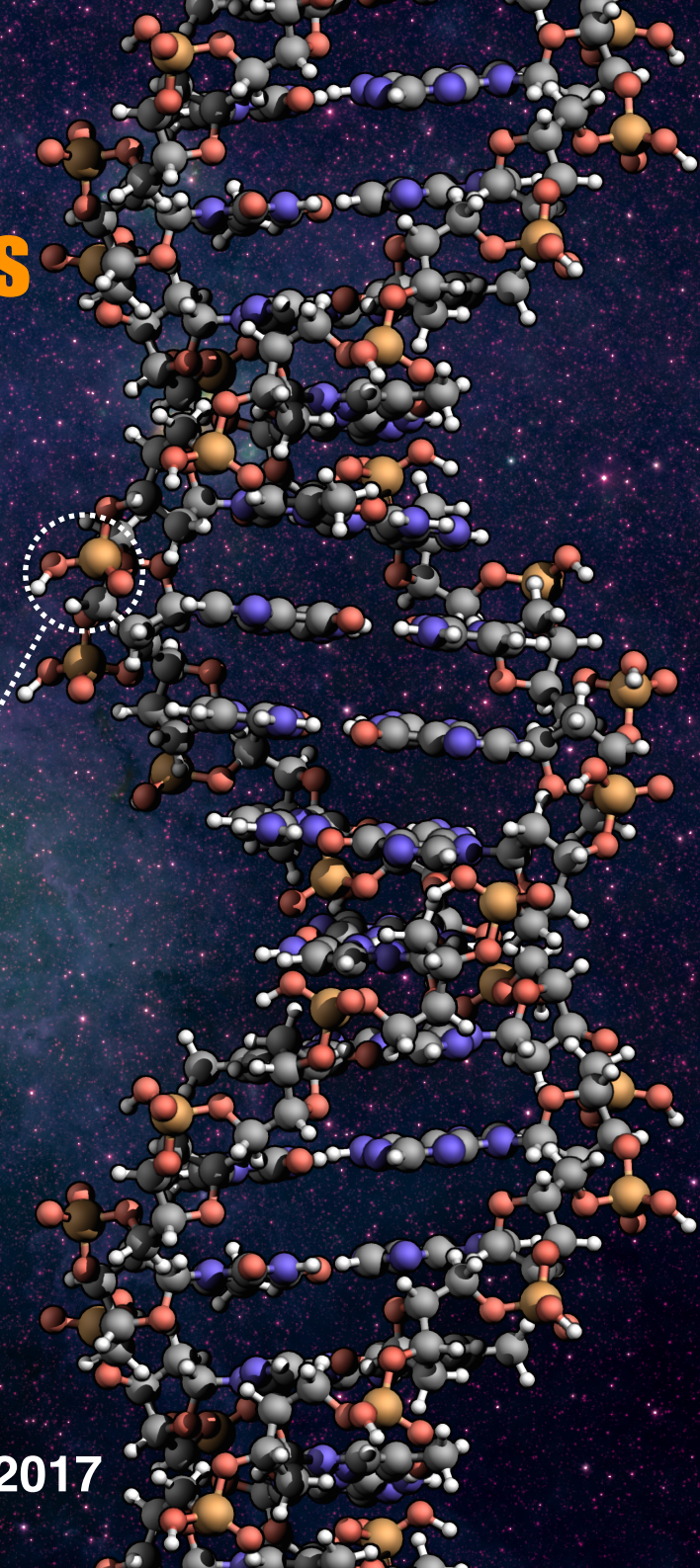
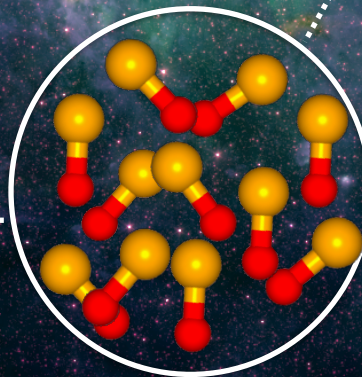
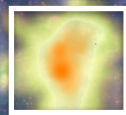


# The formation of prebiotic molecules in star-forming regions

Víctor M. Rivilla

Osservatorio Astrofisico di Arcetri, OAA-INAF



Nitrogen

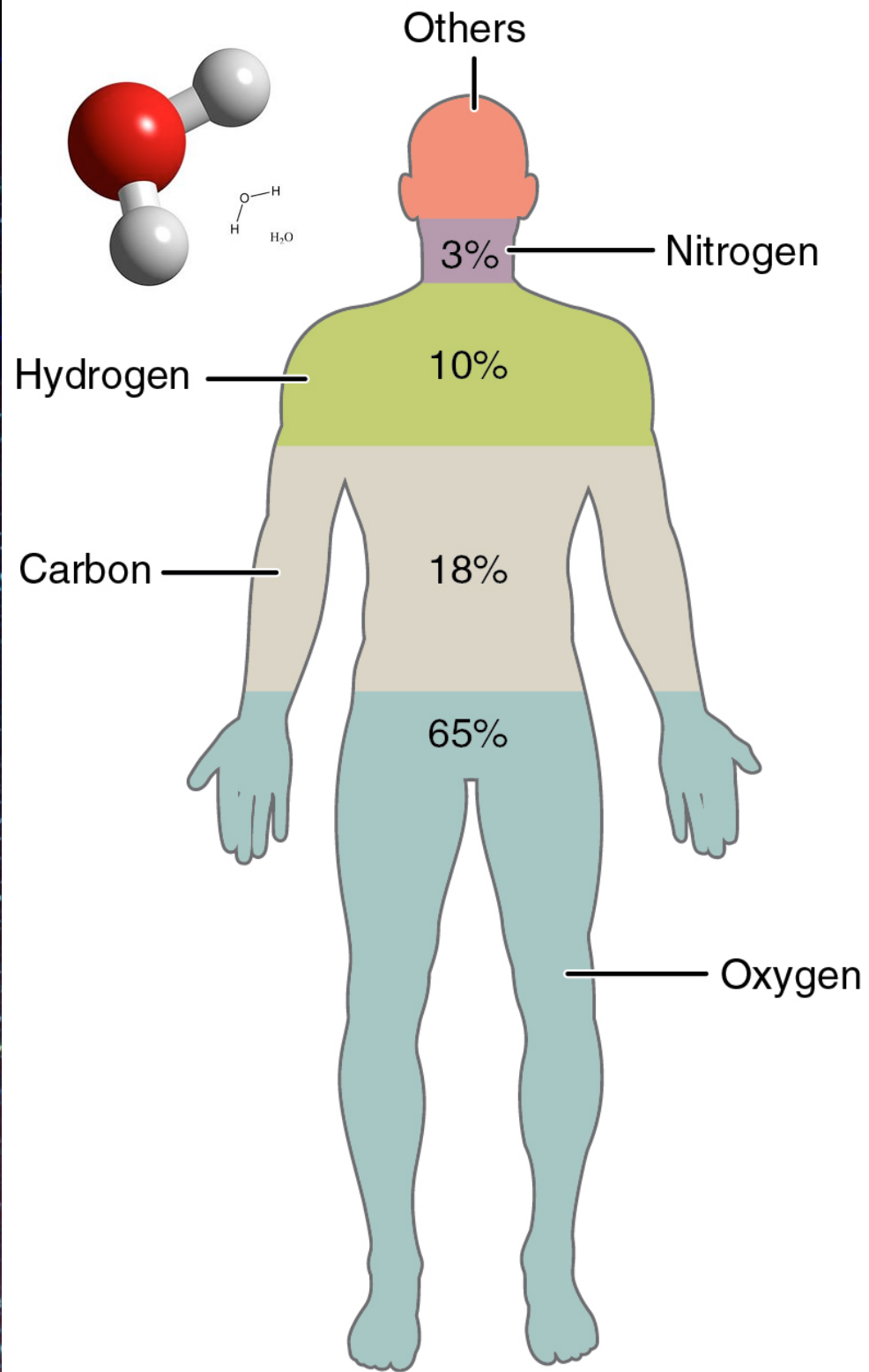


Francesco's Legacy, Florence, June 5-9 2017

**We are chemistry !**

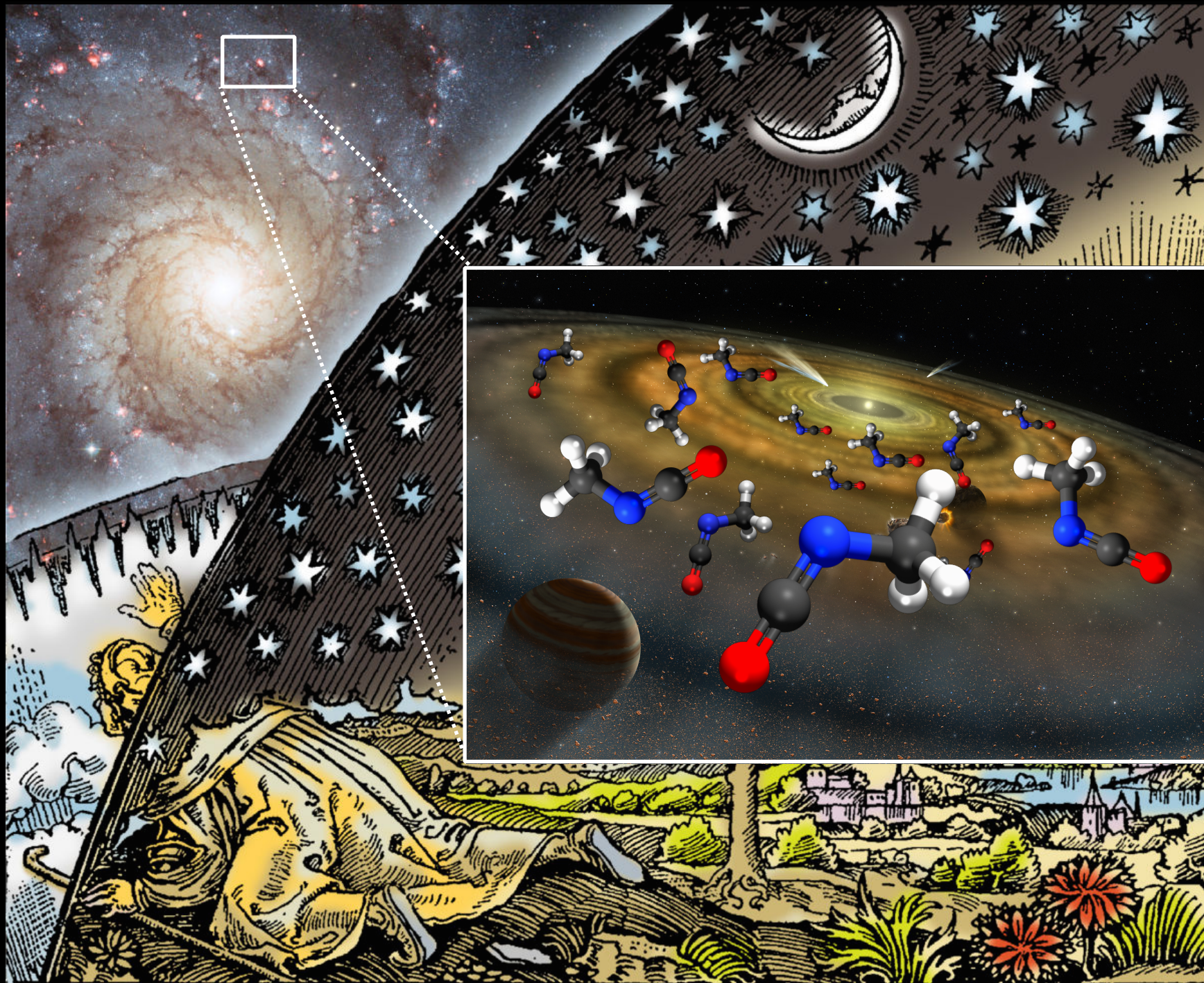
Atoms aggregated in ...

**MOLECULES**









Molecules in the Interstellar Medium or Circumstellar Shells (as of 02/2016)

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>9</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>i</i> -C <sub>3</sub> H	C <sub>4</sub> H	<i>i</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>i</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> ?	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 <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	HCO	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>i</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 2015	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>i</i> -HC <sub>4</sub> H <sup>*</sup>							
KCl	HNC	H <sub>2</sub> CO	H <sub>2</sub> NCN	<i>i</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								
SO	OCS	PH <sub>3</sub>	CH <sub>3</sub> O								
SO <sup>+</sup>	SO <sub>2</sub>	HCNO	NH <sub>4</sub> <sup>+</sup>								
SiN	<i>c</i> -SiC <sub>2</sub>	HOCN	H <sub>2</sub> NCO <sup>+</sup> (?)								
SiO	CO <sub>2</sub> <sup>*</sup>	HSCN	NCCNH <sup>+</sup> 2015								
Sis	NH <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>									
CS	H <sub>3</sub> <sup>+</sup> (*)	C <sub>3</sub> H <sup>+</sup>									
HF	SiCN	HMgNC									
HD	AlNC	HCCO 2015									
FeO ?	SiNC										
O <sub>2</sub>	HCP										
CF <sup>+</sup>	CCP										
SiH ?	AlOH										
PO	H <sub>2</sub> O <sup>+</sup>										
AlO	H <sub>2</sub> Cl <sup>+</sup>										
OH <sup>+</sup>	KCN										
CN <sup>-</sup>	FeCN										
SH <sup>+</sup>	HO <sub>2</sub>										
SH	TiO <sub>2</sub>										
HCl <sup>+</sup>	C <sub>2</sub> N										
TiO	Si <sub>2</sub> C 2015										
ArH <sup>+</sup>											
NO <sup>+</sup> ?											

## Molecules detected in space

Almost 200 molecules have been detected in space

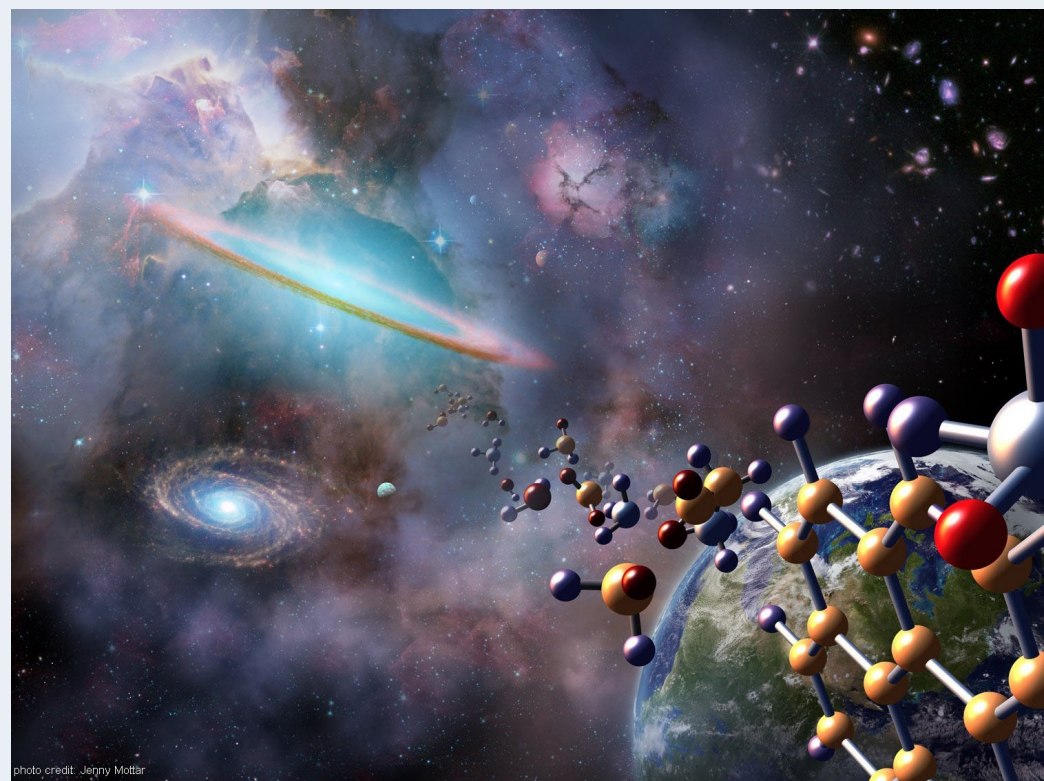


photo credit: Jenny Mottar

# "ASTROCHEMICAL" table of elements

Elements detected in molecules in space

1 H Hydrogen 1.008																	2 He Helium 4.003						
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305																	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798						
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294						
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018						
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [262]	105 Db Dubnium [261]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown						
57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967									
89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]									

# "ASTROBIOLOGICAL" table of key-elements

Basic elements for life

1 H Hydrogen 1.008																	2 He Helium 4.003						
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305																	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
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# Prebiotic molecules: the building blocks of life

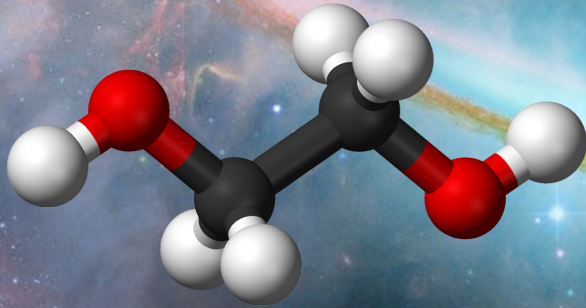
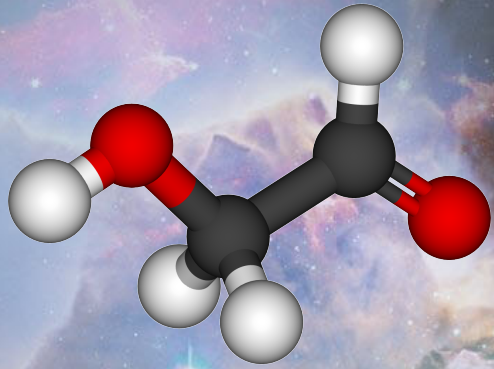
- Molecules containing the 5 key elements for the development of LIFE (C, N, O, S, P).
- Relevant for prebiotic chemistry due to its structural and functional role in DNA, RNA, ATP...
- The detection in **star-forming regions** has open the possibility of understanding how LIFE could emerge on Earth.



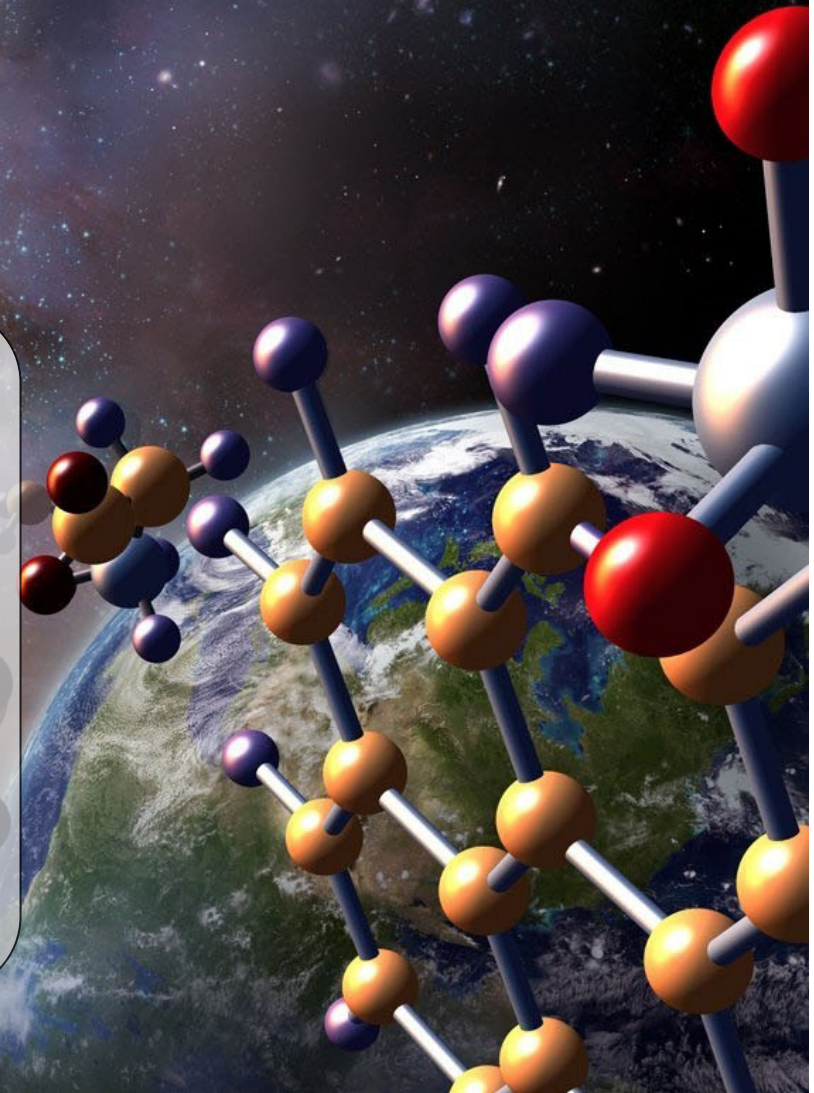
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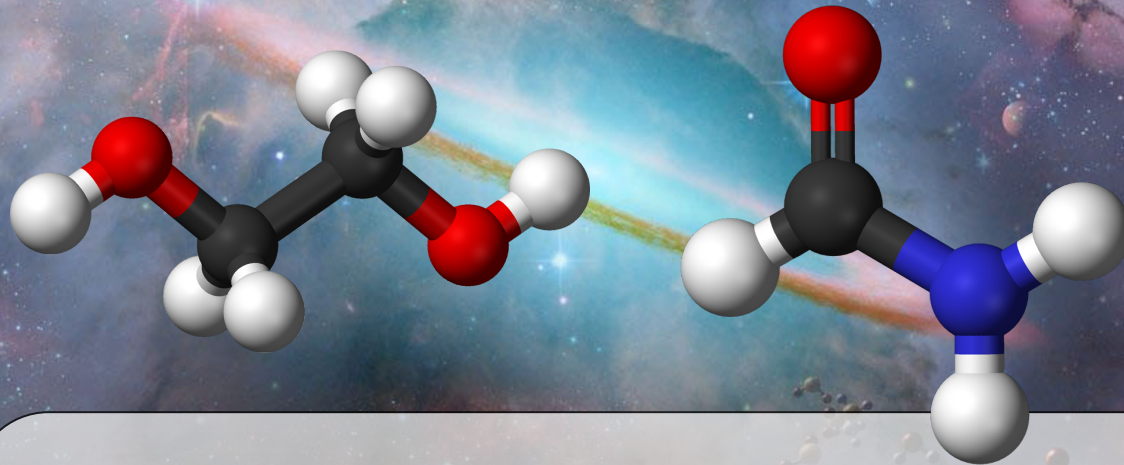
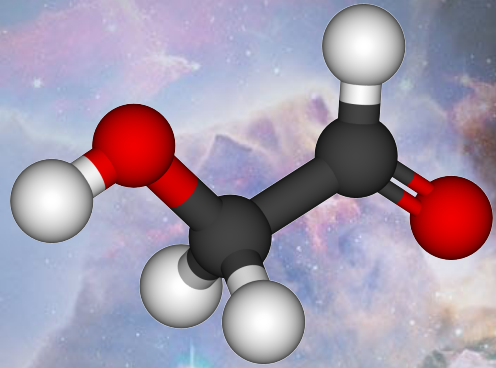
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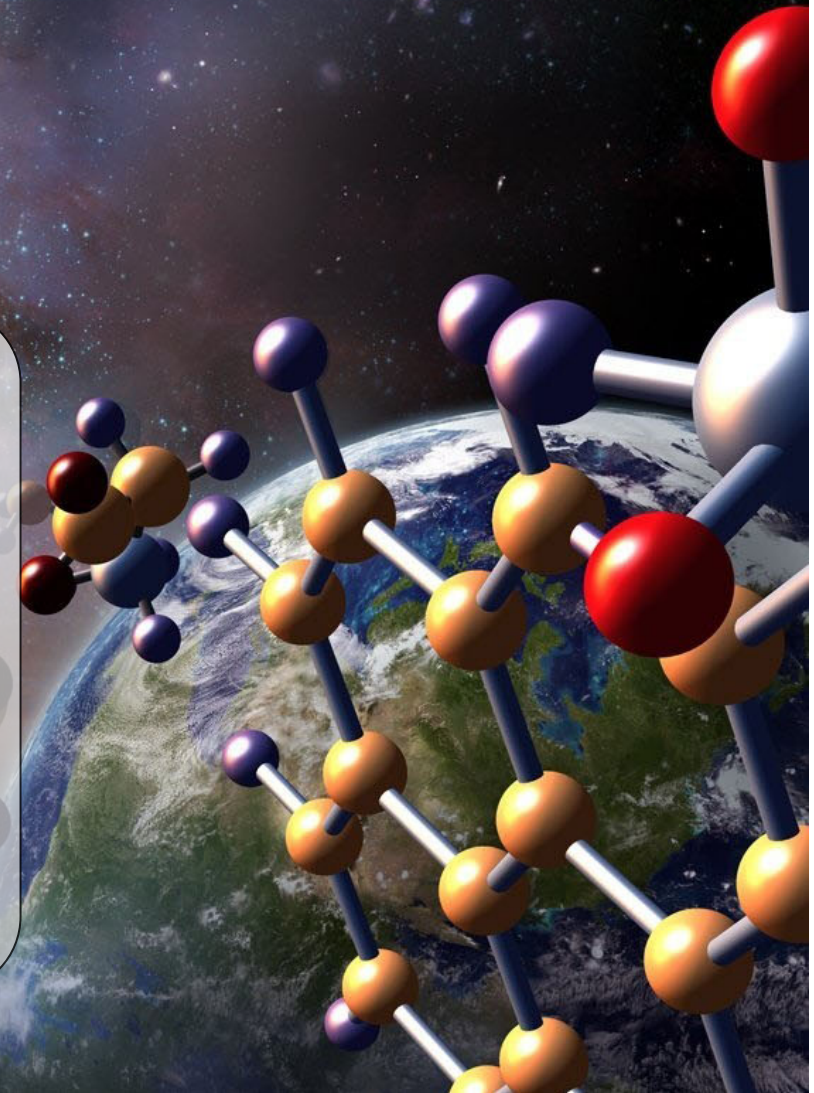
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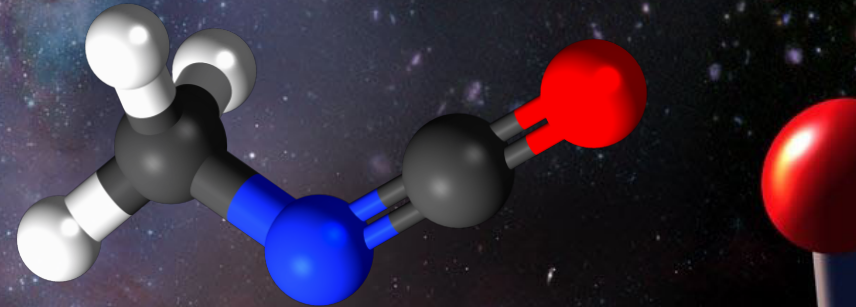
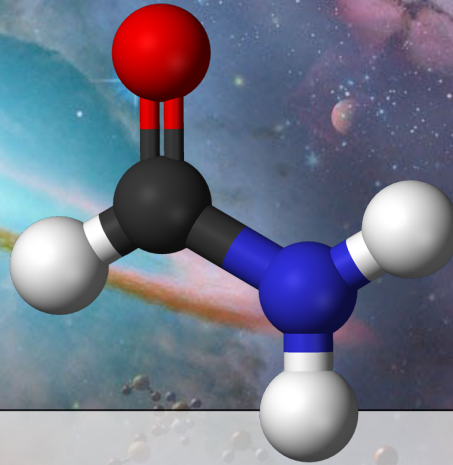
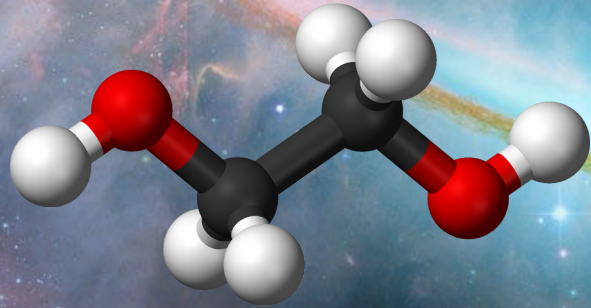
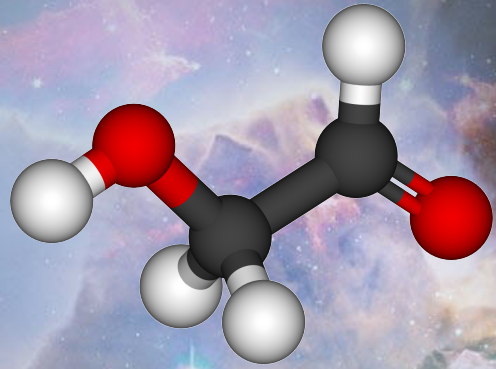
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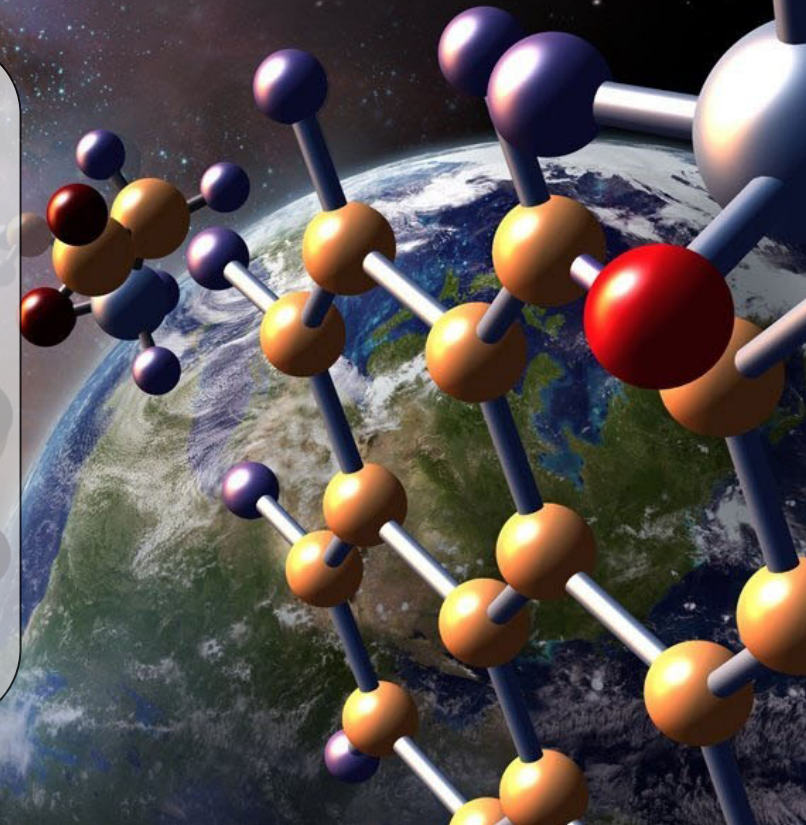
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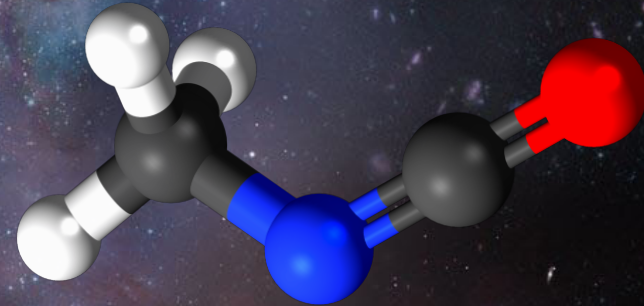
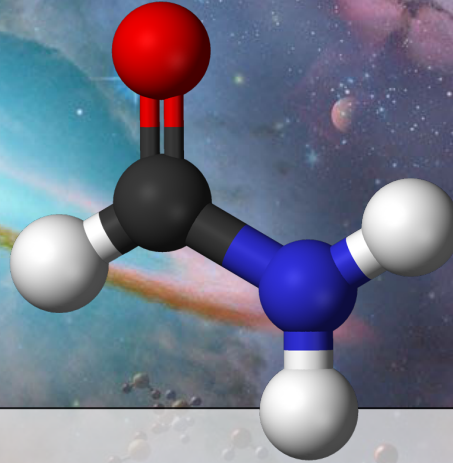
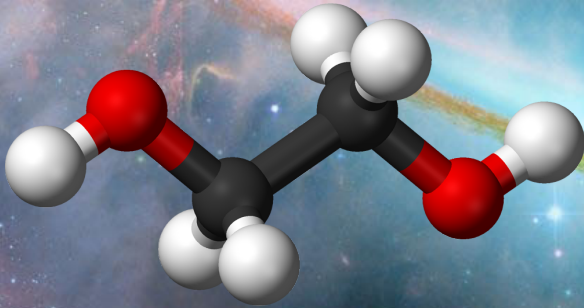
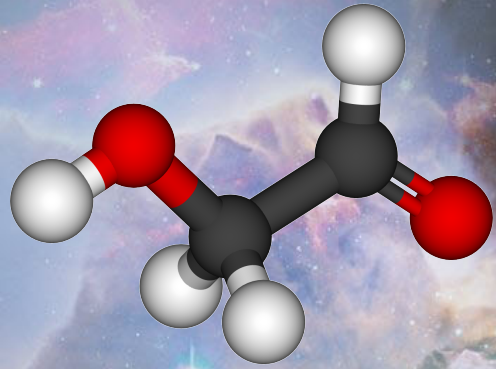
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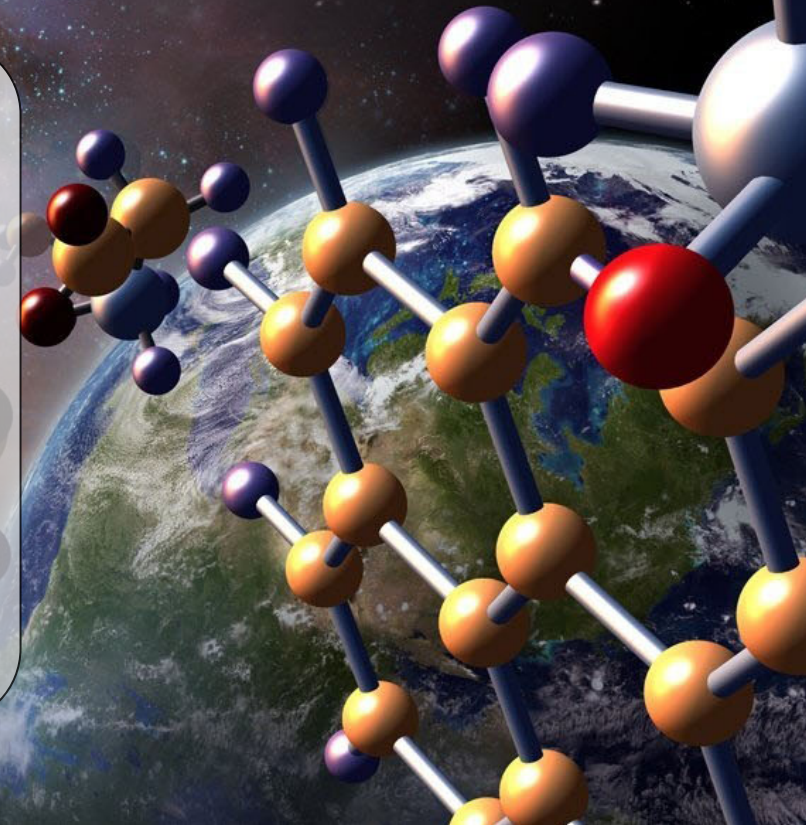
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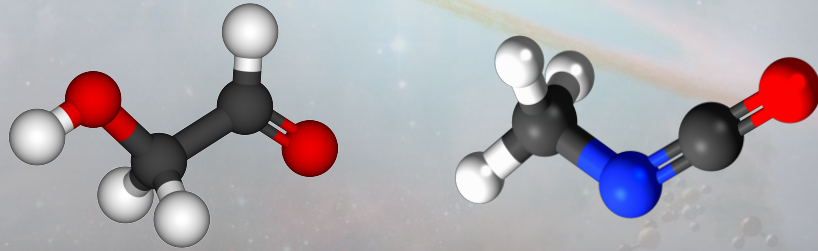


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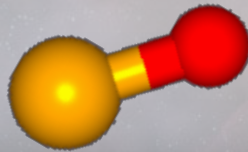


# Prebiotic molecules: the building blocks of life

## COMPLEX ORGANIC MOLECULES



## PHOSPHORUS-BEARING MOLECULES



Osservatorio Astrofisico di Arcetri (Florence) - Star Formation Group:  
**Understanding the formation of prebiotic molecules  
in star-forming regions**

- 1 - **Detection** of prebiotic molecules in star-forming regions
- 2 - Derivation of physical parameters: **molecular abundances** and temperatures.
- 3 - Comparison with **chemical models** → how are they formed?







**COMPLEX ORGANIC MOLECULES (COMs)**

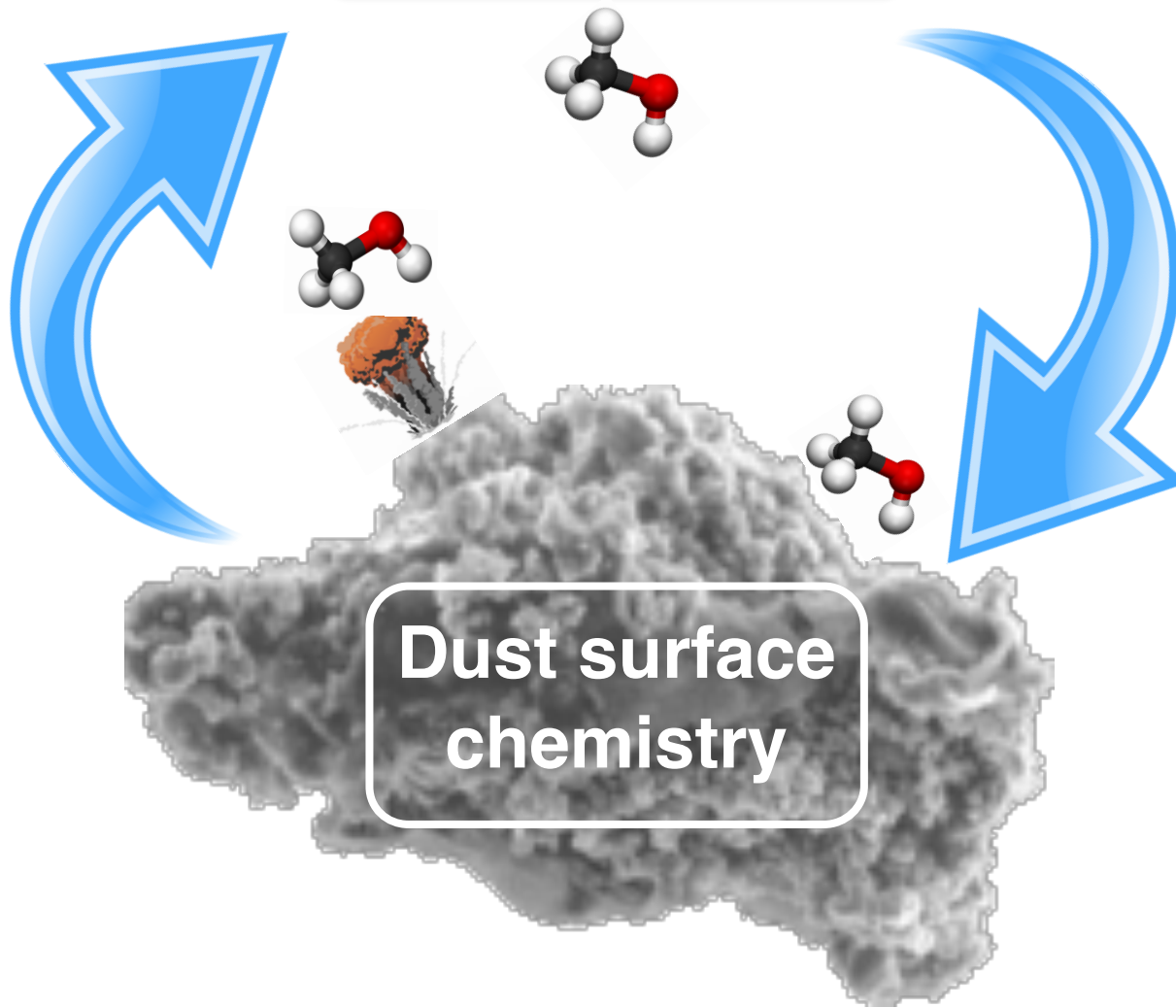
# COMs formation scenarios

Gas phase  
chemistry

Desorption

Depletion

Dust surface  
chemistry





**G31.41+0.31**

## O-bearing

- 2 atoms: CO, C<sup>17</sup>O, C<sup>18</sup>O, C<sup>13</sup>O
- 3 atoms: HCO, HC<sup>18</sup>O<sup>+</sup>, HC<sup>17</sup>O<sup>+</sup>, H<sup>13</sup>CO<sup>+</sup>
- 4 atoms: H<sub>2</sub>CO, H<sub>2</sub><sup>13</sup>CO
- 5 atoms: CH<sub>2</sub>CO, HCOOH
- 6 atoms: CH<sub>3</sub>OH, <sup>13</sup>CH<sub>3</sub>OH
- 7 atoms: CH<sub>3</sub>CHO, c-H<sub>2</sub>COCH<sub>2</sub>
- 8 atoms: CH<sub>3</sub>OCHO, CH<sub>2</sub>OHCHO
- 9 atoms: CH<sub>3</sub>OCH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH,
- 10 atoms: CH<sub>3</sub>COCH<sub>3</sub>, (CH<sub>2</sub>OH)<sub>2</sub>

## N-bearing

- 2 atoms: NH, CN, NS
- 3 atoms: HCN, H<sup>13</sup>CN, HC<sup>15</sup>N, HN<sup>13</sup>C, H<sup>15</sup>NC, N<sup>15</sup>NH<sup>+</sup>
- 4 atoms: HNCO, HNC<sup>18</sup>O
- 5 atoms: HC<sub>3</sub>N
- 6 atoms: NH<sub>2</sub>CHO, CH<sub>3</sub>CN, CH<sub>3</sub><sup>13</sup>CN
- 7 atoms: HC<sub>5</sub>N, CH<sub>3</sub>NCO, C<sub>2</sub>H<sub>3</sub>CN
- 9 atoms: C<sub>2</sub>H<sub>5</sub>CN

## Only C and H

- 3 atoms: CCH
- 5 atoms: c-C<sub>3</sub>H<sub>2</sub>
- 7 atoms: CH<sub>3</sub>CCH

## S-bearing

- 2 atoms: SO, <sup>34</sup>SO, <sup>13</sup>CS, <sup>13</sup>C<sup>34</sup>S, C<sup>34</sup>S
- 3 atoms: SO<sub>2</sub>, <sup>34</sup>SO<sub>2</sub>, H<sub>2</sub>S, OCS, O<sup>13</sup>CS, <sup>18</sup>OCS, OC<sup>34</sup>S, HCS<sup>+</sup>
- 4 atoms: H<sub>2</sub>CS

## Deuterated

- 3 atoms: DCN, DCO<sup>+</sup>
- 4 atoms: NH<sub>2</sub>D
- 6 atoms: CH<sub>2</sub>DCN, CH<sub>2</sub>DOH, CH<sub>3</sub>OD

## Si-bearing

- 2 atoms: SiO, SiS

## P-bearing

- 2 atoms: PN

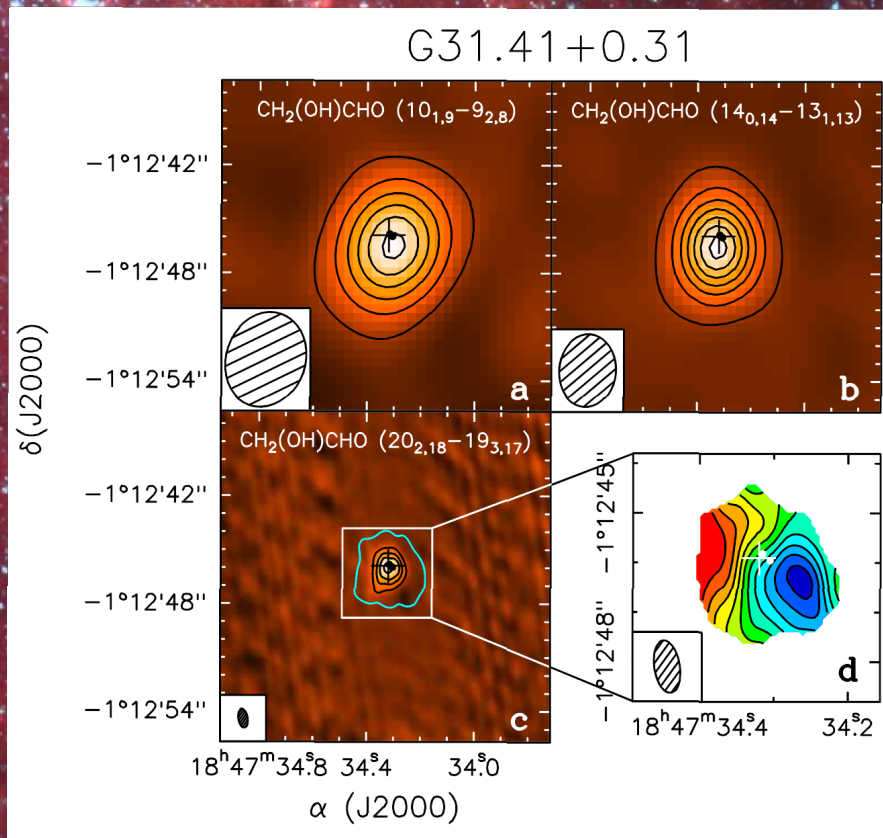
## H recombination lines

- H-alpha
- H-beta
- H-gamma,
- He-alpha

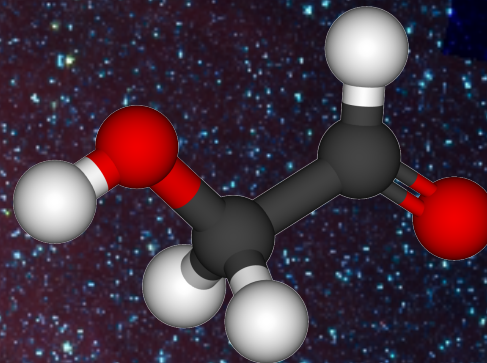
45 molecular species, 16 COMs, 23 isotopologs, 6 deuterated species, 2 cyclic molecules, 4 positive ions and hydrogen recombination lines



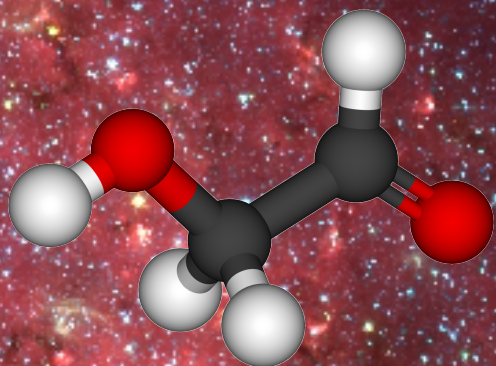
# G31.41+0.31



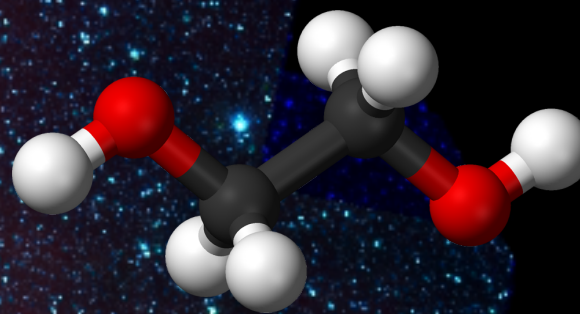
- First detection of glycolaldehyde outside the Galactic Center by Beltrán et al. (2009)



glycolaldehyde  
(8 atoms)

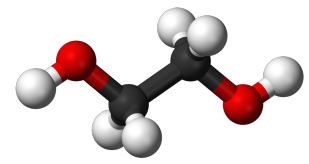


ethylene glycol  
(10 atoms)



# Ethylene glycol ( $\text{CH}_2\text{OH}$ )<sub>2</sub> in G31

---



IRAM 30m



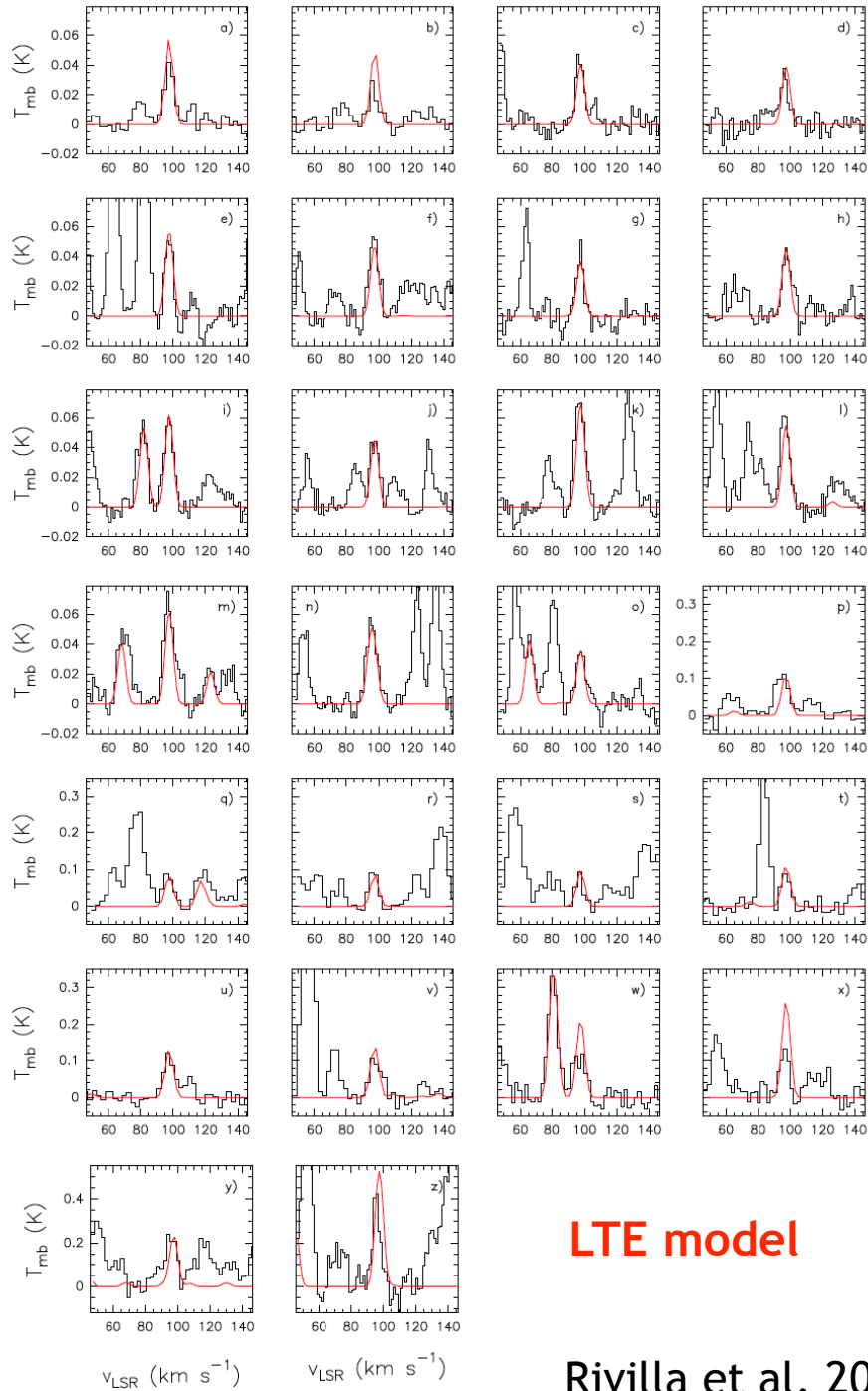
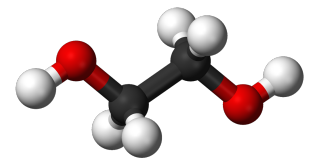
GBT



SMA

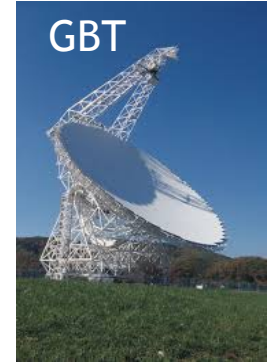
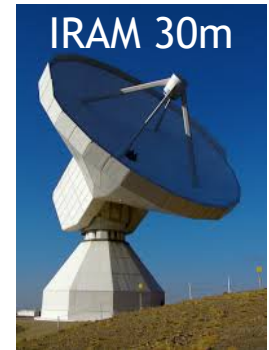


# Ethylene glycol (CH<sub>2</sub>OH)<sub>2</sub> in G31



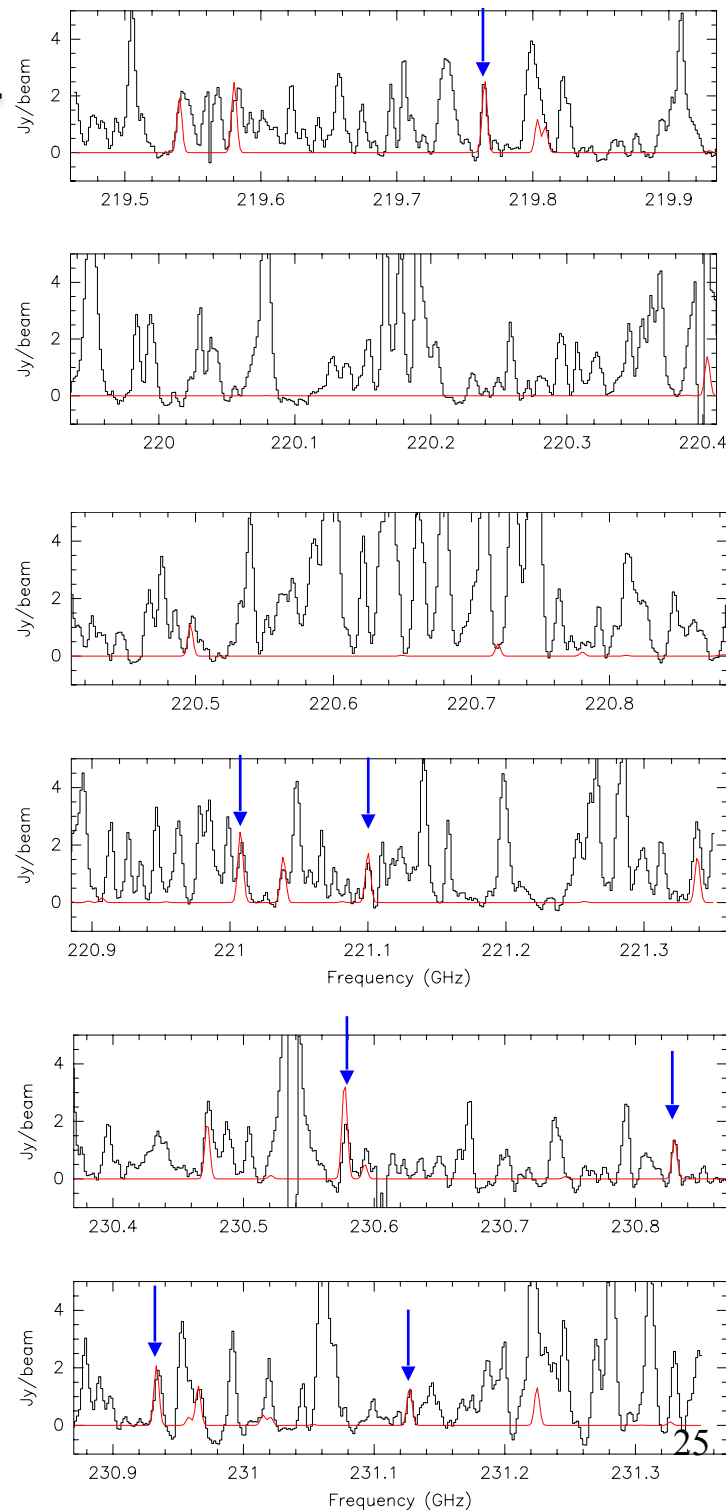
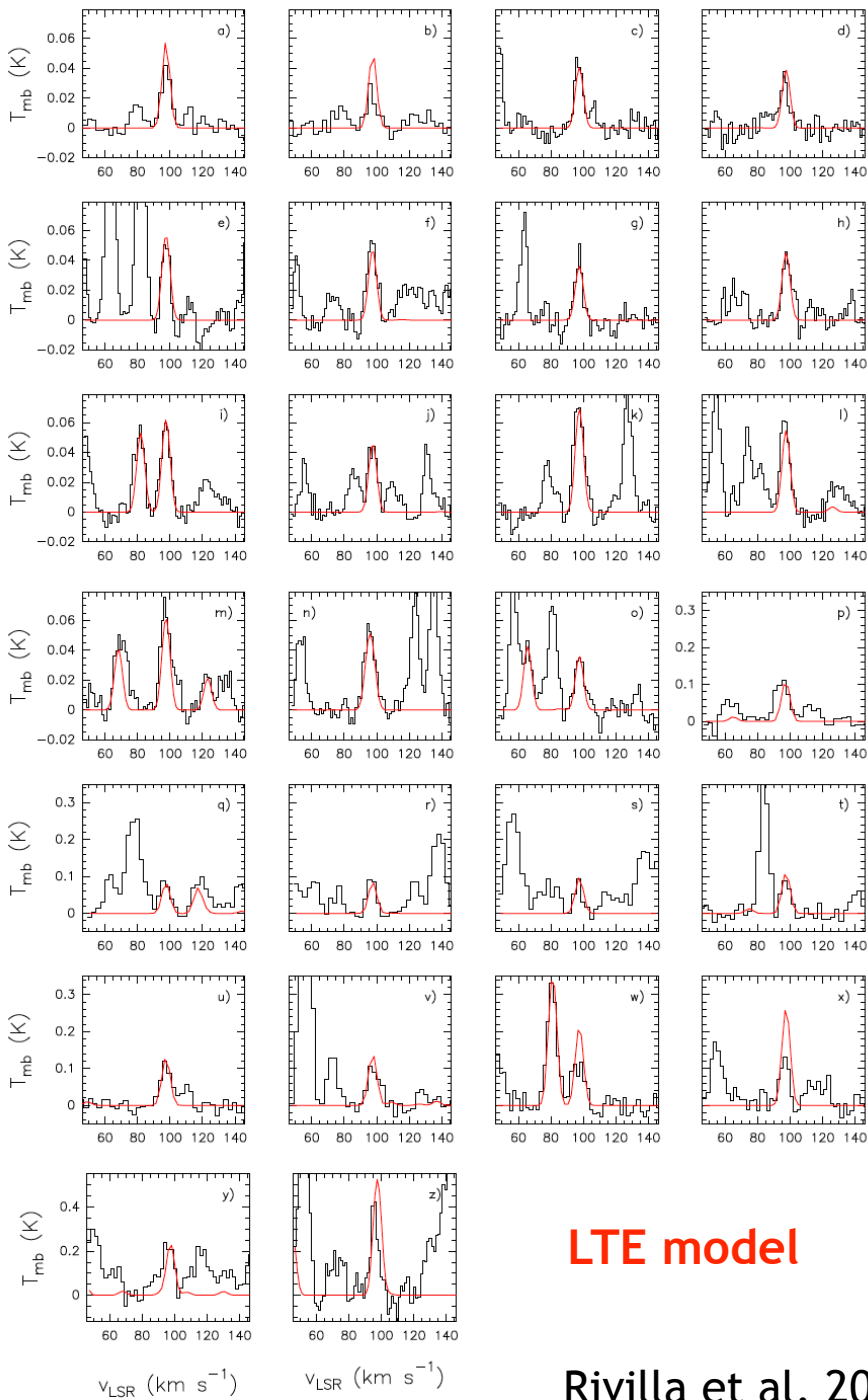
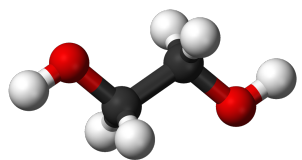
LTE model

Rivilla et al. 2017a



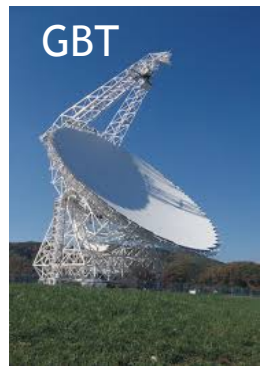
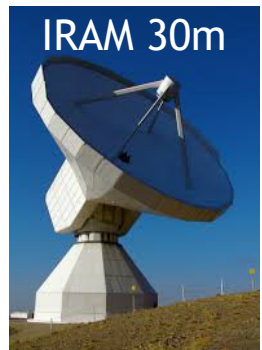


# Ethylene glycol (CH<sub>2</sub>OH)<sub>2</sub> in G31

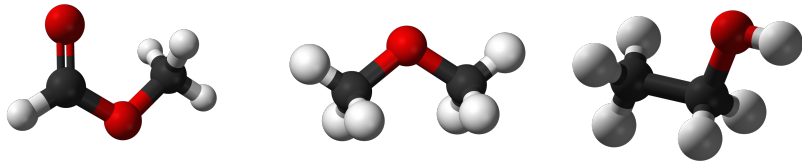


LTE model

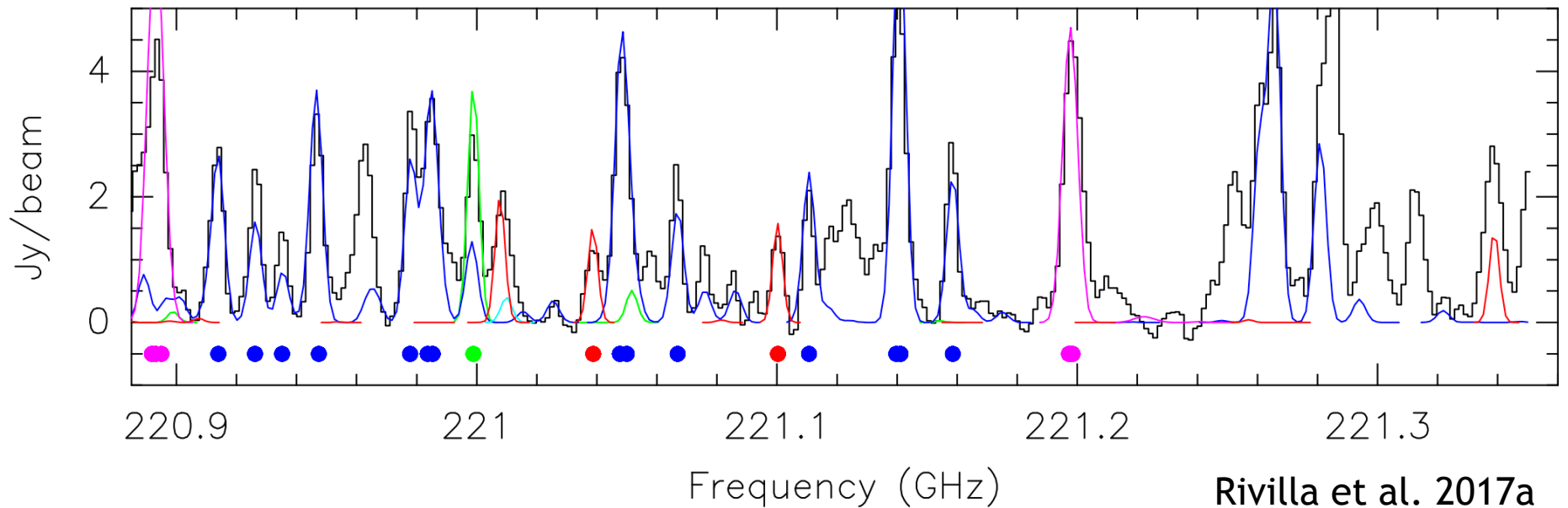
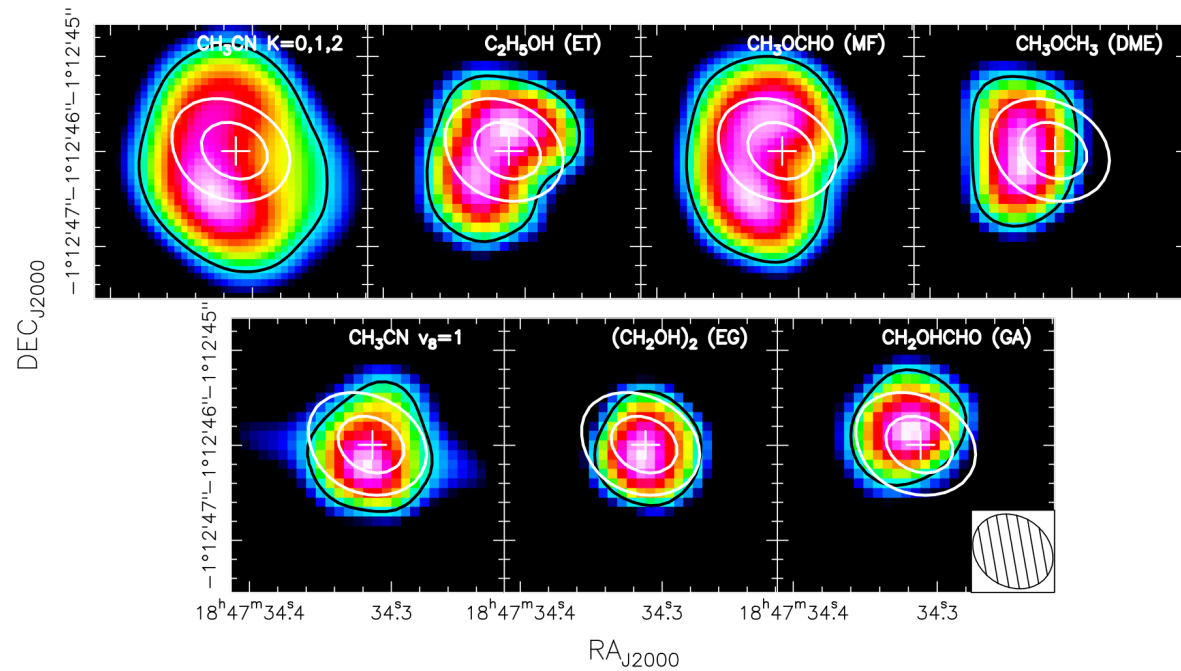
Rivilla et al. 2017a



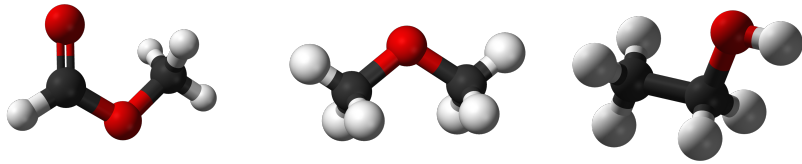
# More COMs in G31.41



Methyl formate Dimethyl ether Ethanol



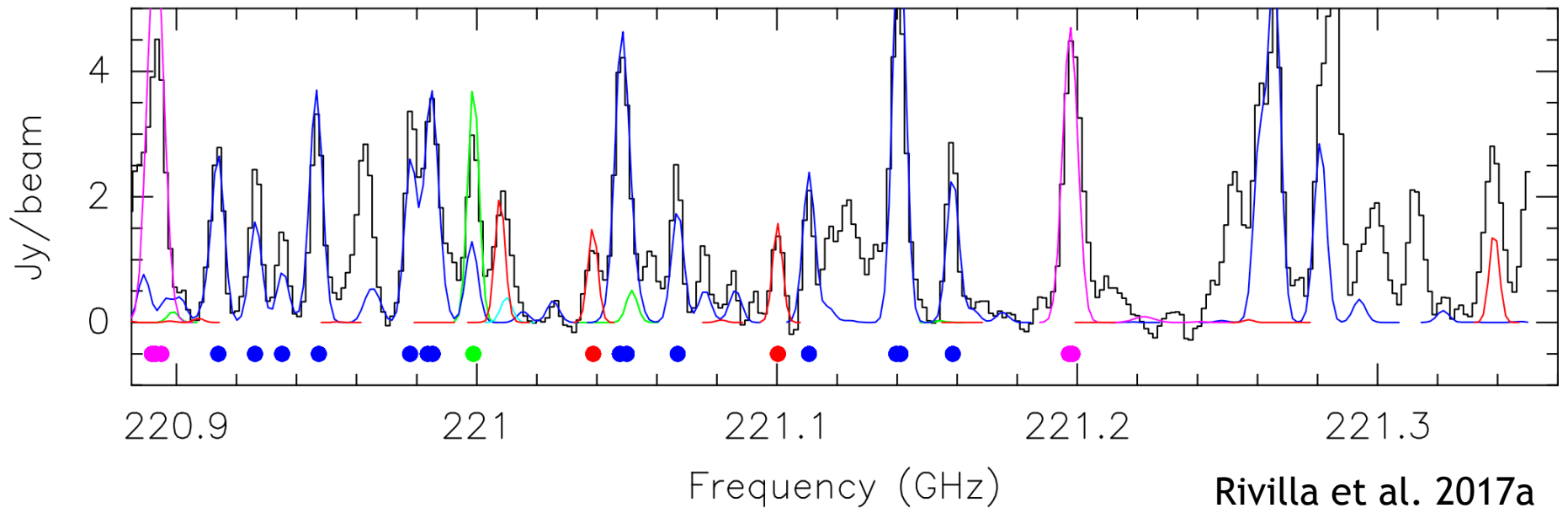
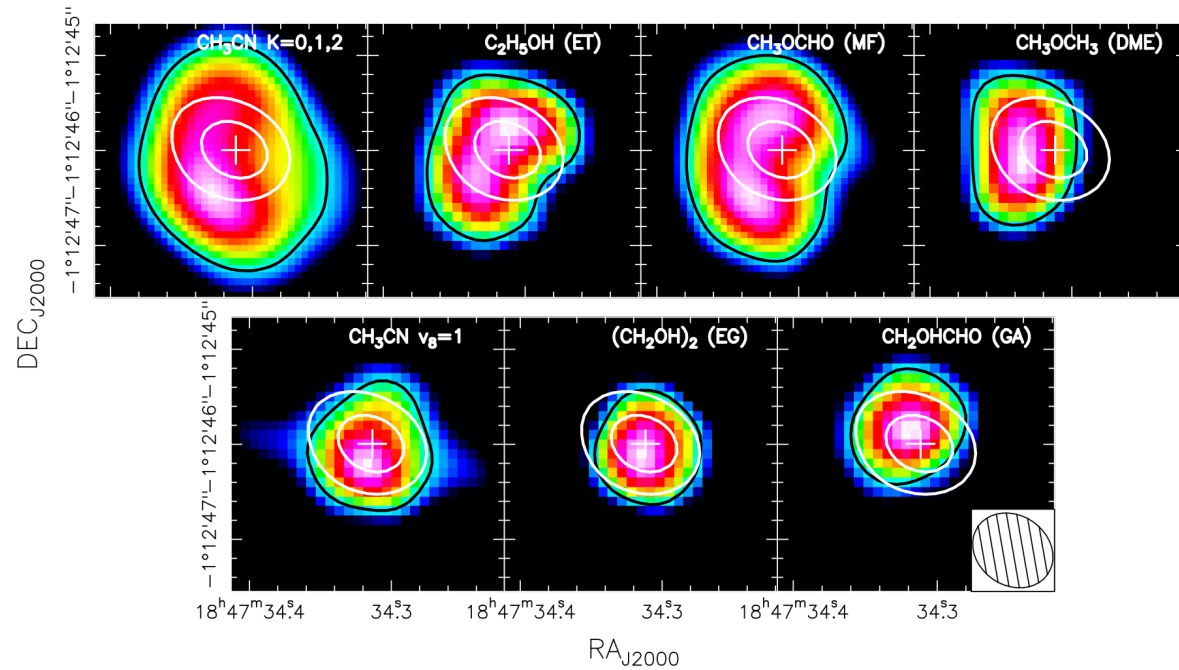
# More COMs in G31.41



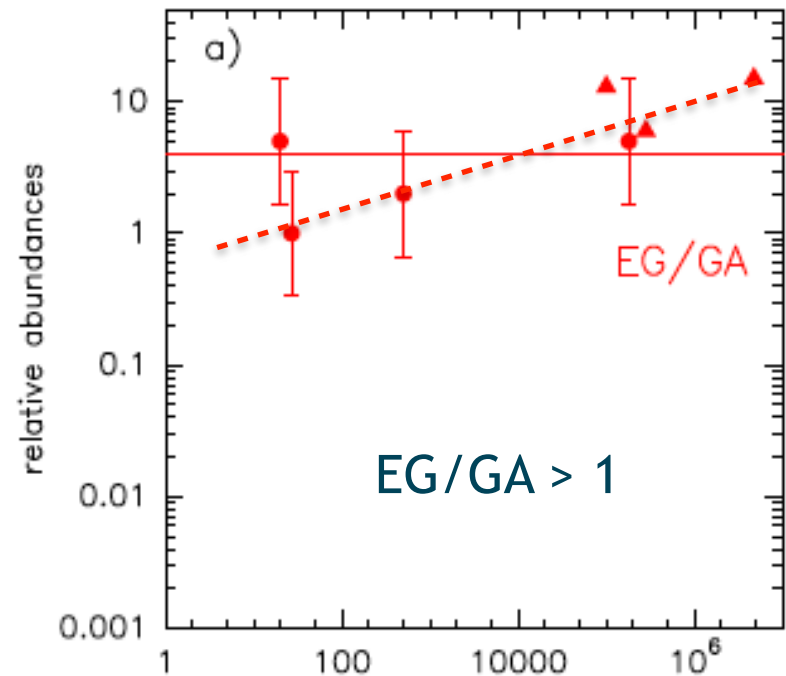
Methyl formate Dimethyl ether Ethanol

## DERIVED PHYSICAL PARAMETERS

	EG	ET	GA	MF	DME
$N$ ( $\times 10^{17}$ cm $^{-2}$ )	6.3	8.5	0.8	19	40
$X$ ( $10^{-8}$ ) <sup>b</sup>	2.1	2.8	0.3	6	13
$T_{\text{ex}}$ (K)	165 <sup>a</sup>	120	165 <sup>a</sup>	165	135
$v_{\text{LSR}}$ (km s $^{-1}$ )	97.6	97.6	96.1	97.6	97.0
$\Delta v$ (km s $^{-1}$ )	5.6	5.4	5.3	4.7	4.4



Source	[EG/GA]
<i>Hale-Bopp (comet)</i>	>6
<i>Lemmon (comet)</i>	>3
<i>Lovejov (comet)</i>	>5
IRAS 16293-2422	1
NGC 1333 IRAS2A	5
NGC7129 FIRS2	2
SgrB2N	1.3
<b>G31.41+0.31</b>	<b>5</b>
Orion hot core	>10
W51e2	>16
G34.3+0.2	>6
<i>G-0.02, G-0.11, G+0.693</i>	1.2-1.6

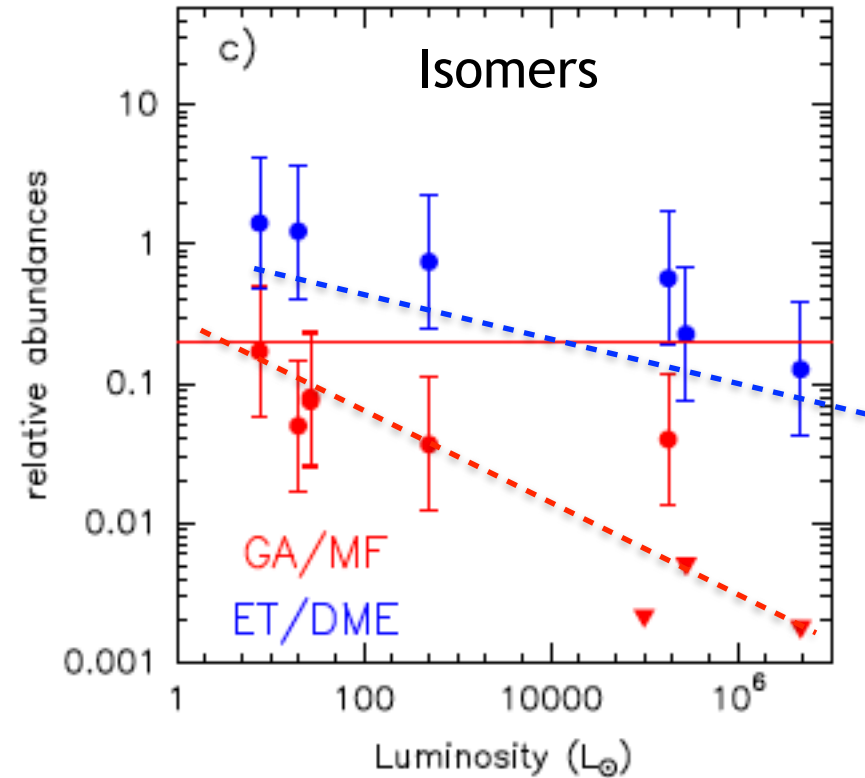
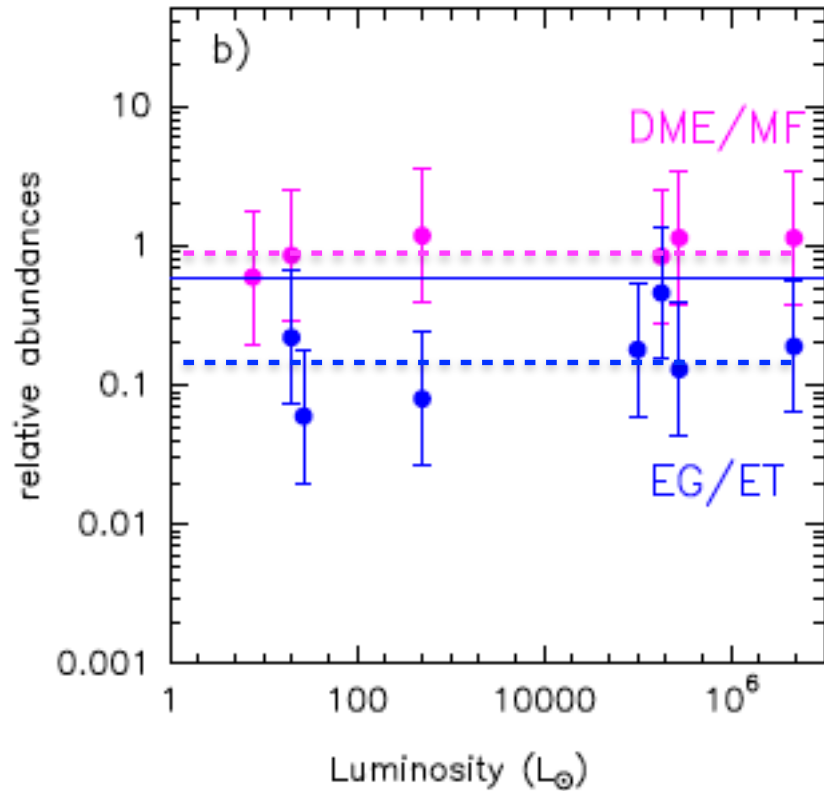


Rivilla et al. 2017a

Hollis+00,02, Crovisier04a, Fuente+04, Requena-Torres08, Beltrán+09, Jørgensen+12, Belloche+13  
 Maury+14, Biver+14, Coutens+15, Brouillet+15, Lykke+15, Taquet+15, Rivilla+17a.

# Observational results: abundances ratios

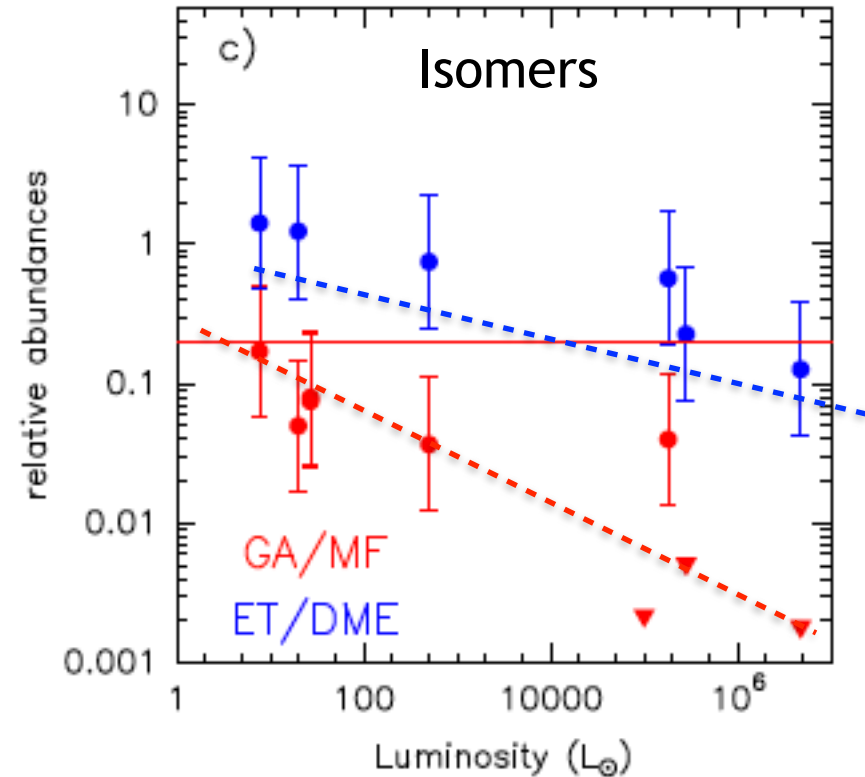
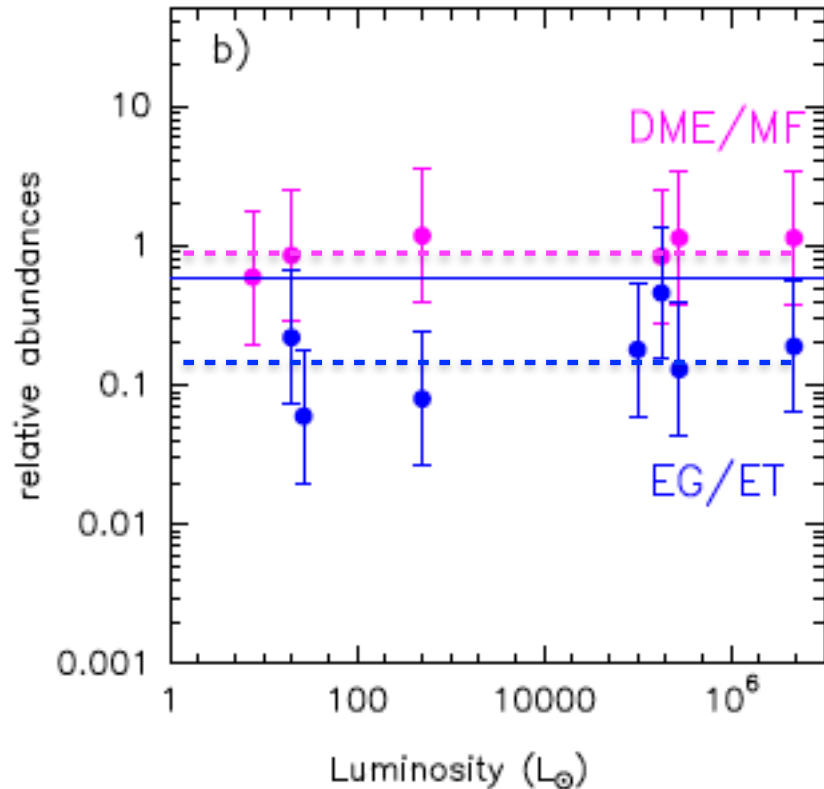
Rivilla et al. 2017a



What can be infer about the formation of COMs from the results of the observations?

# Observational results: abundances ratios

Rivilla et al. 2017a



What can be infer about the formation of COMs from the results of the observations?

If two species are chemically linked (i.e. they have a common precursor and/or one is formed from the other) their relative abundance should be nearly constant regardless the luminosity.

# Chemical pathways

COM		Chemical pathway
(CH <sub>2</sub> OH) <sub>2</sub> (EG)	[1]	CH <sub>2</sub> OHCHO + 2H → (CH <sub>2</sub> OH) <sub>2</sub>
	[2]	CH <sub>2</sub> OH + CH <sub>2</sub> OH → (CH <sub>2</sub> OH) <sub>2</sub>
CH <sub>2</sub> OHCHO (GA)	[3]	2HCO → CO + H <sub>2</sub> CO → HOCCOH; HOCCOH + H → CH <sub>2</sub> OCHO; CH <sub>2</sub> OCHO + H → CH <sub>2</sub> OHCHO
	[4]	HCO + CH <sub>2</sub> OH → CH <sub>2</sub> OHCHO
CH <sub>3</sub> OCHO (MF)	[5]	CH <sub>3</sub> O + HCO → CH <sub>3</sub> OCHO
	[6]	CH <sub>3</sub> OCH <sub>3</sub> + O → CH <sub>3</sub> OCHO + H (gas phase)
CH <sub>3</sub> OCH <sub>3</sub> (DME)	[7]	CH <sub>3</sub> O + CH <sub>3</sub> → CH <sub>3</sub> OCH <sub>3</sub>
CH <sub>3</sub> CH <sub>2</sub> OH (ET)	[8]	CH <sub>2</sub> OH + CH <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> OH

Bennett & Kaiser07

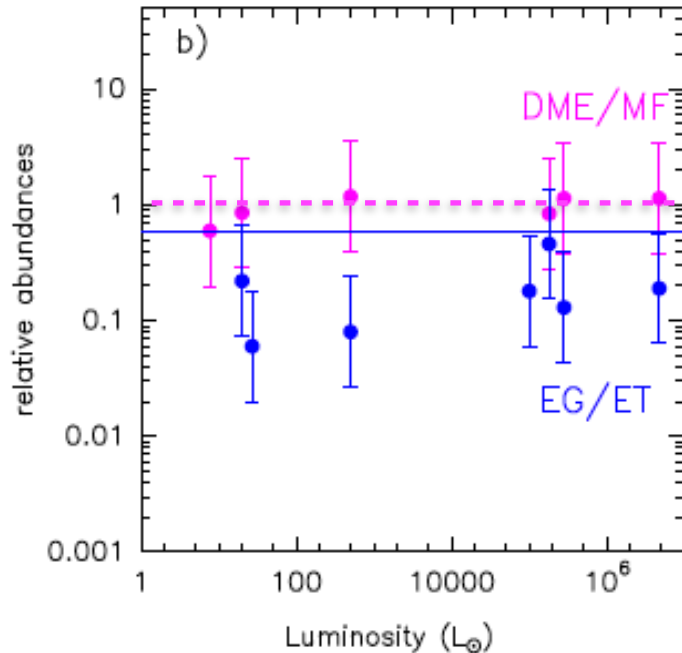
Garrod+08

Woods+13

Balucani+15

Fedoseev+14

Butscher+15



DME and MF formed from the common precursor CH<sub>3</sub>O

# Chemical pathways

COM		Chemical pathway
(CH <sub>2</sub> OH) <sub>2</sub> (EG)	[1]	CH <sub>2</sub> OHCHO + 2H → (CH <sub>2</sub> OH) <sub>2</sub>
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Bennett & Kaiser07

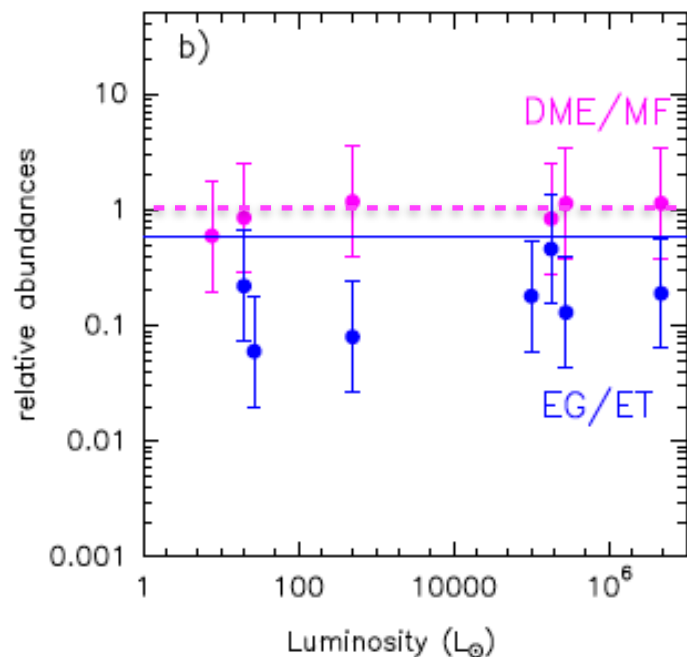
Garrod+08

Woods+13

Balucani+15

Fedoseev+14

Butscher+15



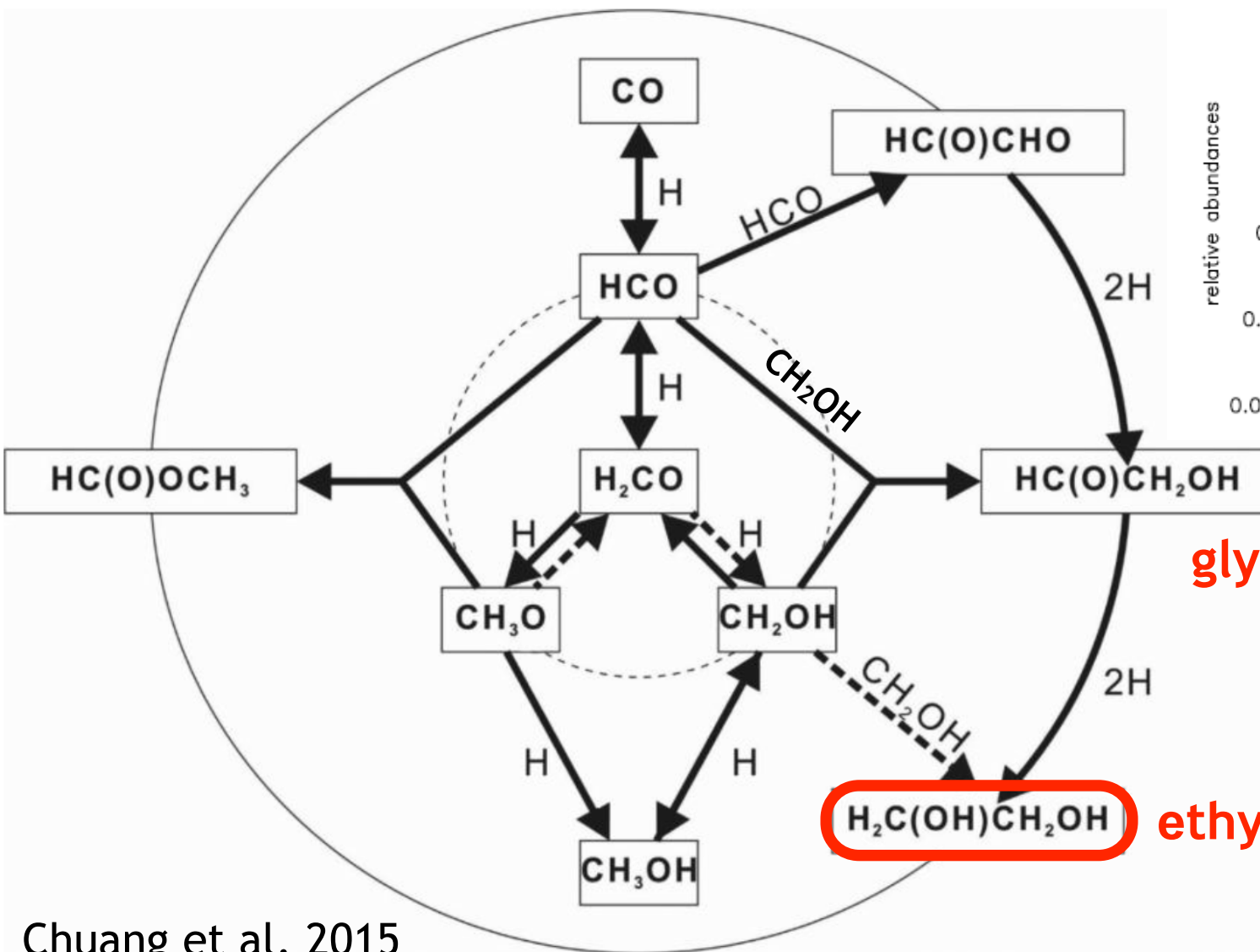
DME and MF formed from the common precursor CH<sub>3</sub>O

MF formed directly from DME in gas-phase (Balucani+2015)



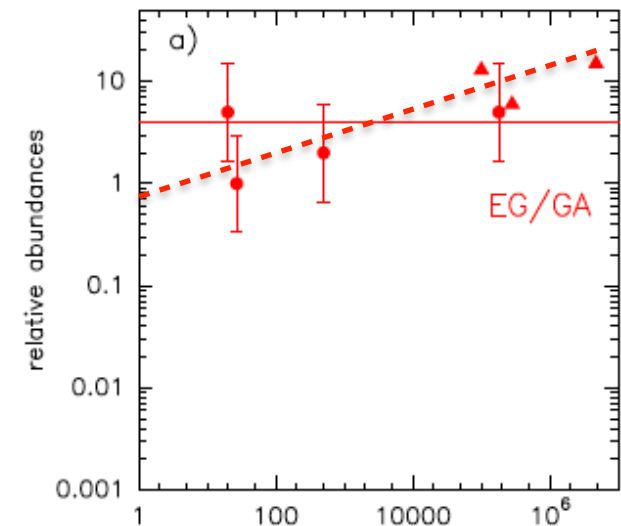


# GAME OF REACTIONS

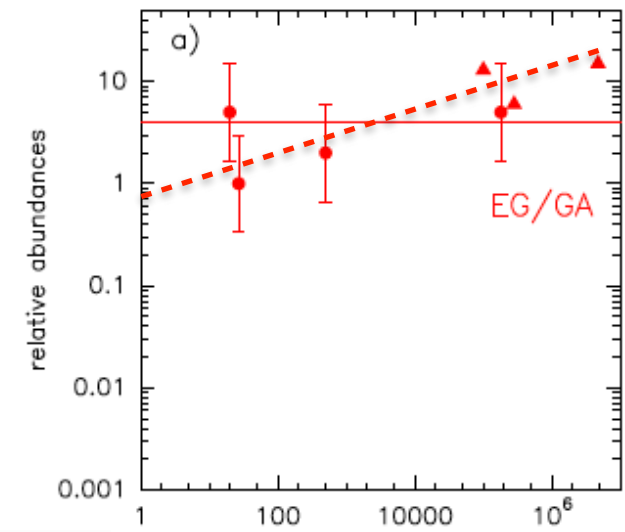
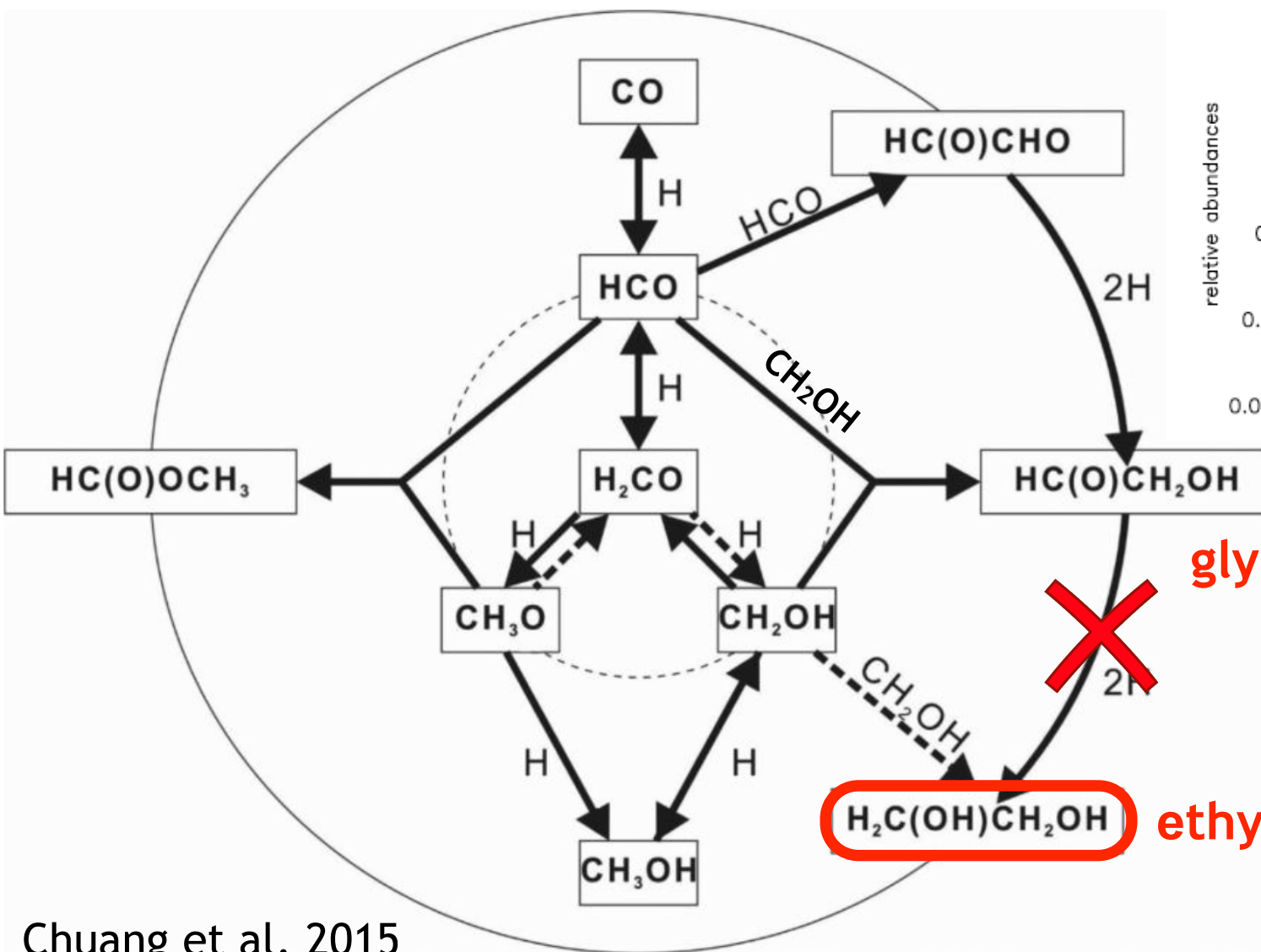


glycolaldehyde

**H<sub>2</sub>C(OH)CH<sub>2</sub>OH** ethylene glycol



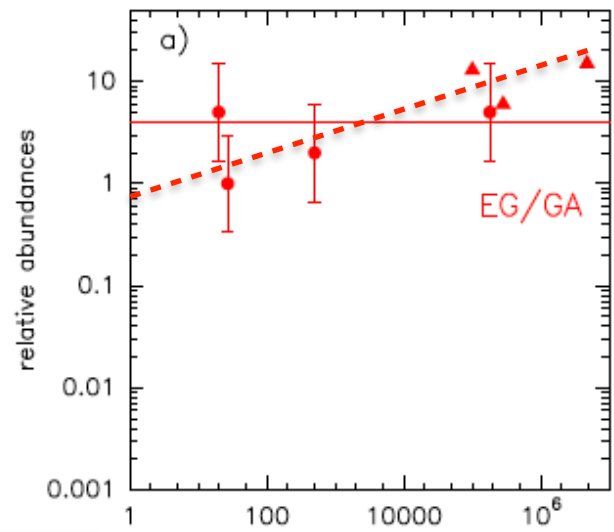
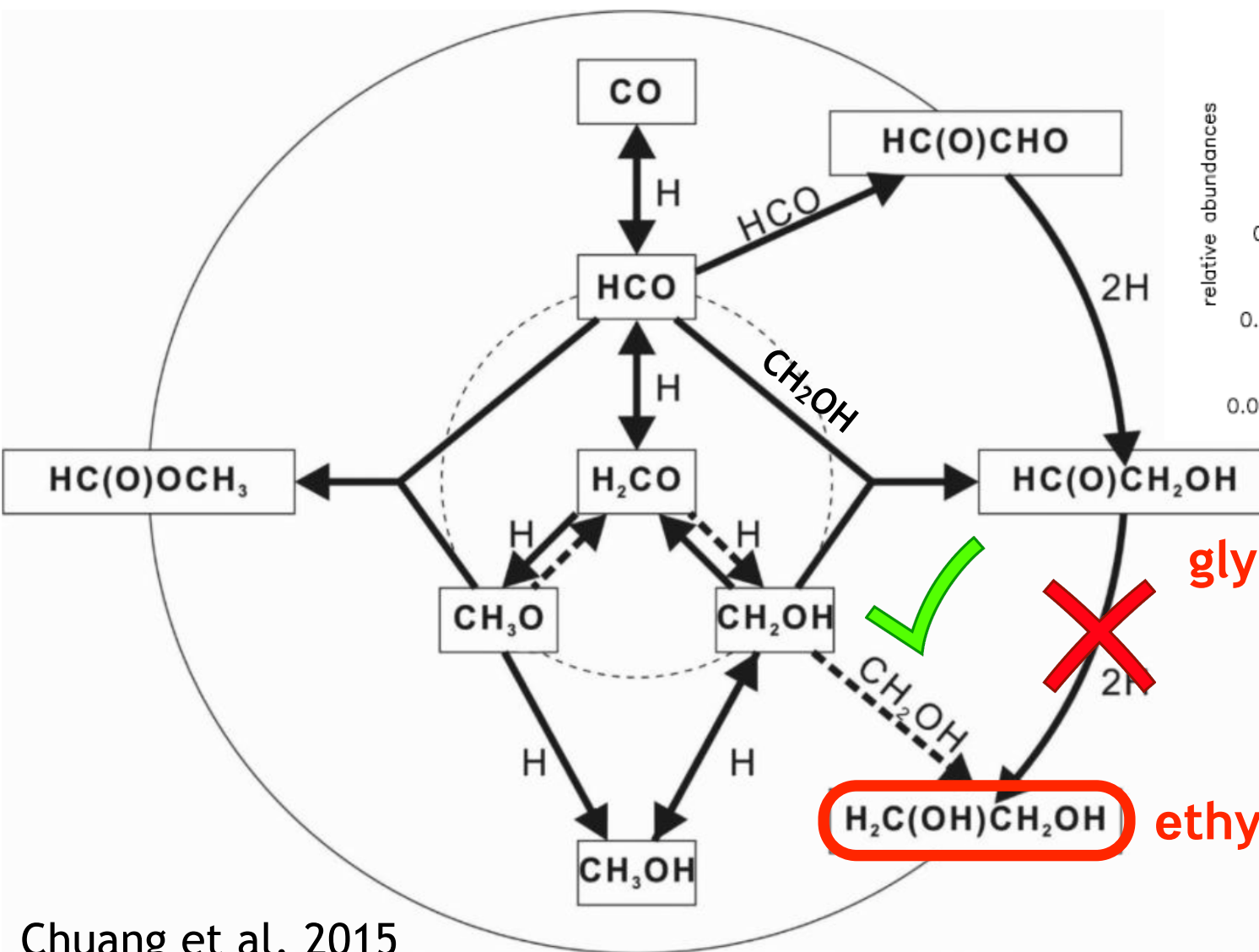
# GAME OF REACTIONS



glycolaldehyde

**H<sub>2</sub>C(OH)CH<sub>2</sub>OH** ethylene glycol

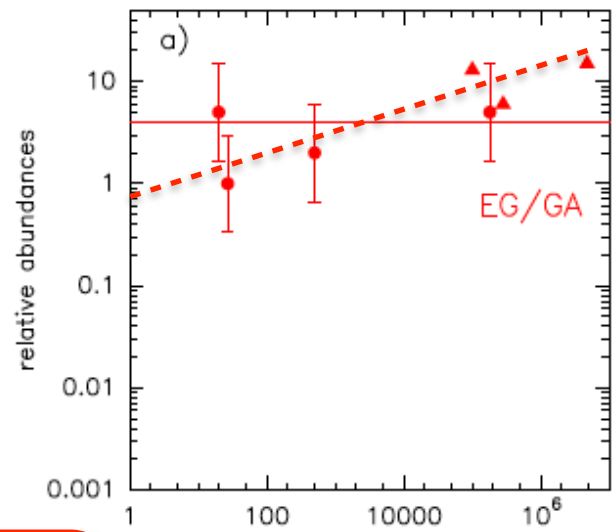
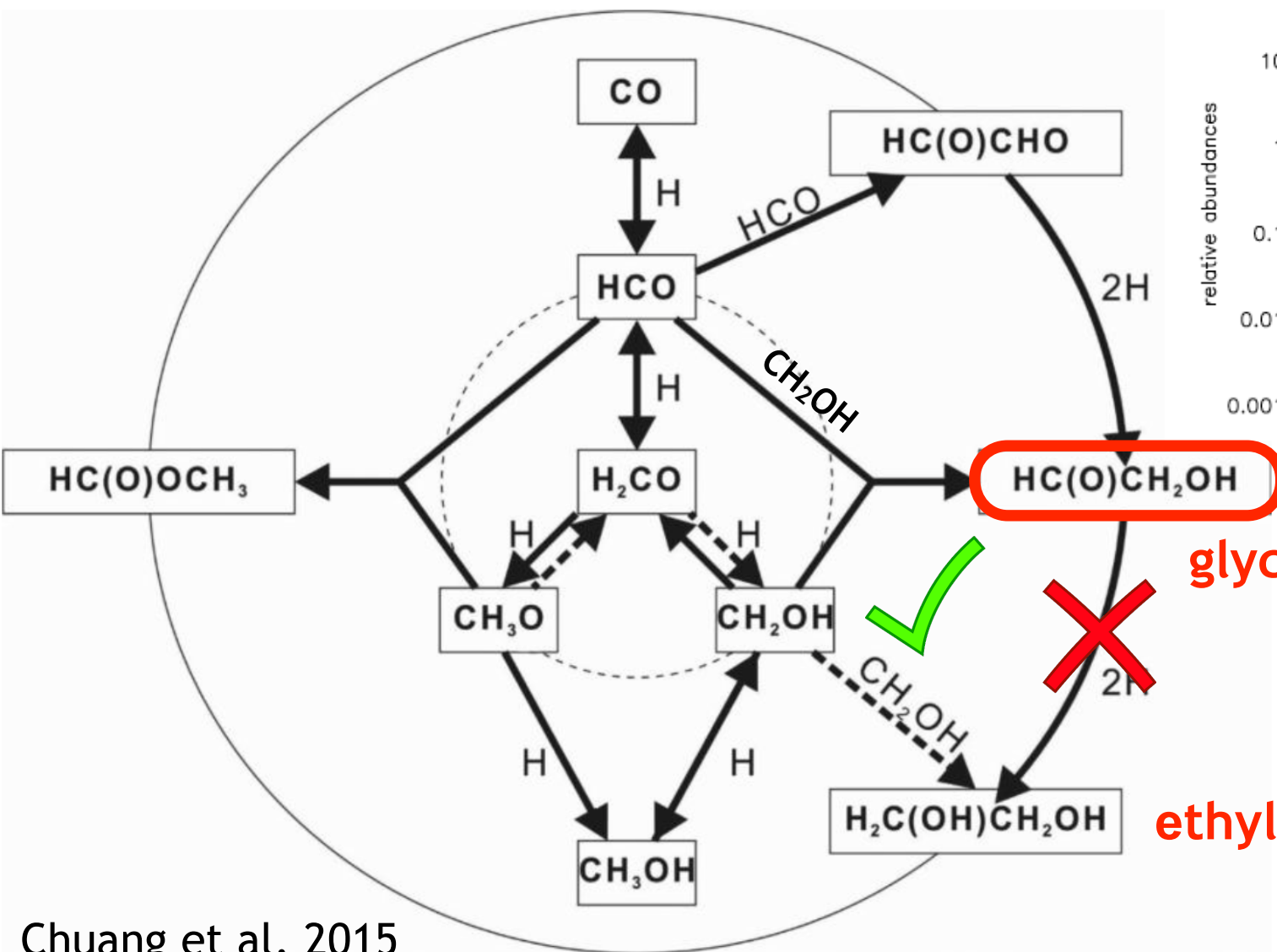
# GAME OF REACTIONS



glycolaldehyde

**H<sub>2</sub>C(OH)CH<sub>2</sub>OH** ethylene glycol

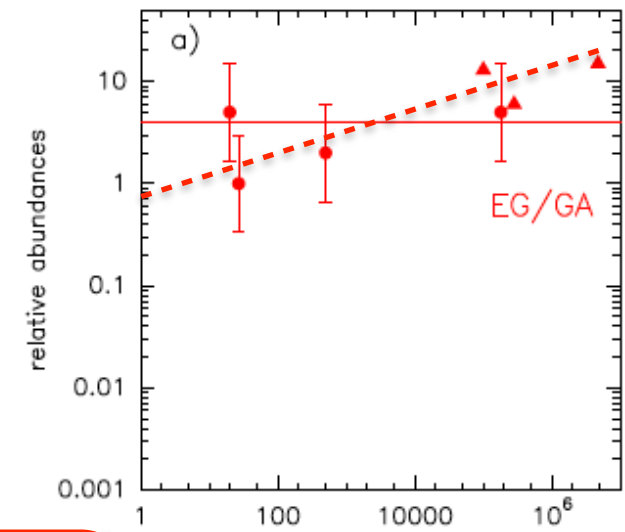
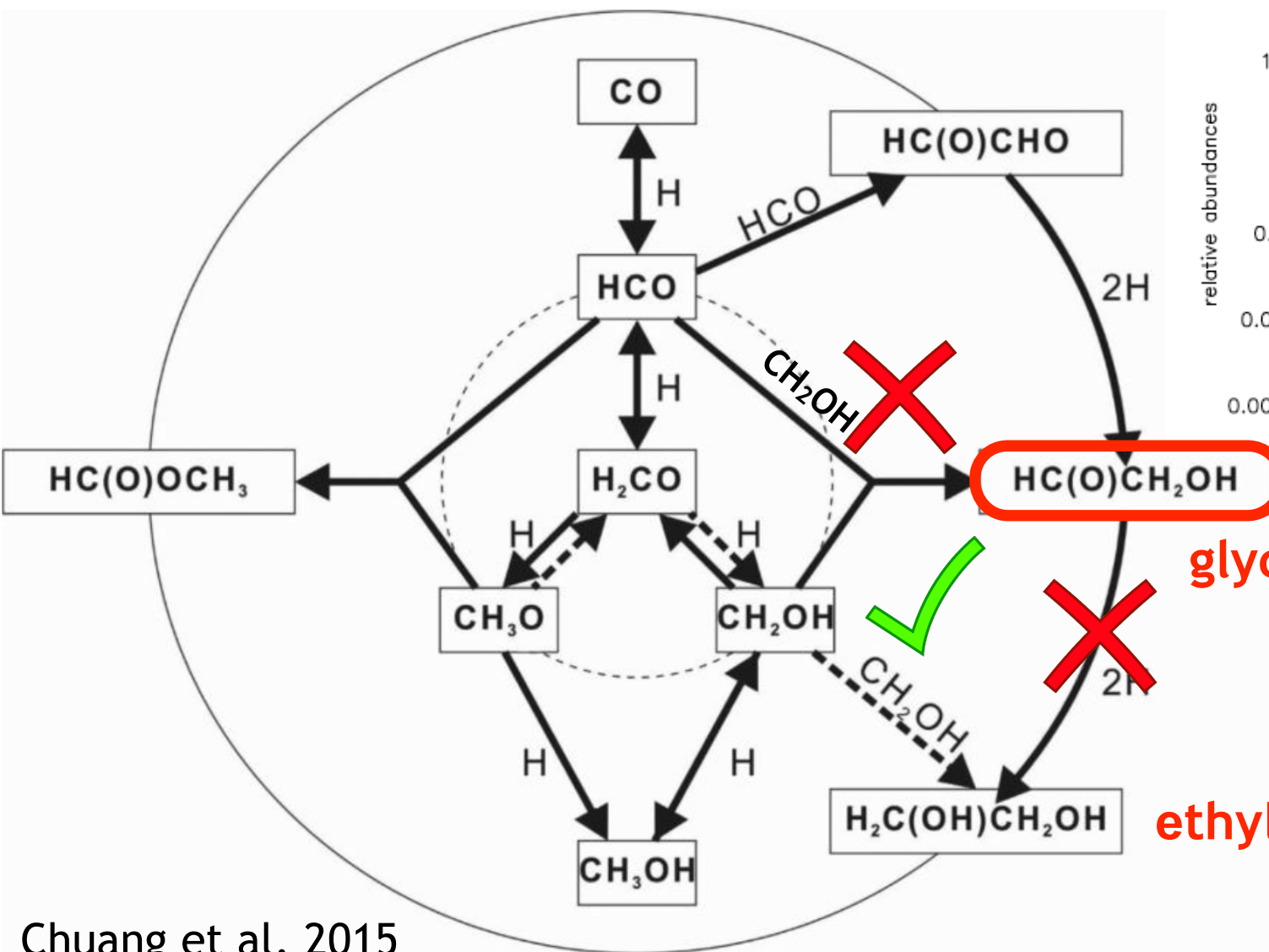
# GAME OF REACTIONS



glycolaldehyde

ethylene glycol

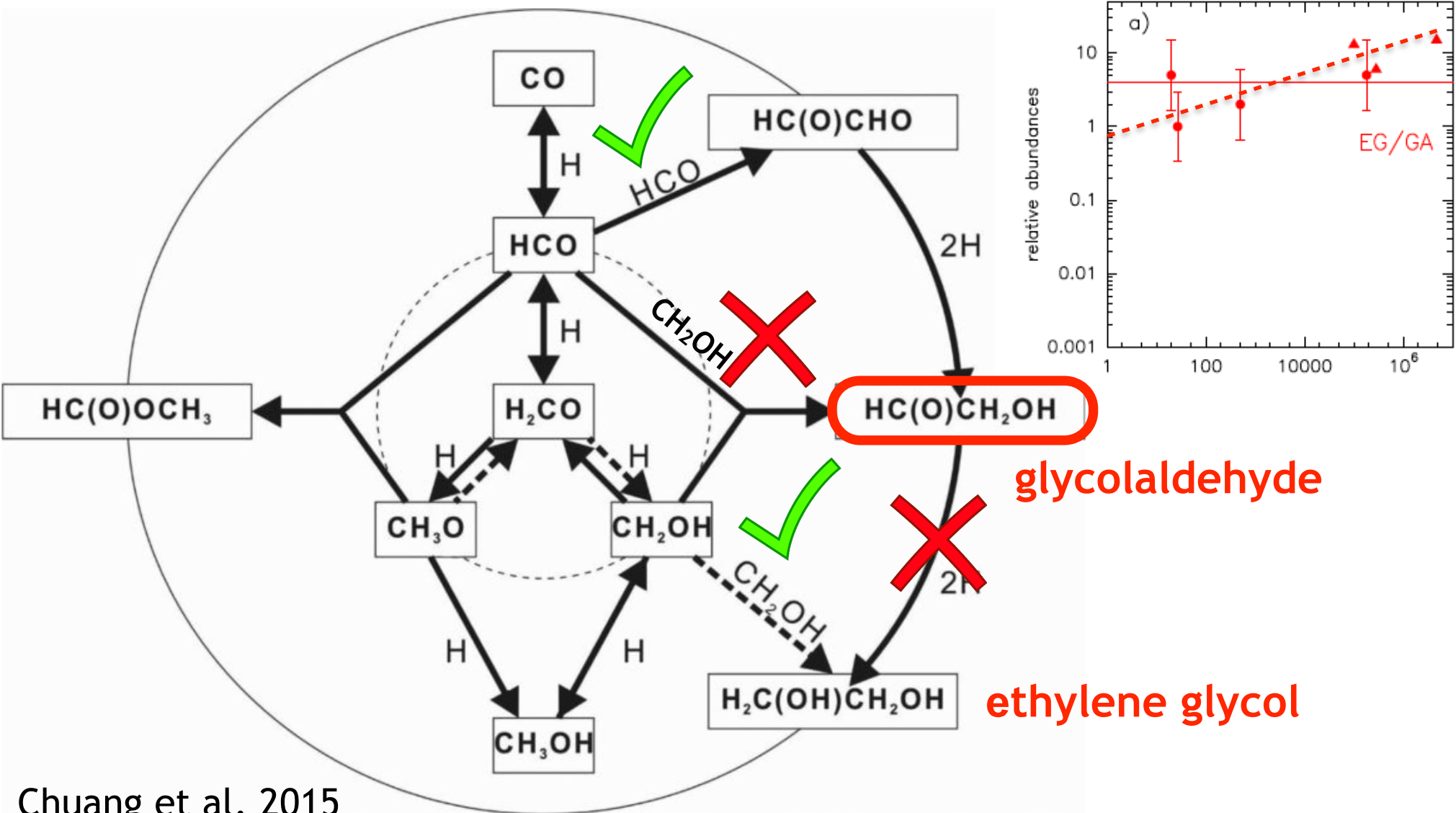
# GAME OF REACTIONS



glycolaldehyde

ethylene glycol

# GAME OF REACTIONS



# Chemical routes

COM	Chemical pathway
$(\text{CH}_2\text{OH})_2$ (EG)	[1] $\text{CH}_2\text{OHCHO} + 2\text{H} \longrightarrow (\text{CH}_2\text{OH})_2$
	[2] $\text{CH}_2\text{OH} + \text{CH}_2\text{OH} \longrightarrow (\text{CH}_2\text{OH})_2$
$\text{CH}_2\text{OHCHO}$ (GA)	[3] $2\text{HCO} \longrightarrow \text{CO} + \text{H}_2\text{CO} \longrightarrow \text{HOCCOH};$ $\text{HOCCOH} + \text{H} \longrightarrow \text{CH}_2\text{OCHO};$ $\text{CH}_2\text{OCHO} + \text{H} \longrightarrow \text{CH}_2\text{OHCHO}$
	[4] $\text{HCO} + \text{CH}_2\text{OH} \longrightarrow \text{CH}_2\text{OHCHO}$
$\text{CH}_3\text{OCHO}$ (MF)	[5] $\text{CH}_3\text{O} + \text{HCO} \longrightarrow \text{CH}_3\text{OCHO}$
	[6] $\text{CH}_3\text{OCH}_3 + \text{O} \longrightarrow \text{CH}_3\text{OCHO} + \text{H}$ (gas phase)
$\text{CH}_3\text{OCH}_3$ (DME)	[7] $\text{CH}_3\text{O} + \text{CH}_3 \longrightarrow \text{CH}_3\text{OCH}_3$
$\text{CH}_3\text{CH}_2\text{OH}$ (ET)	[8] $\text{CH}_2\text{OH} + \text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$

Bennett & Kaiser07

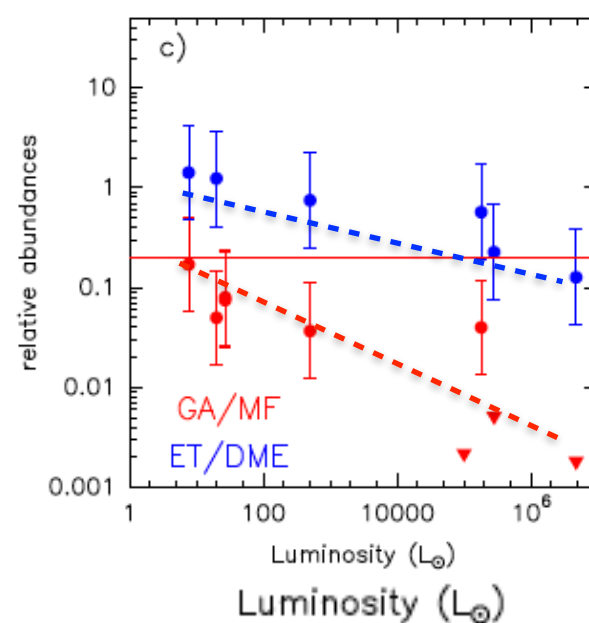
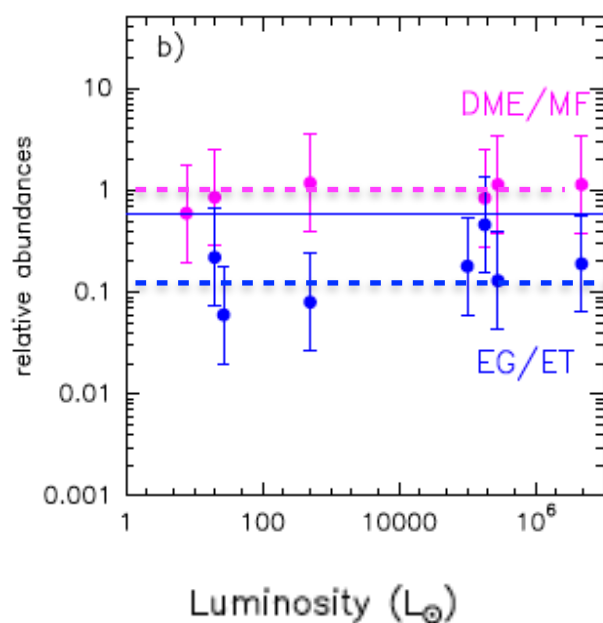
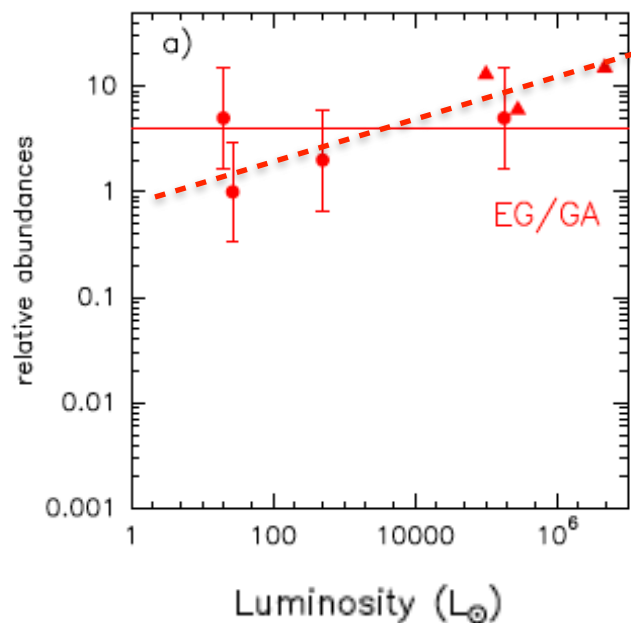
Garrod+08

Woods+13

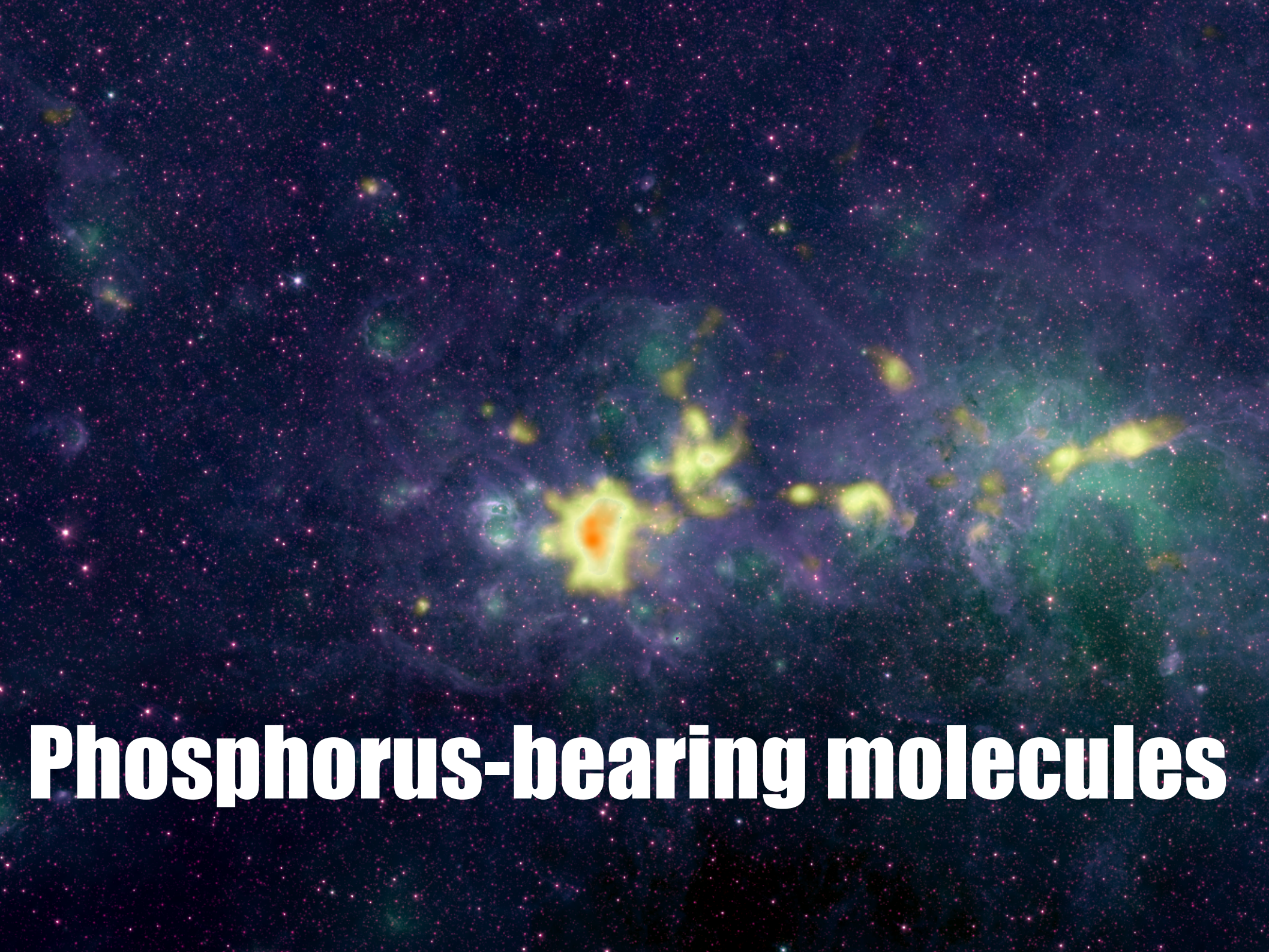
Balucani+15

Fedoseev+14

Butscher+15





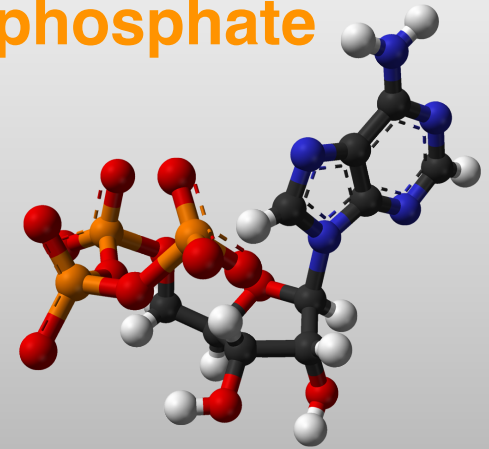
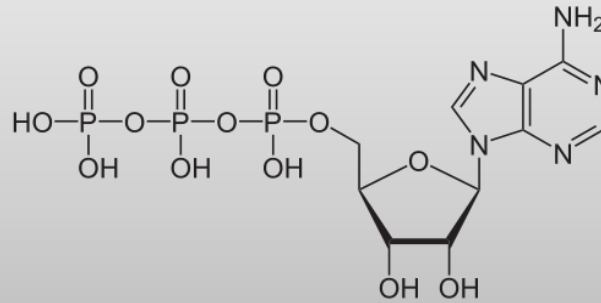


**Phosphorus-bearing molecules**

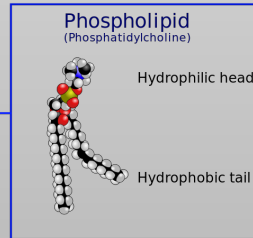
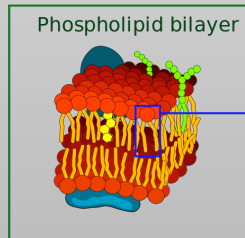
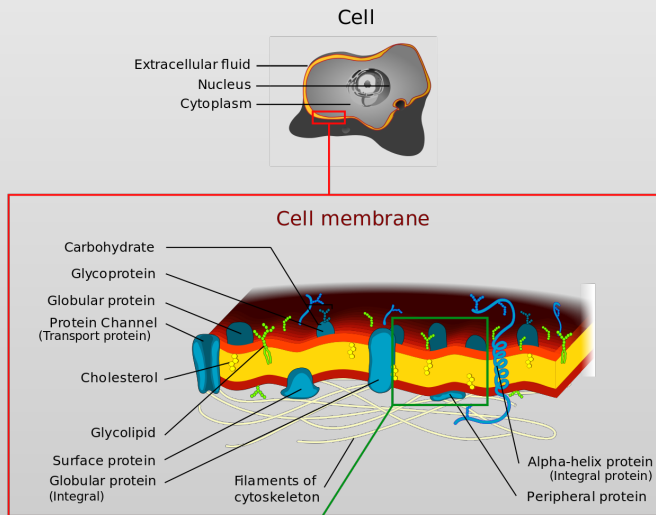
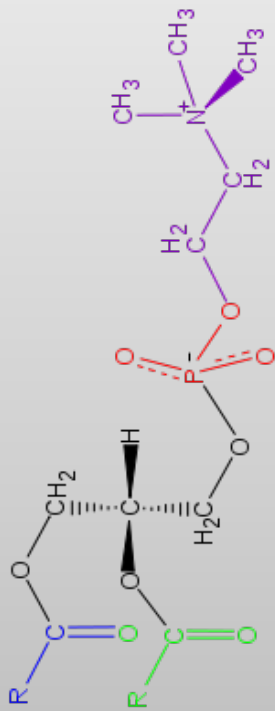
# Phosphorus: key to Life

Chemical reactivity  
Structural stability

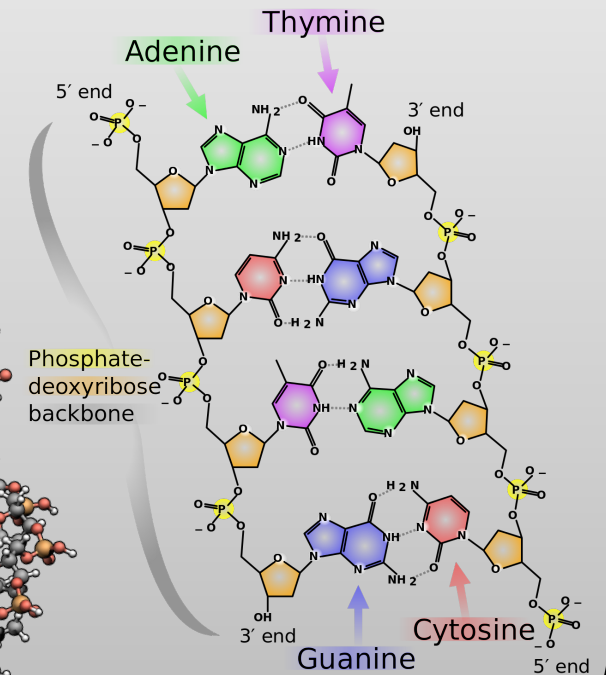
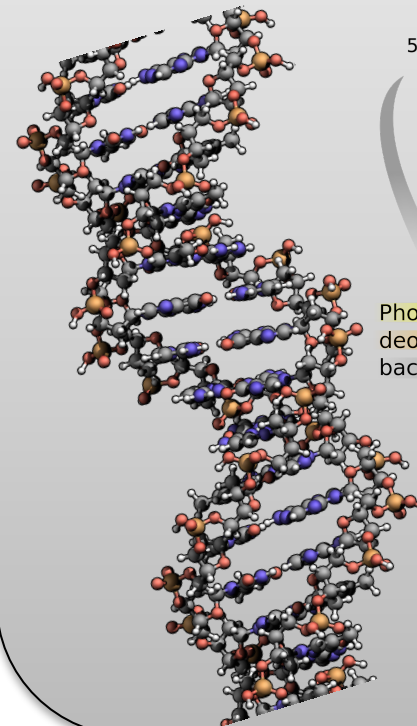
## ATP: Adenosine Triphosphate



## Phospholipids



## DNA





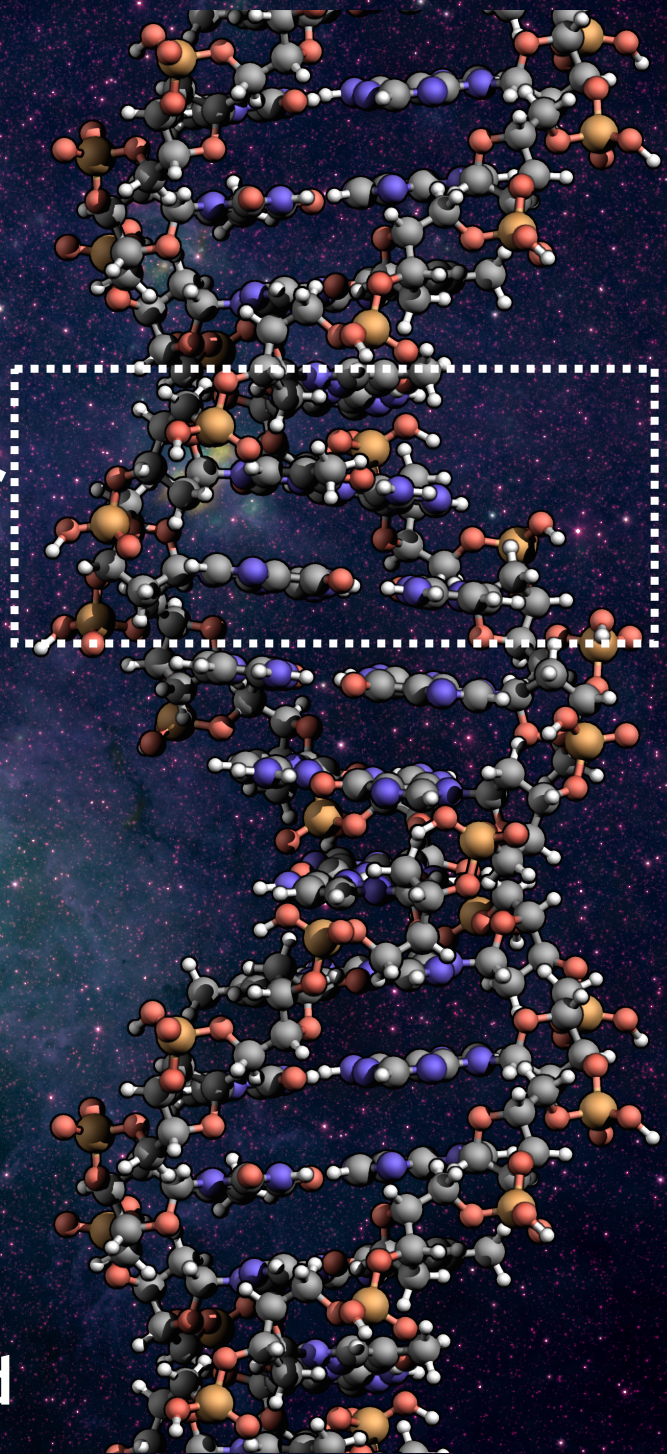
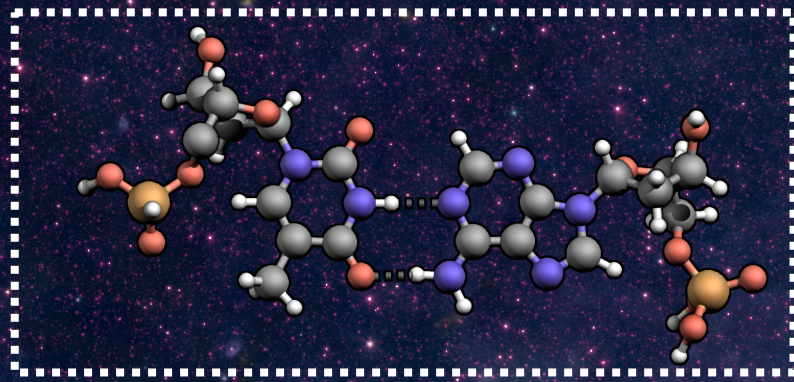
# Phosphorus-bearing molecules: the importance of the P-O bond

- Hydrogen
- Oxygen
- Nitrogen
- Carbon
- Phosphorus



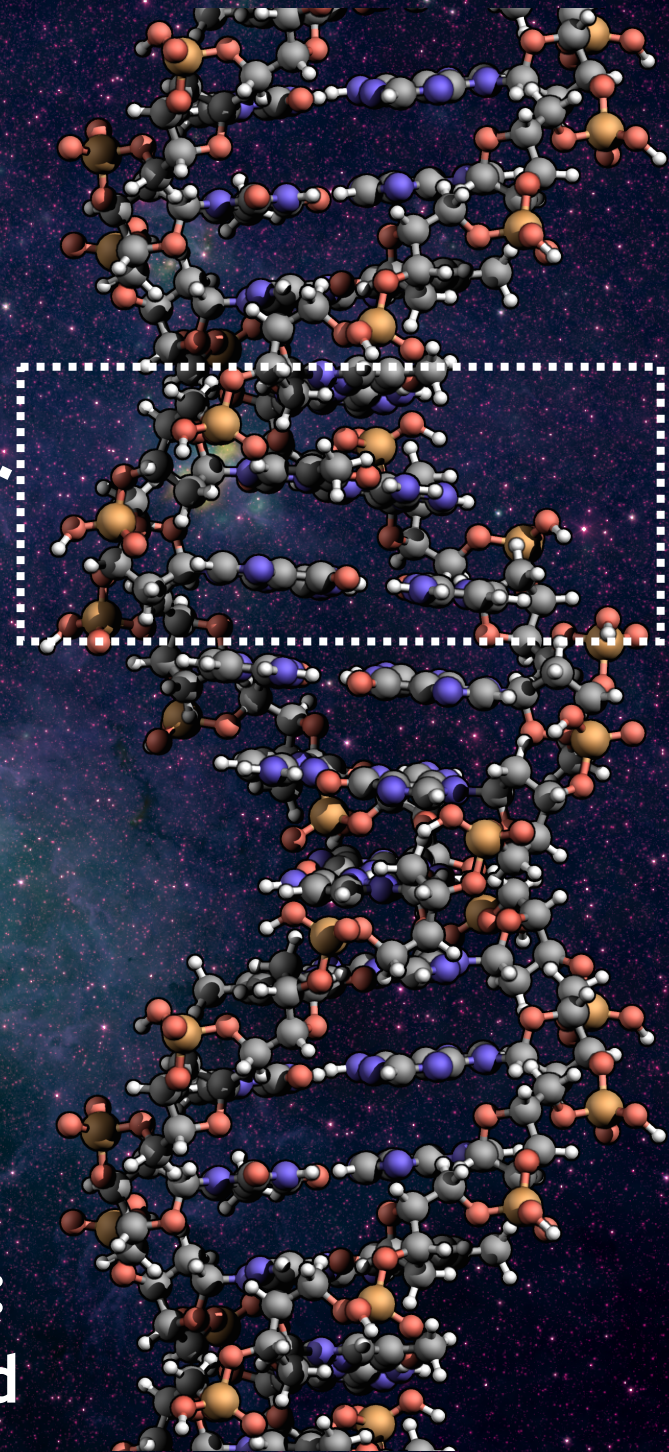
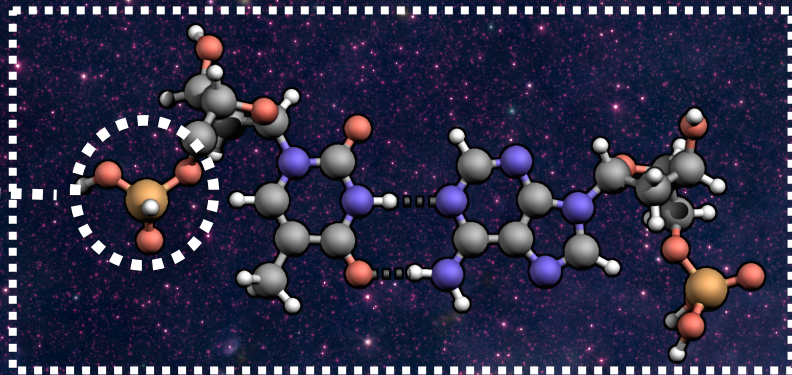
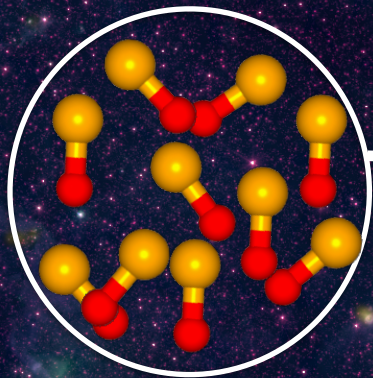
Phosphorus-bearing molecules:  
the importance of the P-O bond

- Hydrogen
- Oxygen
- Nitrogen
- Carbon
- Phosphorus



- Hydrogen
- Oxygen
- Nitrogen
- Carbon
- Phosphorus

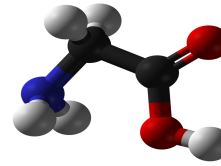
Phosphorus-bearing molecules:  
the importance of the P-O bond



# Phosphorus-bearing molecules: the importance of the P-O bond

- Hydrogen
- Oxygen
- Nitrogen
- Carbon
- Phosphorus

# Prebiotic chemicals—amino acid and phosphorus— in the coma of comet 67P/Churyumov-Gerasimenko

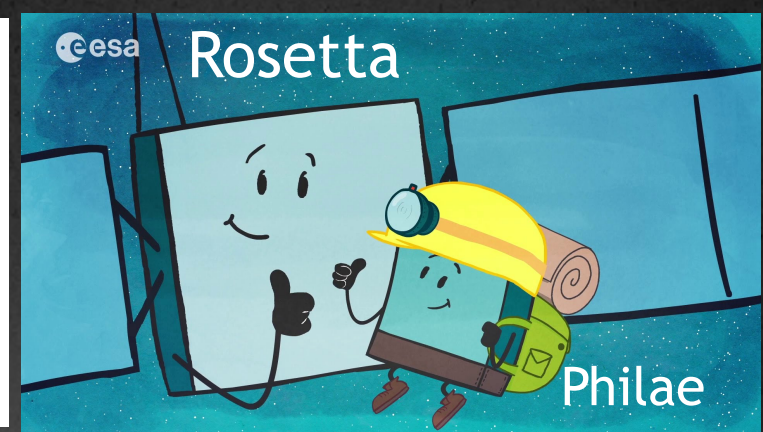
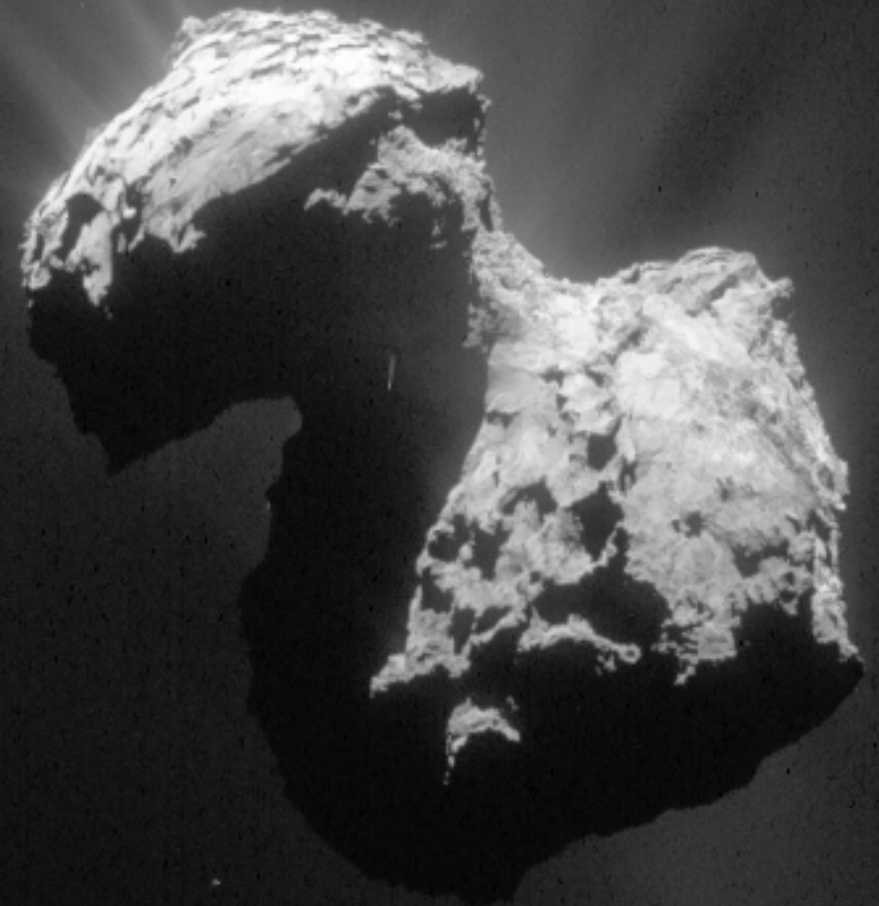


Kathrin Altwegg,<sup>1,2\*</sup> Hans Balsiger,<sup>1</sup> Akiva Bar-Nun,<sup>3</sup> Jean-Jacques Berthelier,<sup>4</sup> Andre Bieler,<sup>1,5</sup> Peter Bochsler,<sup>1</sup> Christelle Briois,<sup>6</sup> Ursina Calmonte,<sup>1</sup> Michael R. Combi,<sup>5</sup> Hervé Cottin,<sup>7</sup> Johan De Keyser,<sup>8</sup> Frederik Dhooghe,<sup>8</sup> Bjorn Fiethe,<sup>9</sup> Stephen A. Fuselier,<sup>10</sup> Sébastien Gasc,<sup>1</sup> Tamas I. Gombosi,<sup>5</sup> Kenneth C. Hansen,<sup>5</sup> Myrtha Haessig,<sup>1,10</sup> Annette Jäckel,<sup>1</sup> Ernest Kopp,<sup>1</sup> Axel Korth,<sup>11</sup> Lena Le Roy,<sup>2</sup> Urs Mall,<sup>11</sup> Bernard Marty,<sup>12</sup> Olivier Mouis,<sup>13</sup> Tobias Owen,<sup>14</sup> Henri Rème,<sup>15,16</sup> Martin Rubin,<sup>1</sup> Thierry Sémon,<sup>1</sup> Chia-Yu Tzou,<sup>1</sup> James Hunter Waite,<sup>10</sup> Peter Wurz<sup>1</sup>

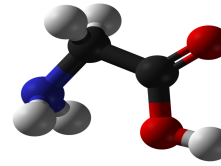
2015

Phosphorus and glycine recently  
detected in the 67P comet !

These prebiotic ingredients are  
present in the pristine material of  
our solar system



# Prebiotic chemicals—amino acid and phosphorus— in the coma of comet 67P/Churyumov-Gerasimenko



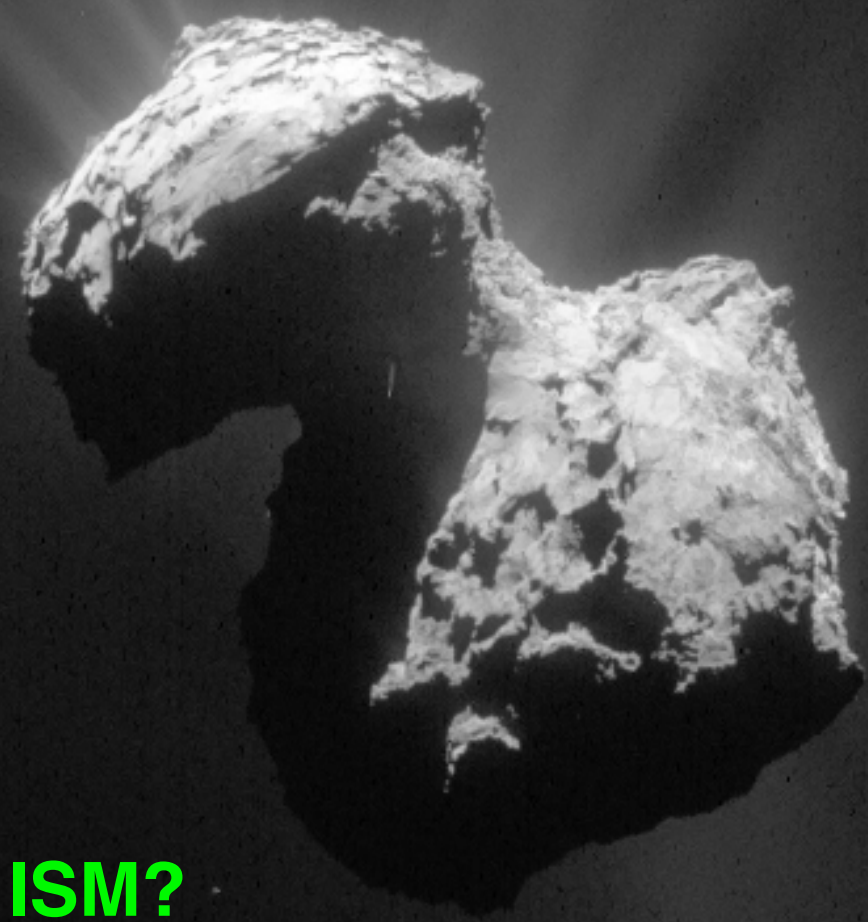
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What about Phosphorus in the ISM?





# P-bearing molecules in the ISM

- P is thought to be synthesised in massive stars and injected to the ISM through supernova explosions (Koo et al., 2013).

- It is **barely detected in space**

P<sup>+</sup> in several diffuse clouds (Jura & York 1978)

PN, PO, CP, HCP, C<sub>3</sub>P and PH<sub>3</sub> in circumstellar envelopes of evolved objects

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Only a very few detections of PN towards hot cores  
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THE ASTROPHYSICAL JOURNAL, 321:L75-L79, 1987 October 1  
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## DETECTION OF INTERSTELLAR PN: THE FIRST IDENTIFIED PHOSPHORUS COMPOUND IN THE INTERSTELLAR MEDIUM

B. E. TURNER

National Radio Astronomy Observatory,<sup>1</sup> Charlottesville

AND

JOHN BALLY

AT & T Bell Laboratories, Holmdel

Received 1987 March 13; accepted 1987 April 17

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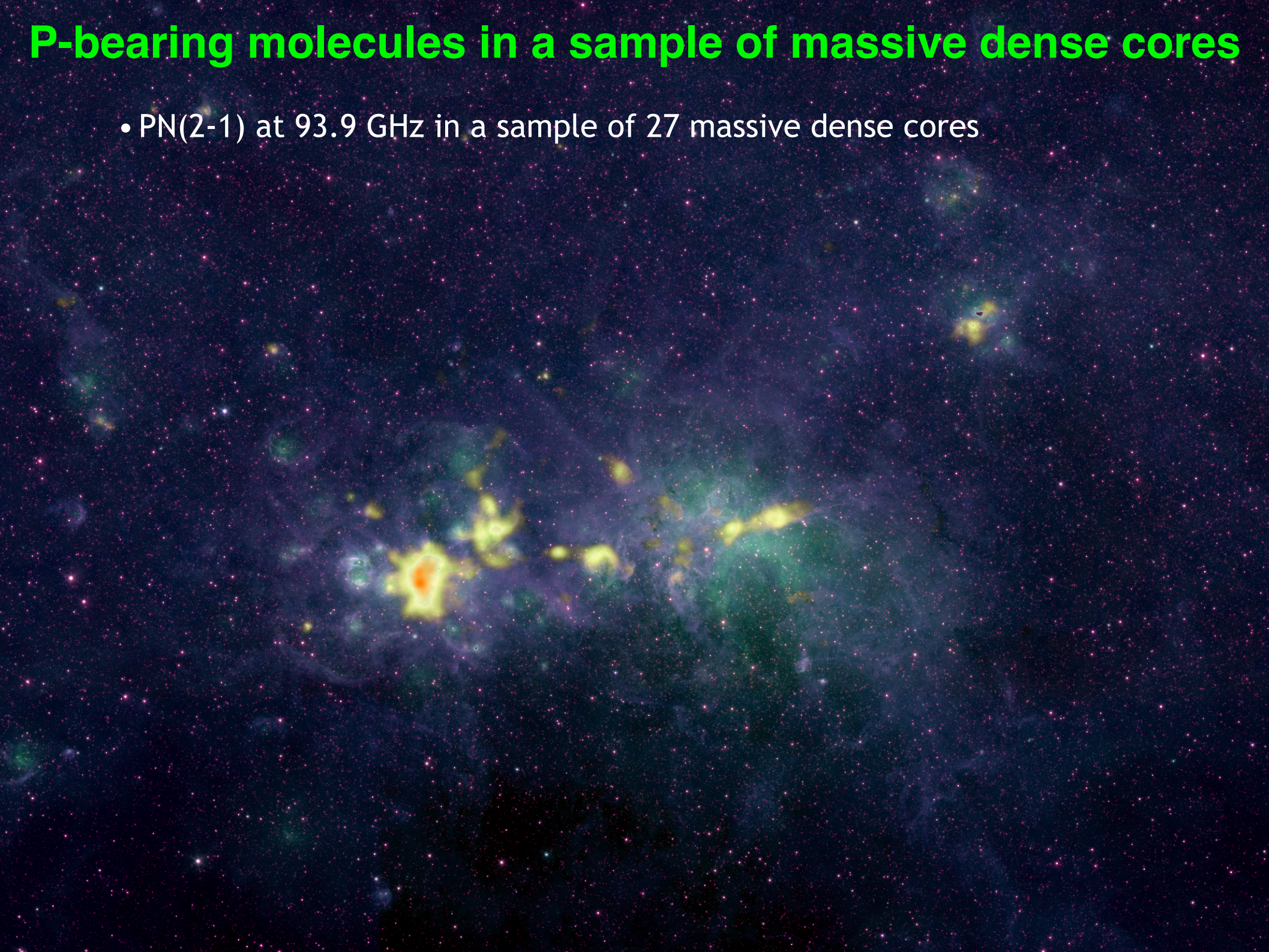
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Our group started a project to study  
P-bearing molecules in star-forming regions

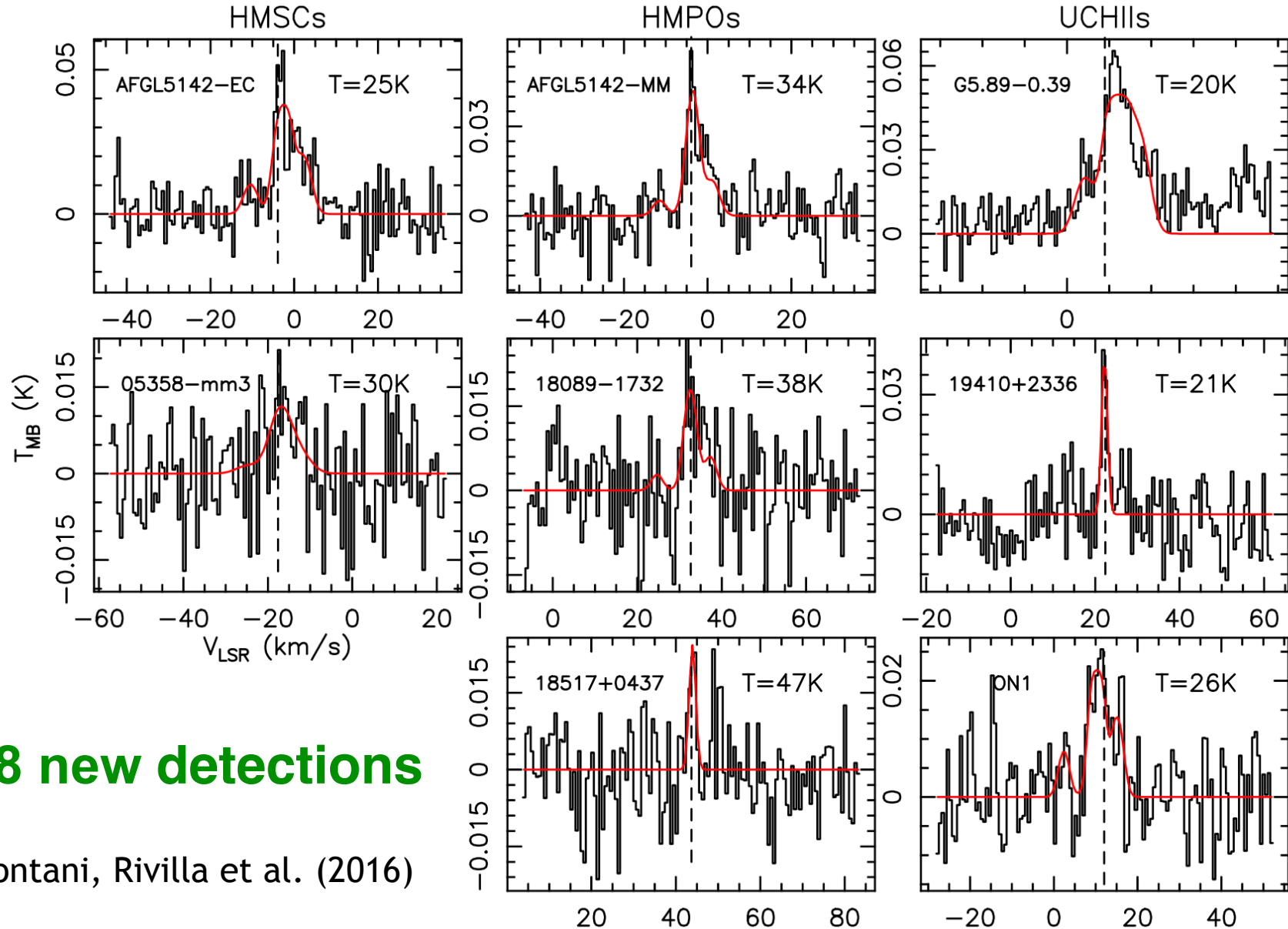
# P-bearing molecules in a sample of massive dense cores

- PN(2-1) at 93.9 GHz in a sample of 27 massive dense cores



# P-bearing molecules in a sample of massive dense cores

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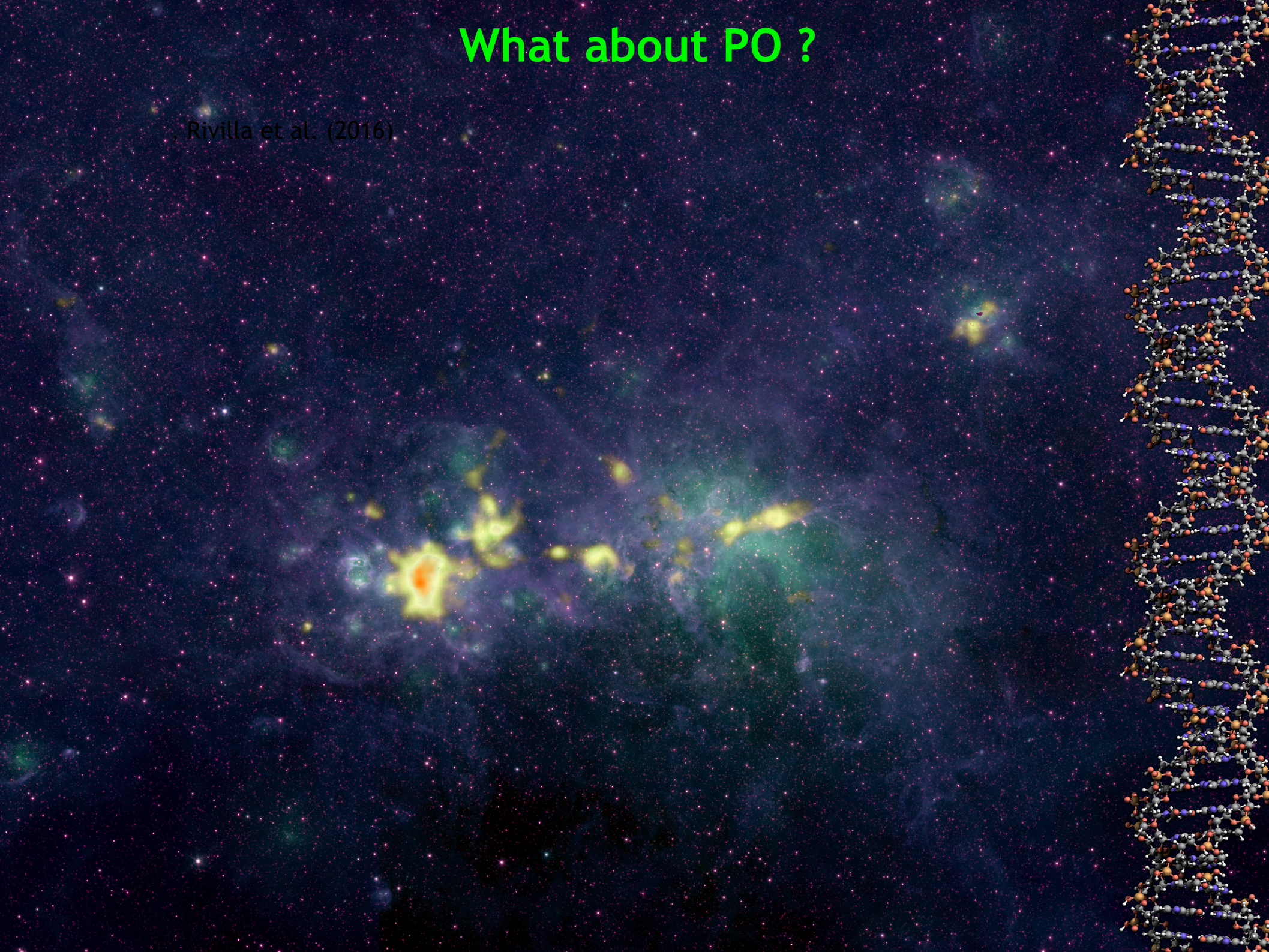
**8 new detections**

Fontani, Rivilla et al. (2016)



# What about PO ?

, Rivilla et al. (2016)

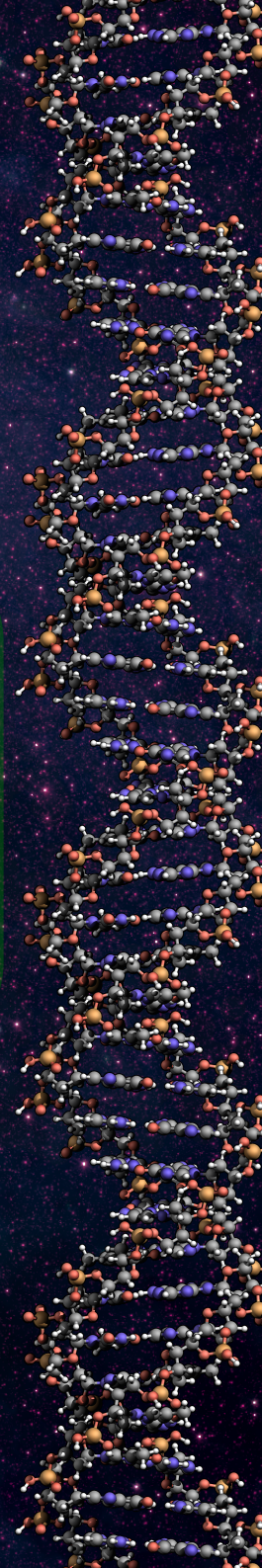


# What about PO ?

Fontani, Rivilla et al. (2016)

source	$\Delta v$ (km s <sup>-1</sup> )	$N(\text{PN})^a$ $\times 10^{11}$ cm <sup>-2</sup>	$N(\text{PO})^a$ $\times 10^{11}$ cm <sup>-2</sup>
00117-MM2	1.6 <sup>a</sup>		
AFGL5142-EC	3.8(0.6)	5.8	< 20
05358-mm3	6(2)	10	< 13
G034-G2	1.6 <sup>a</sup>		
G034-F2	1.6 <sup>a</sup>		
G034-F1	1.6 <sup>a</sup>		
G028-C1	1.6 <sup>a</sup>		
I20293-WC	1.6 <sup>a</sup>		
I22134-G	1.6 <sup>a</sup>		
I22134-B	1.6 <sup>a</sup>		
00117-MM1	2.9 <sup>a</sup>		
AFGL5142-MM	3.7(0.6)	12	< 12
05358-mm1	2.9 <sup>a</sup>		
18089-1732	3(1)	6.3	< 6.3
18517+0437 <sup>d</sup>	<1.8(0.7)	4.4	< 4.4
G75-core	2.9 <sup>a</sup>		
I20293-MM1	2.9 <sup>a</sup>		
I21307	2.9 <sup>a</sup>		
I23385	2.9 <sup>a</sup>		
G5.89-0.39	5.2(0.8)	14.5	< 14
19035-VLA1	3.5 <sup>a</sup>		
19410+2336 <sup>d</sup>	<1.6(0.4)	3.3	< 3.3
ON1	2.9(0.5)	9.5	< 6.3
I22134-VLA1	3.5 <sup>a</sup>		
23033+5951	3.5 <sup>a</sup>		
NGC7538-IRS9	3.5 <sup>a</sup>		

- Not detected
- Good constraint on upper limits



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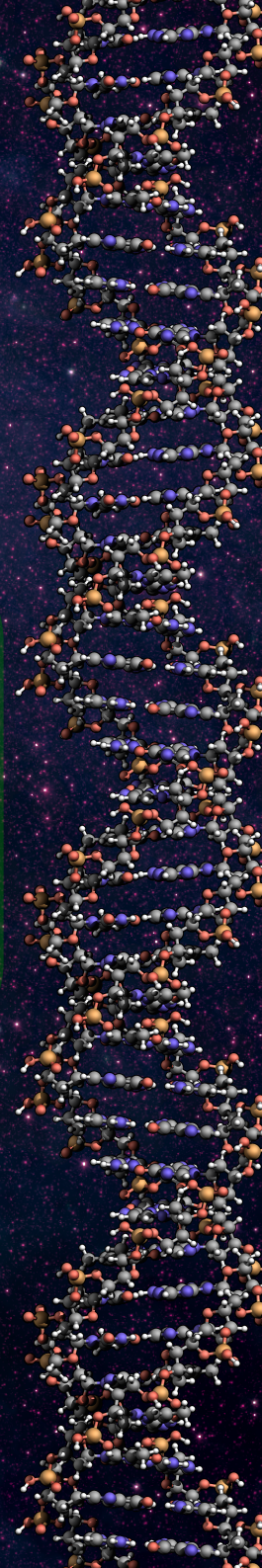
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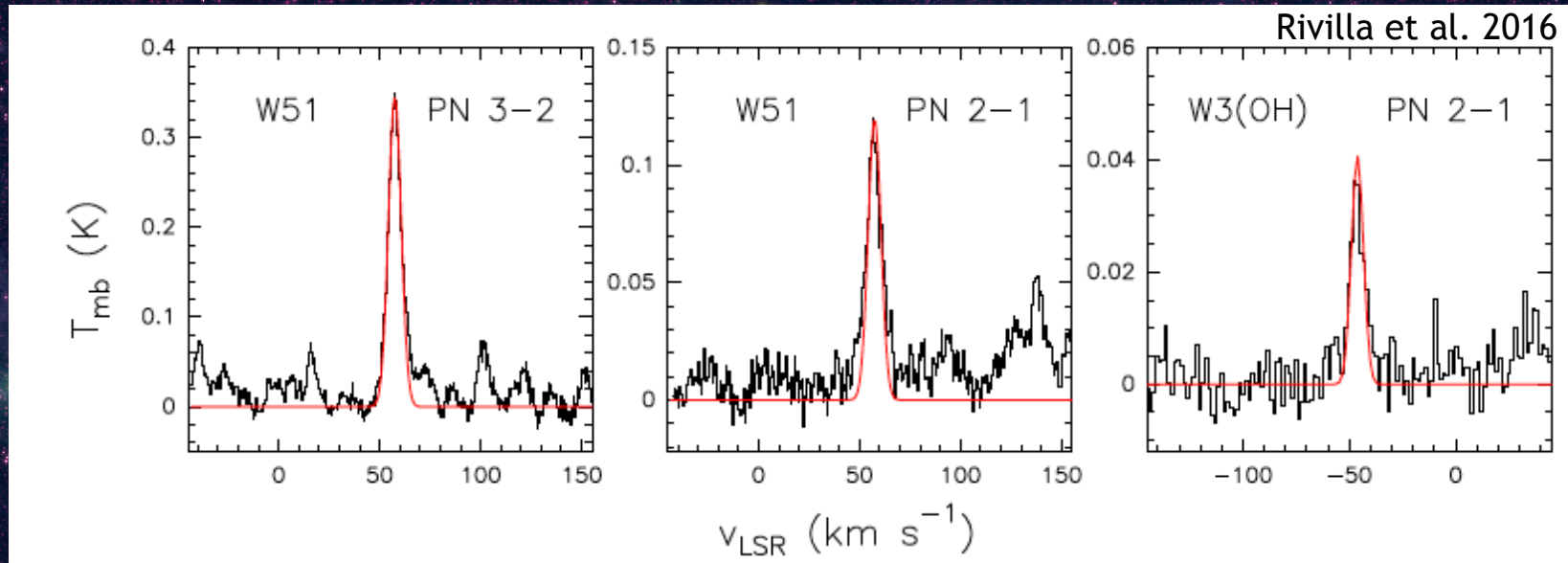


PO could be as abundant as PN



# Searching for PO

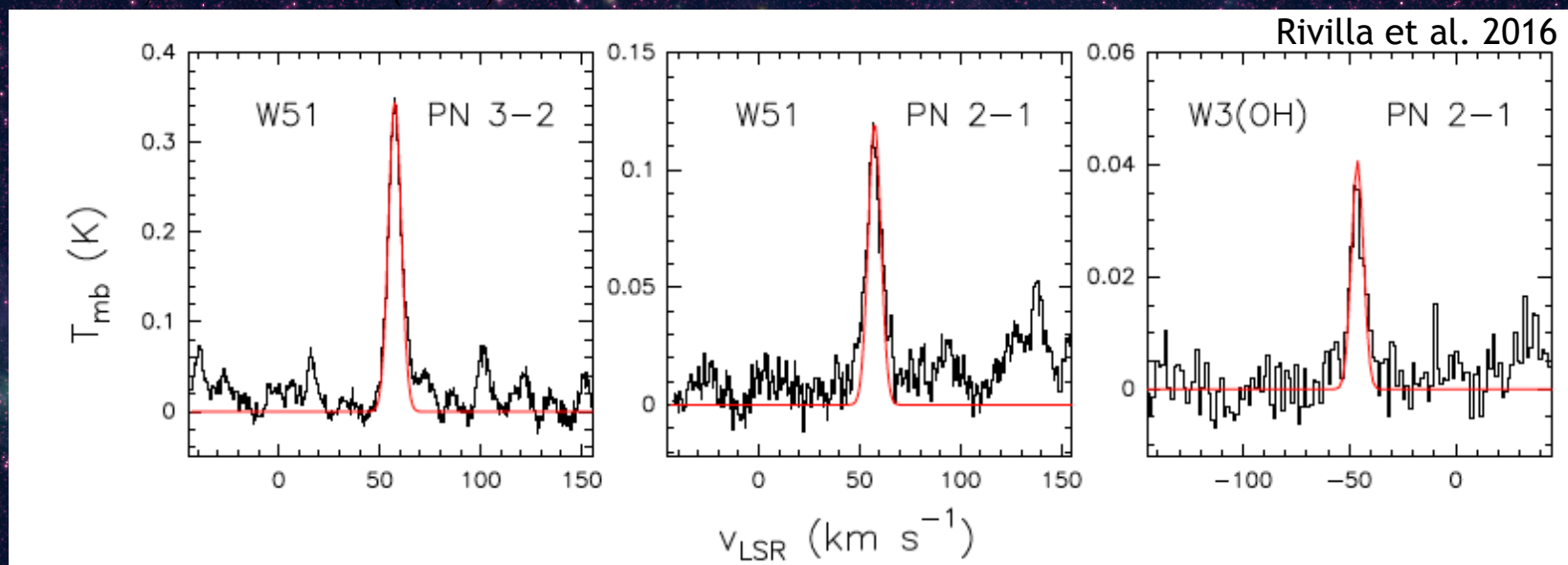
- PN brightest detections of 2 massive star-forming regions.  
Rivilla et al. (2016)



# Searching for PO

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Rivilla et al. (2016)



## New IRAM 30m observations

- 3 PO quadruplets at 1, 2 and 3mm.

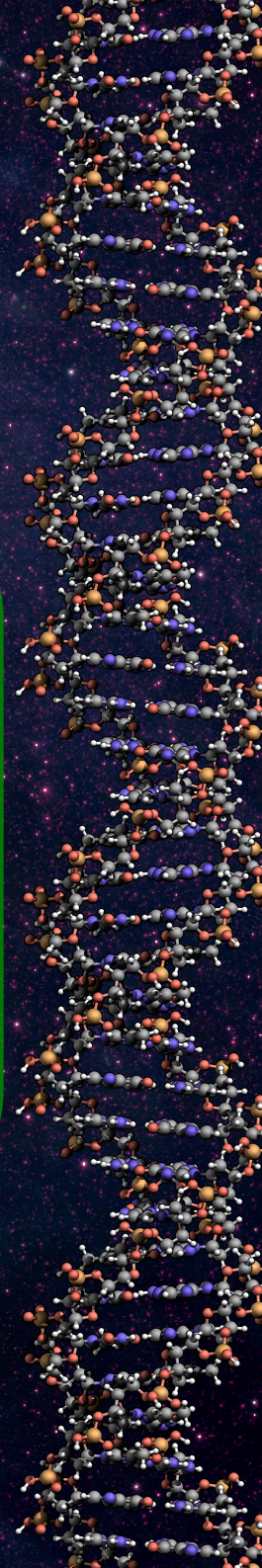
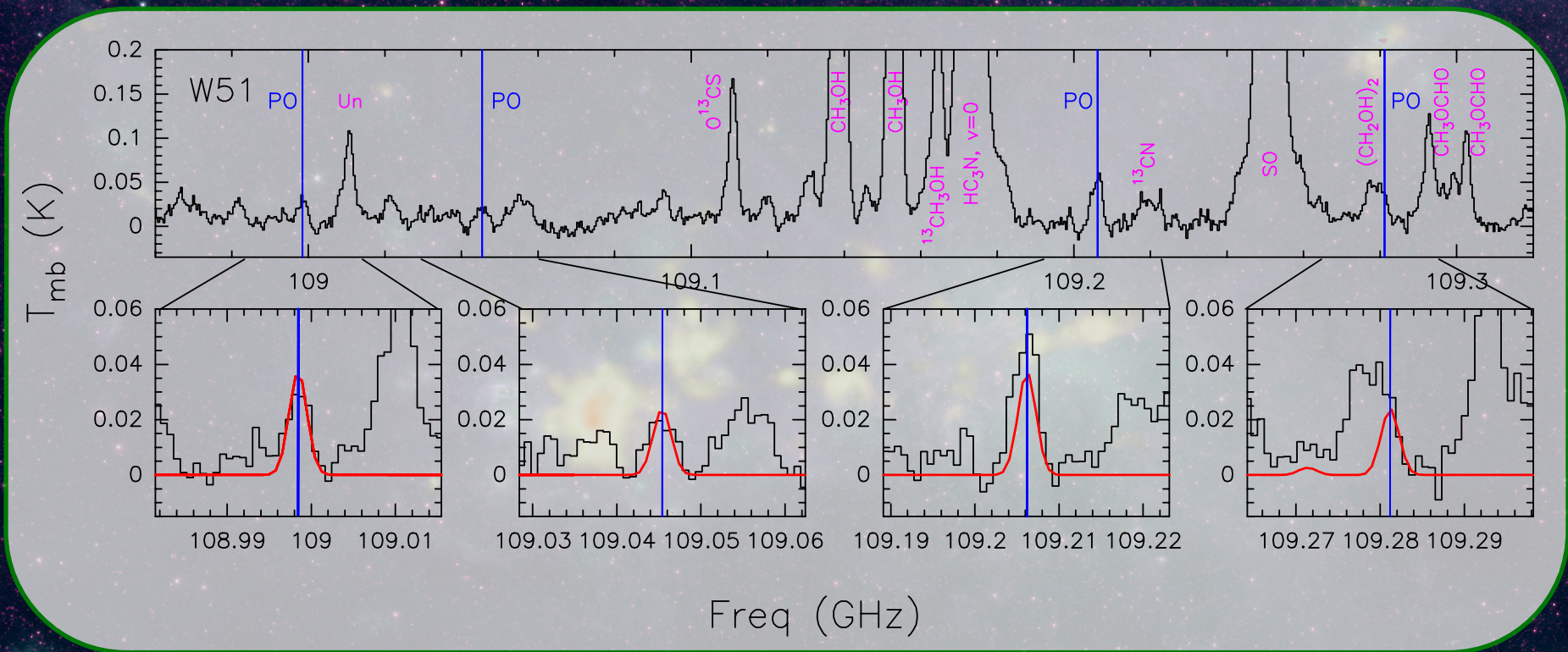
Frequency (GHz)	Transition	$S_{ij}\mu^2$ ( $D^2$ )	$E_{up}$ (K)
$J=5/2-3/2, \Omega=1/2$			
108.99845	F=3-2, l=e	9.9	8.4
109.04540	F=2-1, l=e	6.4	8.4
109.20620	F=3-2, l=f	9.9	8.4
109.28119	F=2-1, l=f	6.4	8.4
$J=7/2-5/2, \Omega=1/2$			
152.65698	F=4-3, l=e	13.6	15.7
152.68028	F=3-2, l=e	10.1	15.7
152.85545	F=4-3, l=f	13.6	15.7
152.88813	F=3-2, l=f	10.1	15.7
$J=11/2-9/2, \Omega=1/2$			
239.94898	F=6-5, l=e	20.9	36.7
239.95810	F=5-4, l=e	17.4	36.7
240.14106	F=6-5, l=f	20.9	36.7
240.15253	F=5-4, l=f	17.4	36.7

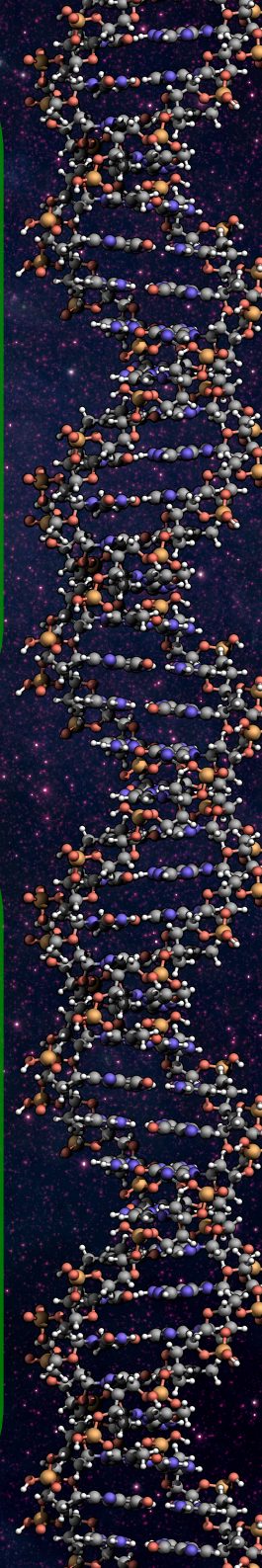
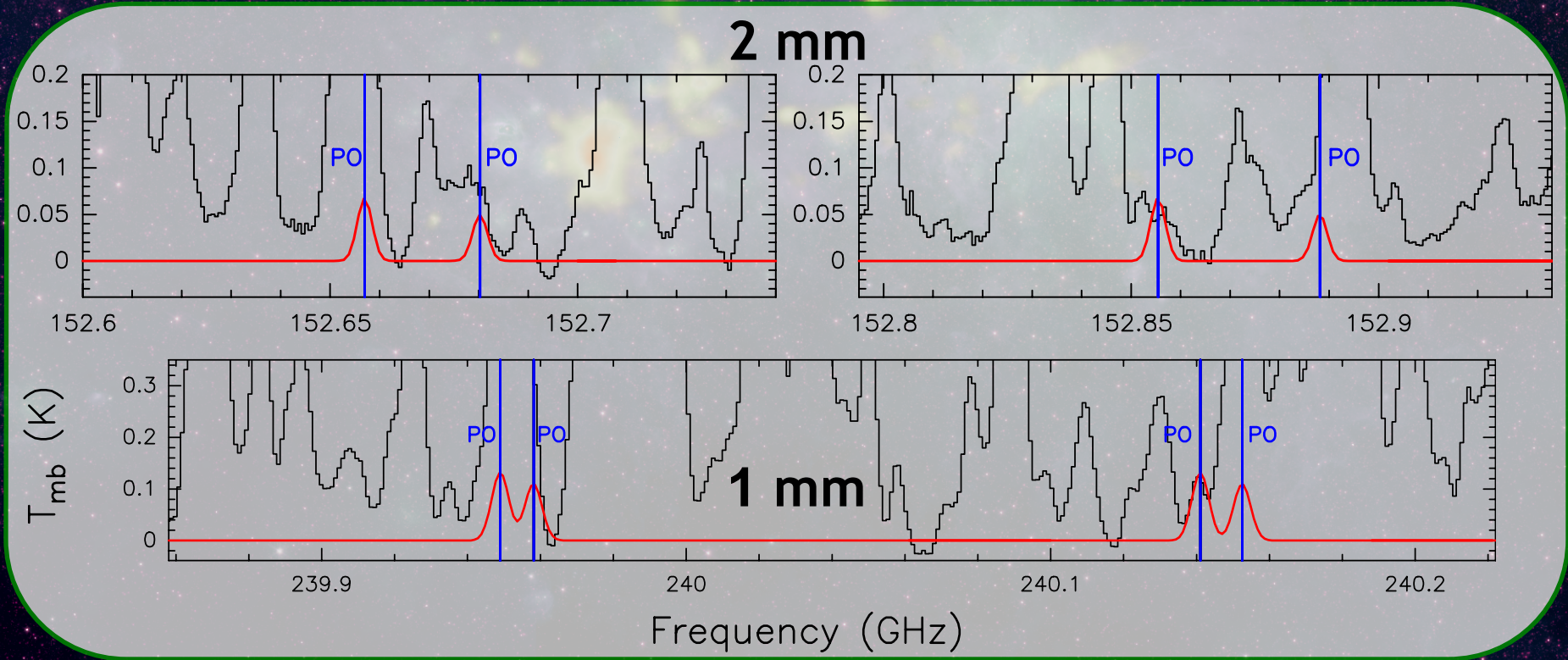
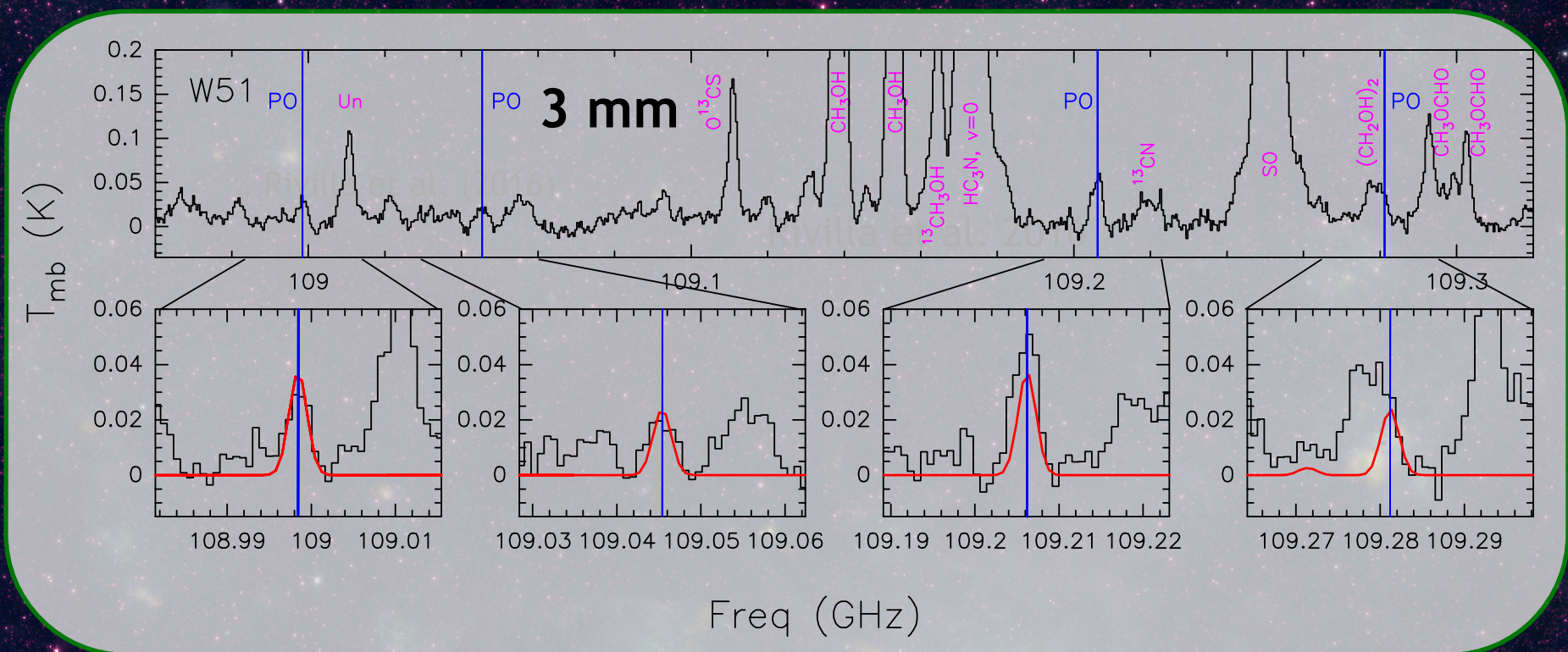
# First detections of PO in star-forming regions

Rivilla et al. (2016)

Rivilla et al. 2016

3 mm

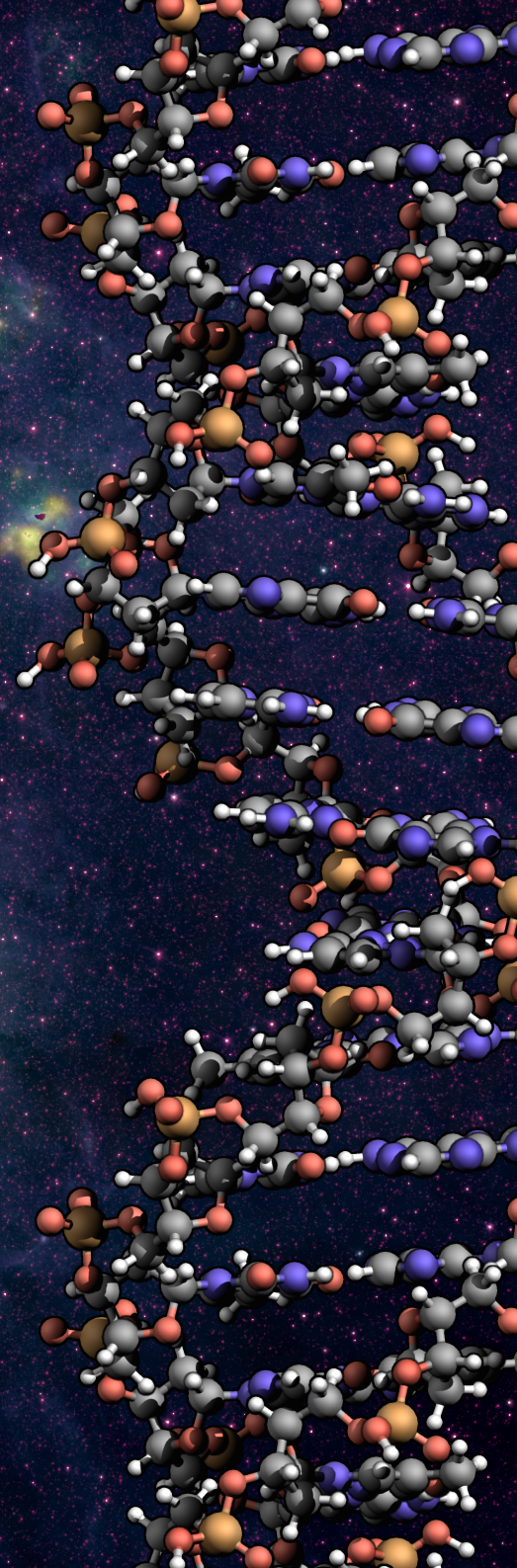




# PO and PN physical parameters

	N ( $\times 10^{13} \text{ cm}^{-2}$ )	Abundance ( $10^{-10}$ )
PN	0.2-2.1	0.4-1.1
PO	0.6-4.0	1.2-2.0

PO is a factor 2-3 more abundant than PN !



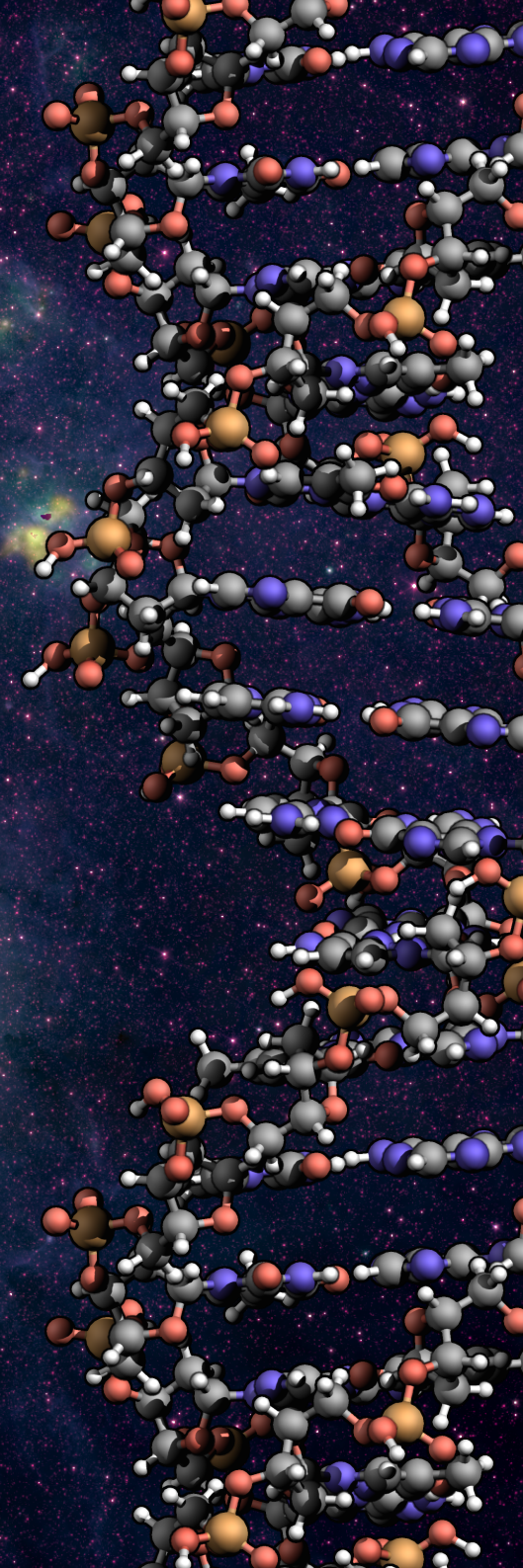


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Lefloch et al. (2016) also found  $\text{PO/PN} \sim 3$  in a protostellar shock



# P-bearing molecules: Chemical modelling

- Very little is known about P-chemistry.
- PN and PO has been already included in the chemical network to explain our detections.

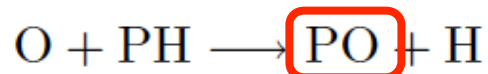
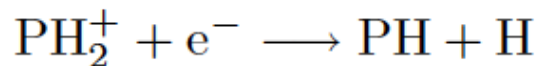
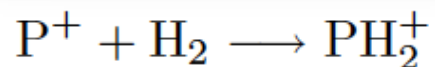
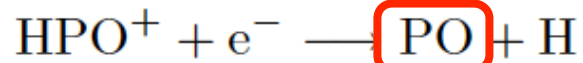
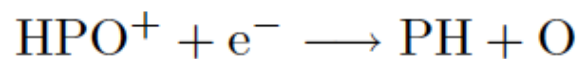
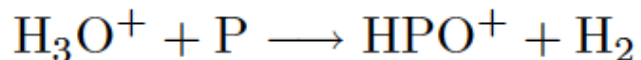
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- The two P-bearing molecules are chemically related and form purely in a sequence of **gas-phase ion-molecule** and **neutral-neutral** reactions during the cold collapse phase.

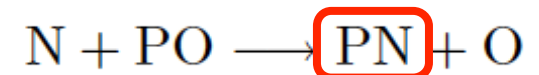
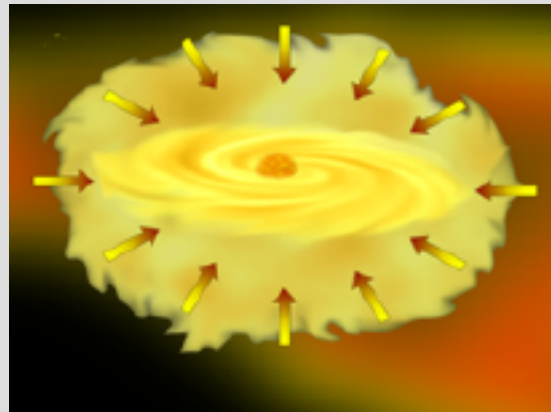
PO formation

GAME OF REACTIONS

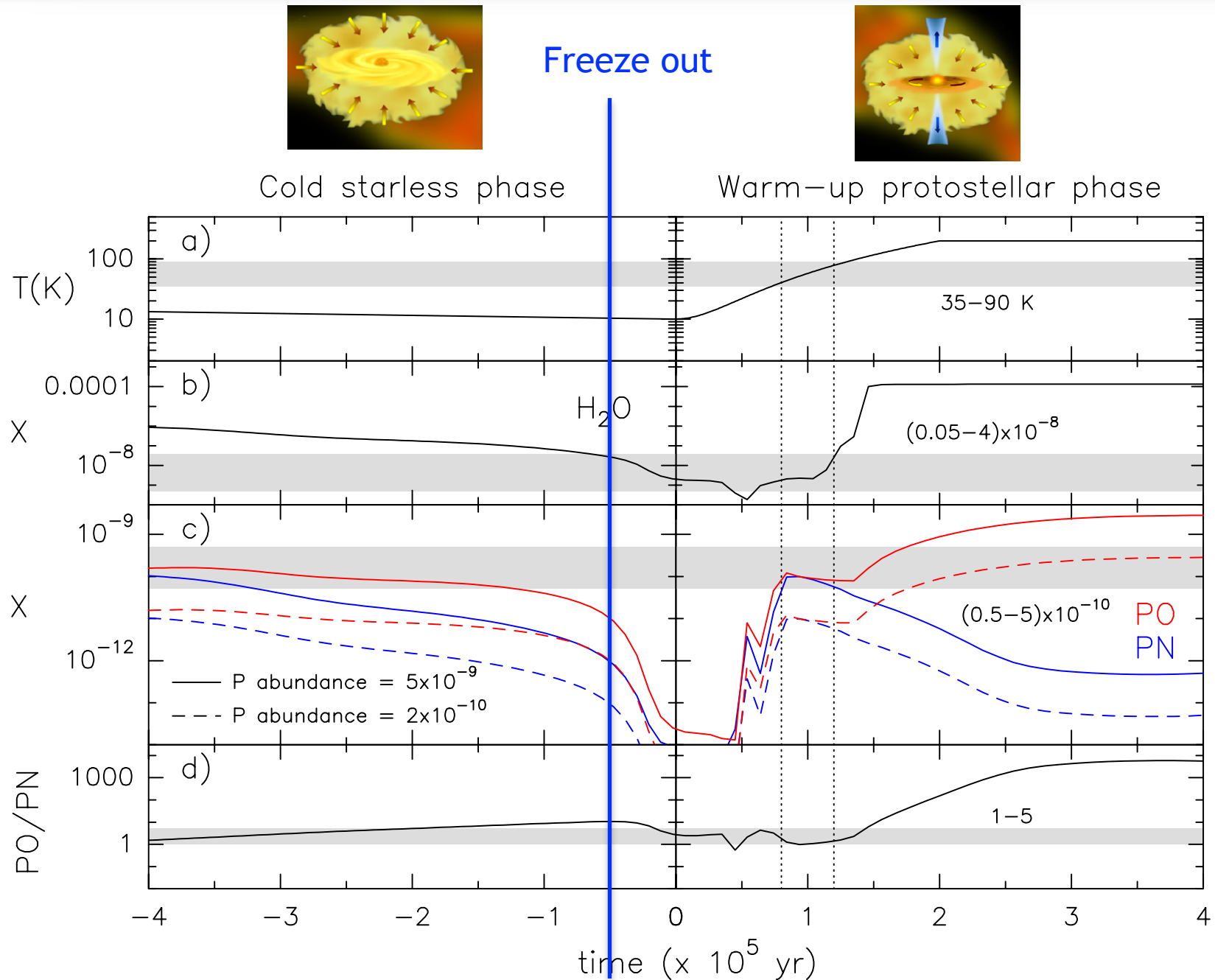
PN formation



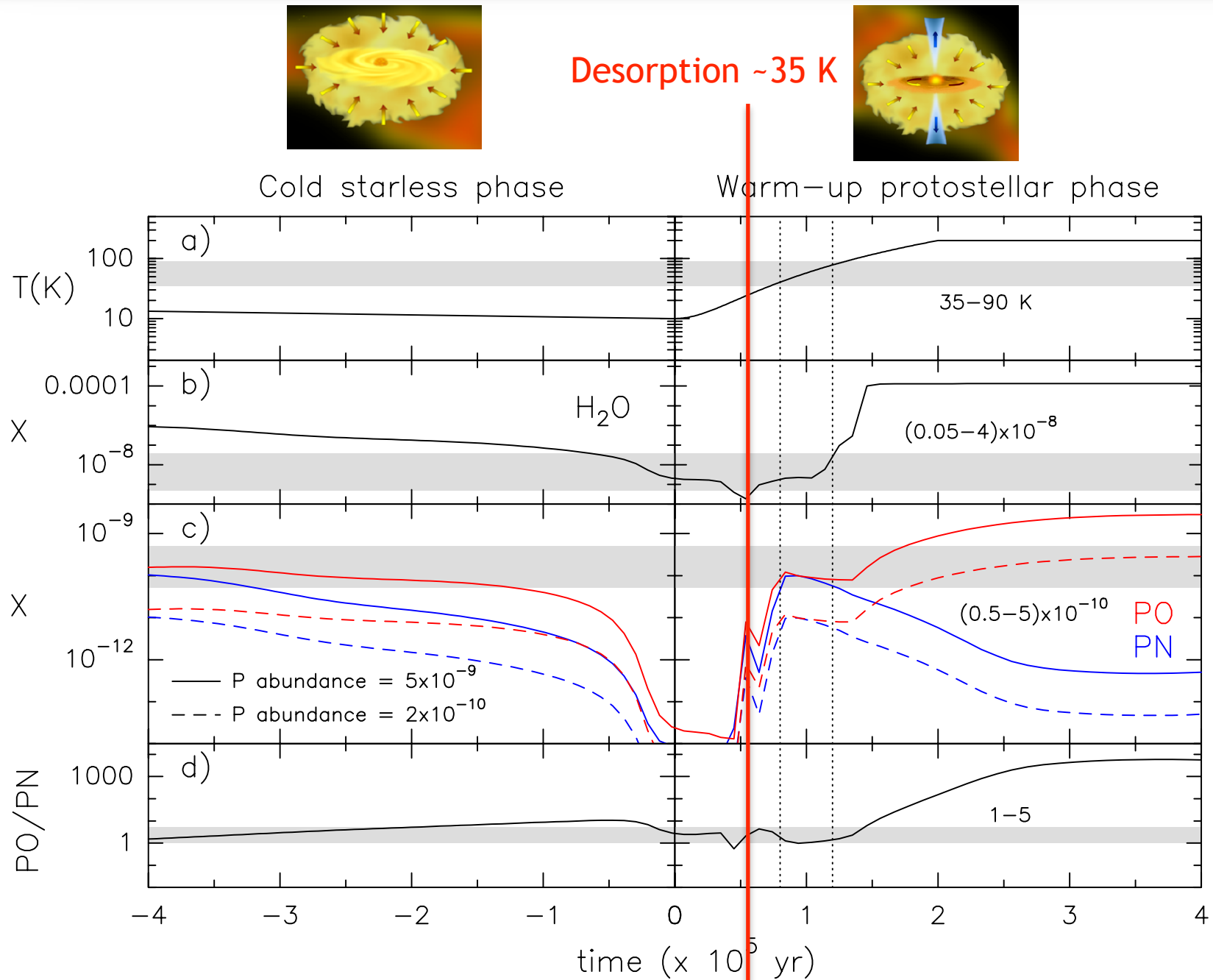
Cold starless phase



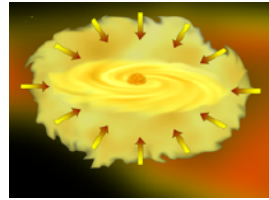
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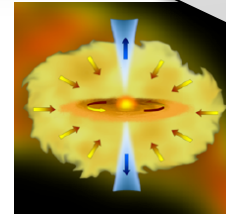
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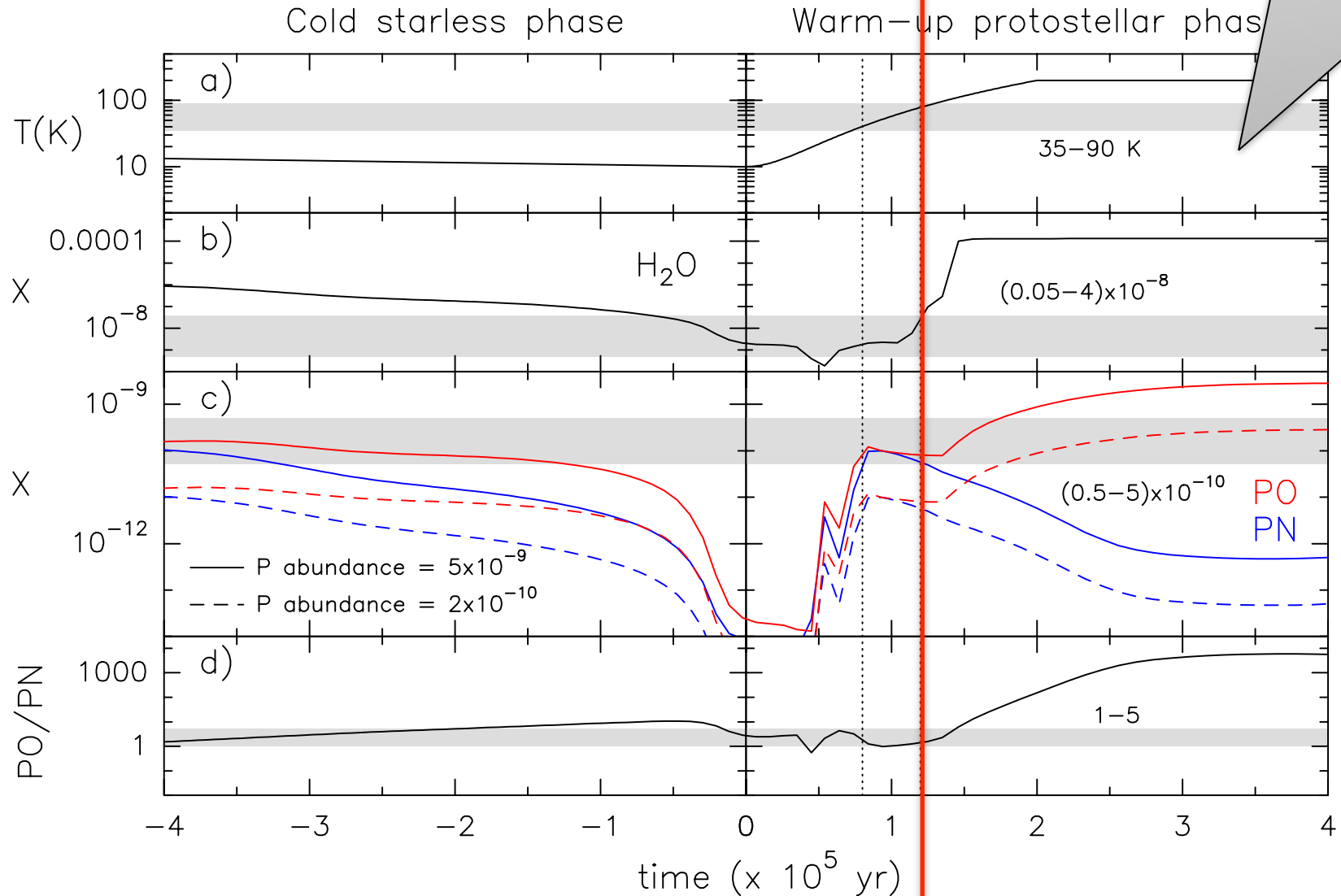
# P-bearing molecules: Chemical modelling



Water ices desorb  
~100 K



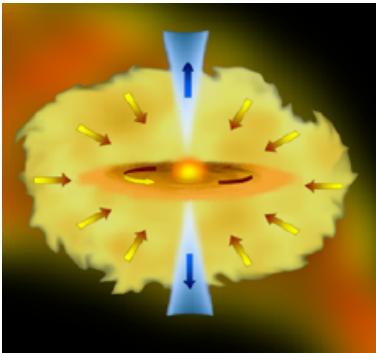
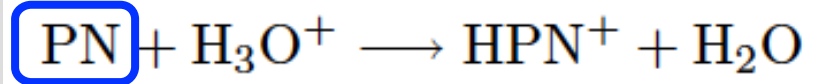
abundance of  
 $\text{H}_3\text{O}^+$  increases



# P-bearing molecules: Chemical modelling

- The abundance of  $\text{H}_3\text{O}^+$  increases:

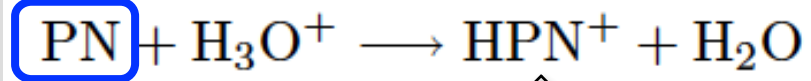
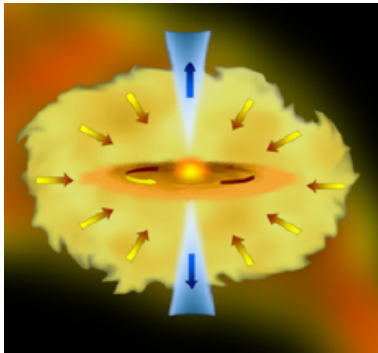
GAME OF REACTIONS



# P-bearing molecules: Chemical modelling

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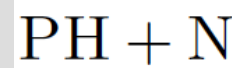
## GAME OF REACTIONS



+ e<sup>-</sup>

+ e<sup>-</sup>

Dissociative recombination  
of  $\text{HPN}^+$

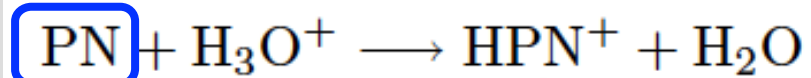
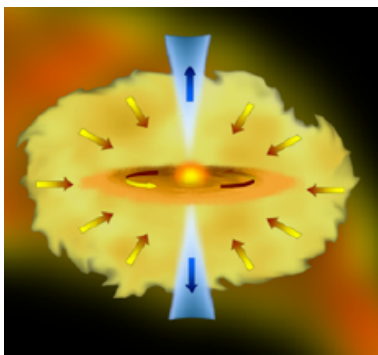




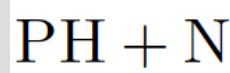
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## GAME OF REACTIONS



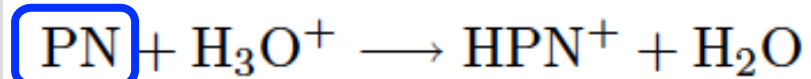
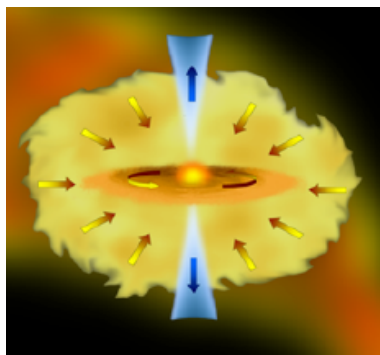
+ e<sup>-</sup>                      + e<sup>-</sup>                      Dissociative recombination  
of  $\text{HPN}^+$



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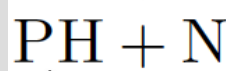
## GAME OF REACTIONS



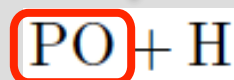
+ e<sup>-</sup>

+ e<sup>-</sup>

Dissociative recombination  
of  $\text{HPN}^+$



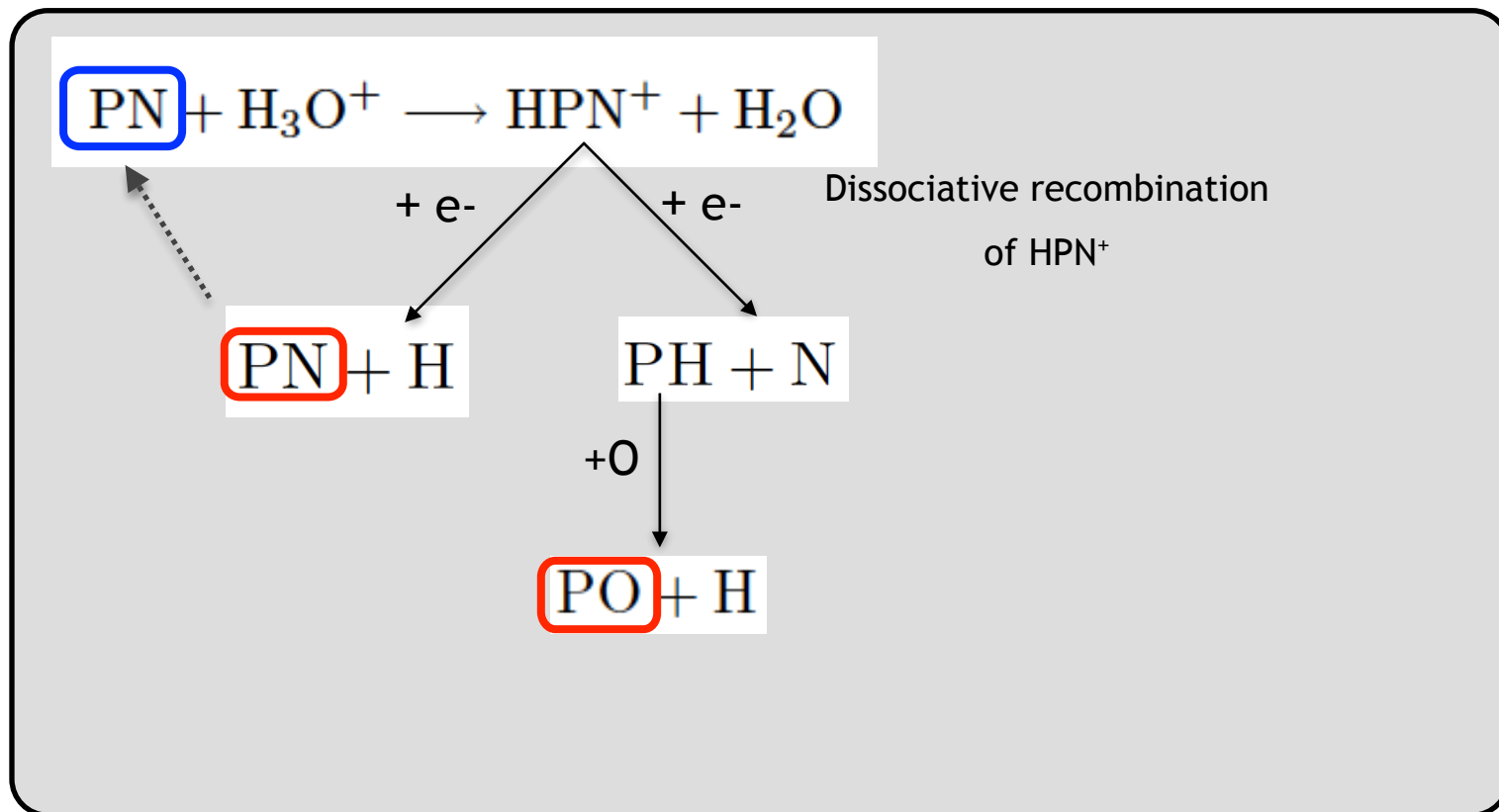
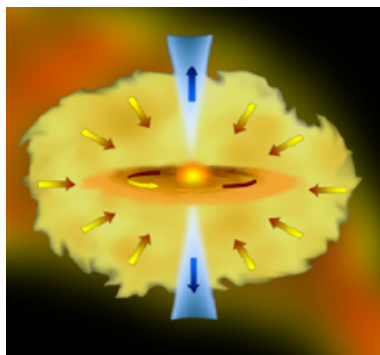
+ O



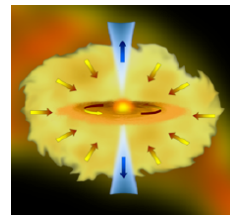
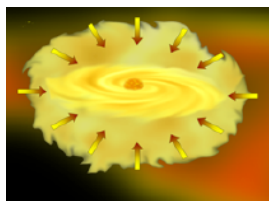
# P-bearing molecules: Chemical modelling

- The abundance of  $\text{H}_3\text{O}^+$  increases:

## GAME OF REACTIONS

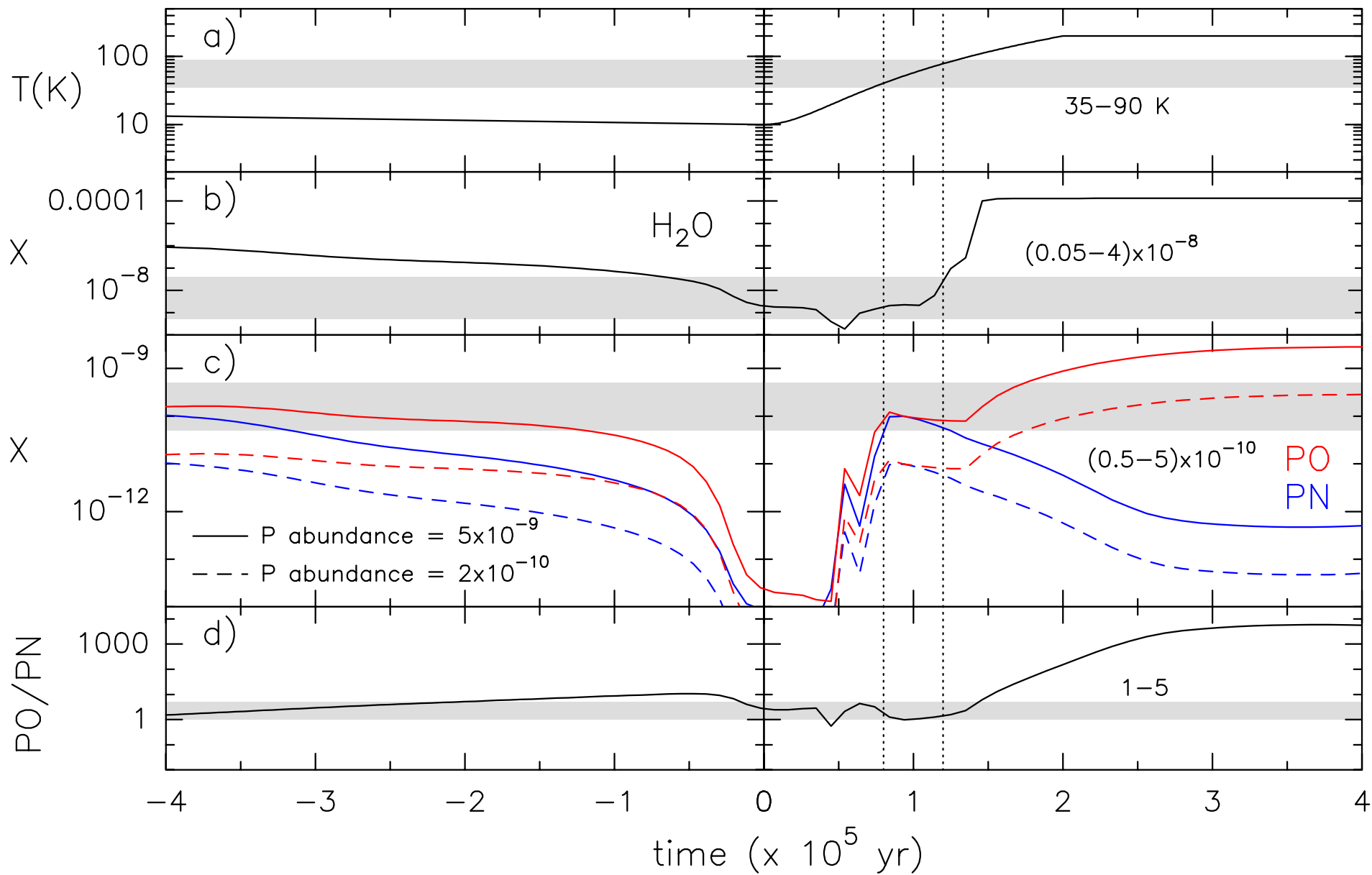


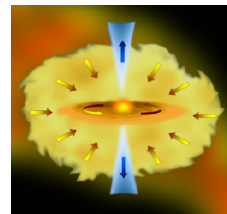
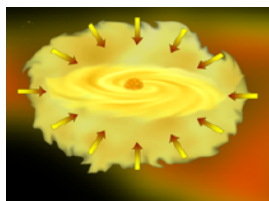
PN is gradually destroyed and PO is additionally produced



Cold starless phase

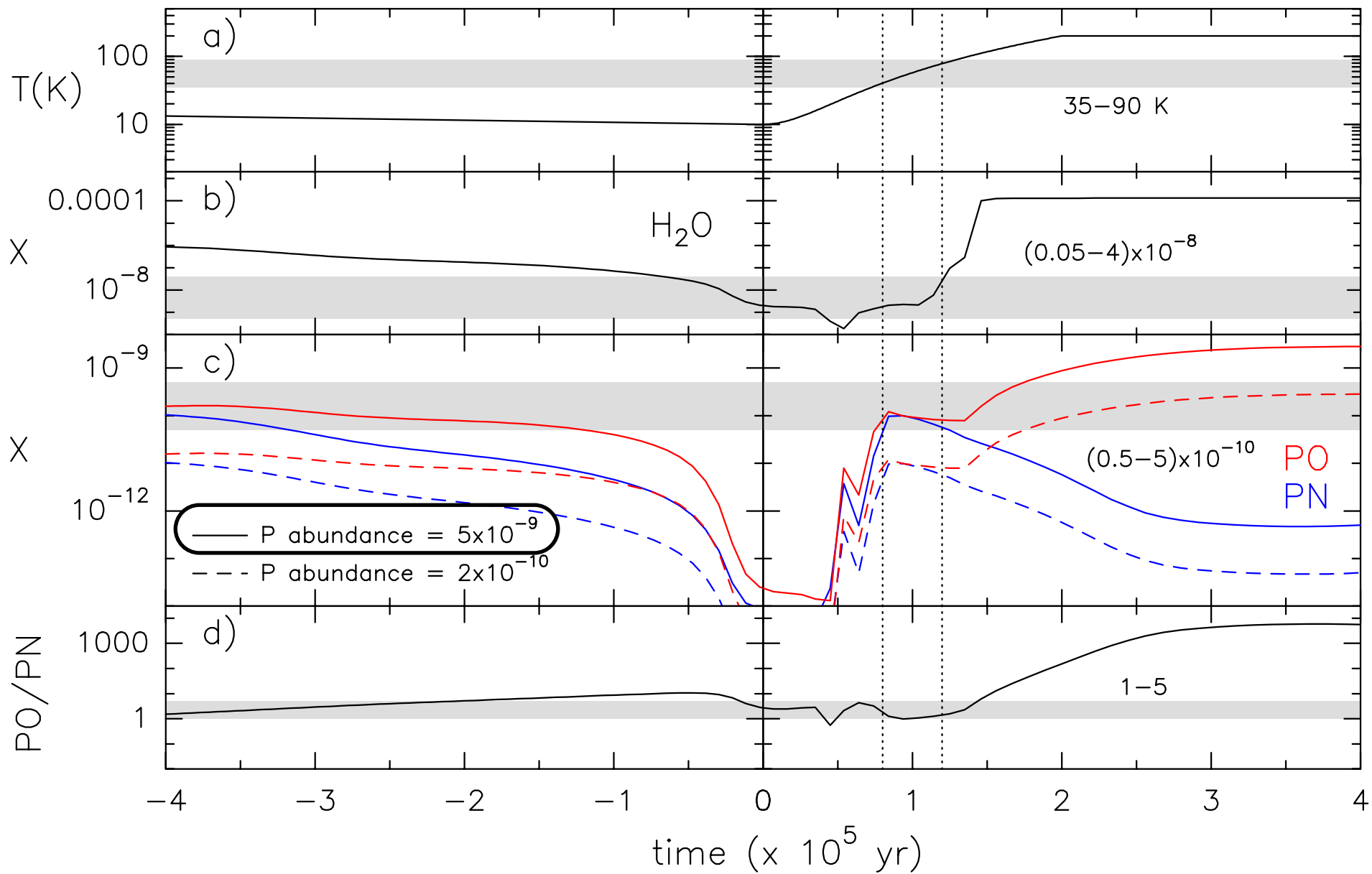
Warm-up protostellar phase

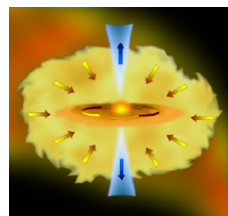
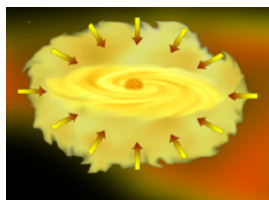




Cold starless phase

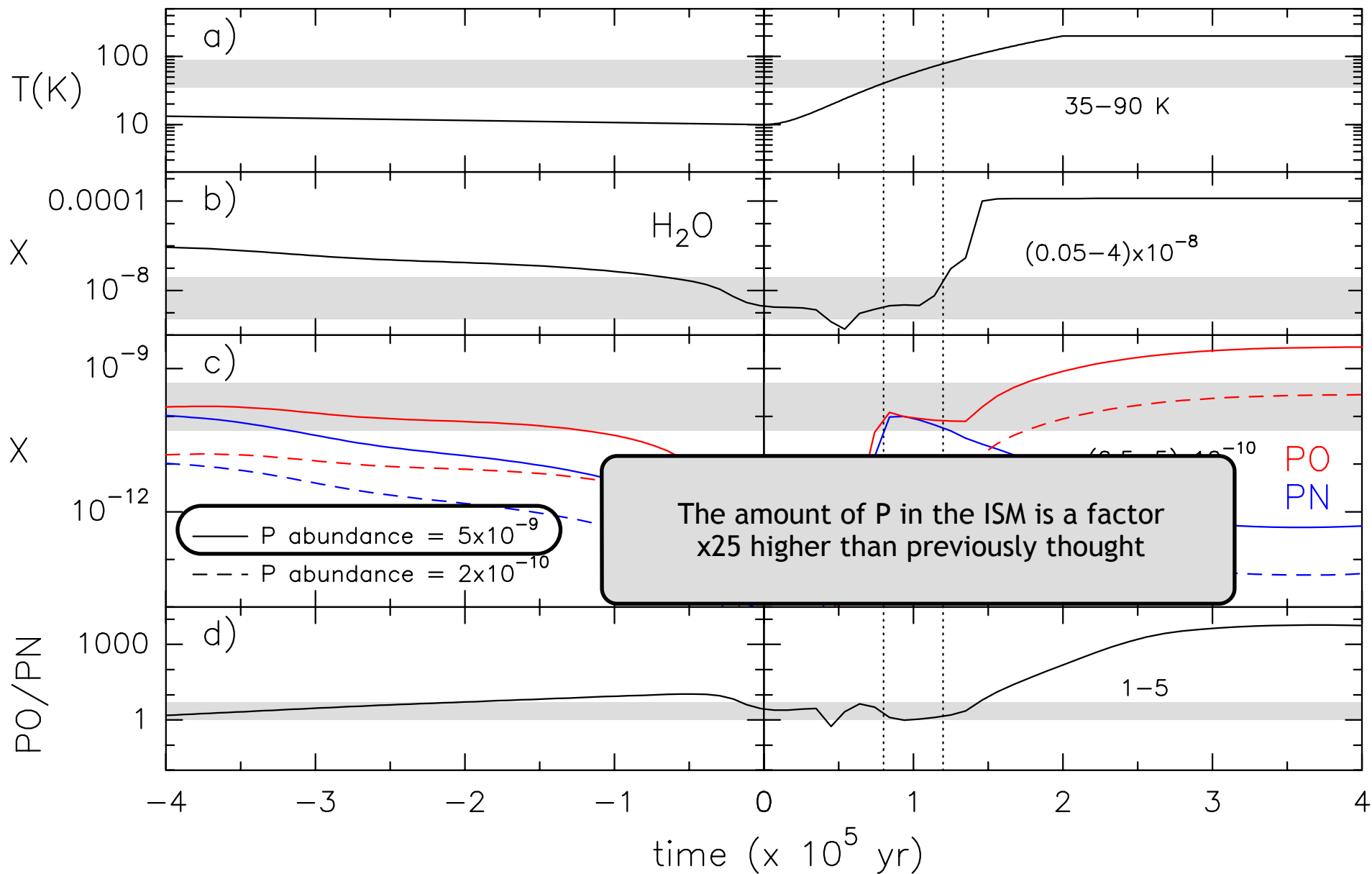
Warm-up protostellar phase

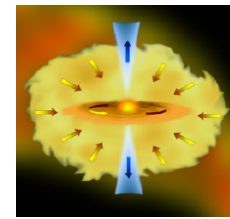
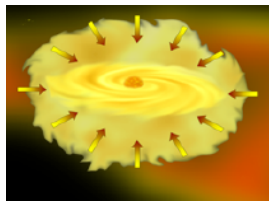




Cold starless phase

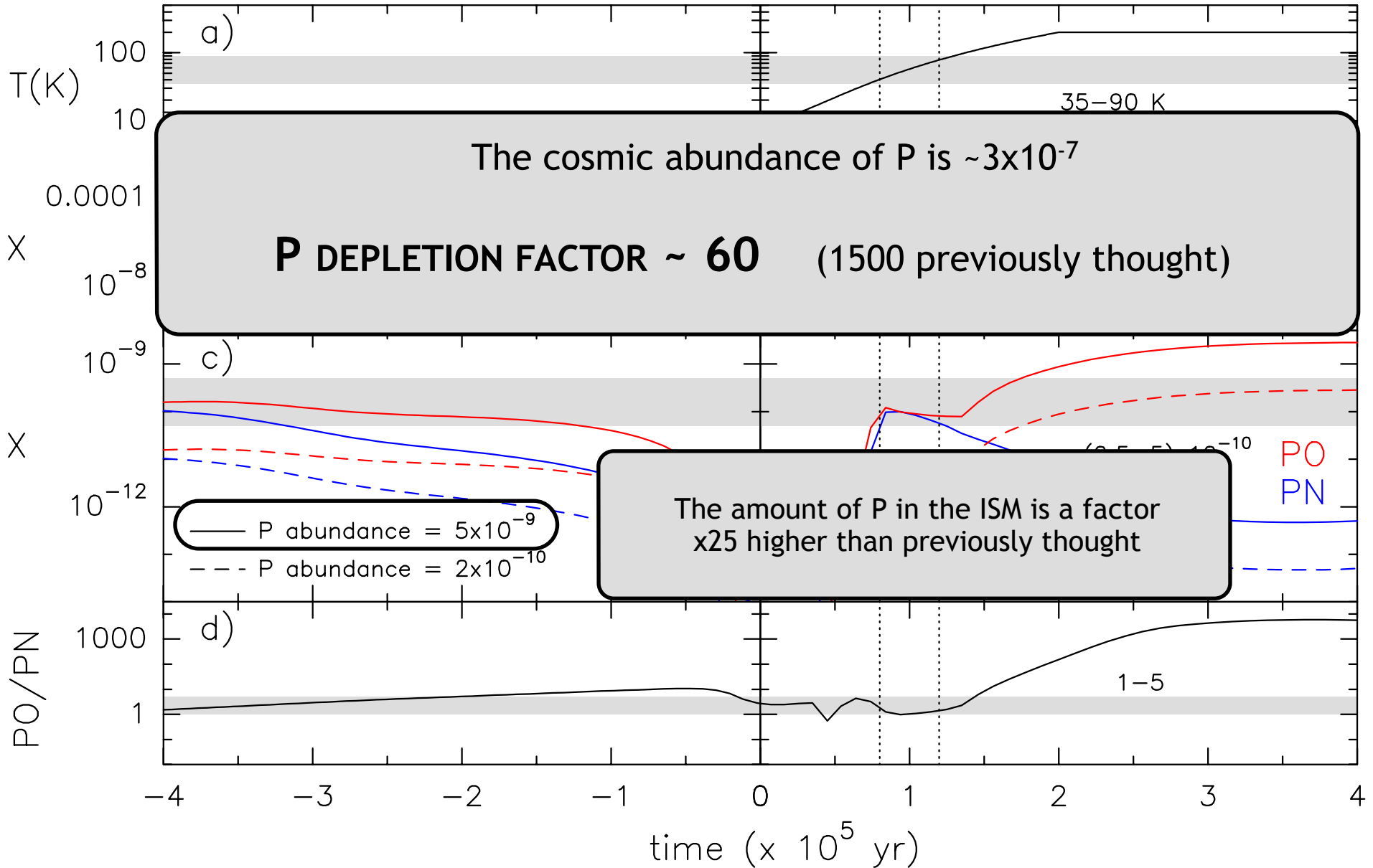
Warm-up protostellar phase





Cold starless phase

Warm-up protostellar phase



# Multi-transition PN analysis: the full sample (18 sources)

(Mininni et al., in prep.)	PN(2-1)	PN(3-2)	PN(6-5)
05358-mm3	✓	✓	✗
AFGL5142-EC	✓	✓	✗
G034-G2/A	✗	✗	✗
18517+0437	✓	✓	✓
AFGL5142-MM	✓	✓	✗
18089-1732	✓	✓	✗
I20293-MM1/B	✗	✗	✗
G75-core	✗	✓	✗
G5.89-0.39	✓	✓	✓
19035-VLA1	✗	✗	✗
19410+2336	✓	✓	✗
ON1	✓	✓	✓
G10.47+0.03	-	✓	✗
G24.78+0.08	-	✓	✗
G29.96-0.02	-	✓	✗
G31.41+0.31	-	✓	✓
W3OH	-	✓	✓
W51	-	✓	✓

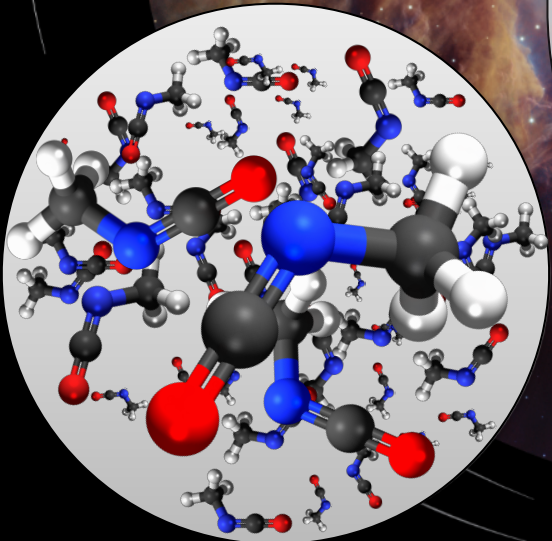


The first stars



The evolution of molecular clouds

# Grazie Francesco!



Young stellar clusters

Protostellar and pre-main sequence evolution



The first stars



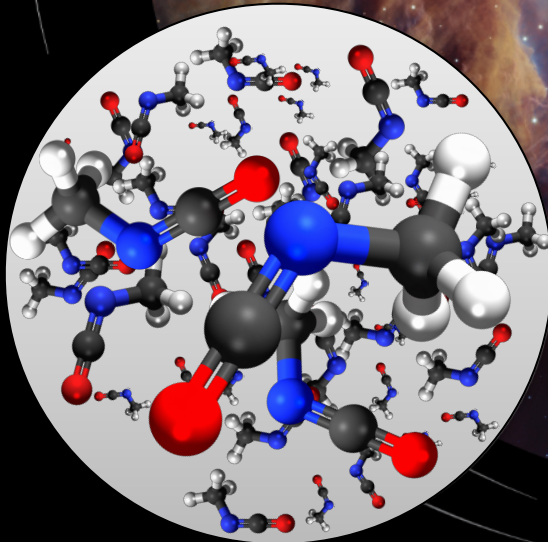
The evolution of molecular clouds

# Grazie Francesco!



Continueremo a osservare il cielo di Arcetri e a rimanere stupiti dai suoi misteri...

We will continue to observe Arcetri's sky and to be amazed by its mysteries...



Young stellar clusters  
Protostellar and pre-main sequence evolution

The first stars



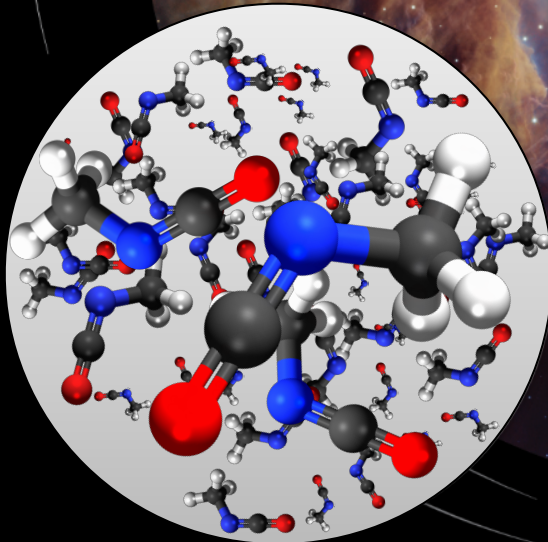
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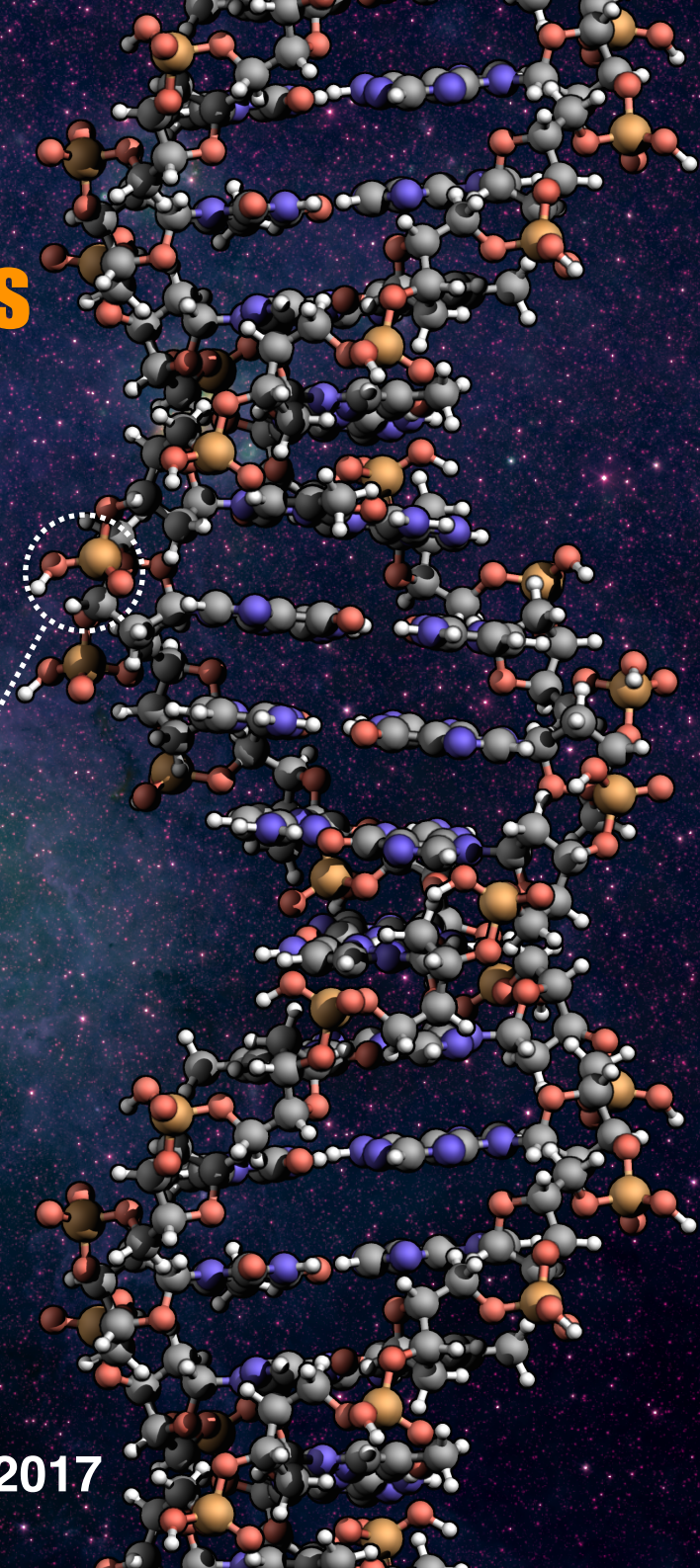
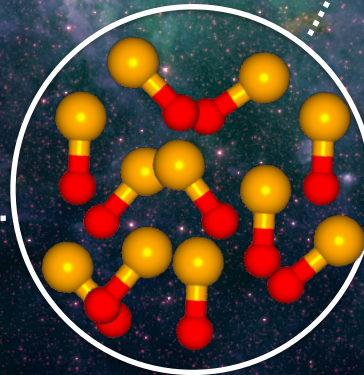
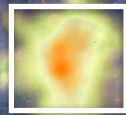


Young stellar clusters  
Protostellar and pre-main sequence evolution

# The formation of prebiotic molecules in star-forming regions

Víctor M. Rivilla

Osservatorio Astrofisico di Arcetri, OAA-INAF



Nitrogen



Francesco's Legacy, Florence, June 5-9 2017