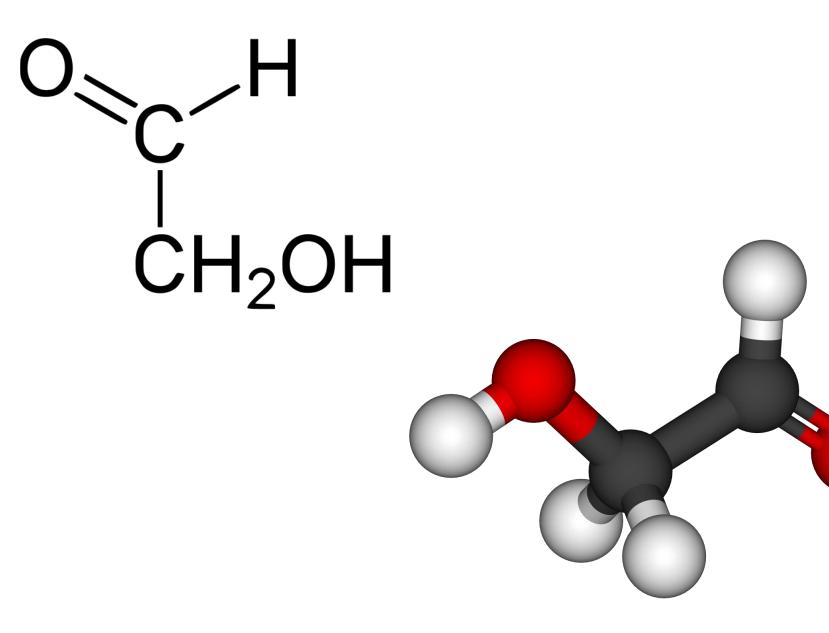
- Respiration
- $CH_2O + O_2 \rightarrow CO_2 + H_2O + Energy$ In reality:
- $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Energy$
- Fermentation
- $C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_6O + Energy$

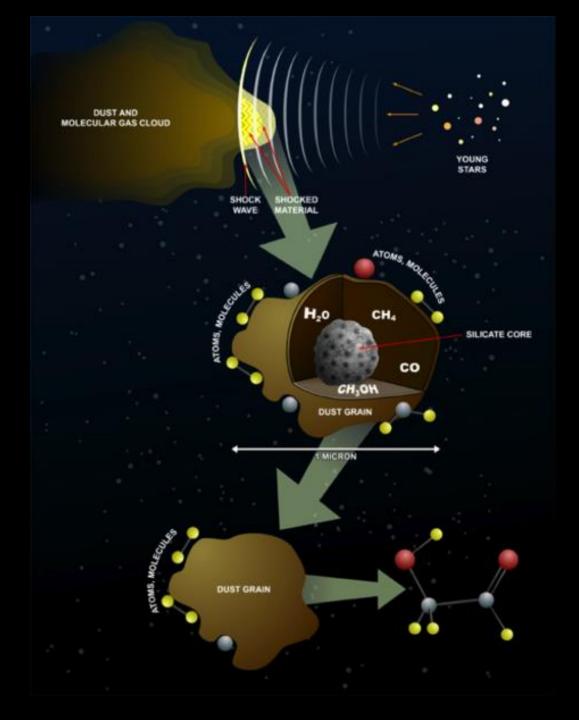
O Universo é úmido

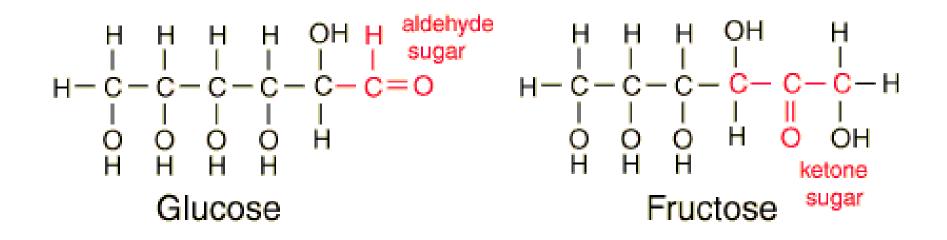
O Universo é doce

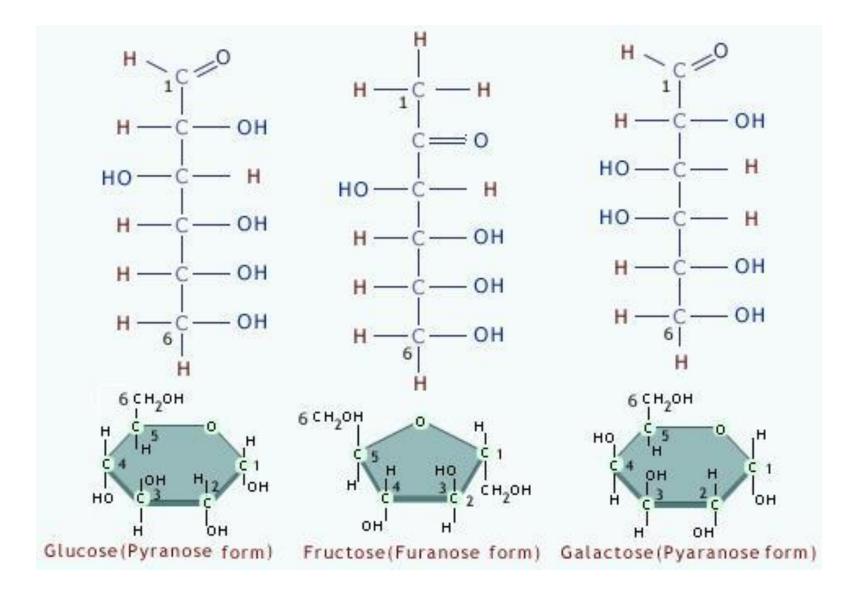
Center of the Milky Way as seen by the Spitzer Space Telescope

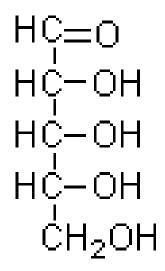


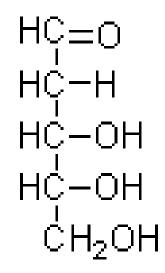


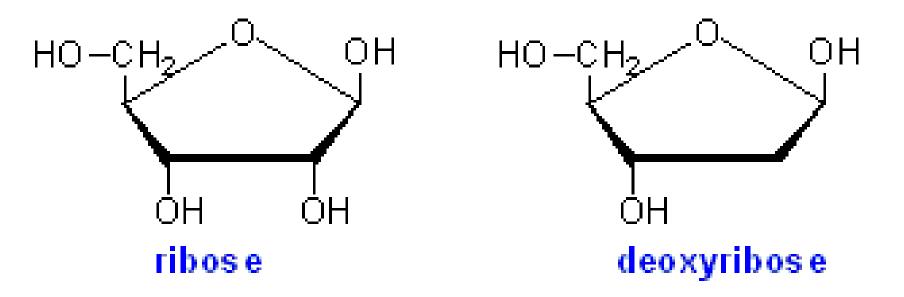












Lipids (fats and oils)

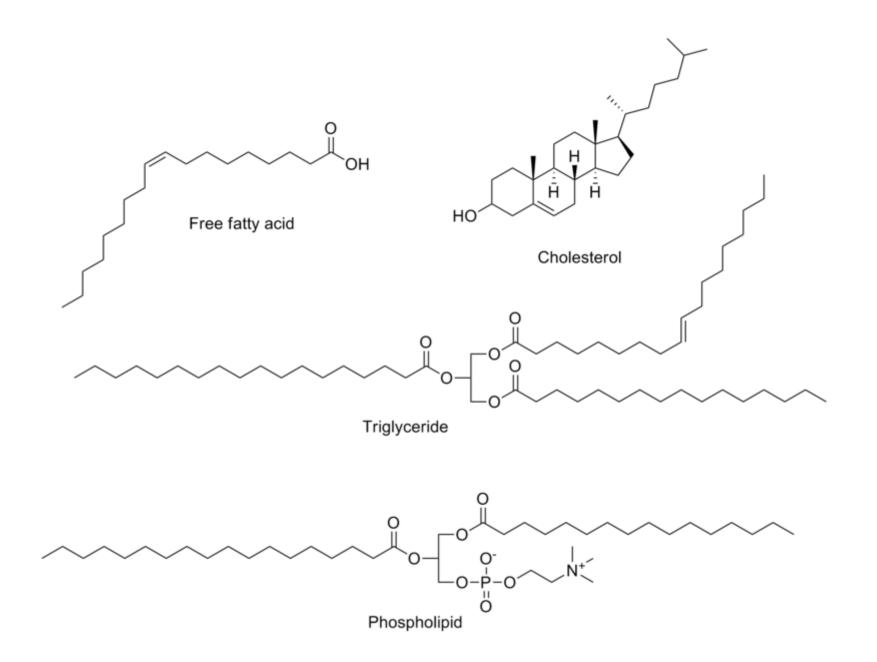
- Representatives: fatty acids and cholesterol
- Poorly soluble in water
- Good (concentrated)

energy source

• Flexible

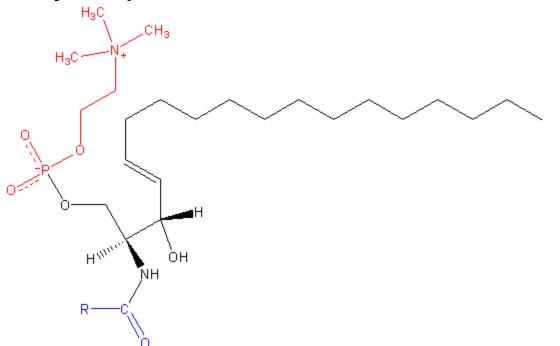
(cell membrane material)



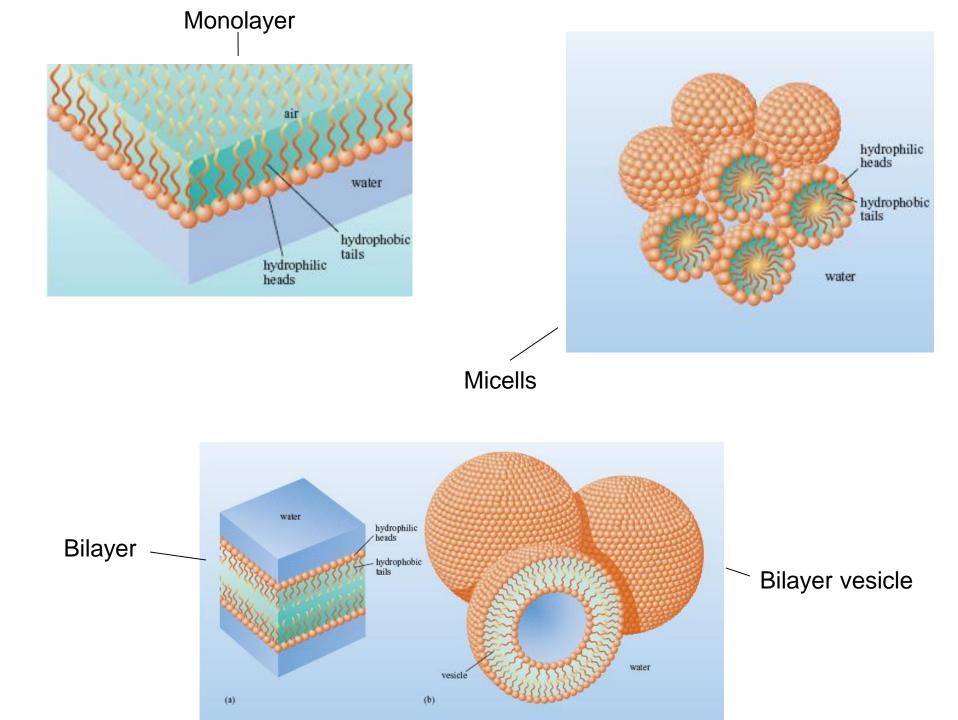


Lipids are important for the formation of the cell membrane

 Some lipids have hydrophilic (love water) head and hydrophobic tail



 In solution these lipids can form monolayers, bilayers and bilayer vesicles spontaneously – pre-cells.

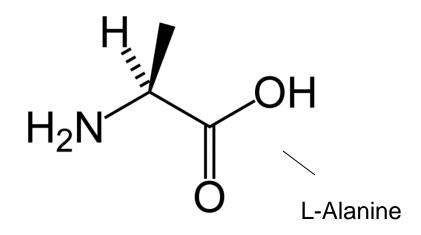


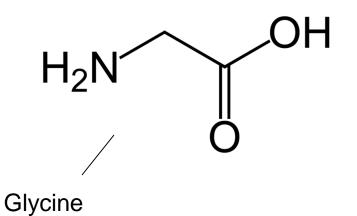
SIGA A VIDA

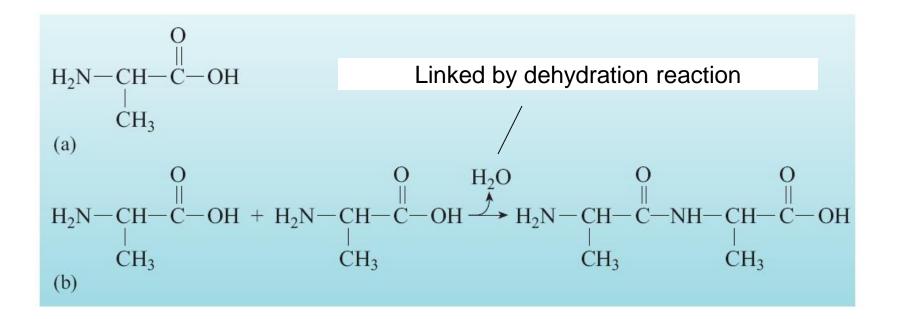
- Siga a água (Follow the water)
- Siga o carbono
- ⇒ Siga o nitrogênio
 - Siga o fósforo
 - Siga a energia
 - Siga a entropia
 - Siga a informação
 - Siga o significado

Proteins

- "Proteios" primary
- Long "trains" of amino acids
- Different proteins have different sequence of amino acids
- 20 amino acids used in any organism
- Some provide structure (fingernails, hair)
- Some serve as catalysts
- Enzymes proteins with catalitic properties







Catalysts in Chemistry

- Suppose chemical reaction:
- $A + B \rightarrow AB$ is a slow reaction
- The same reaction can be accelerated with catalyst (D):
- $A + D \rightarrow AD$ fast step
- $B + AD \rightarrow AB + D$ fast step

The net result is still:

 $A + B \rightarrow AB$ but it is much faster

Proteins (continued)

- Even though there are ~70 amino acids any known life uses only 20
- Amino acids derived abiotically are a mix of both "left-handed" and "right-handed" ones. Biological amino acids are only lefthanded.

Chirality

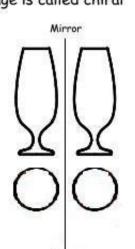
• Was there a common ancestor for all life?

CHIRALITY

An object that cannot be superimposed on its mirror image is called chiral



Chiral objects Nonsuperimposable mirror images



Nonchiral objects Superimposable mirror images

Biology uses only left-handed Alanine соон COOH R R H NH NH

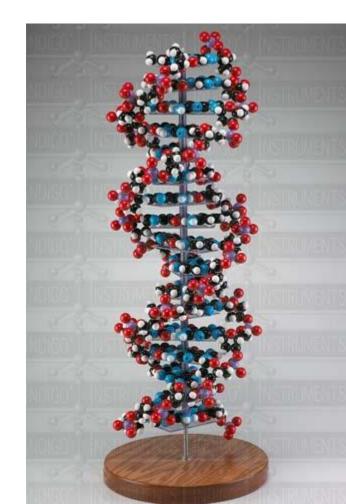
Amino acid	Abundance	Found in proteins on Earth	
	synthesized in the Miller–Urey experiment	Found in the Murchison meteorite	
glycine			yes
alanine			yes
α-amino-N-butyric acid	•••		no
α-aminoisobutyric acid	••••	••	no
valine	•••	••	yes
norvaline	•••		no
isovaline	••	••	no
proline	•••	•	yes
pipecolic acid	•	•	no
aspartic acid	•••		yes
glutamic acid	•••		yes
β-alanine	••	••	no
β-amino-N-butyric acid	••	••	no
β-aminoisobutyric acid	•	•	no
y-aminobutyric acid	•	••	no
sarcosine	••		no
N-ethylglycine	••	••	no
N-methylalanine	••	••	no

 Table 1.5
 Abundances of amino acids synthesized in the Miller–Urey experiment and those found in the Murchison meteorite.

 The number of dots represents relative abundance. Those amino acids used by life (i.e. in proteins) are indicated.

Nucleic acids (DNA/RNA)

- Deoxyribonucleic acid (DNA), is a <u>nucleic acid</u> that contains the (<u>genetic</u>) instructions used in the <u>development</u> and functioning of all known <u>living organisms</u>.
- Collection of nucleotides linked together in long polymers – the largest macromolecule



Nucleotide

Each nucleotide:
1) Five-carbon sugar molecule
2) One or more phosphate groups
3) Nitrogen-containing compound – nitrogenous base

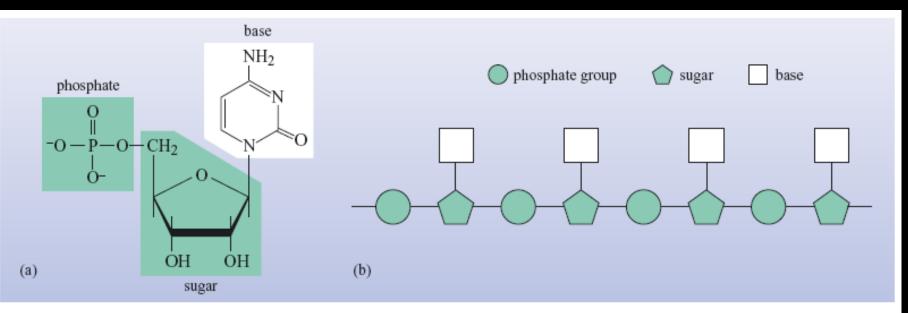


Figure 1.7 (a) The structure of a nucleotide consisting of a phosphate group, sugar molecule and nitrogenous base (cytosine in this instance). (b) Nucleotides polymerize by simple reactions that involve the loss of water to form nucleic acids. ((a) Zubay, 2000)

Watson and Crick (1953) realized that DNA have a double helix.

DNA strand	DNA strand
А	Т
Т	А
G	С
С	G

A can link only with T G can link only with C

Two DNA strands are "complimentary" to each other

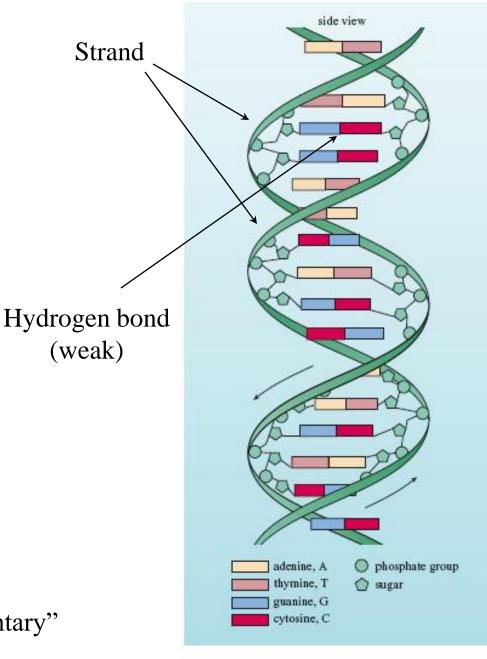
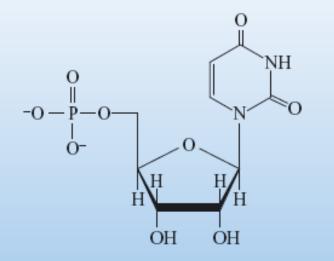
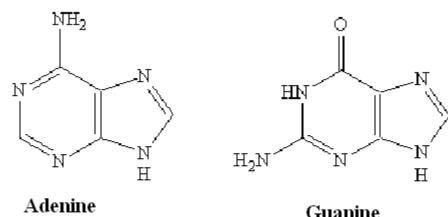


Figure 1.9 The DNA double helix. Note that the 'ribbons' are not real, but are there to illustrate the nature of the double helix.

DNA vs. RNA

- Deoxyribonucleic acid (DNA) deoxyribose sugar
- Ribonucleic acid (RNA) ribose sugar
- Four bases:
- DNA RNA
- A adenine A
- G guanine G
- C cytosine C
- T thymine U uracil





Guanine

О

Л Н

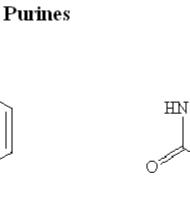
.CH₃



ΗN

Ο

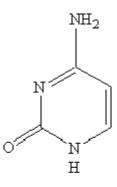
И Н



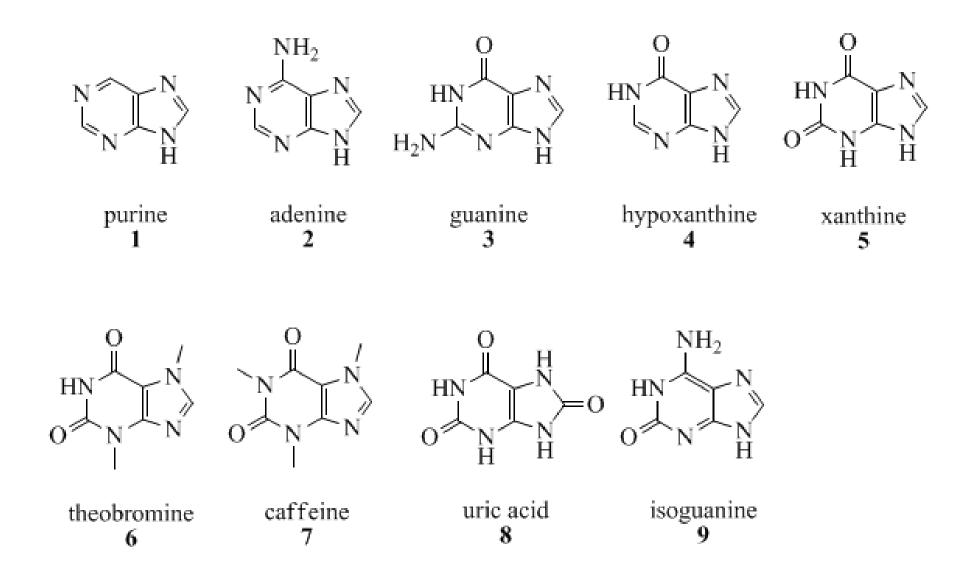
Uracil

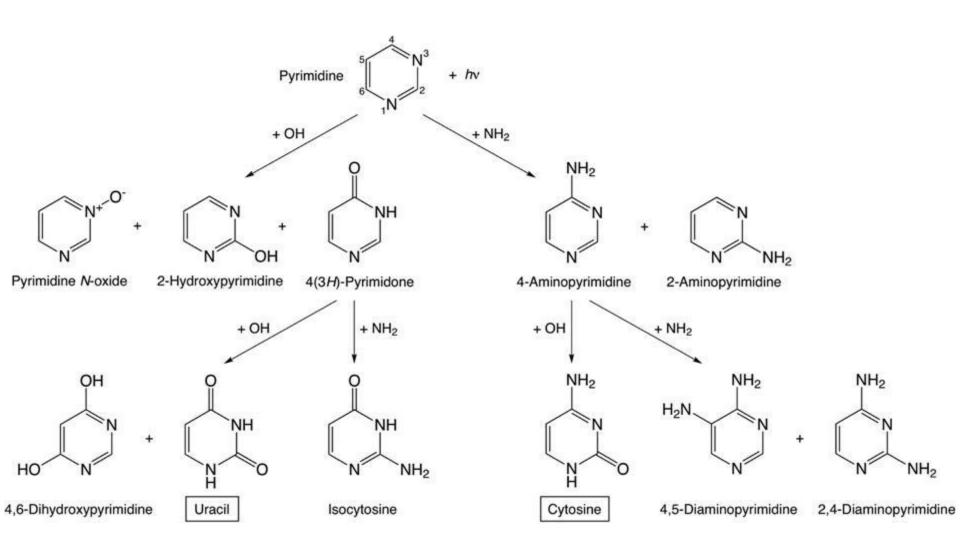
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Thymine Pyrimidines



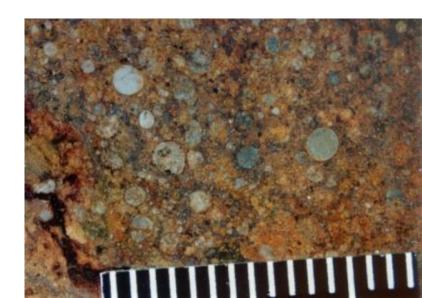
Cytosine





Meteorites

- A meteorite is a natural object originating in outer space that survives an impact with the Earth's surface without being destroyed.
- Chondrites 86%
- (5% Carbonaceous Chondrites)
- Achondrites 8%
- Iron meteorites 5%



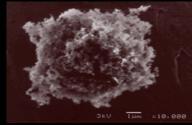
TYPES OF METEORITES

TYPE	SUBTYPE	FREQU	JENCY	COMPOSITION	FORMATION
Stones	Carbonaceous Chondrites)	5 %	Water, carbon silicates, metals	Primitive
	Chondrites	}	81 %	Silicates	Heated under pressure
	Achondrites	J	8 %	Silicates	Heated
Stony in	rons		1 %	50 % silicates, 50 % free metal	Differentiated
Irons			5 %	90 % iron 10 % nickel	Differentiated

Meteorites represent extraterrestrial material which can be studied on Earth !



Insoluble C-fraction: 60-80 % aromatic carbon highly substituted small aromatic moieties branched by aliphatic chains



Murchison (1969, Australia)





Organics Found in Meteorites

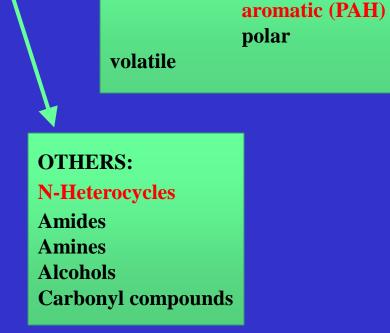
Total Carbon Content: > 3% (by weight); Soluble Fraction: < 30% of total C

COMPONENTS:

ACIDS:

Amino acids Carboxylic acids Hydroxycarboxylic acids Dicarboxylic acids Hydroxydicarboxylic acids Sulfonic acids Phosphonic acids

FULLERENES: C₆₀, C₇₀ He@C₆₀ Higher Fullerenes



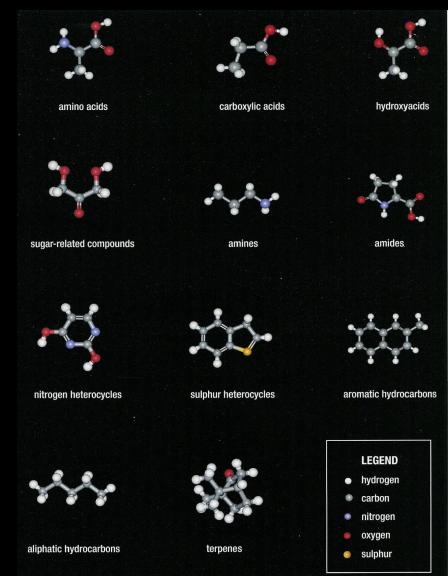
HYDROCARBONS:

non-volatile: aliphatic

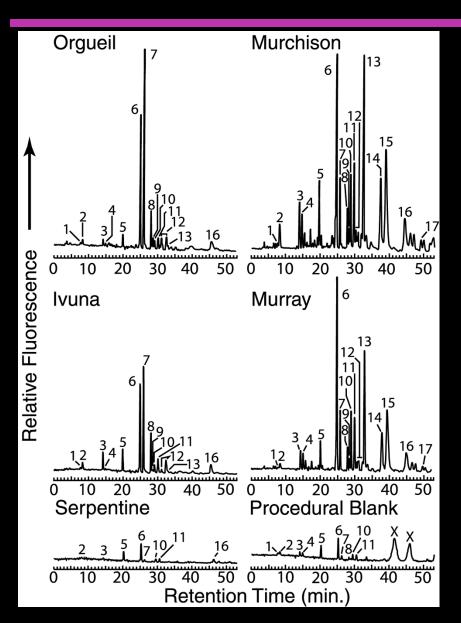
Abundances of soluble organic compounds in the Murchison meteorite (Botta & Bada 2002, Sephton 2002, 2004)

Compound Class Concentration(ppm)

Amino Acids	CM	17-60
	CI	~5
Aliphatic hydro	carbons	>35
Aromatic hydro	carbons	3.3
Fullerenes		>1
Carboxylic acid	> 300	
Hydroxycarbox	15	
Dicarboxylic aci	ds &	
Hydroxydicar	14	
Purines & Pyrin	1.3	
Basic N-heteroc	7	
Amines		8
Amides linear		> 70
cyclic		> 2
Alcohols		11
Aldehydes & Ke	27	
Sulphonic acids	68	
Phosphonic acid	2	



Chromatograms of Meteorite Extracts



- **1 D-Aspartic Acid**
- 2 L-Aspartic Acid
- 3 L-Glutamic Acid
- 4 D-Glutamic Acid
- 5 D,L-Serine
- 6 Glycine
- 7 β -Alanine
- 8 γ-Amino-*n*-butyric Acid (g-ABA)
- 9 D,L-b-Aminoisobutyric Acid (b-AIB)
- **10 D-Alanine**
- 11 L-Alanine
- **12** D,L-β-Amino-n-butyric Acid (b-ABA)
- 13 α-Aminoisobutyric Acid (AIB)
- 14 D,L-α-Amino-n-butyric Acid (a-ABA)
- 15 D,L-Isovaline
- 16 L-Valine
- 17 D-Valine
- X: unknown

Ehrenfreund et al., 2001

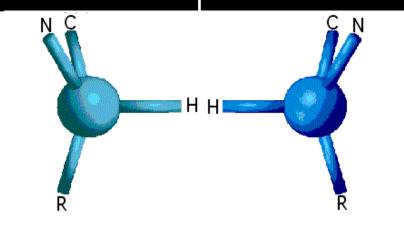
Amino Acids in Carbonaceous Chondrites

- Amino acids are readily synthesized under a variety of plausible prebiotic conditions (e.g. in the Miller-Urey Experiment).
- Amino acids are the building blocks of proteins and enzymes in life on Earth.
- Chirality (handedness) can be used to distinguish biotic vs. abiotic origins.
- Most of the amino acids found in meteorites are very rare on Earth (AIB, isovaline).

Chirality







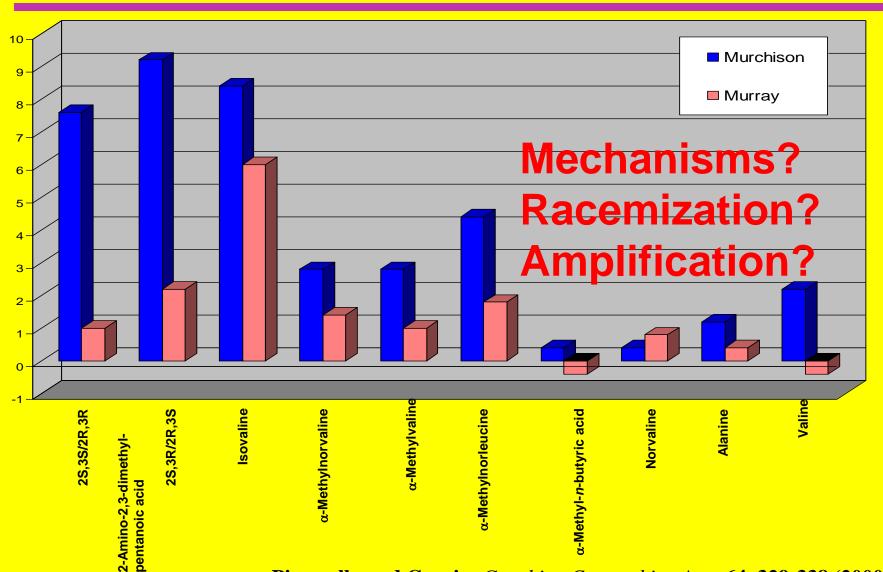
- Left- and right-handed mirror molecules are called enantiomers.
- Enantiomers possess identical physical properties (melting point *etc.*).
- They rotate the plane of planarpolarized light in opposite directions.
- They cannot be chromatographically separated on a non-chiral column.

Separation on chiral column

or

Derivatization to form diastereoisomers, separation on non-chiral column

Enantiomeric Excesses in Meteoritic Amino Acids



Pizzarello and Cronin, Geochim. Cosmochim. Acta 64, 329-338 (2000)

Racemic amino acids from the ultraviolet photolysis of interstellar ice analogues

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The delivery of extraterrestrial organic molecules to Earth by meteorites may have been important for the origin and early evolution of life1. Indigenous amino acids have been found in meteorites²-over 70 in the Murchison meteorite alone³. Although it has been generally accepted that the meteoritic amino acids formed in liquid water⁴ on a parent body, the water in the Murchison meteorite is depleted in deuterium⁵ relative to the indigenous organic acids6,7. Moreover, the meteoritical evidence8 for an excess of laevo-rotatory amino acids is hard to understand in the context of liquid-water reactions on meteorite parent bodies. Here we report a laboratory demonstration that glycine, alanine and serine naturally form from ultraviolet photolysis of the analogues of icy interstellar grains. Such amino acids would naturally have a deuterium excess similar to that seen in interstellar molecular clouds, and the formation process could also result in enantiomeric excesses if the incident radiation is circularly polarized. These results suggest that at least some meteoritic amino acids are the result of interstellar photochemistry, rather than formation in liquid water on an early Solar System body.

As the most ancient and pristine bulk material studied in the laboratory, primitive meteorites are the clearest windows to the birth of the Solar System. Planetary systems such as our own are believed to form from the collapse of an interstellar dense molecular cloud composed of gas and sub-micrometre sized grains. In such 'dark' clouds the temperatures are low (T < 50 K), and all but the most volatile species (that is, H₂, He, Ne) condense onto grains, coating them with a thin layer of ice⁹. This ice is composed primarily of amorphous H₂O, but usually also contains a variety of other simple molecules^{9,10}, such as CO₂, CO, CH₃OH, and NH₃. Laboratory studies¹¹ and astronomical observations^{10,12} indicate that radiation processing of such ices can create complex organic compounds¹³. Many of the organic molecules that are present in carbonaceous chondrites (primitive carbon-rich meteorites) and comet and asteroid dust are thought to come, at least in part, from the ice and complex compounds constructed in the interstellar medium (ISM).

Perhaps the most convincing molecular evidence for the interstellar heritage of meteoritic molecules is their high deuterium (D) enrichment3714. At the low temperatures in dense molecular clouds deuterium fractionation is efficient and elevated D/H ratios are seen in grain mantles15; such increased ratios are also found in several gas-phase interstellar molecules, including amino acid precursors, such as formaldehyde and ammonia¹⁶. Although it had been accepted that the deuterium in meteoritic organics indicated that their precursors formed in the ISM, the actual hydroxy and amino acids are still commonly believed to have formed on the asteroid or comet parent body from reactions in liquid water4 that, at least in Murchison, was apparently deuterium poor5. It is difficult to explain how these compounds retain relatively high amounts of deuterium, let alone how it is distributed. For example, it seems contradictory that the hydroxy acids in the Murchison meteorite have one-third as much deuterium as the amino acids, and yet have a lower rate of deuterium exchange in water than amino acids3,7. If, however, the hydroxy and amino acids had formed in the ISM their deuterium enrichment would be a logical consequence of the photochemistry of already deuterium-enriched pre-solar ices.

The laboratory experiments described here were designed to elucidate potential pathways from interstellar chemistry to the organic molecules extracted from meteorites. We have conducted laboratory experiments at temperatures, pressures and radiation conditions that are representative of the interstellar clouds from which planetary systems form. In a series of experiments, gases were vapour deposited onto a substrate at 15K forming an ice film consisting primarily of amorphous H₂O with other compounds over a range of concentrations $(0.5-5\% \text{ NH}_3, 5-10\% \text{ CH}_3\text{OH})$ and 0.5-5% HCN, relative to H₂O). These solid mixtures are

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Comets & Astrobiology



- Comets are the key to understanding the Solar Nebula & its evolution.
- Comets could serve as probes of chemical processes occurring in the midplanes of astronomical disks
- Comets may have provided key organic nutrients required to jump start life on Earth.

MOLECULAR STRUCTURE OF THE COMA

 O^+

 H_2O CO CO_2 CH₃OH NH₃ CS_2 HCN SO₂ CH_4 C_2H_2 C_2H_6 H_2CO OCS

 H_2O^+ H_3O^+ OH HI NH_2 S_2 CN SO NS HNC C₂, C₃

H₂CO CO

CO+

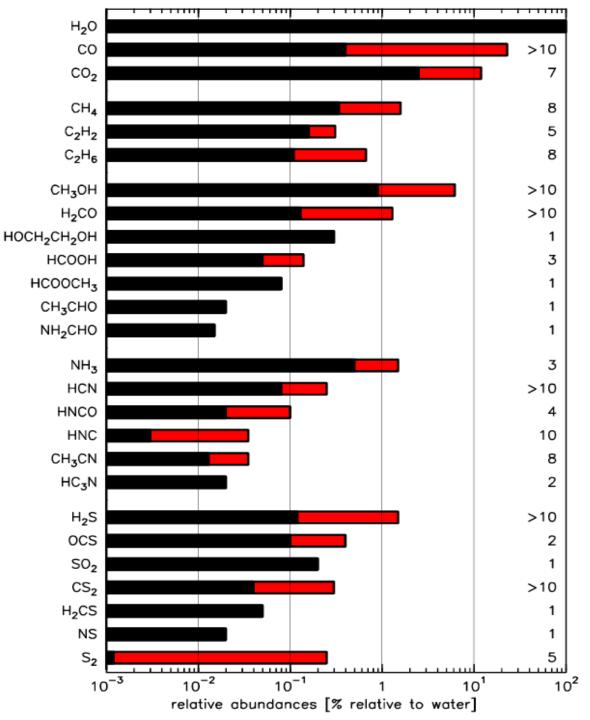
 CO_2^+

Evidence for chemical diversity

Diversity among Oort cloud comets

No systematic differences between Oort cloud and

« Kuiper belt » comets



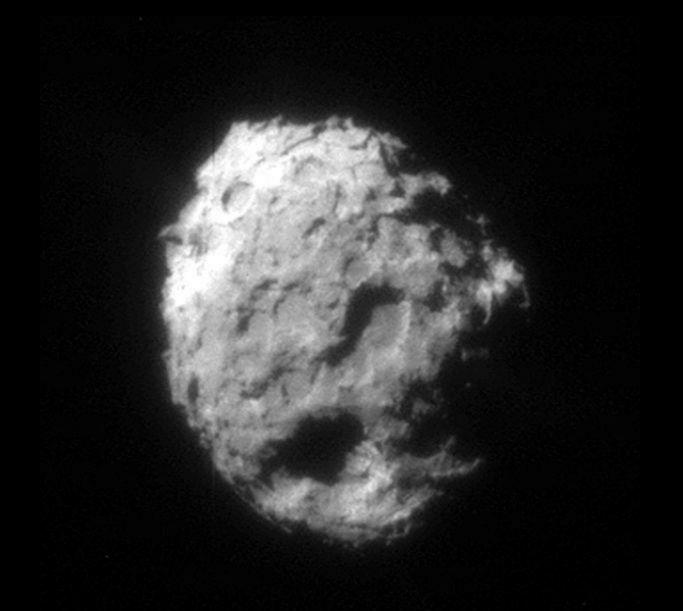
Crovisier 2005

Wild 2 (Jan 17, 2010)

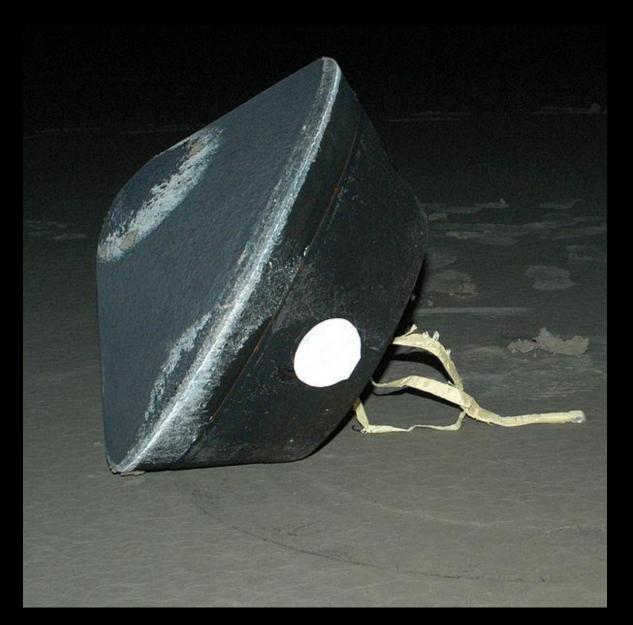




Stardust (launched Feb 7, 1999)



Wild 2 (Stardust, January 2, 2004)



Stardust Sample Return (Jan 16, 2006)



16:00 GMT/17:00 CET (Time signal expected on Earth)

Touchdown

CIVA Panoramic image **COSAC & PTOLEMY** Gas measurements MUPUS Measurement of harpoon deceleration, surface & subsurface properties ROLIS Close-up image of surface **ROMAP** Magnetic field measurements SESAME Properties of surface

eesa



TOUCHDOWN

2014/11/23 16:03 GMT **TELEMETRY OK 16:09 GMT**



A piece of interplanetary dust

PROCESSING ISM TO ORGANIC POLYMERS ?

COMETS: HC¹⁴N/HC¹⁵N~400 C¹⁴N/C¹⁵N~140

PROTOSOLAR ¹⁴N/¹⁵N~400

(TERRESTRIAL ¹⁴N/¹⁵N~270)

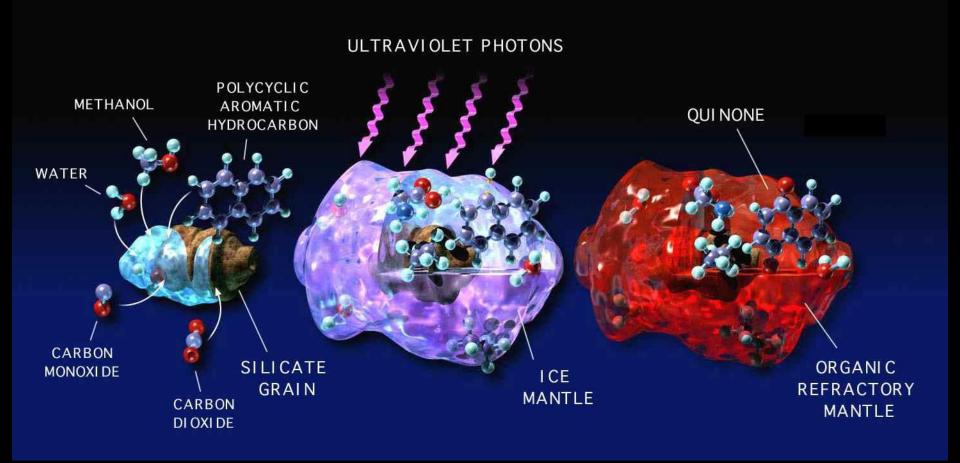
NITROGEN ISOTOPE RATIOS

ISM DEPLETION CORES ¹⁴NH₃/¹⁵NH₃~140

IDPs

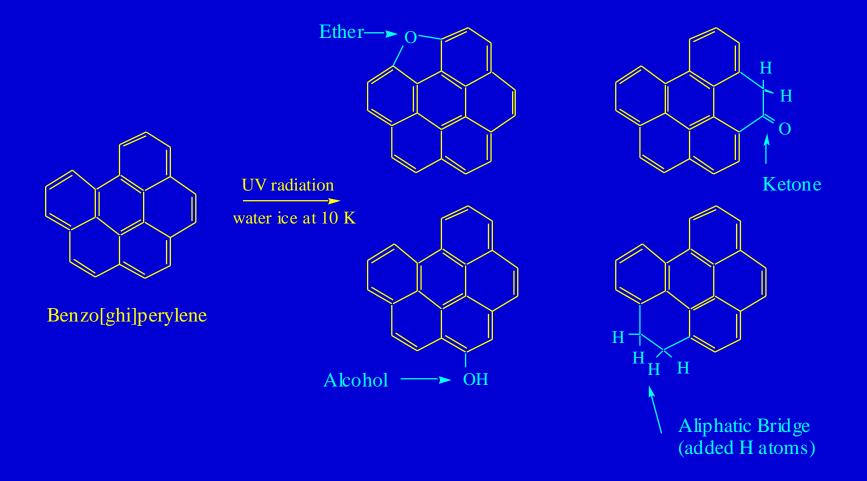
¹⁴N/¹⁵N~140

Interstellar Dust: ice mantle evolution



Bernstein, Sandford, Allamandola, Sci. Am. 7,1999, p26

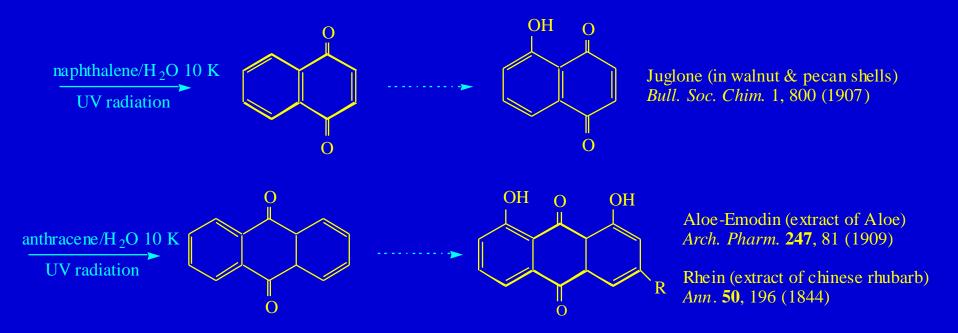
Photolysis of PAHs in Water Ice Produces Alkanes, Ketones, Ethers, and Alcohols.



Both oxidation (alcohol, ether and ketone formation) and reduction (addition of hydrogen) reactions occur on photolysis of water ices containing PAHs. These are the same kinds of compounds observed in meteorites, fit spectra of emission objects and, in some cases, have biochemical significance.

Bernstein et al.Science 283, 1135 (1999)

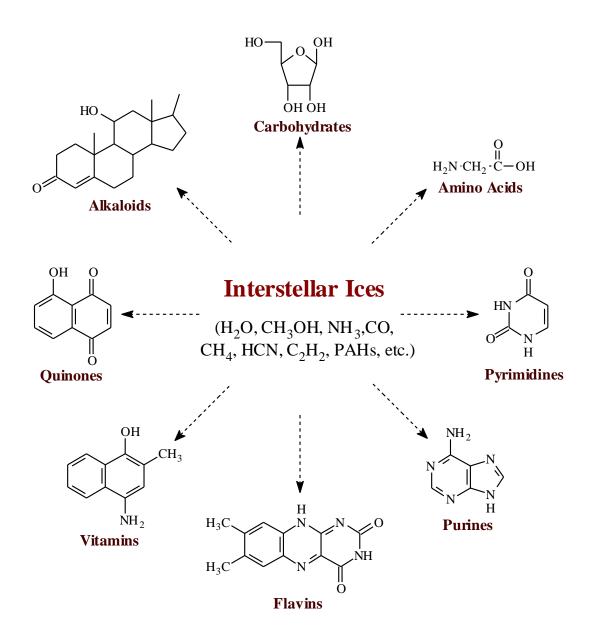
Photochemistry of PAHs in Ice: Abiotic Synthesis of Biogenic Compounds



These quinone type structures are very important in many living systems. For example, naphthaquinones (like juglone above) are essential for electron transport in simple organisms.

Juglone: Bernstein et al.Met. & Planet. Sci. 36, 351 (2001) Anthroquinone: Ashbourne et al. in prep

Abiotic Synthesis of Biogenically Useful Molecules in Cometary and Interstellar Ices



Courtesy Jason Dworkin