



# The Miller & Urey Experiment Shaping a Life-friendly Universe

Janot-Pacheco E.<sup>1</sup>, Fornazier K.S.F.<sup>1</sup>, and Lage C.<sup>2</sup>

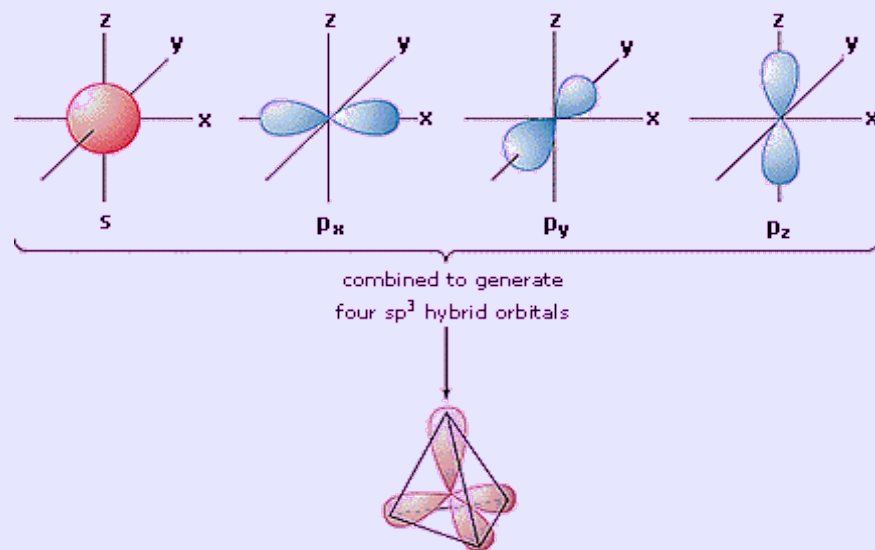
<sup>1</sup>IAG-USP, Brazil

<sup>2</sup>Carlos Chagas Filho Institute of Biophysics, UFRJ, Brazil



# WHY carbon ??

**carbon's hybrid orbitals = geometrical asymmetries**



**Carbon valence electrons: displaced in a tetrahedron geometry**

⇒ **covalent bonds to escape the XYZ  $90^\circ$  monotonous angles** ⇒

⇒ **asymmetrical** chemical structures.

**Structural variety = richer information**

but other elements contribute to complexity...

**nitrogen** = asymmetric bonds

with charge displacements

Nitrogen is more **electronegative** than C and H

so ⇒ asymmetries

**oxygen** ⇒ induces charges dynamics

Oxygen is also very **electronegative** so ⇒

⇒ nitrogen- and oxygen-harboring

compounds are **very polar** e.g. **water**

**hydrogen** = keeps reagents reduced

**Hydrogen** functions as a “**bonding buffer**” ⇒

⇒ reagents kept in reduced form.

Whenever a reagent reacts with other compound ⇒ a proton is released when the covalent bonding is formed.

# RELATIVE ABUNDANCES (% TOTAL)

EARTH		HUMAN BODY		SUN	
O	47.00	H	63.00	H	71.00
Si	28.00	C	25.50	He	27.10
Al	7.90	N	9.50	C	0.97
Fe	4.50		1.40	N	0.40
Ca	3.50	Ca	0.31		0.10
Na	2.50	P	0.22	Si	0.10
K	2.50	Cl	0.08	Mg	0.08
Mg	2.20	K	0.06	Ne	0.06
Ti	0.50	S	0.05	Fe	0.01
H	0.20	Na	0.03	S	0.04
C	0.20	Mg	0.01		

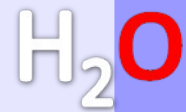
The chemical elements present in your body today were formed inside stars !!!



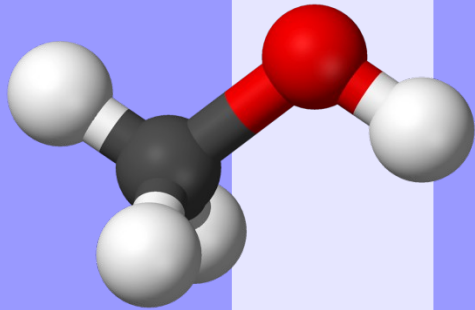


# Basic chemistry, from simple to complex

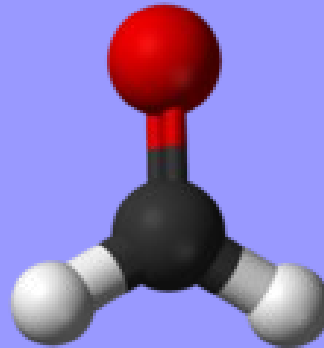
Two-element primary compounds:



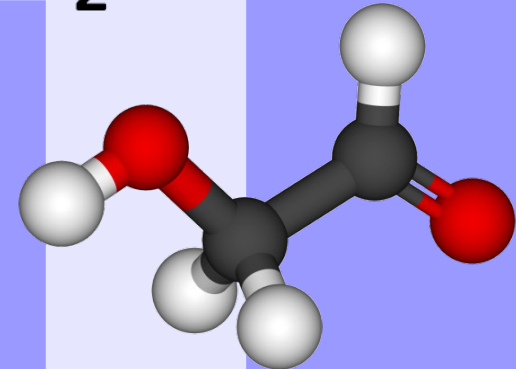
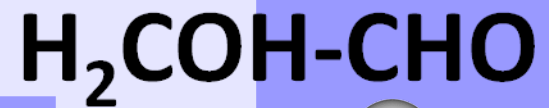
Three-element pre-biotic compounds:



methanol



formaldehyde



glycoaldehyde



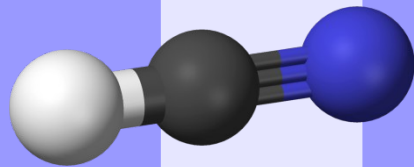


# Basic chemistry, from simple to complex

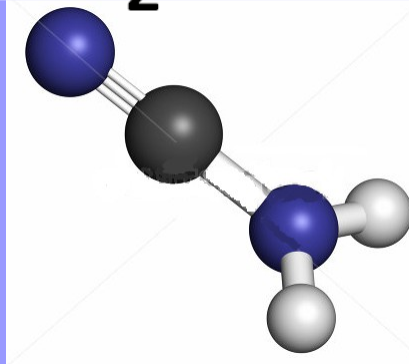
Two-element primary compounds:



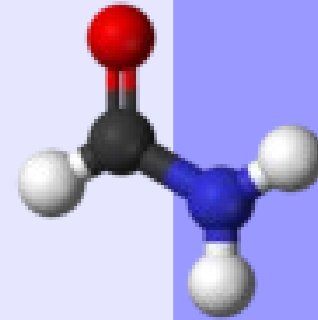
Three-element pre-biotic compounds:



hydrogen cyanide



cyanamide

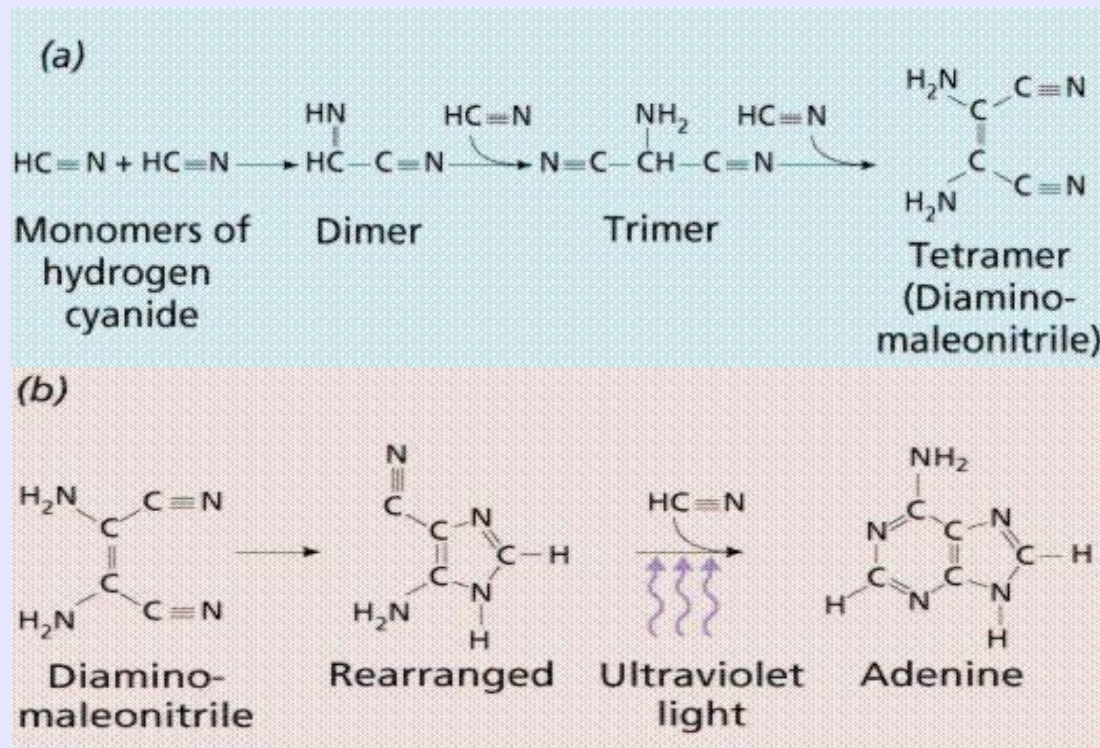


formamide

# From simple to complex ...

**Primitive abiogenic reactions supposed to have generated life building blocks**

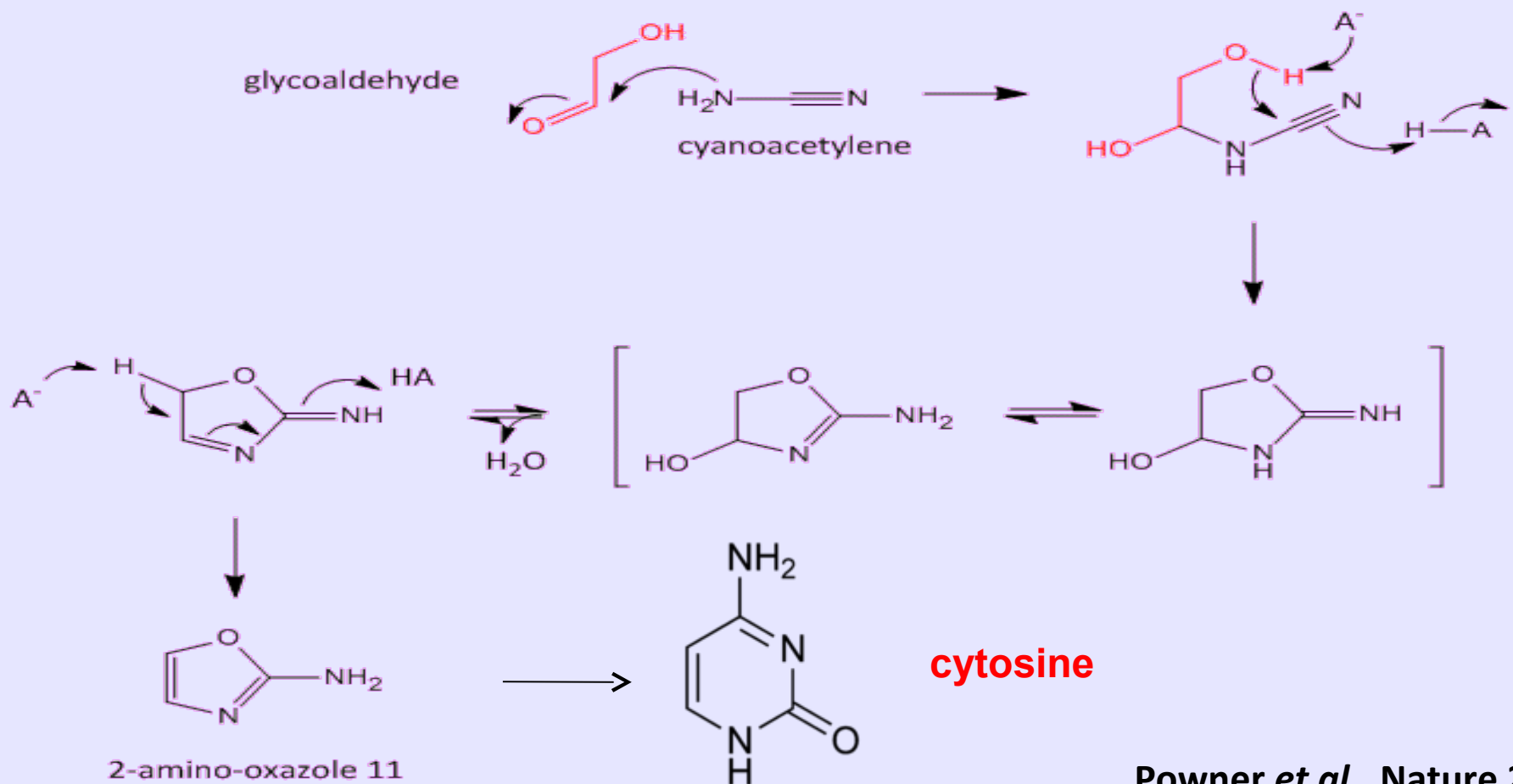
**[HCN]<sub>8</sub> ⇒ purine (DNA nucleobase)**



# From simple to complex ...

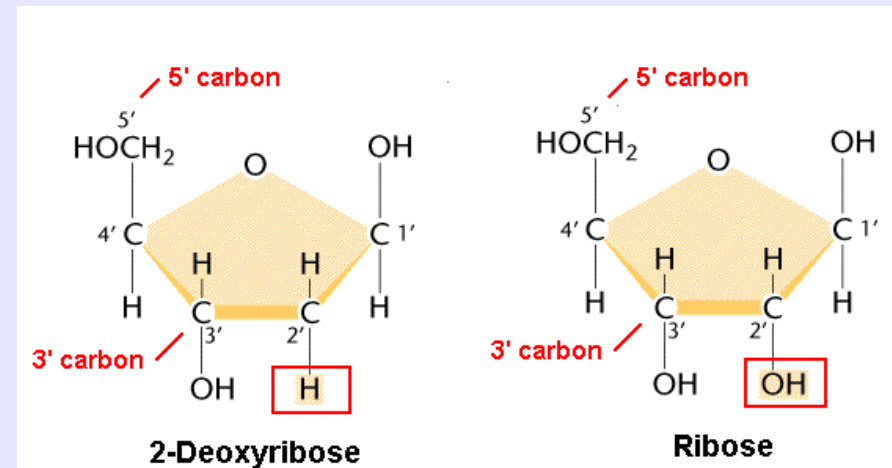
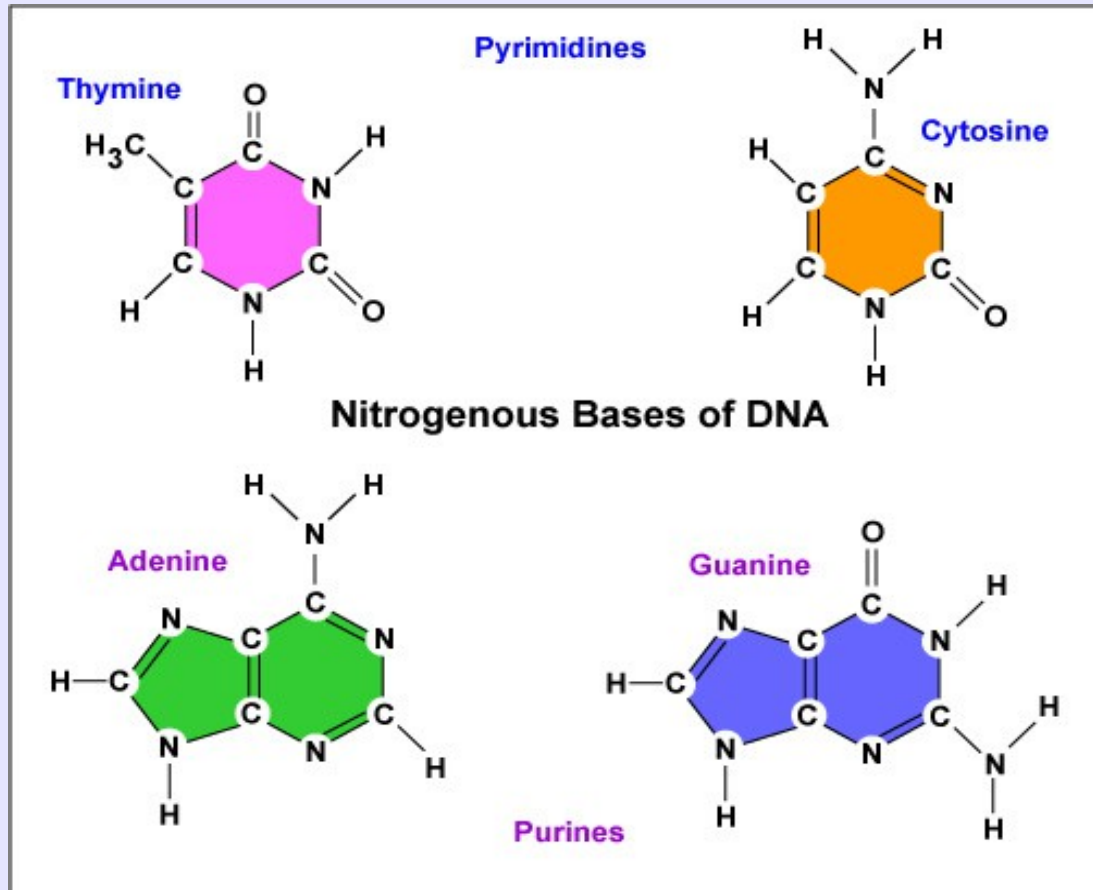
Primitive abiogenic reactions supposed to have generated life building blocks

[?] ⇒ pyrimidine (DNA nucleobase)

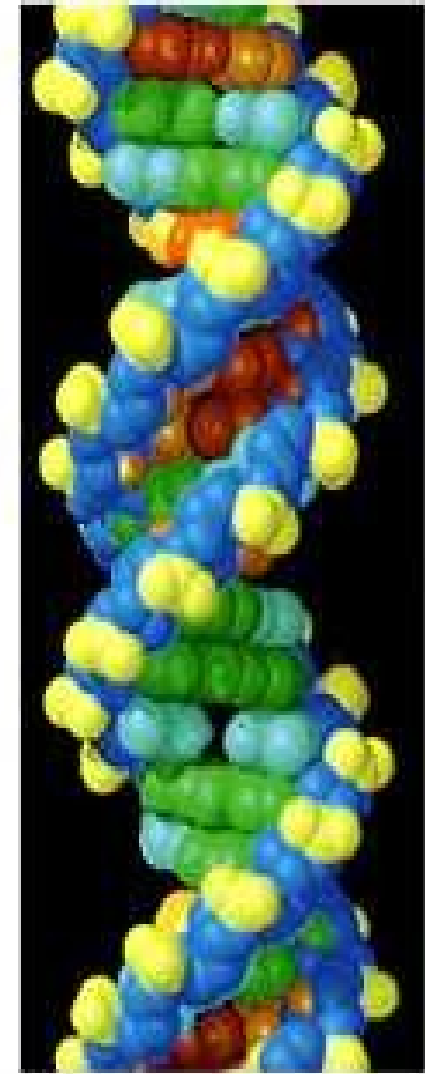
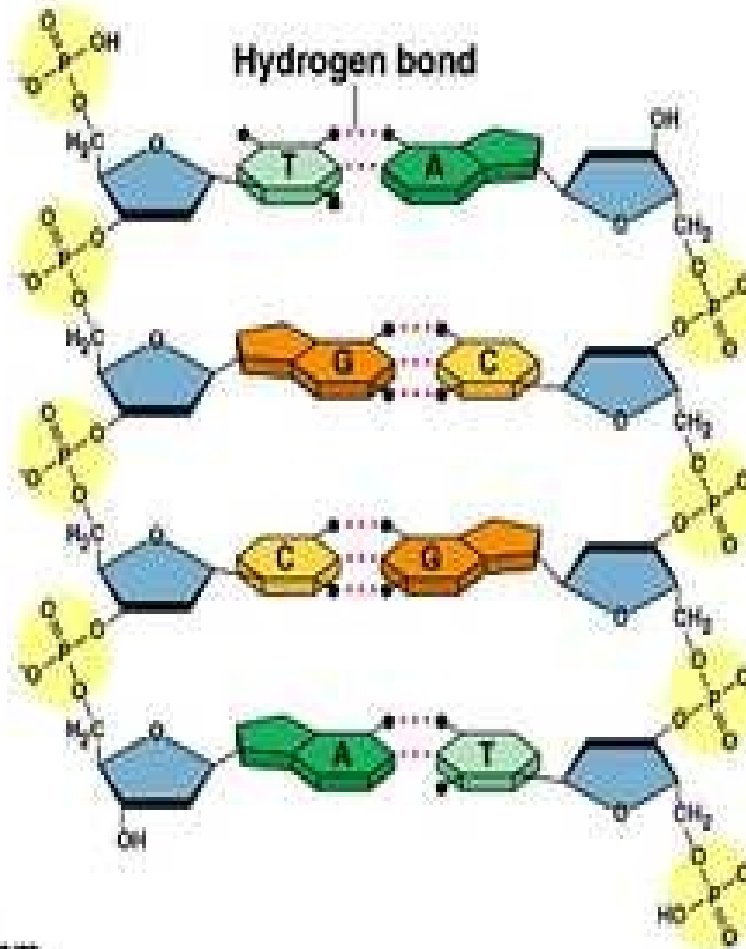
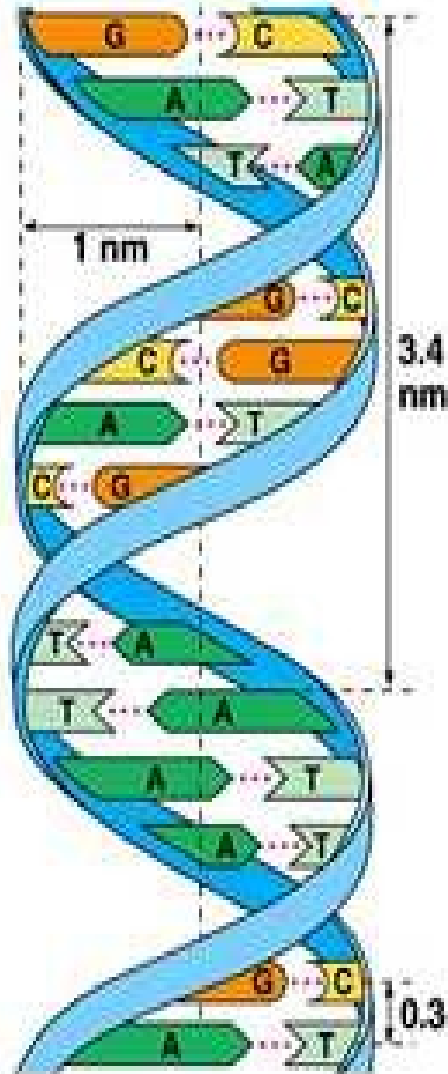


H<sub>2</sub>O, CH<sub>4</sub>, CO, NH<sub>3</sub> ⇒ prebiotic compounds ⇒

⇒ LIFE BUILDING BLOCKS, NUCLEOBASES, SUGARS, AMINOACIDS.



# DNA complex structure



(a)

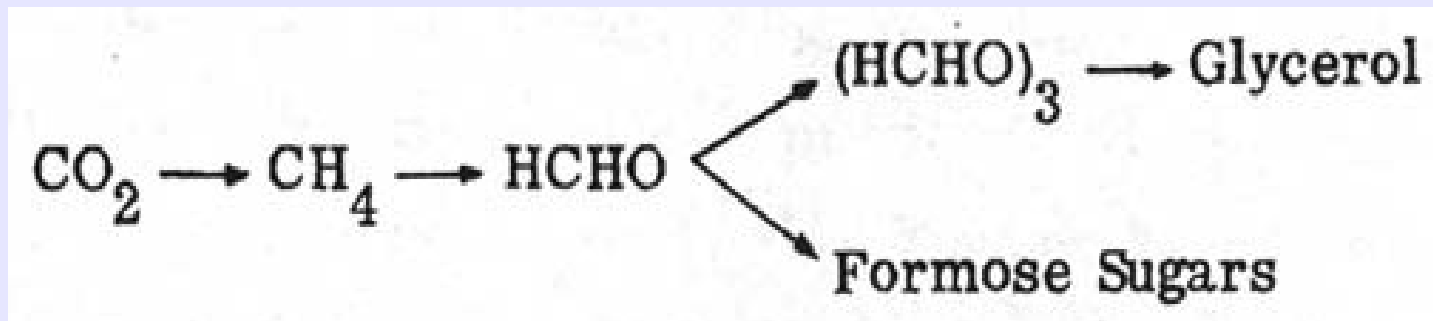
(b)

(c)

# From simple to complex ...

**Primitive abiogenic reactions supposed to have generated life building blocks**

**HCHO  $\Rightarrow$  simple sugars (energy feeding compounds)**  
**formaldehyde**



Prebiotic synthesis of simple sugars by an interstellar formose reaction.

Jalbout AF. Orig Life Evol Biosph, 2008, 38(6):489-497

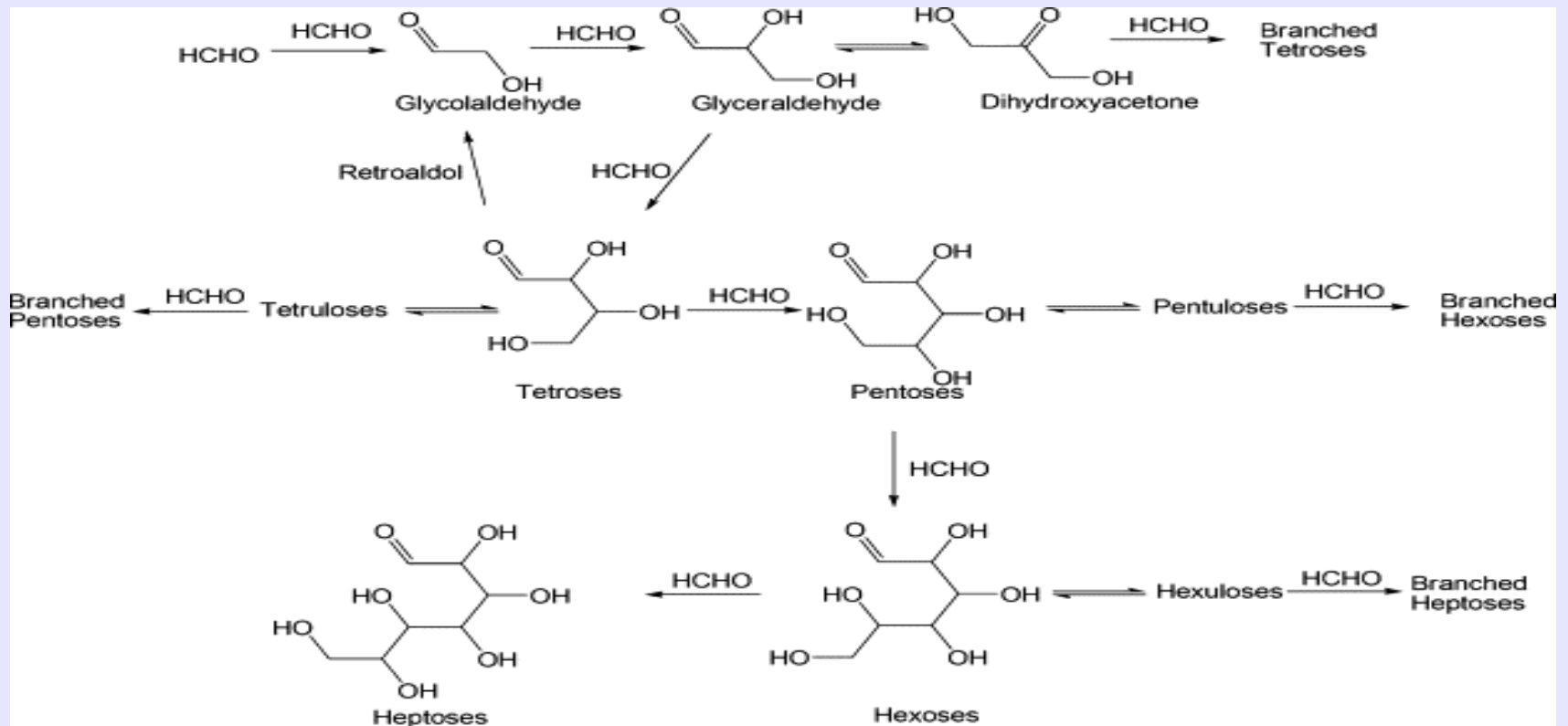
Sugar synthesis from a gas-phase formose reaction. Jalbout AF, Abrell L, Adamowicz L, Polt R, Apponi AJ, Ziurys LM. Astrobiology, 2007, 7(3):433-442.



# From simple to complex ...

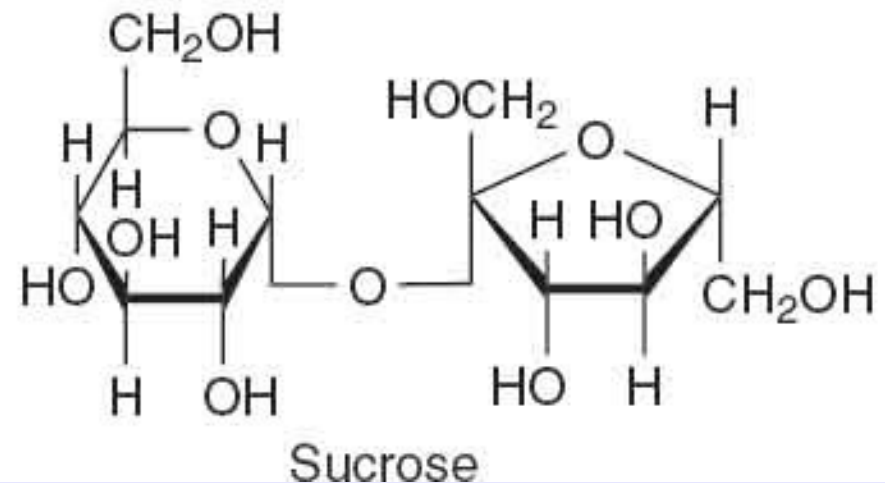
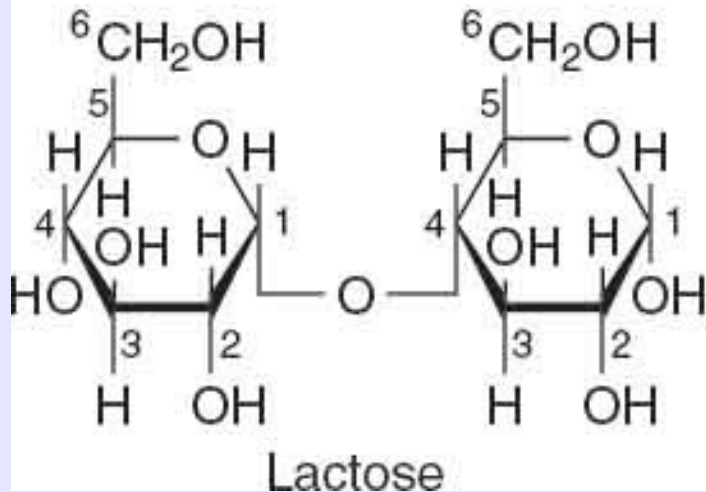
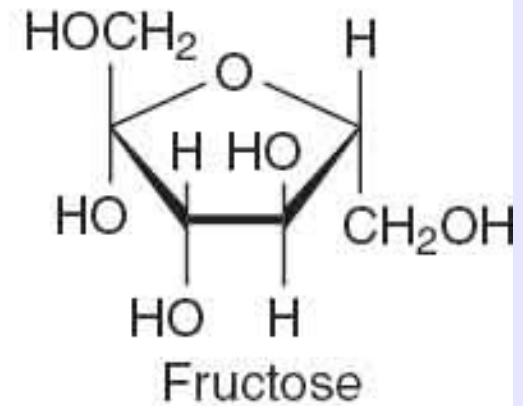
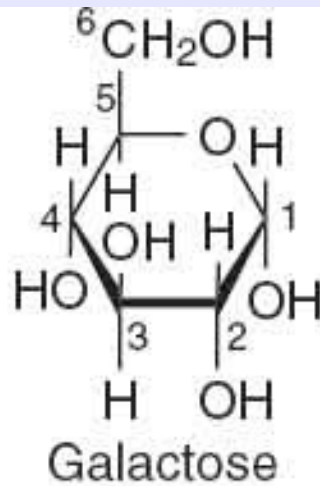
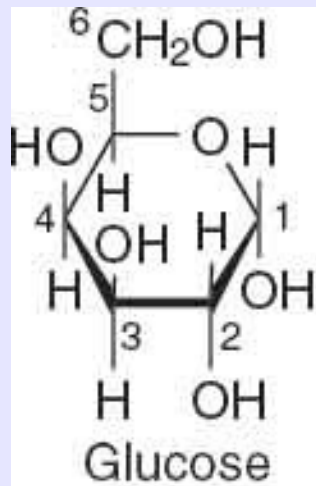
**Primitive abiogenic reactions supposed to have generated life building blocks**

**HCHO  $\Rightarrow$  simple sugars  $\Rightarrow$  complex sugars**



Sugars play a fundamental role in the energetic metabolism of every living being.

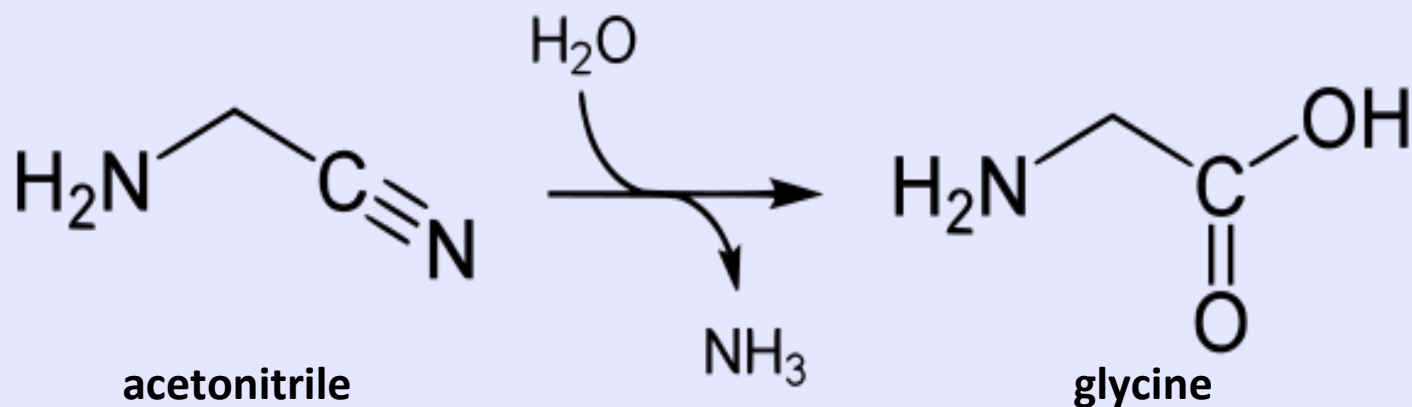
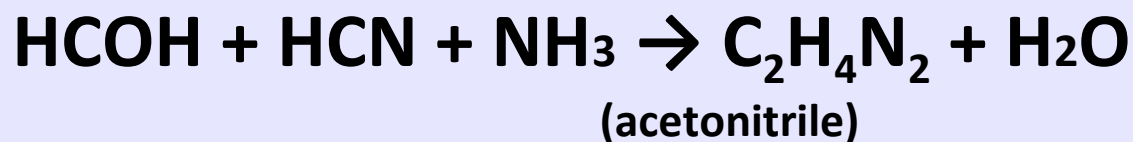
# Chemical structures of compounds belonging to the hexose sugars



## From simple to complex ...

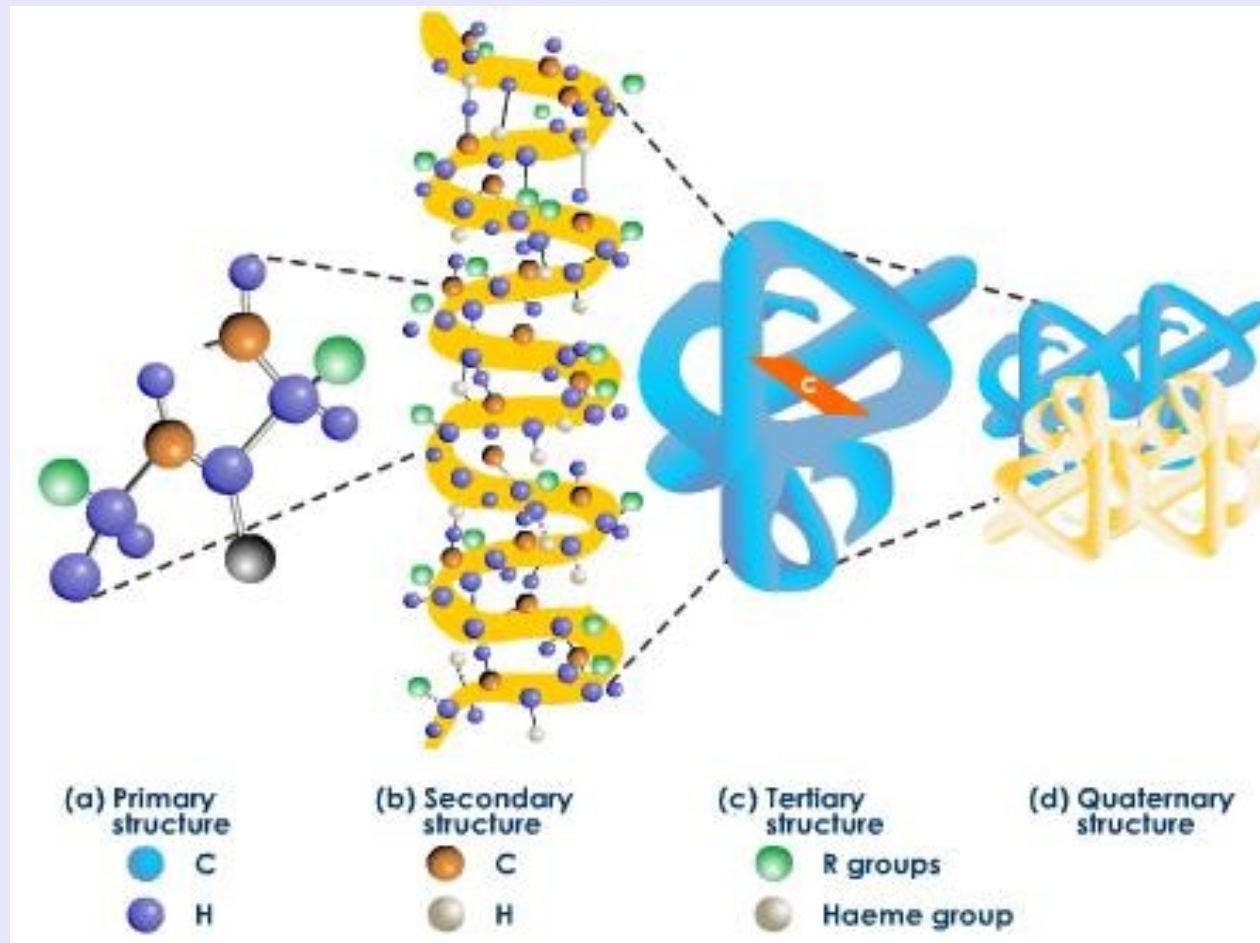
**Primitive abiogenic reactions supposed to have generated life building blocks**

**HCHO + HCN  $\Rightarrow$  simple aminoacids**



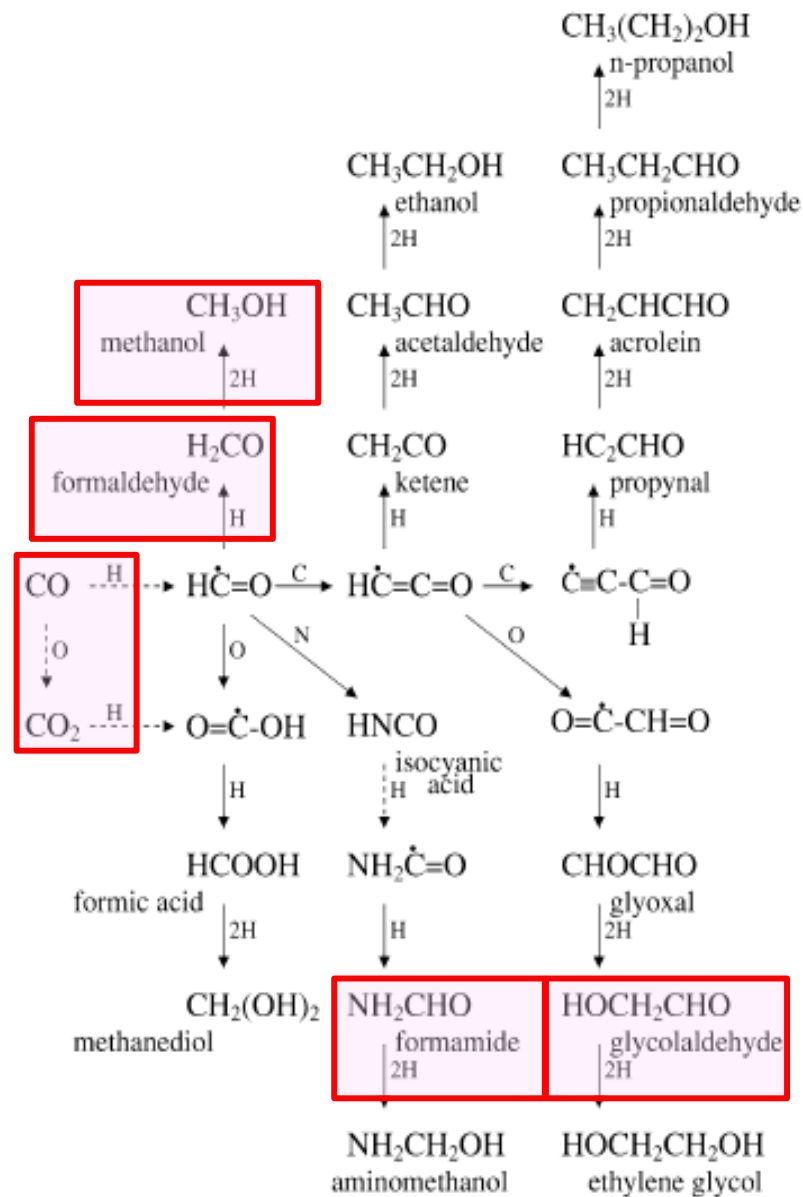
# From simple to complex ...

**Primitive abiogenic reactions supposed to have generated life building blocks:**



**aminoacids & proteins**

# Reaction channels from CO/CO<sub>2</sub> on grain surfaces generating main pre-biotic compounds



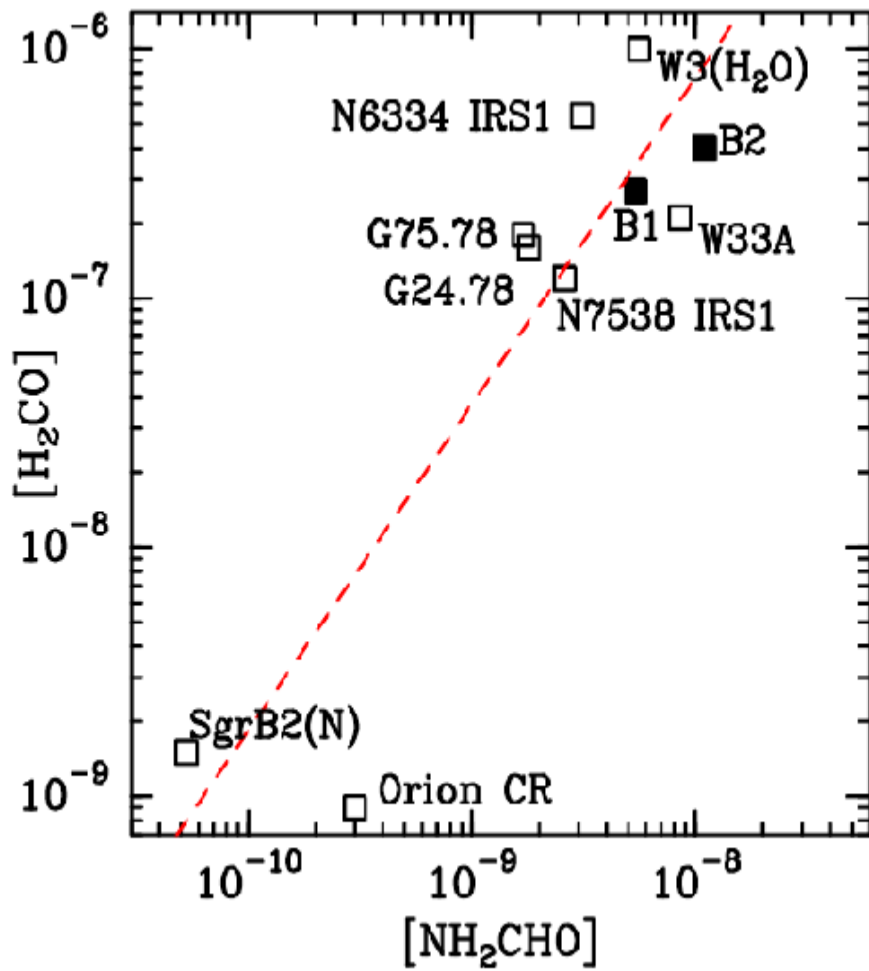
**Fig. 1** Grain-surface atom addition reactions starting from CO as proposed by Charnley et al. (2001). Figure adapted from Charnley and Rodgers (2005)

**Table 1** Interstellar ice feature inventory with respect to H<sub>2</sub>O ice towards dark clouds, low- and high-mass YSOs

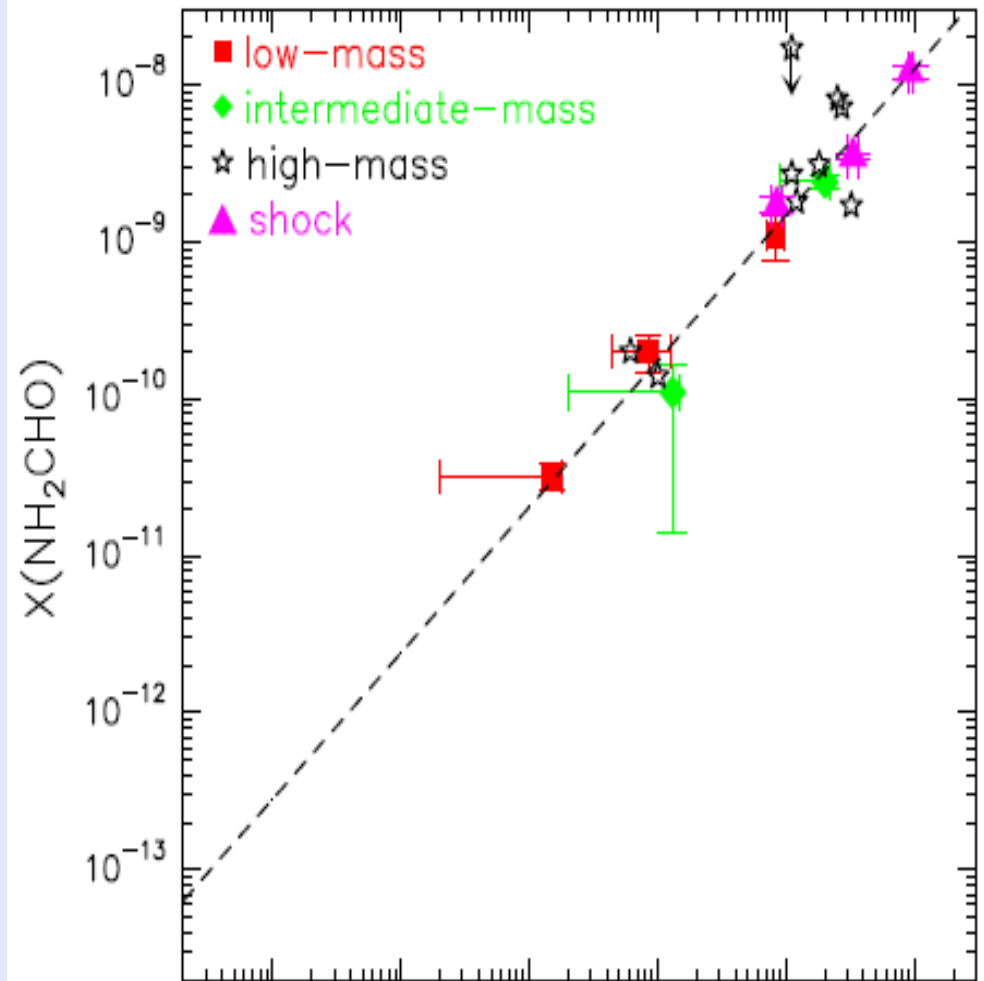
Species	$\lambda$ ( $\mu\text{m}$ )	Dark cloud (Elias 16)	L-m YSO (HH 46)	H-m YSO (W33A)
H <sub>2</sub> O	3.05	100	100	100
CO	4.67	26 <sup>a</sup>	20 <sup>b</sup>	8.1 <sup>c</sup>
CO <sub>2</sub>	4.27	24 <sup>d</sup>	21.6 <sup>e</sup>	14.1 <sup>e</sup>
HCOOH	5.85	$\leq 1.4^f$	2.7 <sup>f</sup>	5.2 <sup>f</sup>
H <sub>2</sub> CO	3.47, 3.54	...	6.0 <sup>f</sup>	3.1 <sup>c</sup>
CH <sub>3</sub> OH	3.08	$< 2.3^f$	6.1 <sup>g</sup>	14.7 <sup>f</sup>
NH <sub>3</sub>	2.96	$\leq 8^d$	6.1 <sup>g</sup>	15 <sup>c</sup>
NH <sub>4</sub> <sup>+</sup>	6.85	5.2 <sup>fj</sup>	6.3 <sup>f,i</sup>	8.1 <sup>fj</sup>
CH <sub>4</sub>	3.32	$< 3^d$	5.0 <sup>h</sup>	1.5 <sup>c</sup>
OCN <sup>-</sup>	4.62	$< 2.3^d$	$\leq 0.6^j$	1.9 <sup>j</sup>
OCS	4.92	$< 0.27^c$	$< 0.04^k$	0.2 <sup>c</sup>

Ioppolo et al. (2011)

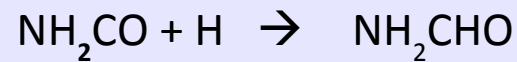
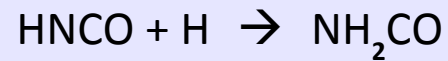




Mendoza et al. (2014)

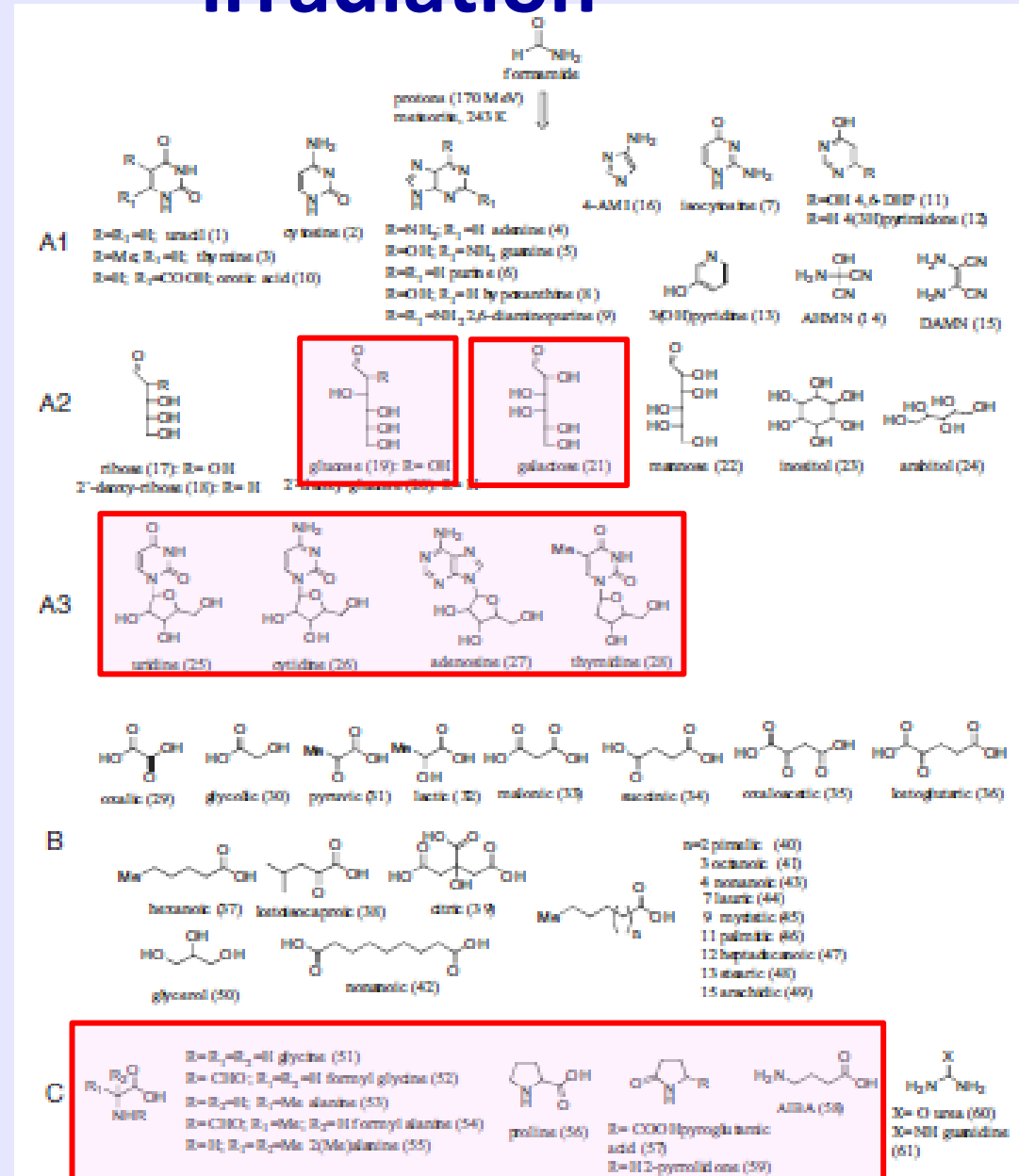
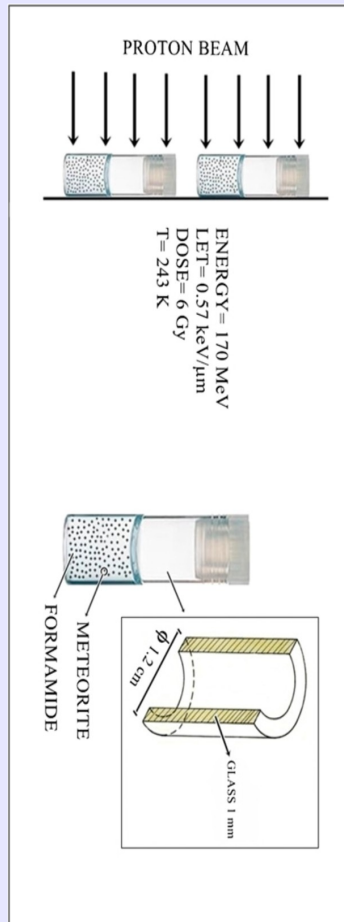


X(HNCO)  
López-Sepulcre et al. (2015)



# Lots of building blocks formed through meteoritic-catalyzed synthesis from formamide under proton irradiation

Saladino et al. (2015)



sugars

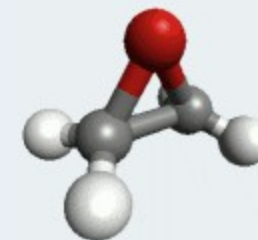
nucleobases

aminoacids

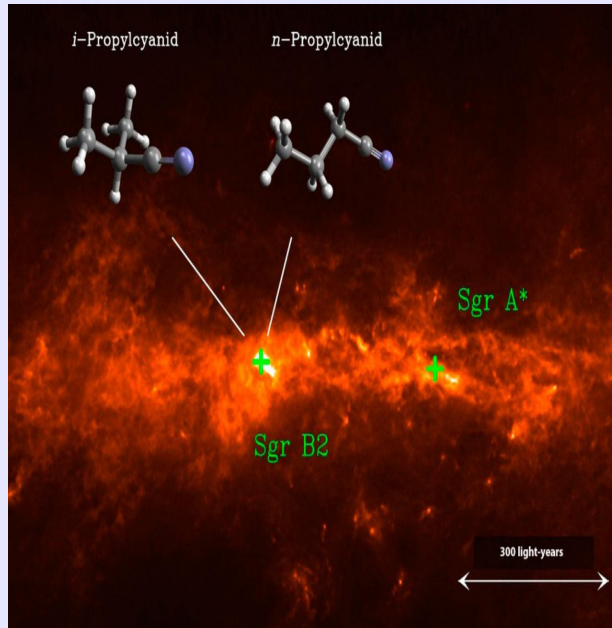
# The Cologne Database of detected molecules

Molecules in the Interstellar Medium or Circumstellar Shells (as of 06/2016)

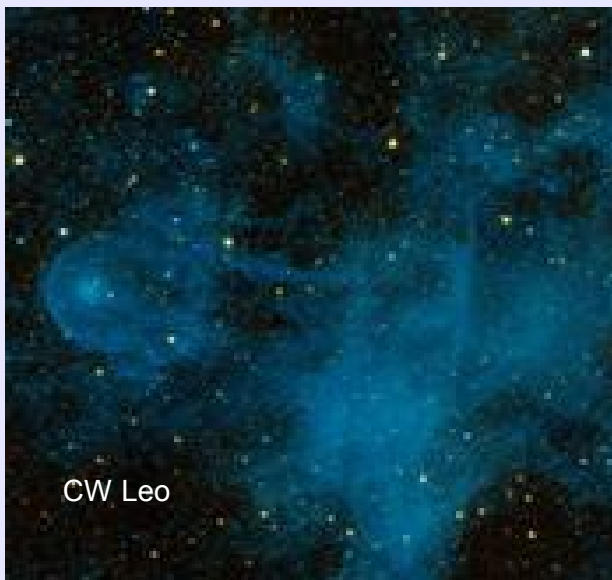
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H <sub>2</sub>	C <sub>3</sub> <sup>*</sup>	<i>c</i> -C <sub>3</sub> H	C <sub>5</sub> <sup>*</sup>	C <sub>5</sub> H	C <sub>6</sub> H	CH <sub>3</sub> C <sub>3</sub> N	CH <sub>3</sub> C <sub>4</sub> H	CH <sub>3</sub> C <sub>5</sub> N	HC <sub>6</sub> N	<i>c</i> -C <sub>6</sub> H <sub>6</sub> <sup>*</sup>	HC <sub>11</sub> N
AlF	C <sub>2</sub> H	<i>l</i> -C <sub>3</sub> H	C <sub>4</sub> H	<i>l</i> -H <sub>2</sub> C <sub>4</sub>	CH <sub>2</sub> CHCN	HC(O)OCH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CN	(CH <sub>3</sub> ) <sub>2</sub> CO	CH <sub>3</sub> C <sub>6</sub> H	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CN	C <sub>60</sub> <sup>*</sup>
AlCl	C <sub>2</sub> O	C <sub>3</sub> N	C <sub>4</sub> Si	C <sub>2</sub> H <sub>4</sub> <sup>*</sup>	CH <sub>3</sub> C <sub>2</sub> H	CH <sub>3</sub> COOH	(CH <sub>3</sub> ) <sub>2</sub> O	(CH <sub>2</sub> OH) <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OCHO	<i>i</i> -C <sub>3</sub> H <sub>7</sub> CN	C <sub>70</sub> <sup>*</sup>
C <sub>2</sub> <sup>**</sup>	C <sub>2</sub> S	C <sub>3</sub> O	<i>l</i> -C <sub>3</sub> H <sub>2</sub>	CH <sub>3</sub> CN	HC <sub>5</sub> N	C <sub>7</sub> H	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> CH <sub>2</sub> CHO	CH <sub>3</sub> OC(O)CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OCH <sub>3</sub> <sup>?</sup>	C <sub>60</sub> <sup>**</sup>
CH	CH <sub>2</sub>	C <sub>3</sub> S	<i>c</i> -C <sub>3</sub> H <sub>2</sub>	CH <sub>3</sub> NC	CH <sub>3</sub> CHO	C <sub>6</sub> H <sub>2</sub>	HC <sub>7</sub> N	CH <sub>3</sub> CHCH <sub>2</sub> O			
CH <sup>+</sup>	HCN	C <sub>2</sub> H <sub>2</sub> <sup>*</sup>	H <sub>2</sub> CCN	CH <sub>3</sub> OH	CH <sub>3</sub> NH <sub>2</sub>	CH <sub>2</sub> OHCHO	C <sub>8</sub> H				
CN	HCC	NH <sub>3</sub>	CH <sub>4</sub> <sup>*</sup>	CH <sub>3</sub> SH	<i>c</i> -C <sub>2</sub> H <sub>4</sub> O	<i>l</i> -HC <sub>6</sub> H <sup>*</sup>	CH <sub>3</sub> C(O)NH <sub>2</sub>				
CO	HCO <sup>+</sup>	HCCN	HC <sub>3</sub> N	HC <sub>3</sub> NH <sup>+</sup>	H <sub>2</sub> CCHOH	CH <sub>2</sub> CHCHO(?)	C <sub>8</sub> H <sup>-</sup>				
CO <sup>+</sup>	HCS <sup>+</sup>	HCNH <sup>+</sup>	HC <sub>2</sub> NC	HC <sub>2</sub> CHO	C <sub>6</sub> H <sup>-</sup>	CH <sub>2</sub> CCHCN	C <sub>3</sub> H <sub>6</sub>				
CP	HOC <sup>+</sup>	HNCO	HCOOH	NH <sub>2</sub> CHO	CH <sub>3</sub> NCO	H <sub>2</sub> NCH <sub>2</sub> CN	CH <sub>3</sub> CH <sub>2</sub> SH(?)				
SiC	H <sub>2</sub> O	HNCS	H <sub>2</sub> CNH	C <sub>5</sub> N		CH <sub>3</sub> CHNH					
HCl	H <sub>2</sub> S	HOCO <sup>+</sup>	H <sub>2</sub> C <sub>2</sub> O	<i>l</i> -HC <sub>4</sub> H <sup>*</sup>							
KCl	HNC	H <sub>2</sub> CO	H <sub>2</sub> NCN	<i>l</i> -HC <sub>4</sub> N							
NH	HNO	H <sub>2</sub> CN	HNC <sub>3</sub>	<i>c</i> -H <sub>2</sub> C <sub>3</sub> O							
NO	MgCN	H <sub>2</sub> CS	SiH <sub>4</sub> <sup>*</sup>	H <sub>2</sub> CCNH(?)							
NS	MgNC	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> COH <sup>+</sup>	C <sub>5</sub> N <sup>-</sup>							
NaCl	N <sub>2</sub> H <sup>+</sup>	<i>c</i> -SiC <sub>3</sub>	C <sub>4</sub> H <sup>-</sup>	HNCHCN							
OH	N <sub>2</sub> O	CH <sub>3</sub> <sup>*</sup>	HC(O)CN								
PN	NaCN	C <sub>3</sub> N <sup>-</sup>	HNCNH								



# Organics everywhere !



$c\text{-H}_2\text{C}_3\text{O}$ ,  $\text{H}_2\text{NCH}_2\text{CN}$ ,  $\text{NH}$ ,  $\text{C}_3$ ,  $\text{C}_2\text{H}$ ,  $\text{H}_2\text{C}$ ,  $\text{HNC}$ ,  $\text{HCO}^+$ ,  $\text{NH}_2$ ,  
 $\text{HCCN}$ ,  $\text{HCNO}$ ,  $\text{HOCN}$ ,  $\text{NH}_3$ ,  $c\text{-C}_3\text{H}_2$ ,  $\text{H}_2\text{CCN}$ ,  $\text{CH}_3\text{CN}$ ,  
 $\text{H}_2\text{C}_2\text{CHO}$ ,  $c\text{-C}_2\text{H}_4\text{O}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{HCONH}_2$ ,  $\text{HC}_2\text{nN}$ ,  $\text{CH}_3\text{C}_2\text{N}$ ,  
 $\text{C}_2\text{H}_3\text{CN}$ ,  $\text{H}_2\text{COHCHO}$ ,  $\text{HCOOCH}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_2\text{CHCHO}$ ,  
 $\text{CH}_3\text{CHNH}$ ,  $\text{H}_2\text{NCH}_2\text{CN}$ ,  $(\text{NH}_2)_2\text{CO}$ ,  $\text{HCOOCH}_3$ ,  $\text{C}_2\text{H}_5\text{CN}$ ,  
 $\text{CH}_3\text{CONH}_2$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{CO}$  ...



$\text{CN}$ ,  $\text{C}_3$ ,  $\text{C}_2\text{H}$ ,  $\text{HNC}$ ,  $c\text{-C}_3\text{H}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{CH}_3\text{CN}$ ,  $\text{C}_7\text{H}$ ,  
 $\text{HC}_5\text{N}$ ,  $i\text{-C}_3\text{H}$ ,  $c\text{-C}_3\text{H}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{H}_2\text{CCN}$ ,  $i\text{-H}_2\text{C}_4$ ,  
 $\text{CH}_2\text{CHCN}$ ,  $\text{HC}_2\text{H}$ ,  $\text{HC}_2\text{nH}$ ,  $\text{HNC}$ ,  $\text{HCCN}$ ,  $\text{H}_2\text{C}_2\text{O}$ ,  $\text{C}_5\text{H}$ ,  $\text{C}_6\text{H}$ ,  
 $\text{C}_2\text{H}_5\text{CN}$ ,  $\text{HCNO}$ ,  $\text{NH}_3$ ,  $\text{C}_5$ ,  $\text{C}_4\text{H}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{C}_5\text{N}$ ,  $\text{CH}_3\text{CHO}$ ,  
 $\text{CH}_8$

# Mapping the presence of organics with ALMA

Walsh et al. *Ap J* 823, L10 (May, 2016)

a

## Detection of gas-phase methanol in the TW Hydrae with ALMA

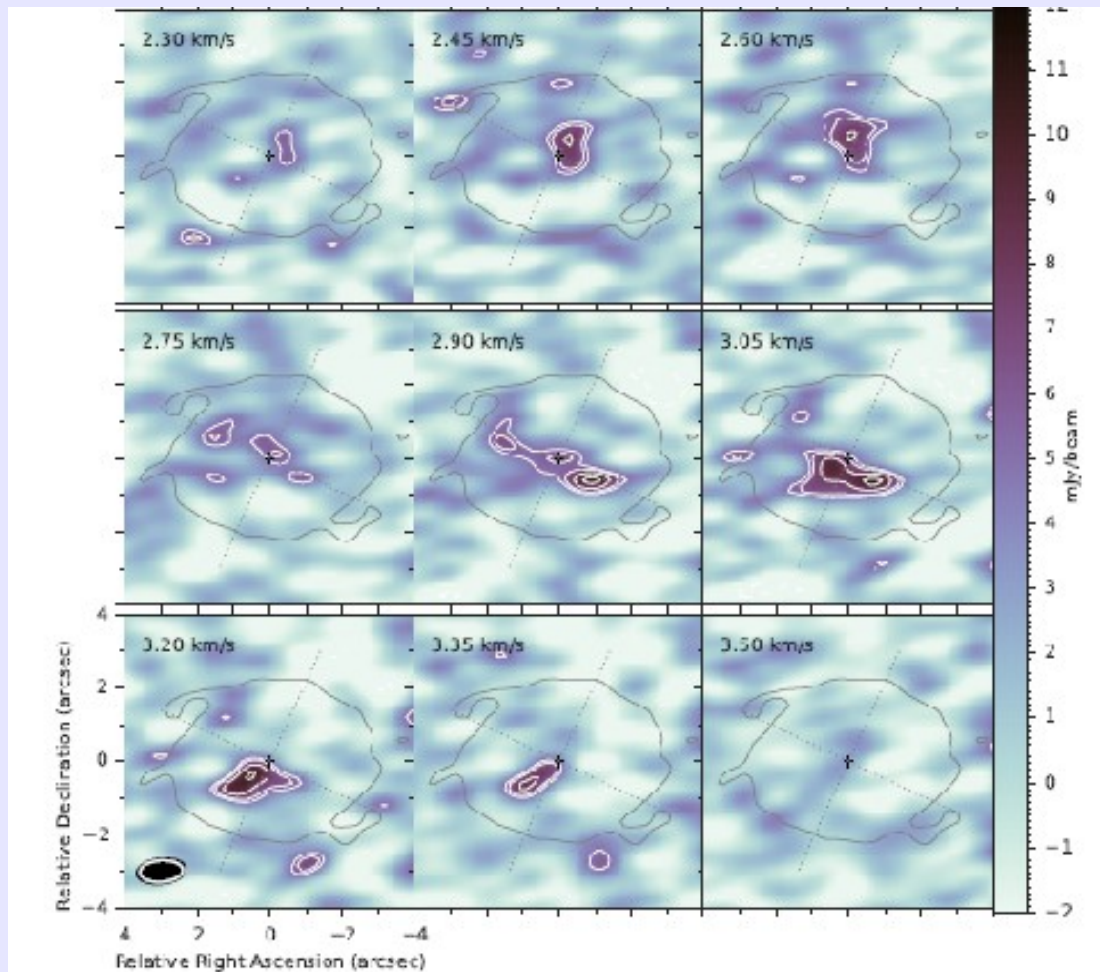


Fig. 1.— Channel maps for the stacked observed B7  $\text{CH}_3\text{OH}$  line emission. The white contours show the 2.5, 3.0, 4.0 and 5.0 $\sigma$  levels for the  $\text{CH}_3\text{OH}$  data and the gray contour shows the 3 $\sigma$  extent of the 317 GHz continuum. The black cross denotes the stellar position, and the dashed gray lines show the disk major and minor axes. The synthesised beams for the continuum (open ellipse) and line (filled ellipse) emission are shown in the bottom-left panel.

**MILLER & UREY  
REACTIONS IN THE  
UNIVERSE !**

),



“All the world began with a *yes*.  
One molecule said *yes* to another  
molecule and life was born...

[...] Make no mistake, I only achieve  
simplicity with enormous effort.”

Clarice Lispector  
“The Hour of the Star”

## Abstract

The atomic composition of the present Universe is largely dominated by hydrogen and helium that were formed in the Big Bang. Heavier elements form through nucleosynthesis inside stars and in Supernovae explosions. From those, a rich chemistry comes out in particular in astrophysical locations as molecular clouds and the interstellar gas. Therewith, simpler elements recombine in successive reaction paths, generating two-, three- and even four-atom compounds. Hydrogen, carbon, oxygen and nitrogen easily react forming  $H_2O$ ,  $NH_3$ ,  $CO$ ,  $CH_4$ , and  $CO_2$ . From these simple molecules, more complex organics such as formaldehyde ( $HCOH$ ), hydrogen cyanide ( $HCN$ ), methanol ( $CH_2OH$ ), formic acid ( $HCOOH$ ) and glycoaldehyde ( $HCOH_2$ ) are shown to appear driven by proper catalysis, as it was successfully showed in several Miller & Urey-like laboratory experiments. This contribution is intended to feed evidence on how those robust prebiotic reactions could have shaped a life-friendly Universe, providing solid arguments for future observations and science development.