



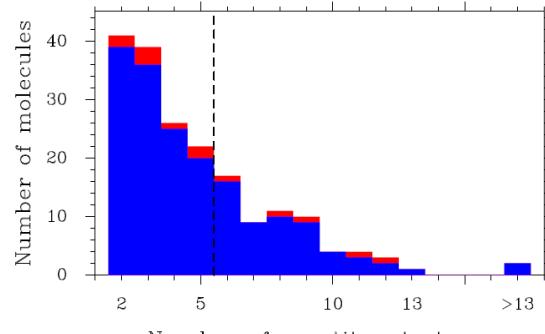
Emergence of Molecular Complexity in Solar-Type Star Forming Regions

B. Lefloch

Institute of Planetology and Astrophysics of Grenoble (France)

Molecular Complexity in the ISM

2	3	4	5	6	7	8	9	10	11	12	13
H ₂	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	C ₆ H ₆	c-C ₆ H ₅ CN
AlF	C ₂ H	1-C ₃ H	C ₄ H	1-H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	C ₂ H ₅ OCH ₃	
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	CH ₃ COOH?	(CH ₃) ₂ O	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	i-C ₃ H ₇ CN	
C ₂	C ₂ S	C ₃ O	1-C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ CHCH ₂ O	n-C ₃ H ₇ CN	
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	CH ₃ CHO	C ₆ H ₂	HC ₇ N	C ₈ H	CH ₃ OCH ₂ OH	+ C ₆₀ , C ₇₀	
CH ⁺	HCN	C ₂ H ₂	CH ₂ CN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO					
CN	HCO	NH ₃	CH ₄	CH ₃ SH	c-C ₂ H ₄ O	I-HC ₆ H	CH ₃ CONH ₂				
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	CH ₂ CHOH	CH ₂ CHCHO	C ₈ H ⁻				
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN	C ₃ H ₆				
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO		NH ₂ CH ₂ CN					
CSi	H ₂ O	HNCS	H ₂ CNH	C ₅ N		CH ₃ CHNH					
HCl	H ₂ S	HOOC ⁺	H ₂ C ₂ O	I-HC ₄ H							
KCl	HNC	H ₂ CO	H ₂ NCN	I-HC ₄ N							
NH	HNO	H ₂ CN	HNC ₃	c-H ₂ C ₃ O							
NO	MgCN	H ₂ CS	SiH ₄	H ₂ CCNH							
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻							
NaCl	N ₂ H ⁺	c-SiC ₃	C ₄ H ⁻	HNHCN							
OH	N ₂ O	CH ₃	HCOCN								
PN	NaCN	C ₃ N ⁻	HNCNH								
SO	OCS	PH ₃	CH ₃ O								
SO ⁺	SO ₂	HCNO	NH ₄ ⁺								
SiN	c-SiC ₂	HOCN	H ₂ NCO ⁺								
SiO	CO ₂	C ₃ H ⁺									
SiS	NH ₂	HMgNC									
CS	H ₃ ⁺	HSCN									
HF	SiCN										
HD	AINC										
FeO?	SiNC										
O ₂	CCP										
CF ⁺	AlOH										
SiH	H ₂ O ⁺										
PO	H ₂ Cl ⁺										
AlO,	KCN										
OH ⁺ ,	FeCN										
CN ⁻	HO ₂										



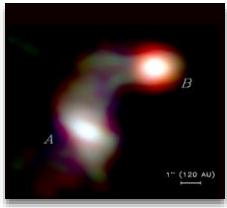
Around 200 molecules discovered mainly in massive star-forming regions (SgrB2, Orion), evolved stars, dark clouds, diffuse medium.

Complex Organic Molecules : ≥ 6 atoms + C atoms (*Herbst & van Dishoeck, 2009*)
One third of detected molecules are COMs.

The Bricks of Organic Chemistry are detected in the ISM

Pre-biotic molecules (HCOCH₂OH, NH₂CHO,...) but no amino acid !

Key Questions

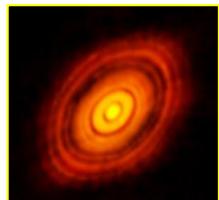


COMs and Prebiotic chemistry around Sun-like Protostars: What evidence ?

A handful of hot corino sources are known: how well ?

IRAS16293-2422: TIMASS (Caux et al. 2011), PILS (Jorgensen et al. 2016)

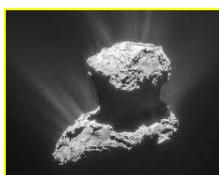
How and when do Complex Organic Molecules form around Sun-like systems ?



Which heritage to (exo)planetary systems ?

What is the ultimate molecular complexity that can be reached in SFRs ?

→ Origin of cometary material ? Amino-acids ?





The IRAM Large Program ASAI



(Astrochemical Surveys At IRAM)

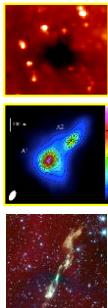
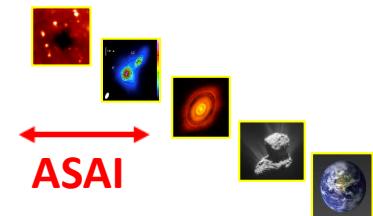
(Lefloch, Bachiller et al. 2018)

Goals:

- Evolutionary view on chemistry along Solar-type Star Formation:
- Influence of environmental conditions: feedback processes

Unbiased, high sensitivity spectral line surveys from 70 to 280GHz

ASAI Source Sample: 10 templates illustrative of the different chemical stages of a sun-like protostar



Sources	Coordinates (J2000)	d (pc)	Lum. (L_{\odot})	3 mm (mK)	2 mm (mK)	1.3 mm (mK)	$\delta\nu$ (kHz)	Comment
TMC1	04 ^h 41 ^m 41.90 ^s +25 °41'27.1"	140	–	–	4.2–4.2	–	48.8, 195.3	Early prestellar core
L1544	05 ^h 04 ^m 17.21 ^s +25 °10'42.8"	140	–	2.1–7.0	–	–	48.8	Evolved prestellar core
B1b	03 ^h 33 ^m 20.80 ^s +31 °07'34.0"	230	0.77	2.5–10.6(*)	4.4–8.0	4.2–4.6	195.3	First Hydrostatic Core
L1527	04 ^h 39 ^m 53.89 ^s +26 °03'11.0"	140	2.75	2.1–6.7(*)	4.2–7.1	4.6–4.1	195.3	Class 0 WCCC
IRAS4A	03 ^h 29 ^m 10.42 ^s +31 °13'32.2"	260	9.1	2.5–3.4	5.0–6.1	4.6–3.9	195.3	Class 0 Hot Corino
L1157mm	20 ^h 39 ^m 06.30 ^s +68 °02'15.8"	250	3	3.0–4.7	5.0–6.5	3.8–3.5	195.3	Class 0
SVS13A	03 ^h 29 ^m 03.73 ^s +31 °16'03.8"	260	34	2.0–4.8	4.2–5.1	4.6–4.3	195.3	Class I
AB Aur (†)	04 ^h 55 ^m 45.84 ^s +30 °33'33.04"	145	–	4.6–4.3	4.8–3.9	2.1–4.3	195.3	protoplanetary disk
L1157-B1	20 ^h 39 ^m 10.20 ^s +68 °01'10.5"	250	–	1.1–2.9	4.6–7.2	2.1–4.2	195.3	Outflow shock spot
L1448-R2	03 ^h 25 ^m 40.14 ^s +30 °43'31.0"	235	–	2.8–4.9	6.0–9.7	2.9–4.9	195.3	Outflow shock spot



3mm band: chemical content

After analysing the 3mm line surveys (1% U lines)

2	3	4	5	6	7	8	9	10	11	12	13
H ₂	C ₃	c-C ₃ H	C ₅	C ₅ H	C ₆ H	CH ₃ C ₃ N	CH ₃ C ₄ H	CH ₃ C ₅ N	HC ₉ N	C ₆ H ₆	c-C ₆ H ₅ CN
AlF	C ₂ H	I-C ₃ H	C ₄ H	I-H ₂ C ₄	CH ₂ CHCN	HCOOCH ₃	CH ₃ CH ₂ CN	(CH ₃) ₂ CO	CH ₃ C ₆ H	C ₂ H ₅ OCH ₃	
AlCl	C ₂ O	C ₃ N	C ₄ Si	C ₂ H ₄	CH ₃ C ₂ H	HC ₅ N	CH ₃ COOH?	(CH ₂ OH) ₂	C ₂ H ₅ OCHO	i-C ₃ H ₇ CN	
C2	C ₂ S	C ₃ O	I-C ₃ H ₂	CH ₃ CN	HC ₅ N	C ₇ H	CH ₃ CH ₂ OH	CH ₃ CH ₂ CHO	CH ₃ CHCH ₂ O	n-C ₃ H ₇ CN	
CH	CH ₂	C ₃ S	c-C ₃ H ₂	CH ₃ NC	CH ₃ CHO	C ₆ H ₂	HC ₇ N	CH ₃ CONH ₂			
CH ⁺	HCN	C ₂ H ₂	CH ₂ CN	CH ₃ OH	CH ₃ NH ₂	CH ₂ OHCHO	C ₈ H	C ₈ H ⁻			
CN	HCO	NH ₃	CH ₄	CH ₃ SH	c-C ₂ H ₄ O	I-HC ₆ H	C ₃ H ₆				
CO	HCO ⁺	HCCN	HC ₃ N	HC ₃ NH ⁺	CH ₂ CHOH	CH ₂ CHCHO					
CO ⁺	HCS ⁺	HCNH ⁺	HC ₂ NC	HC ₂ CHO	C ₆ H ⁻	CH ₂ CCHCN					
CP	HOC ⁺	HNCO	HCOOH	NH ₂ CHO	CH ₃ NCO	NH ₂ CH ₂ CN					
CSi	H ₂ O	HNCS	H ₂ CNH	C ₅ N		CH ₃ CHNH					
HCl	H ₂ S	HOCO ⁺	H ₂ C ₂ O	I-HC ₄ H							
KCl	HNC	H ₂ CO	H ₂ NCN	I-HC ₄ N							
NH	HNO	H ₂ CN	HNC ₃	c-H ₂ C ₃ O							
NO	MgCN	H ₂ CS	SiH ₄	H ₂ CCNH							
NS	MgNC	H ₃ O ⁺	H ₂ COH ⁺	C ₅ N ⁻							
NaCl	N ₂ H ⁺	c-SiC ₃	C ₄ H ⁻	HNCHCN							
OH	N ₂ O	CH ₃	HCOCN								
PN	NaCN	C ₃ N ⁻	HNCNH								
SO	OCS	PH ₃	CH ₃ O								
SO ⁺	SO ₂	HCNO	NH ₄ ⁺								
SiN	c-SiC ₂	HOCH ₃	H ₂ NCO ⁺								
SiO	CO ₂	C ₃ H ⁺									
SiS	NH ₂	HMgNC									
CS	H ₃ ⁺	HSCN									
HF	SiCN										
HD	AINC										
FeO?	SiNC										
O ₂	CCP										
CF ⁺	AlOH										
SiH	H ₂ O ⁺										
PO	H ₂ Cl ⁺										
AlO,	KCN										
OH ⁺ ,	FeCN										
CN ⁻	HO ₂										

First S-bearing COM detected in low-mass SFRs: CH₃SH

(also Majumdar et al. 2016)

No evidence for COMs larger than glycolaldehyde, dimethyl ether, ethanol

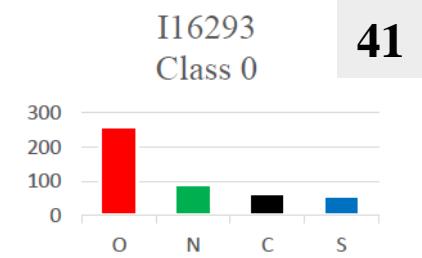
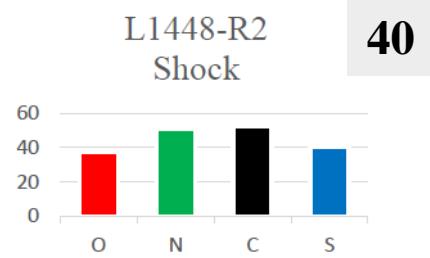
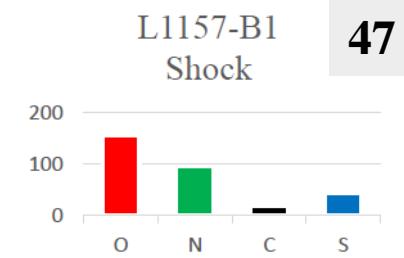
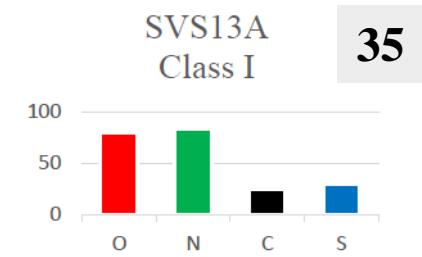
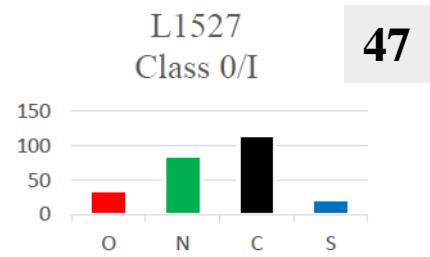
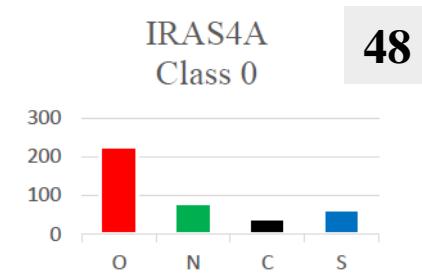
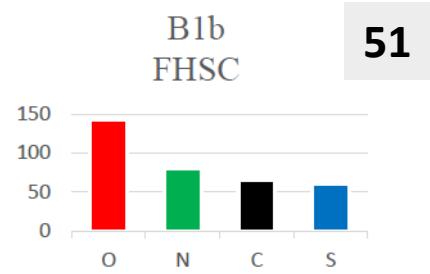
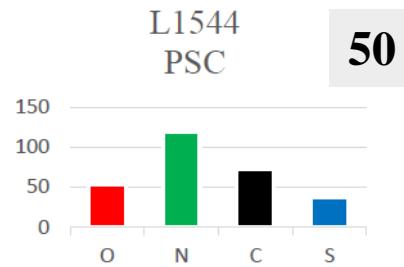
New molecular species: NO⁺, NS⁺ (Cernicharo et al. 2014, 2018),





Statistics

Time



ASAI sample

Number of *detected* molecular species : 35 – 51

Number of molecular lines : 178 – 413 ($\sigma = 5\text{-}12 \text{ GHz}^{-1}$)

Orion

43

SgrB2

56

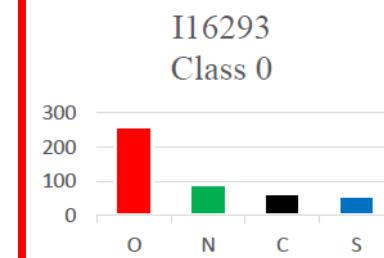
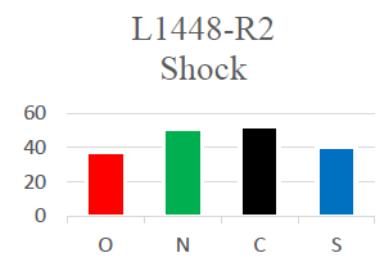
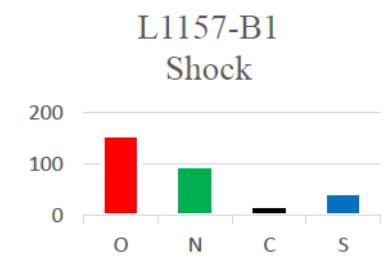
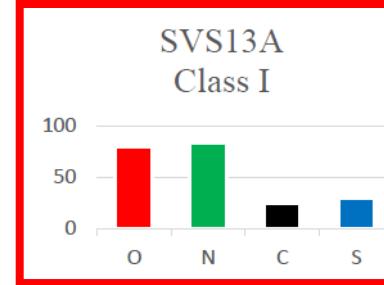
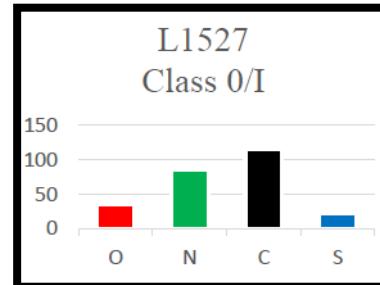
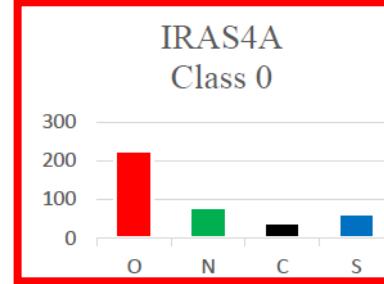
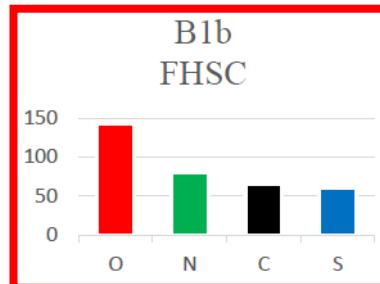
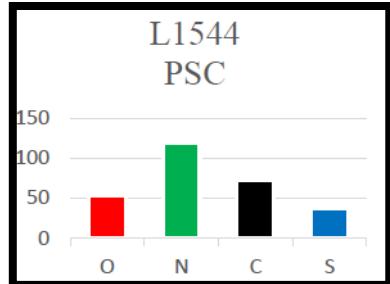
3200

3700



Two Chemical Classes

Time



$r = N(O)/N(C) = 1$ defines two chemical classes:

O-rich : hot corino sources : $r = O/C > 1.5$

C-rich : WCCC : $r = O/C < 1.5$



SVS13A : hot corino
L1157-mm : WCCC



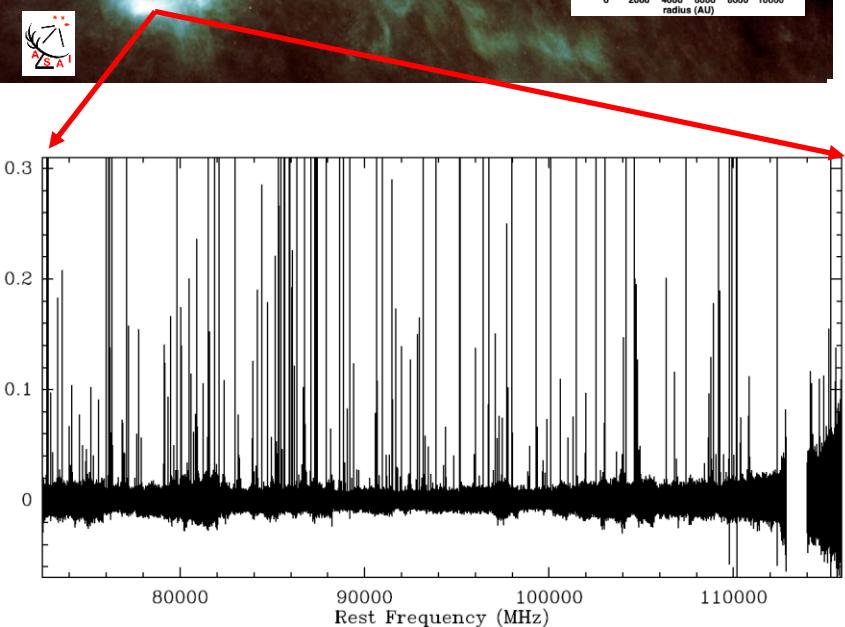
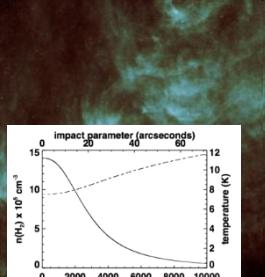
COMs in the Prestellar Phase

COMs are present at the prestellar stage

Bacmann et al. (2012), Cernicharo et al. (2012), Oberg et al. (2010)

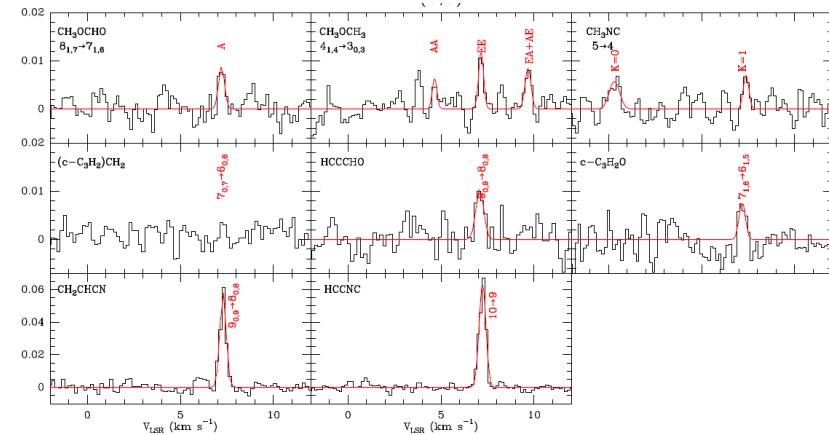
Vastel et al. (2014), Jimenez-Serra et al. (2015)

L1544



First systematic census of COMs in a PSC
CH₃OH, CH₃CHO, CH₃OCHO, CH₃OCH₃,
H₂CCO, HCOOH

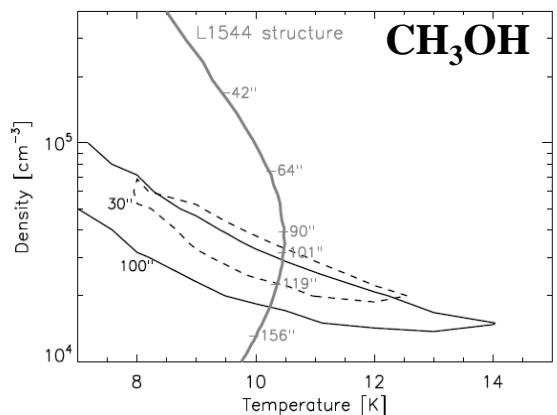
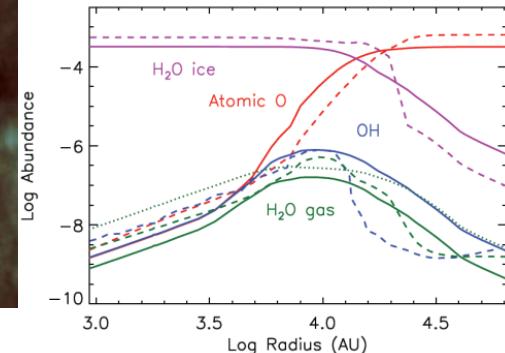
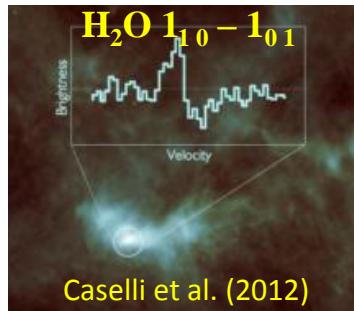
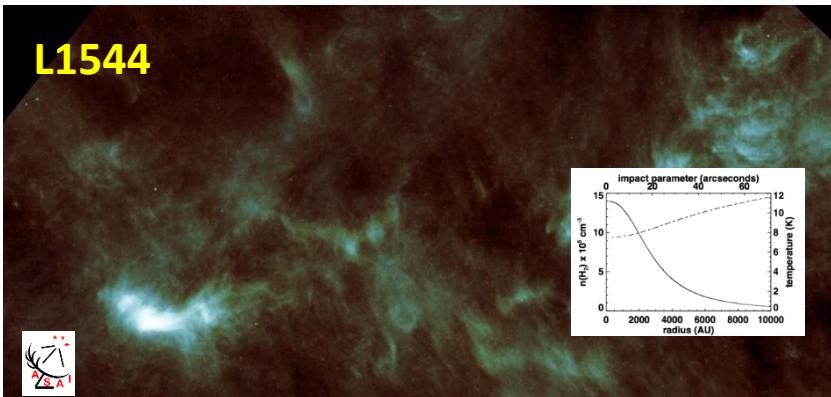
CH₃CN, CH₃NC, CH₂CHCN





COMs in the Prestellar Phase

Vastel et al. (2014), Jimenez-Serra et al. (2015)



Emission of CH_3OH and other COMs arise from the outer layers where strong UV-photodesorption of water ice is observed

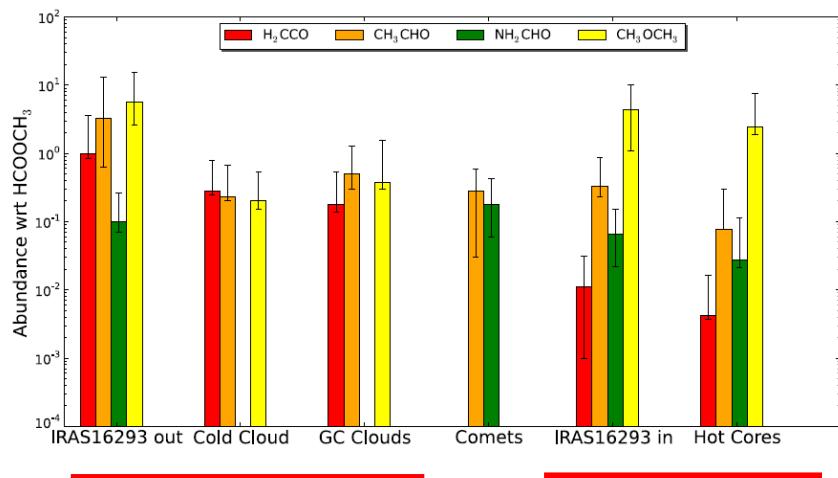
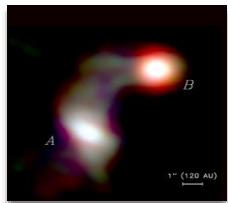
Vastel et al. (2014), Bizzochi et al. (2014)

Origin of COMs is a challenge
→ Non-thermal desorption of CH_3OH and C_2H_4 from grain mantles + gas phase reactions could account for the formation of some COMs *in the gas phase* : CH_3CHO , H_2CCO ?



COMs around Solar-Type Protostars

IRAS16293-2422



Ketene/Methyl Formate : Cold / Hot objects

(Jaber et al. 2014, Kahane et al. 2013, Jorgensen et al. 2012)

TIMASS (Caux et al. 2011) :

H_2CCO , CH_3CHO , NH_2CHO , HCOOCH_3 ,
 CH_3OCH_3 , CH_3CN , HOCH_2CHO

Two contributions :

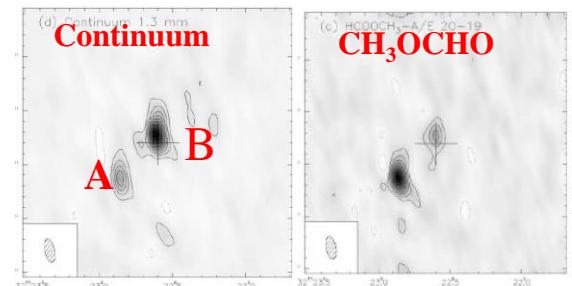
Compact, Hot, dense region : **Hot corino**

$T_d \geq 100\text{K}$: $X = 1(-9) - 1(-8)$

Extended, **Cold Envelope** :

$X = 3(-12) - 2(-10)$

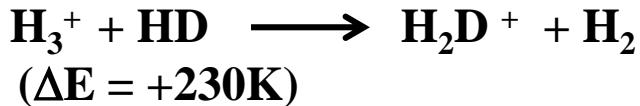
I16293 Hot Corino



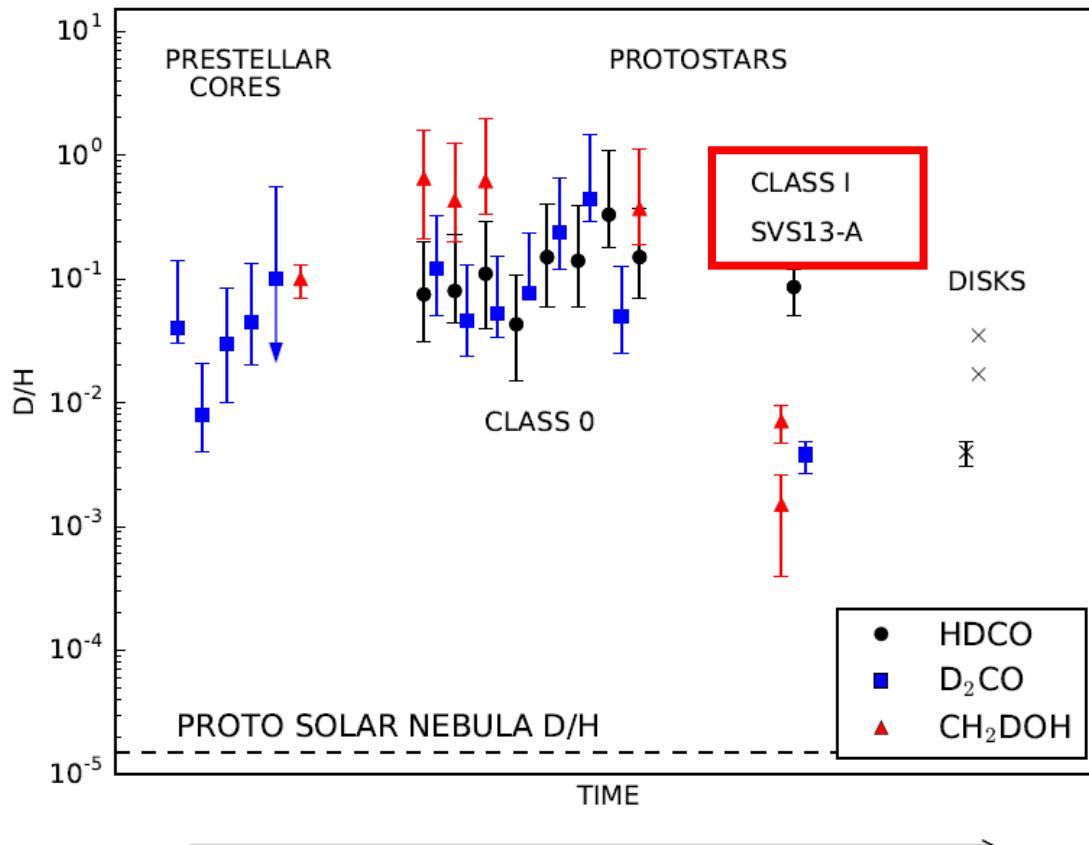
(Bottinelli et al. 2007)



Molecular Deuteriation



Enhanced molecular D/H in cold gas



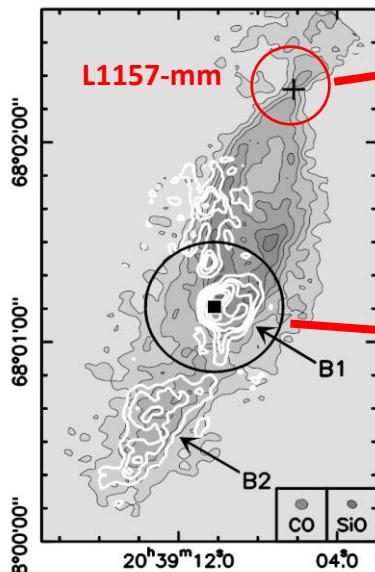
Decrease of molecular deuteriation in Class I - SVS13A

Bianchi et al. (2017)



Shocks as COM factories

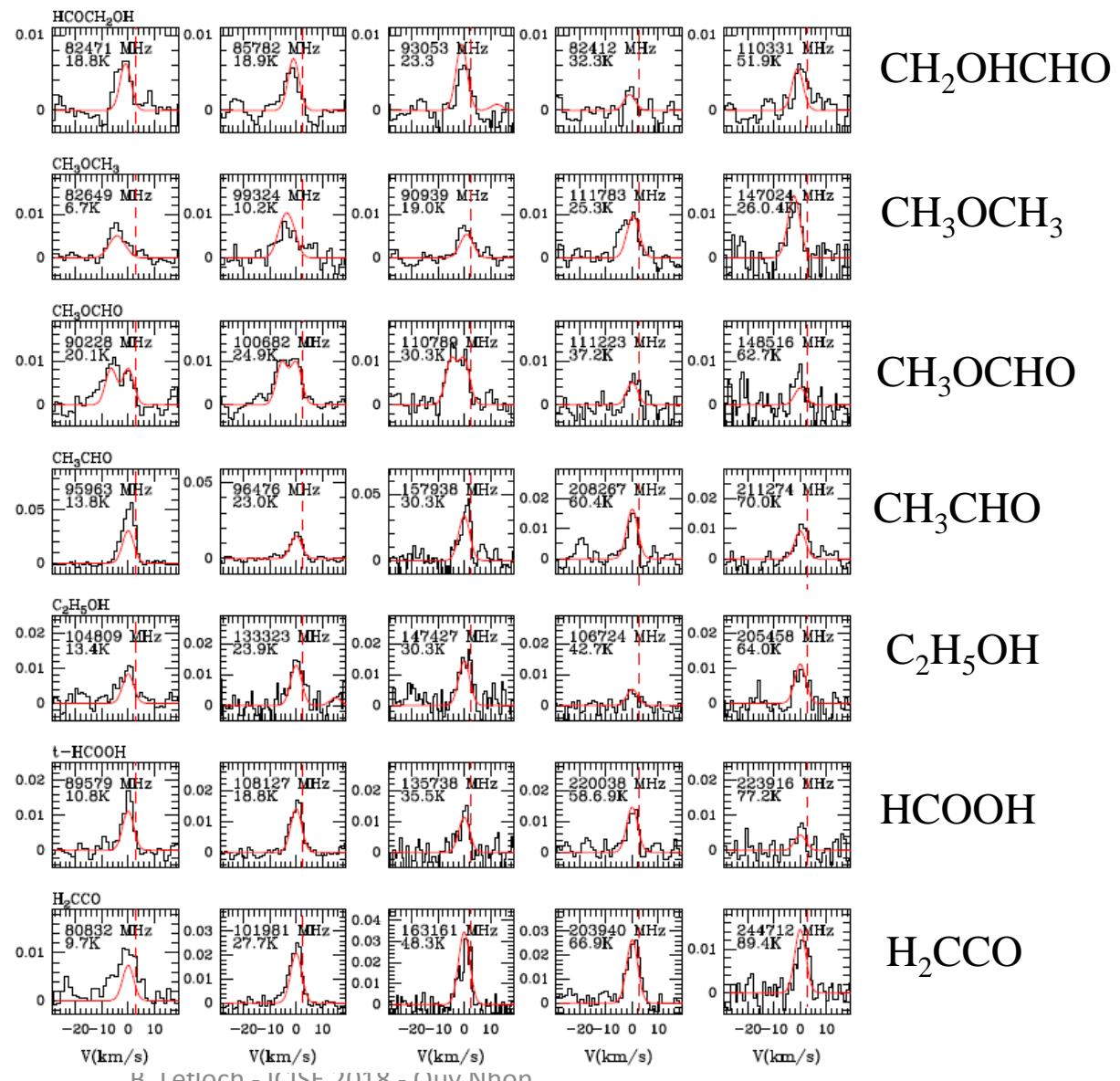
Lefloch et al. (2017)



Gueth et al. (1996,98)

N-bearing:
 NH_2CHO , CH_3CN ,
 $\text{C}_2\text{H}_3\text{CN}$, HC_5N

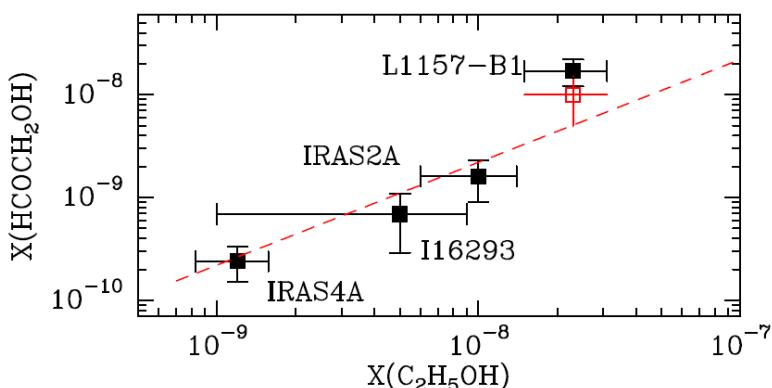
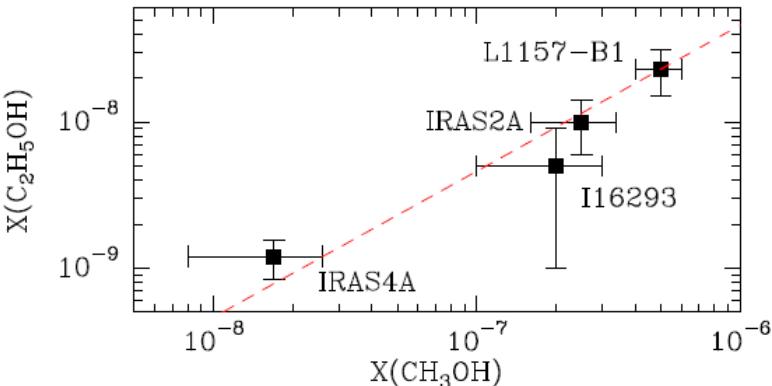
S-bearing: CH_3SH





Shocks as COM factories

Abundances are all similar (but NH_2CHO) : 10^{-8} [H₂]
 Relatively to CH₃OH: X = 2% - 5 % X[CH₃OH]

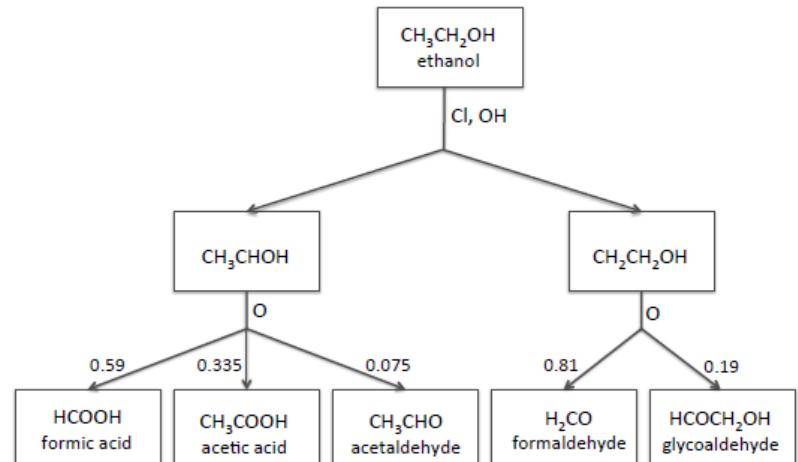


Linear correlations: chemical families:
 a common origin ?

Which formation route for glycolaldehyde ?
 Grain surface (CH₃OH + HCO) ?
 Gas phase (H₂CO⁺ + H₂CO) ?

Woods et al. (2012, 2013)

A New Scheme: The Ethanol Tree
(Skouteris et al. 2017)



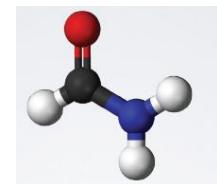


Prebiotic Molecules: NH₂CHO

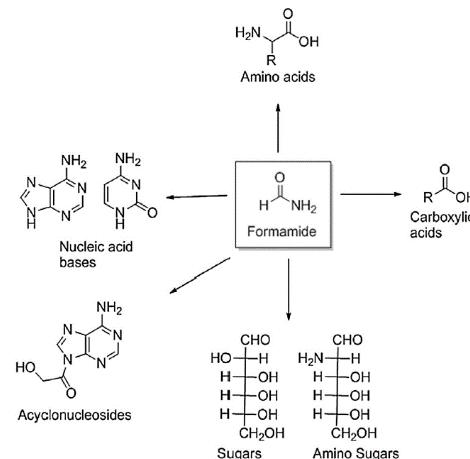


Formamide NH₂CHO: an important molecule for prebiotic chemistry

- the four most abundant elements of biological systems: C,H,O,N
- the simplest molecule with a peptide bond



A precursor of prebiotic chemistry (Saladino et al. 2012)



Detected in Comets: Hale-Bopp (Bockelee-Morvan et al. 2000), **81P/Wild2** (Elsila 2009), **67P** (Altweig 2016)
→ Exogenous delivery on Earth (Ferus et al. 2014) ?

Detected in high-mass SFRs (Bisschop et al. 2007)
solar-type protostar IRAS16293-2422 (Kahane et al. 2013).

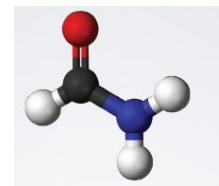


Prebiotic Molecules: NH₂CHO



Formamide NH₂CHO: an important molecule for prebiotic chemistry

- the four most abundant elements of biological systems: C,H,O,N
- the simplest molecule with a peptide bond



Lopez-Sepulcre *et al.* (2015)

ASA I: Search for NH₂CHO in solar-type environments

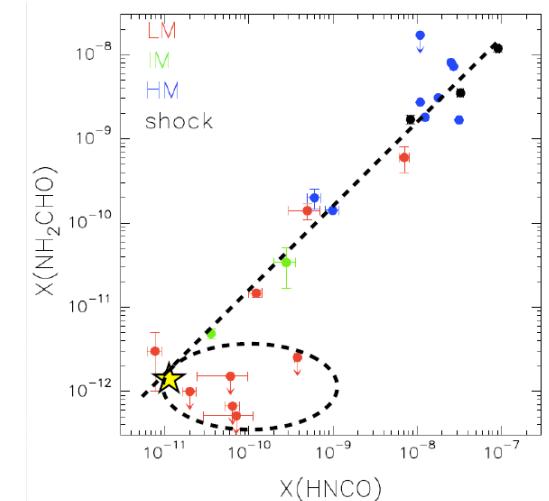
Not detected

Source	<i>d</i> (pc)	<i>M</i> (M _⊙)	<i>L</i> _{bol} (L _⊙)	Type
TMC1	140	21	—	PSC - young
L1544	140	2.7	1.0	PSC - evolved
B1	200	1.9	1.9	Class 0 - early
L1527	140	0.9	1.9	Class 0, WCCC
L1157-mm	325	1.5	4.7	Class 0, WCCC?
IRAS 4A	235	5.6	9.1	Class 0, HC
SVS 13A	235	0.34	21	Class 0/1
OMC-2 FIR 4	420	30	100	IM proto-cluster
Cep E	730	35	100	IM protostar
L1157-B1	250	—	—	outflow shock

Detected

NH₂CHO is detected only in hot corinos and shocks
Not in PSC and WCCC sources

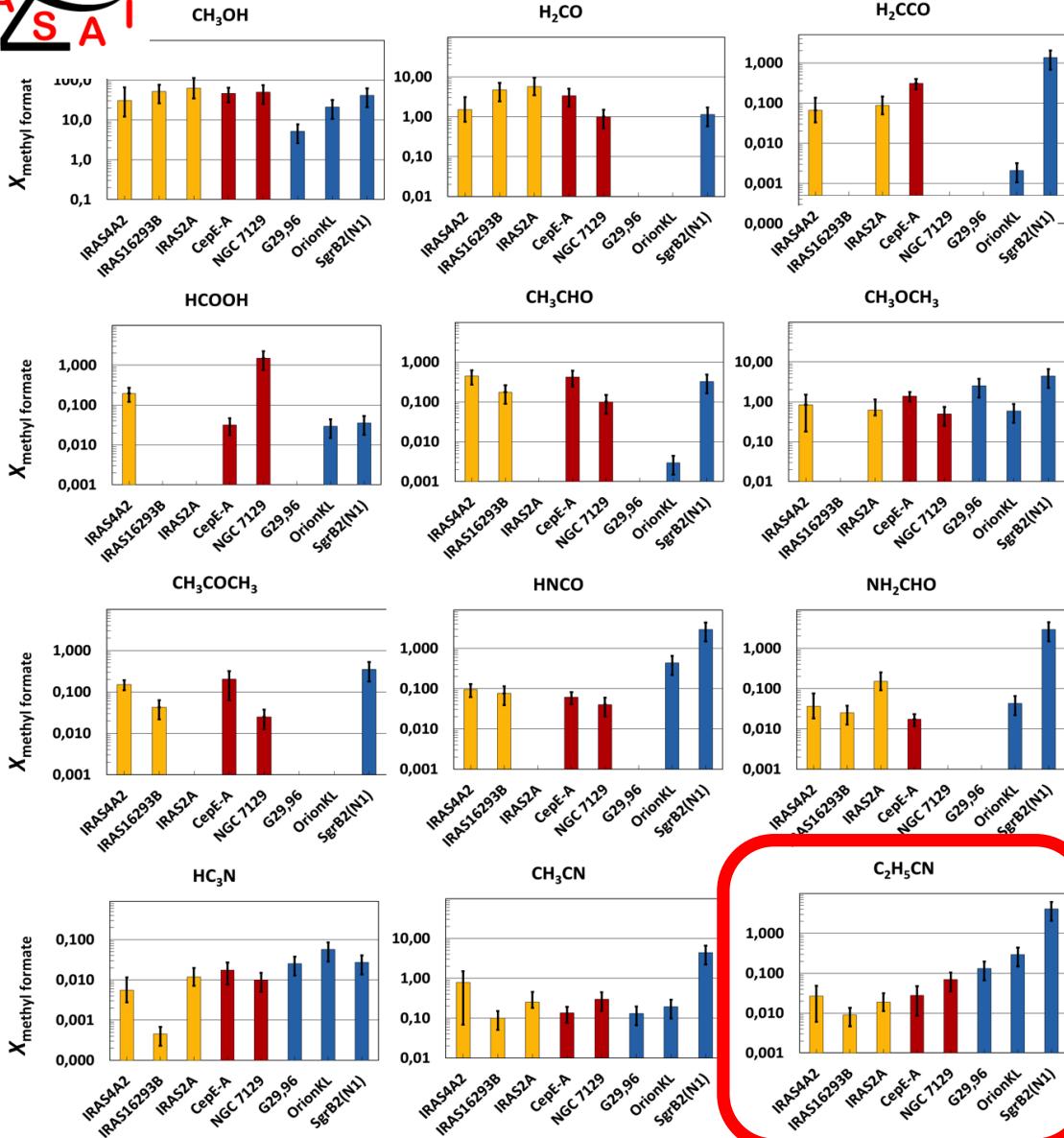
NH₂CHO/HNCO = 0.1



NH₂CHO and HNCO are chemically related
Several formation pathways for HNCO (also : Marcelino 2009)



From hot corinos to hot cores



Relative O-bearing
abundances vary little
with respect to luminosity
But : H_2CCO and CH_3CHO

Good correlation between
 CH_3OCH_3 and CH_3OCHO :
a common origin ?
(Balucani et al. 2016)

Relative $\text{C}_2\text{H}_5\text{N}$ abundance
increases with luminosity

(Ospina-Zamudio et al. 2018)



Conclusions and Future Prospects

Single-dish line surveys such as ASAI show that

- Molecular complexity is already present in the earliest phases of star formation, at a degree comparable to that of massive SFRs.
- No leap in molecular complexity from low- to high-mass Star Forming Regions.
- Molecules of prebiotic interest are discovered, complex and simple!
- Shocks are as chemically rich as protostellar envelopes; act a major factor of chemical feedback. They are true laboratories which help to characterize molecule formation pathways.

High-angular resolution observations with NOEMA and ALMA are opening a new window for the (astro)chemistry of Star Forming Regions.

Thanks

Thanks to all the ASA1 collaborators for this fantastic and so successful journey :

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