From Astrochemistry to Astrobiology: the importance of cosmic ices in astrochemistry and prebiotic evolution

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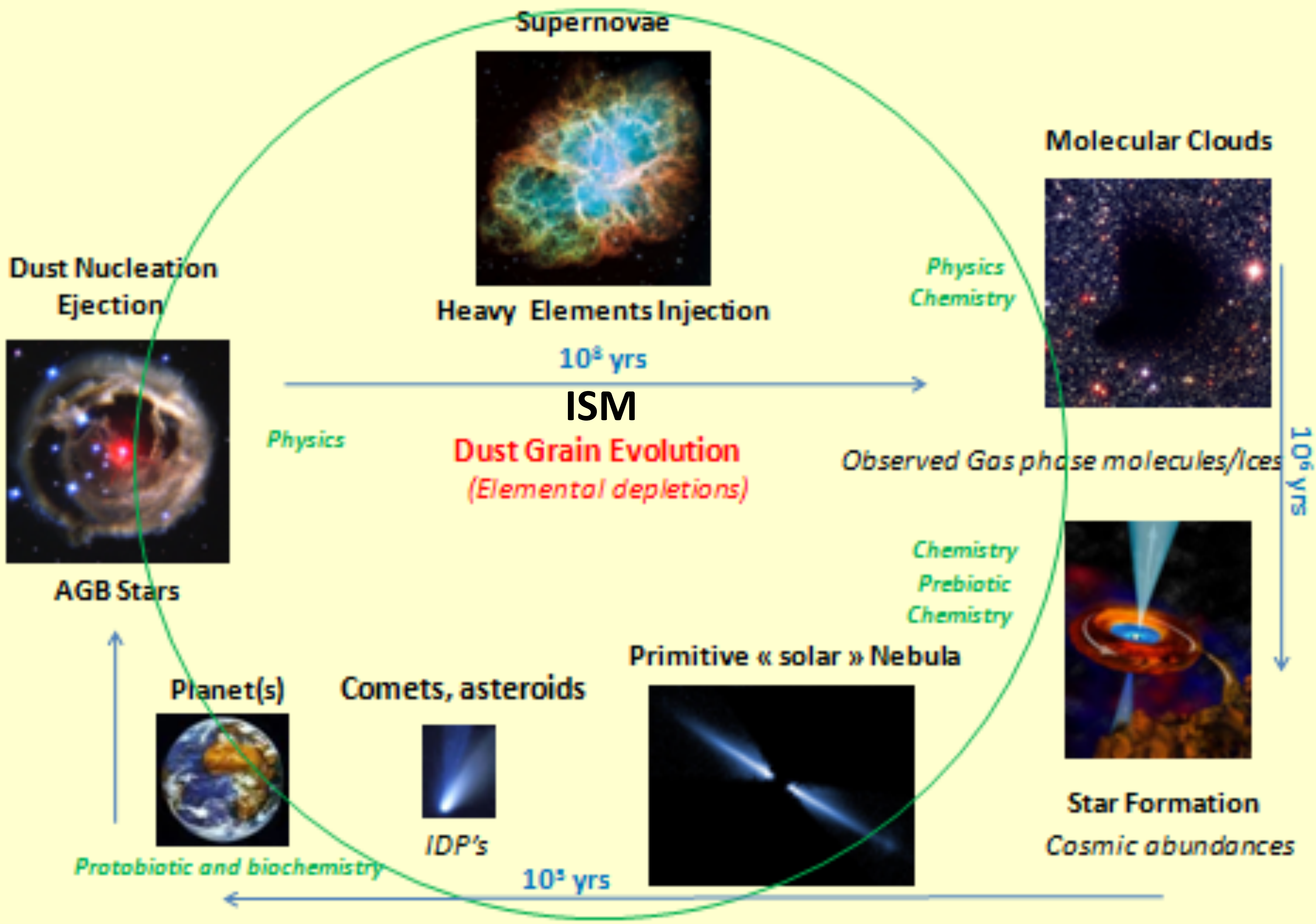
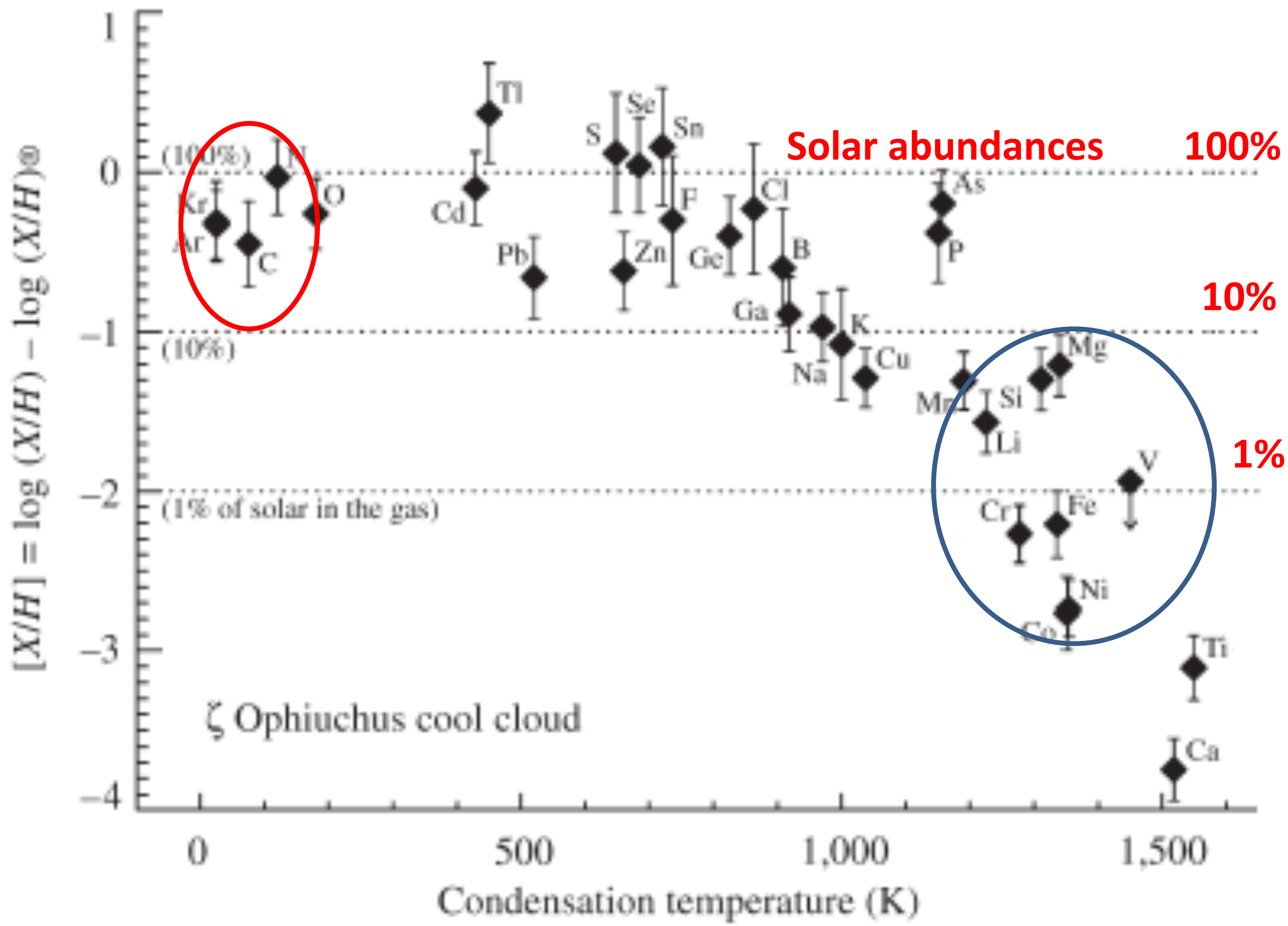
THE CYCLE OF SOLID STATE MATTER IN THE GALAXY

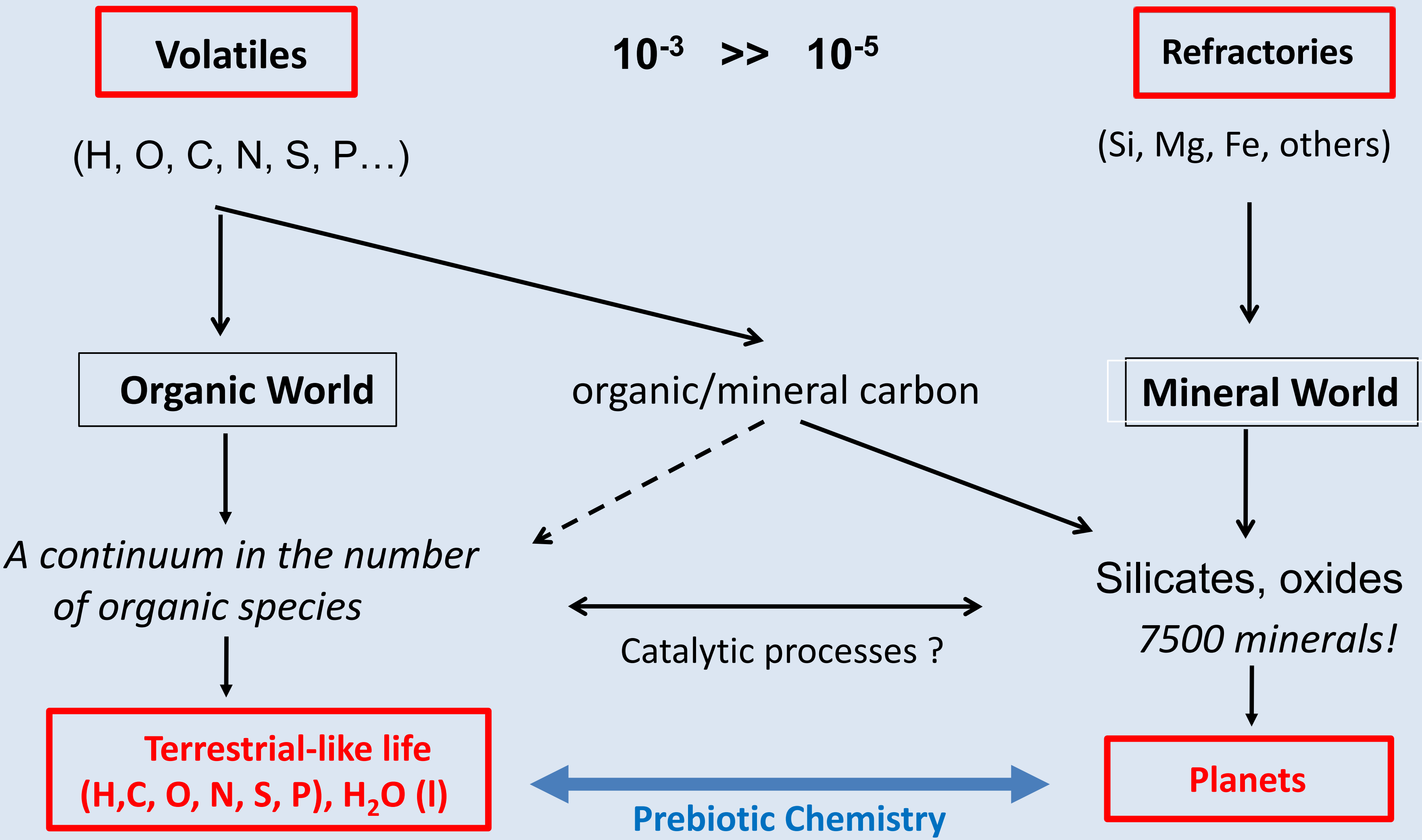


Elemental fractionation (*depletions)* observed in the diffuse ISM gas



…and *cosmic abundances*, H>O>C>N>S>P (CHNOPS for astronomers)

Chemistry in the Galaxy: the solid state factor



Molecules detected ‘gas phase) in the Interstellar medium (radioastronomy)

2 atomes	3 atomes	4 atomes	5 atomes	6 atomes	7 atomes	8 atomes	9 atomes	10 à 13 atomes
H_2	**H_2O**	**NH_3**	**CH_4**	**CH_3OH**	CH_2CHOH	H_2C_6	$(CH_3)_2O$	$(CH_3)_2CO$
CO	H_2S	**H_2CO**	SiH_4	CH_3SH	c-C_2H_4O	$HCOOCH_3$	CH_3CH_2CN	$HOCH_2CH_2OH$
CSi	HCN	H_2CS	CH_2NH	C_2H_4	$HCOCH_3$	CH_2OHCHO	CH_3CH_2OH	CH_3CH_2CHO
CP	HNC	C_2H_2	NH_2CN	H_2C_4	CH_3CCH	CH_3C_3N	CH_3C_4H	CH_3C_5N
CS	**CO_2**	HNCO	CH_2CO	CH_3CN	CH_3NH_2	CH_3COOH	HC_7N	HC_9N
NO	SO_2	HNCS	**HCOOH**	CH_3NC	CH_2CHCN	CH_2CHCHO	C_8H	CH_3C_6H
NS	MgCN	H_3O^+	HC_3N	NH_2CHO	HC_5N	CH_2CCHCN	C_8H^-	C_2H_5OCHO
SO	MgNC	SiC_3	HC_2NC	HC_2CHO	C_6H	C_7H	CH_3CONH_2	C_6H_6
HCl	NaCN	C_3S	c-C_3H_2	HC_3NH^+	C_6H^-	NH_2CH_2CN	CH_2CHCH_3	C_3H_7CN
NaCl	N_2O	H_2CN	l-C_3H_2	HC_4N				$HC_{11}N$
KCl	NH_2	c-C_3H	CH_2CN	C_5N				
AlCl	**OCS**	l-C_3H	H_2COH^+	C_5H				
AlF	CH_2	HCCN	C_4Si	H_2C_4				
PN	HCO	CH_3	C_5	C_5N^-				
SiN	C_3	C_2CN	HNC_3	c-H_2C_3O				
SiO	C_2H	C_3O	C_4H					
SiS	C_2O	$HCNH^+$	C_4H^-					
NH	C_2S	$HOCO^+$	CNCHO					
OH	AlNC	C_3N^-						
C_2	HNO	HCNO						
CN	SiCN	HSCN						
HF	N_2H^+							
FeO	SiNC							
LiH	c-SiC_2							
CH	HCO^+							
CH^+	HOC^+							
CO^+	HCS^+							
SO^+	H_3^+							
SH	**OCN^-**							
O_2	HCP							
N_2	CCP							
CF^+								
PO								
AlO								

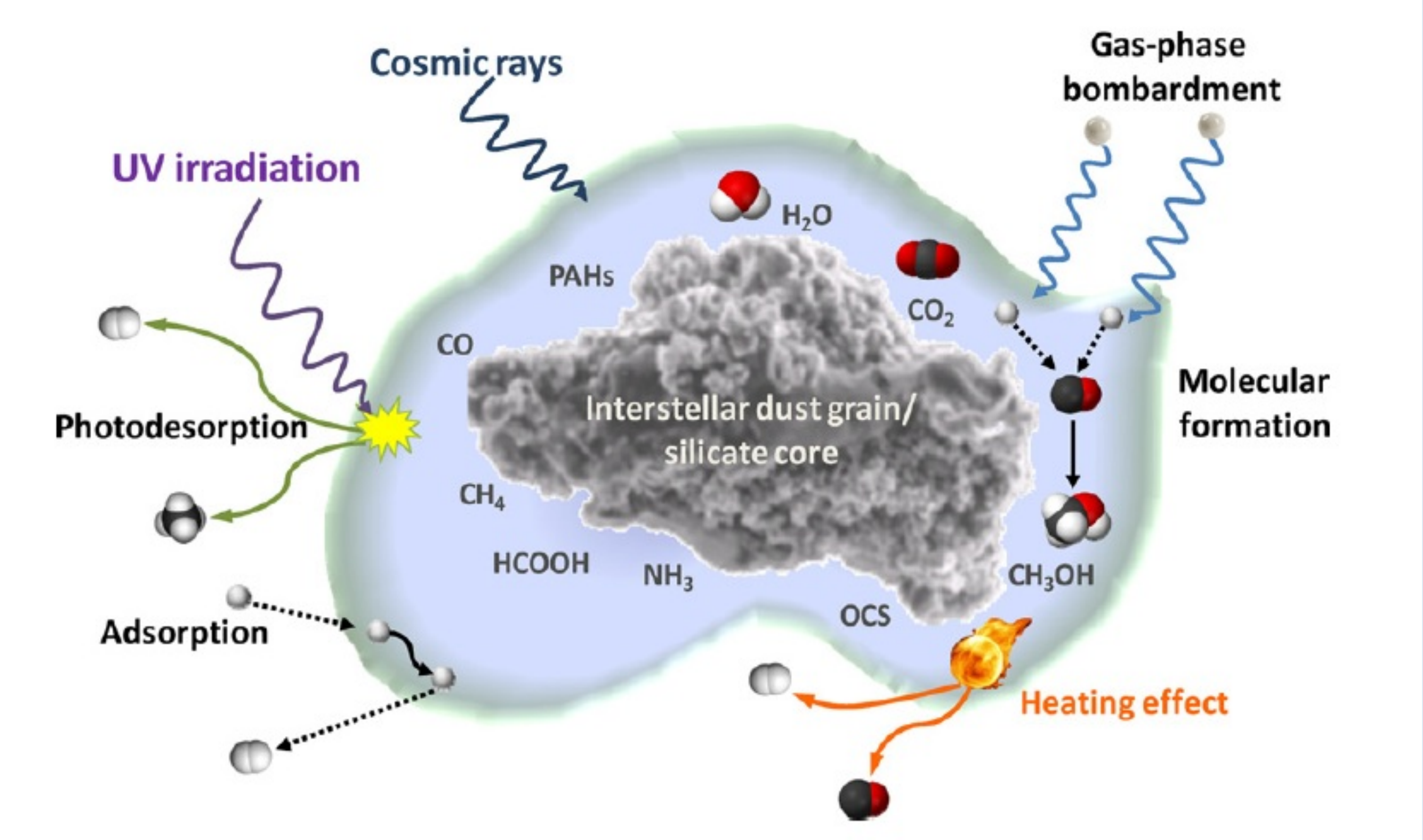
Organic molecules dominate by far

In an H-rich medium, atoms like O, C, N will easily make simple **hydrides** like H_2O, CH_4, NH_3 and **in presence of cold surfaces,** will give **ICES** (Oort and van de Hulst, 1947)

Interstellar Ices

Observed in molecular clouds, places of star formation
the *most* abundant molecular species

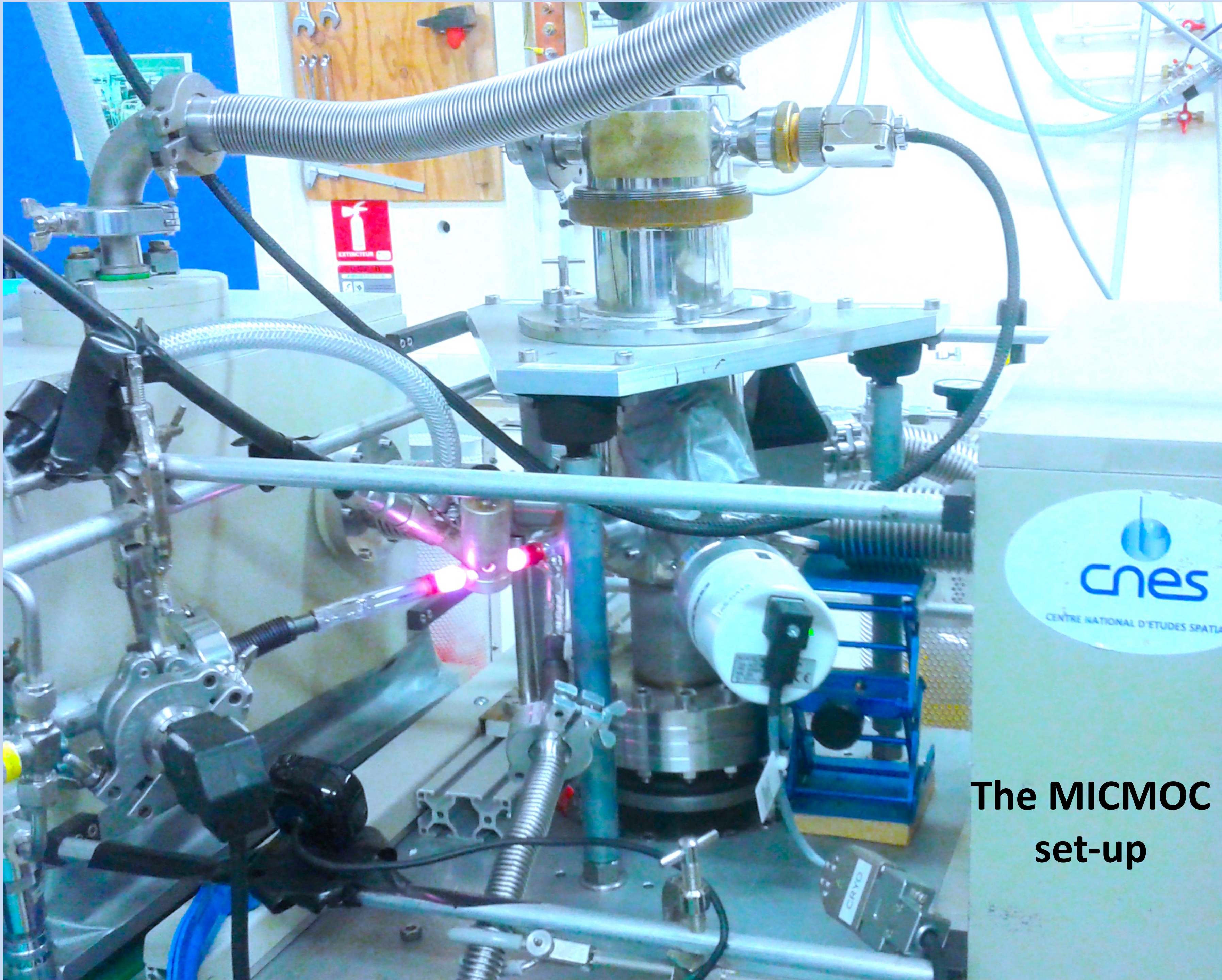
Dust grains: a simple view



T ≈ 10/40 K

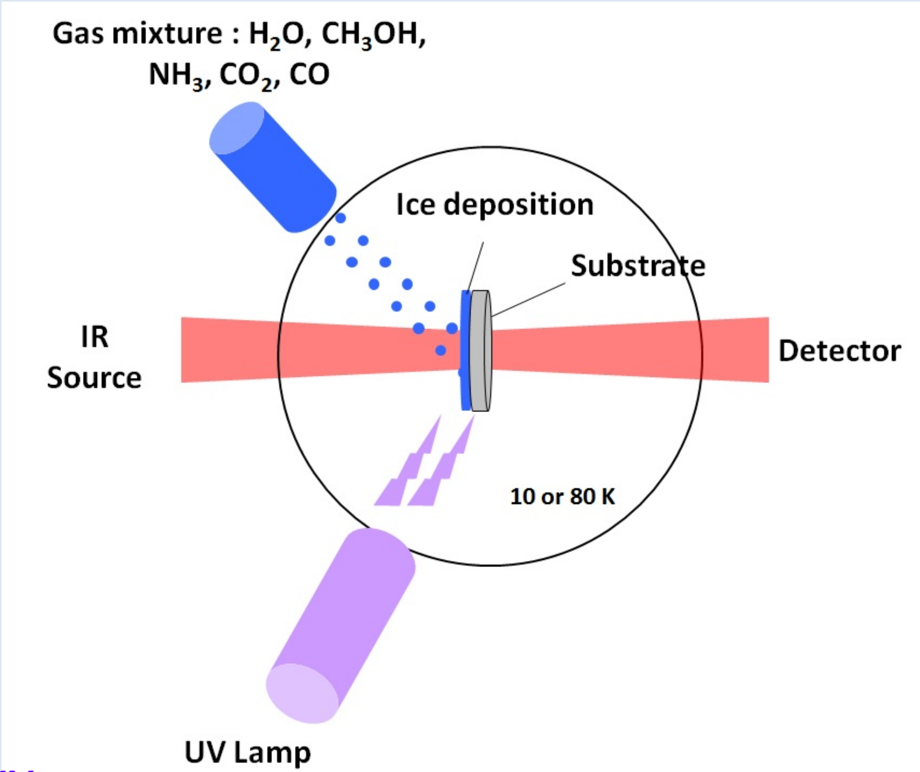
Meinert et al., Phys Life Rev (2011)

→ Surface and solid-state - bulk chemistry

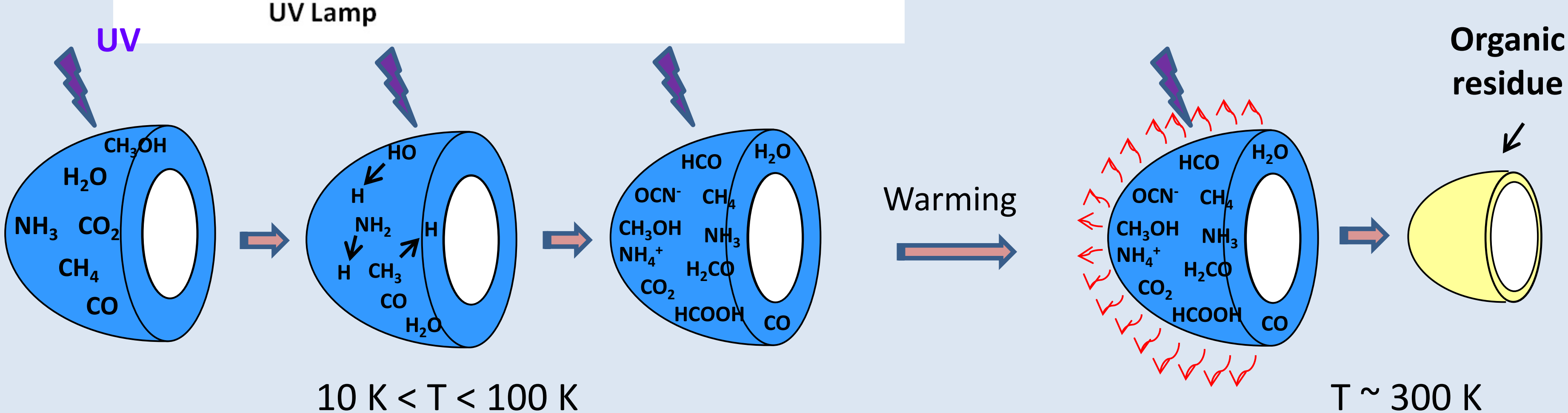


The MICMOC set-up

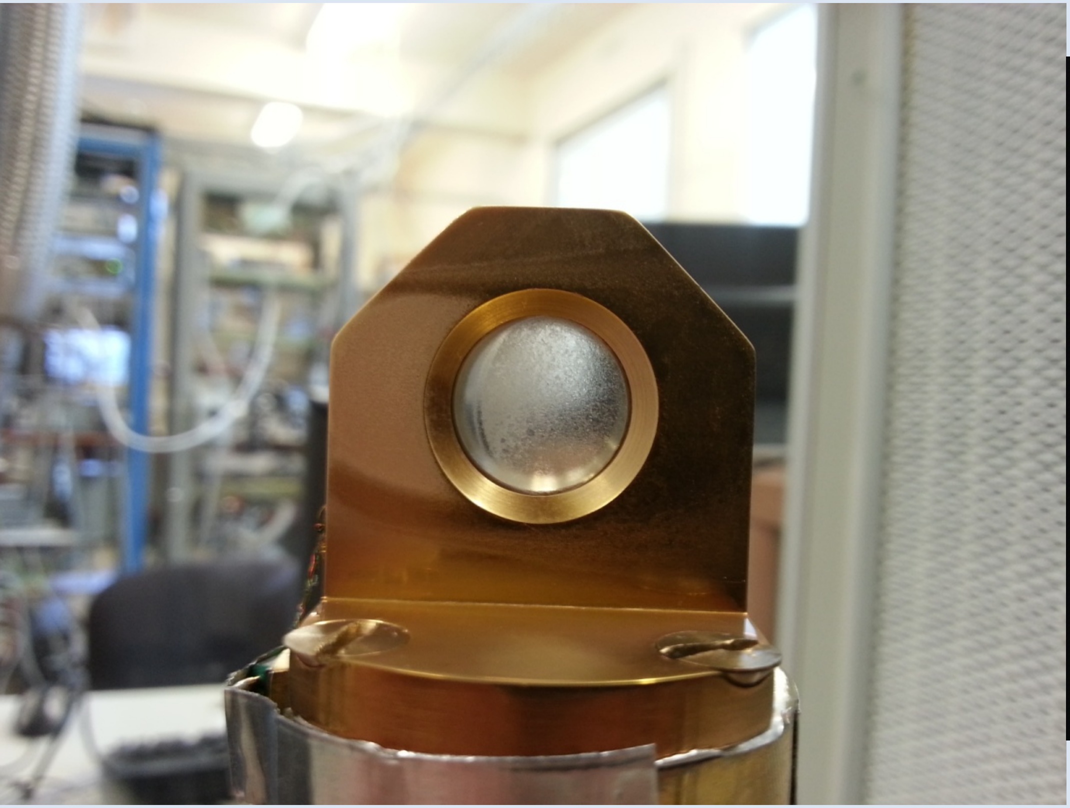
Schematics of the MICMOC experiment

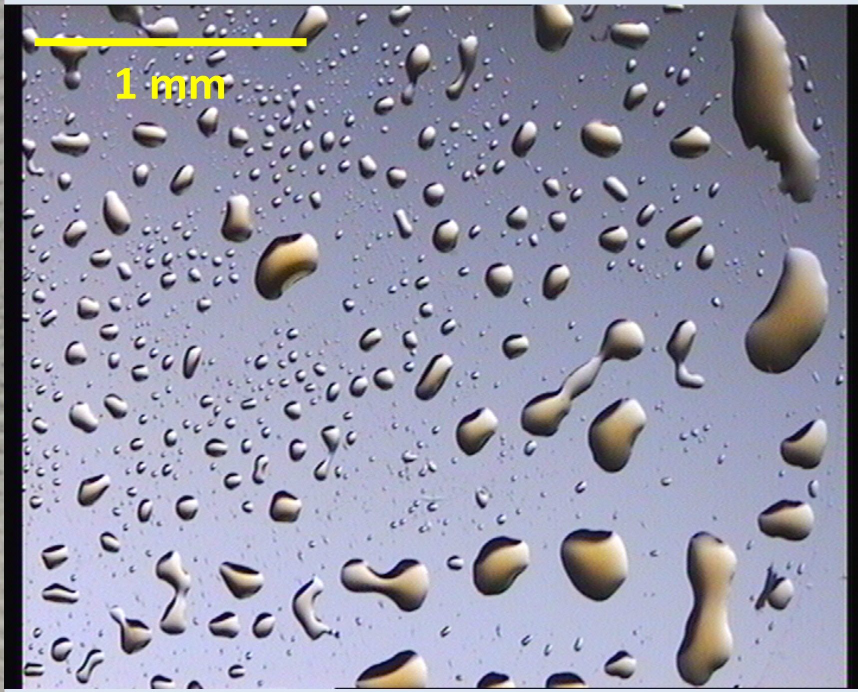


- Duration : 24 to 96h
- Monitoring of the quality of the mixture and of the deposition rate by FT-IR



The organic residue

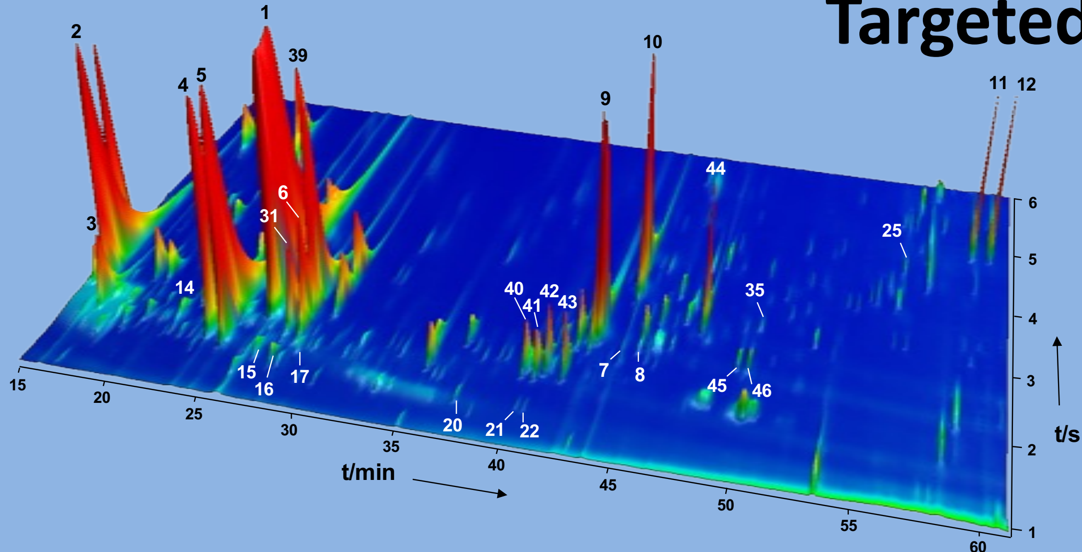




Microscope (visible) X60 (P. Modica, IAS)

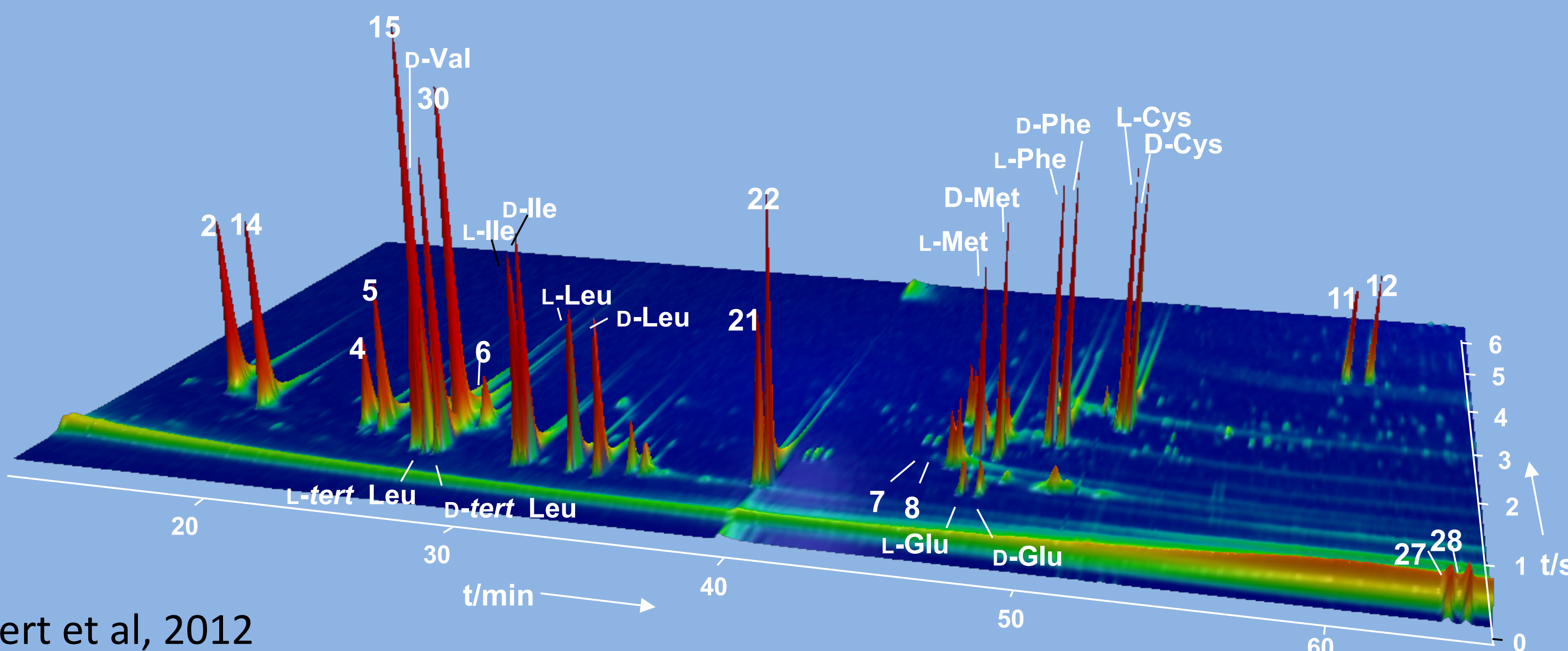
- totally soluble in usual solvents (water, methanol) – SOM
- 50 to 300 µg in each experiment (1 week to 1 month)
- Macromolecular material *(Danger et al., GCA, 2013)* + free molecules

Targeted search for amino acids



20 amino acids
(up to 6 C atoms)
+
6 di-amino acids
+
~ 10 'unknown' species

GCxGC-MS of the organic residue



Meinert et al, 2012

CHEMPLUSCHEM

ChemPlusChem 2012, 77, 186 – 191

DOI: 10.1002/cplu.201100048

N-(2-Aminoethyl)glycine and Amino Acids from Interstellar Ice Analogues

Cornelia Meinert,*[a] Jean-Jacques Filippi,[a] Pierre de Marcellus,[b] Louis Le Sergeant d'Hendecourt,[b] and Uwe J. Meierhenrich*[a]

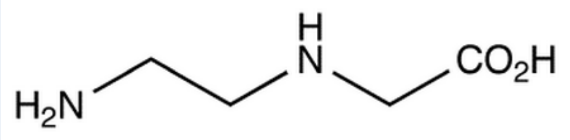
Glycine
Sarcosine
N-Methyl-D,L-alanine
α-L-Alanine
α-D-Alanine
β-Alanine
L-Serine[f]
D-Serine[f]
D,L-Amino (methylamino) acetic acid
N-Aminomethyl glycine
L-2,3-Diaminopropanoic acid
D-2,3-Diamino-propanoic acid
Triaminopropane
N-Ethylglycine
L-2-Aminobutyric acid
D-2-Aminobutyric acid
D,L-3-Aminoisobutyric acid
L-3-Aminobutyric acid
D-3-Aminobutyric acid
4-Aminobutyric acid
L-Aspartic acid
D-Aspartic acid
L-Pyroglutamic acid[h]
D-Pyroglutamic acid[h]
N-(2-aminoethyl) glycine
3-Amino-2-(aminomethyl) propionic acid[i]
L-2,4-Diaminobutyric acid[j]
D-2,4-Diaminobutyric acid[j]
Glycine-glycine[j]
D,L-Proline
L-Norvaline
D-Norvaline
Aminomethyl butanoic acid[k]
5-Aminovaleric acid
D,L-Hydroxyproline
L-Aminomethyl pentanoic acid[l]
D-Aminomethyl pentanoic acid[l]
Aminomethyl pentanoic acid[l]
Unidentified

N-(2-Aminoethyl)glycine and D,L-2,4-diamino-butyric acid may be involved in PNA prior to RNA world.

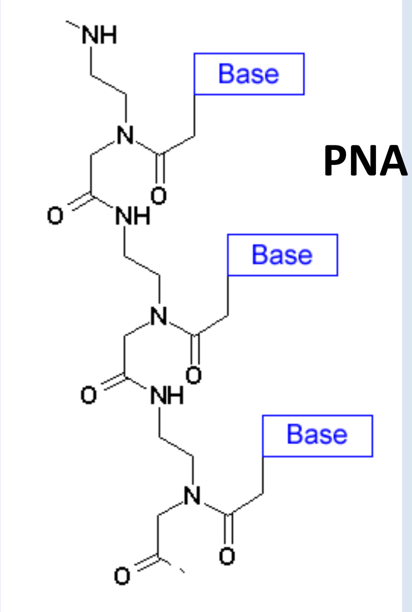
Numerous «prebiotic» molecules

- About 30 **amino** and **di-amino acids**

N-(2-aminoethyl)glycine



Meinert et al., ChemPlusChem, 77, 186 (2012)

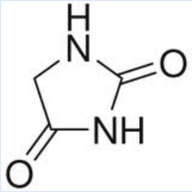


PNA

Nielsen, OLEB (1993)

- Important **intermediates/precursors**

Hydantoin



(Formation of poly- and oligo-peptides)

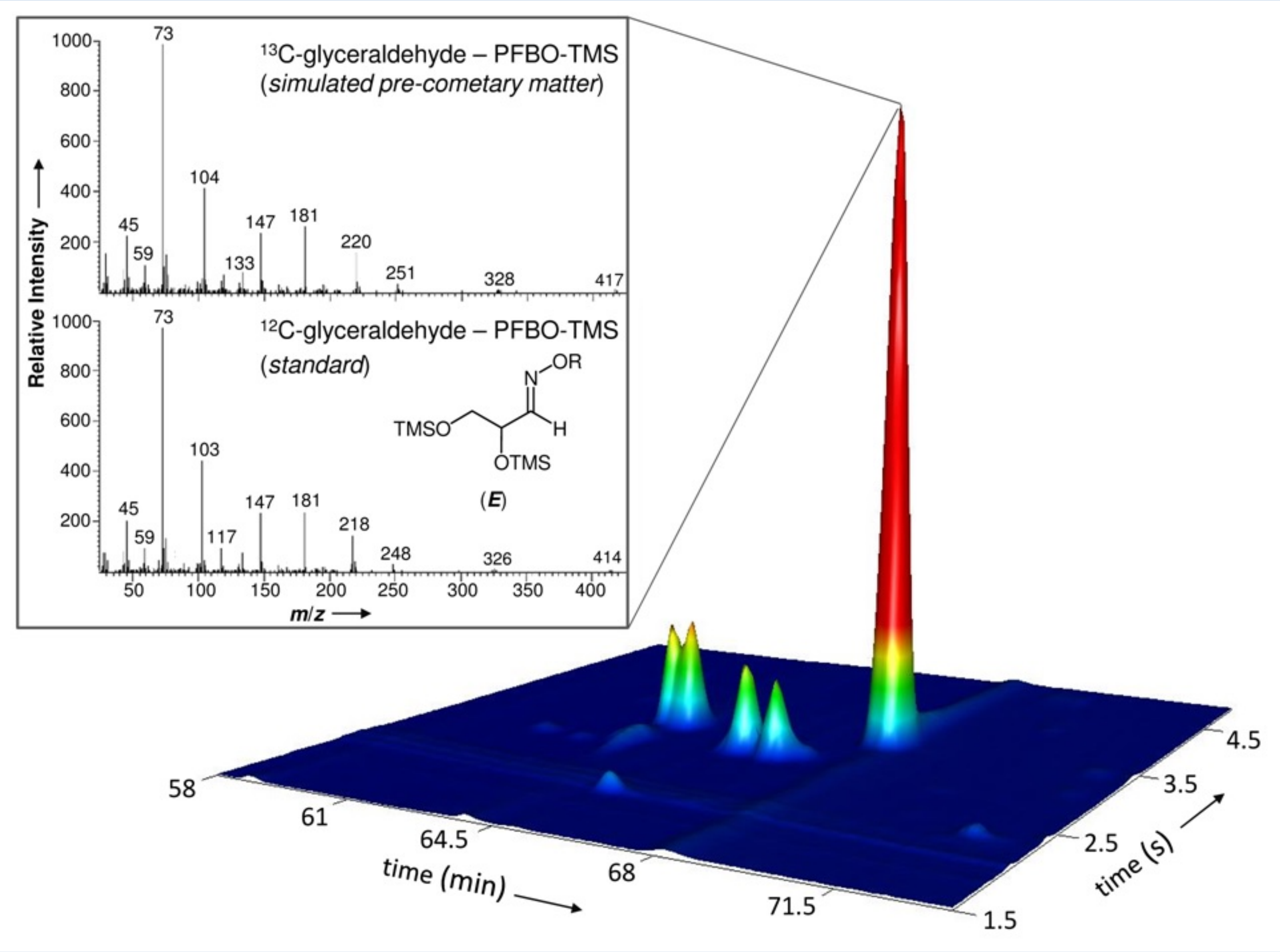
de Marcellus et al., Astrobiology, 11, 847 (2011)

Follow-up work

➔ Analogue of **soluble organic matter (SOM)** of meteorites (carbonaceous chondrites) and **comets** (ROSETTA)? Precursor of **insoluble organic matter (IOM) ?** (*de Marcellus et al, MNRAS, 2017*)

➔ **Search for sugars**

Targeted search for glycolaldehyde and glyceraldehyde



de Marcellus, Meinert et al, PNAS, *112 , 965 (2015)*

Detection of ribose in ices-organic residues

RESEARCH

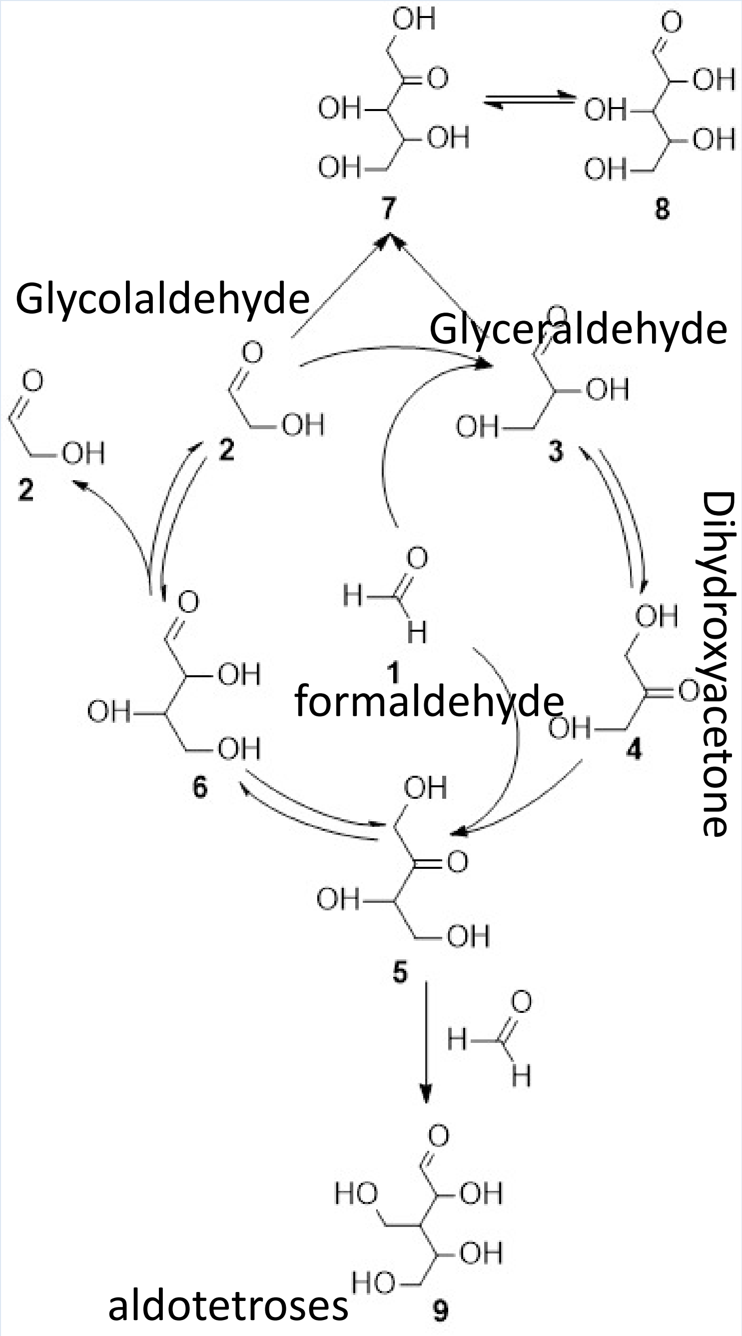
REPORT

ASTROCHEMISTRY

Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs

Cornelia Meinert,[1*] Iuliia Myrgorodska,[1,2] Pierre de Marcellus,[3] Thomas Buhse,[4] Laurent Nahon,[2] Soeren V. Hoffmann,[5] Louis Le Sergeant d'Hendecourt,[3] Uwe J. Meierhenrich[1*]

Meinert et al, Science, 352 (2016)



Other aldopentoses detected : threose, arabinose, lyxose)
➔ different nucleic acids possible

« Formose » autocatalytic reaction ?

Non-directed and natural reaction (MIS, comets)
as proposed by the MICMOC simulations
Miller-type approach at the « cosmic » scale

Significance for Prebiotic Chemistry

Ices non-directed simulations (MICMOC)

Inert 0

Astrochemistry

Amino Acids → Oligopeptides → Proteins → Proto-metabolism

Pre-prebiotic Chemistry
(space environments)

Sugars → Ribonucleotides → ARN → Proto-genes

0

Prebiotic Chemistry
(planetary environments)

0.1

0.5

Co-evolution?

Proto-metabolism ↔ Proto-genes

0.9

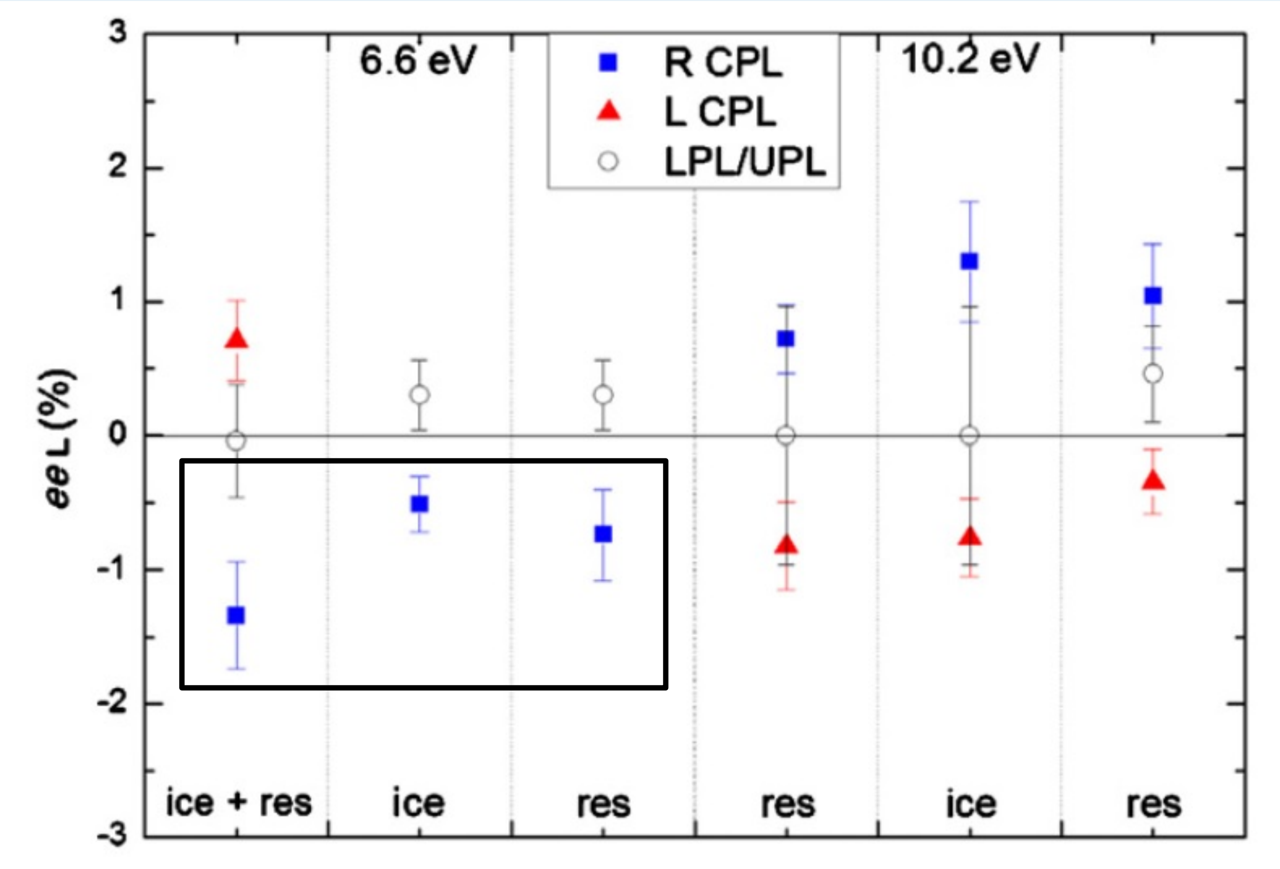
Living 1

Metabolism

Biology

Genetic Code

Enantiomeric excesses in ^{13}C-Alanine



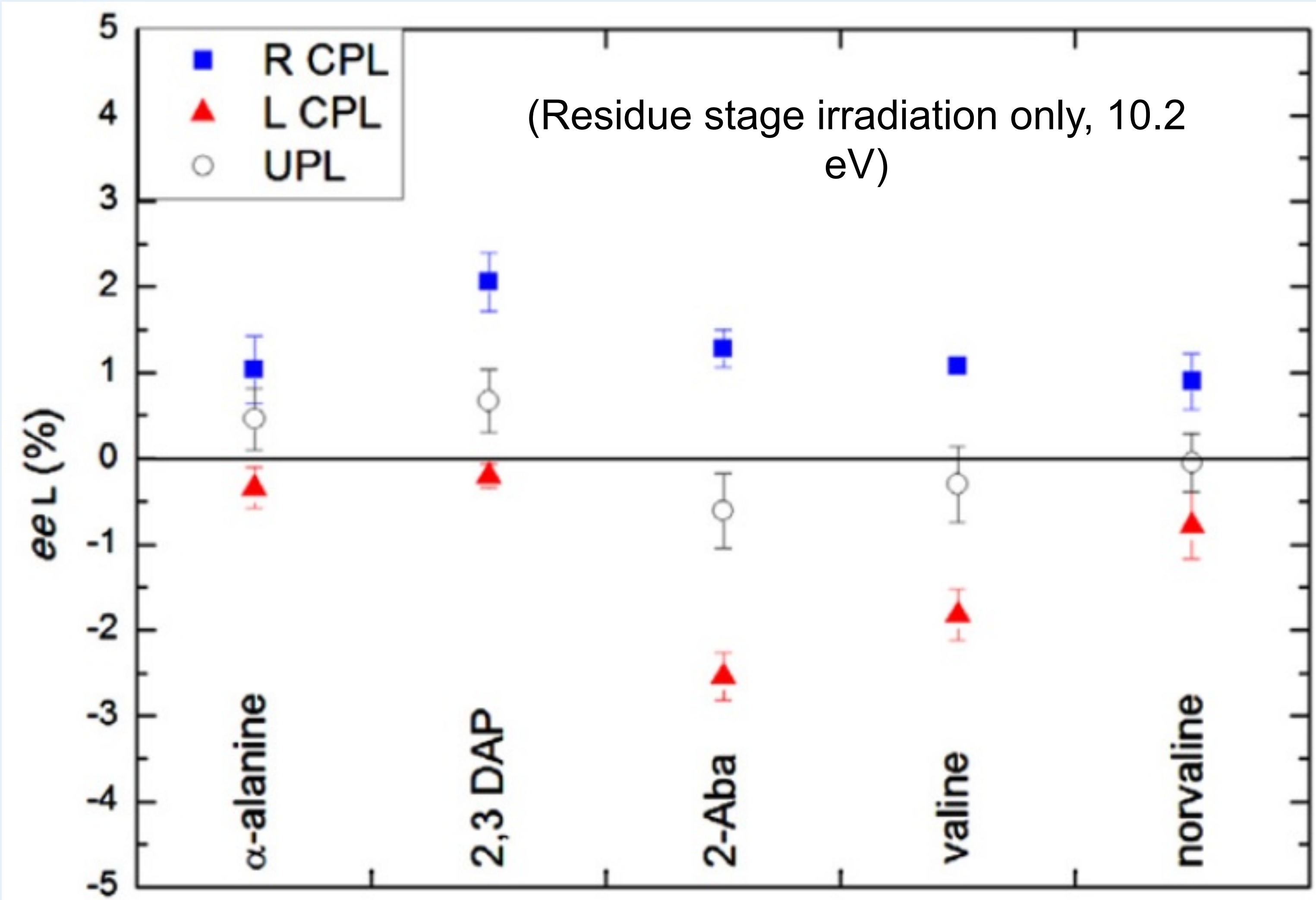
• R-CPL irradiation, same wavelength (6.6 eV)
- ice only
- residue only

} e.e. of the same sign

de Marcellus et al 2011

➔ **Chiral precursors** (of amino acids) already **formed in the ice** (78 K)
➔ **Chiral molecules** should be **present in the ISM**

Enantiomeric excesses in ^{13}C-amino acids



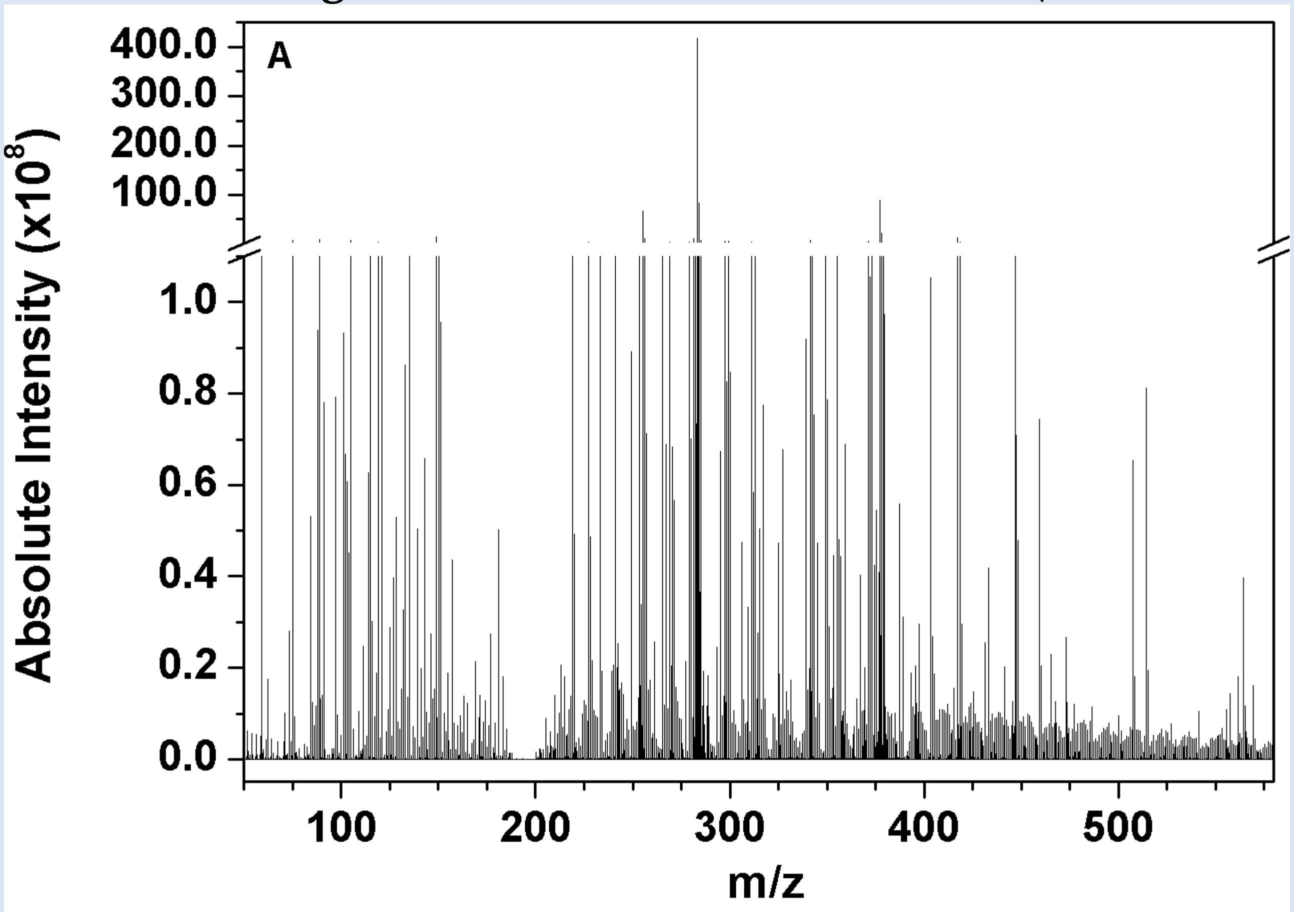
Sign of the e.e.s

- Depends on the helicity of CPL
- Constant for the 5 amino acids

Modica et al, 2014

VHRMS (orbitrap) analyses of organic residues ($H_2O/NH_3/CH_3OH$ =3/1/1)

Collaboration with G. Danger, PIIM, Marseille, R. Thissen (IPAG, Grenoble, France)

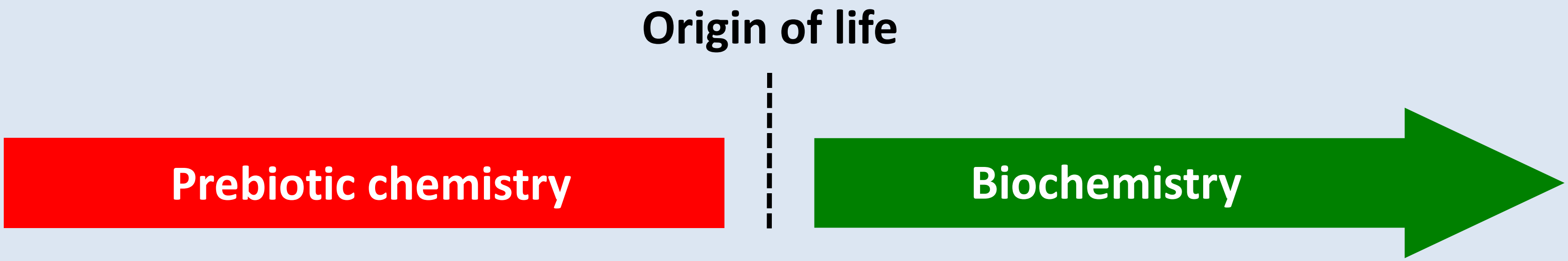


Negative ESI mode = [M-H]$^-$ analysis

Molecules with proton donor chemical functions (e.g. carboxylic acid –COOH)

Danger et al., 2013, 2016, GCA, 118 **, 184-201;** 189, **184 – 196, for comparison with meteoritic SOM (large molecules up to 4000 uma are also detected)**

A search for the origin of life



Prebiotic chemistry: How form complex structures in molecular terms or chemical networks.
How can evolve these chemical networks toward biochemical network
(chemical evolution, selectivity, replication…).

A search for the origin of life

Origin of life

Prebiotic chemistry | **Biochemistry**

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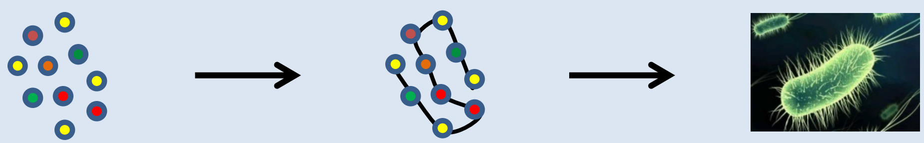
1- Building blocks from extraterrestrial and planetary reservoir.



A search for the origin of life

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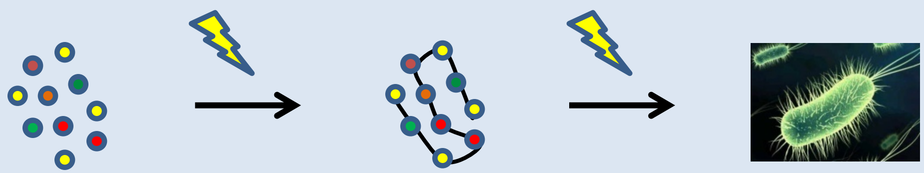

2- Free energy (UV/Vis photons, Pascal (2017)

A search for the origin of life

Origin of life

Only in specific environment

Prebiotic chemistry | **Biochemistry**

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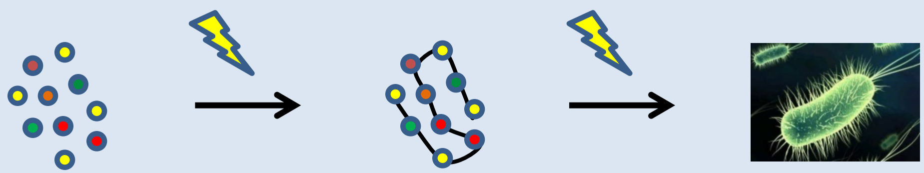


2- Free energy (low entropy, (UV-Vis photons) R. Pascal 2017

3- Self-organization of organic matter and emergence of far from equilibrium chemical systems

Chemical evolution and selectivity.

Pascal R., *J.Syst.Chem.*, **3** (2012) 3

Pross A., *J.Syst.Chem.*, **2** (2011) 1-14

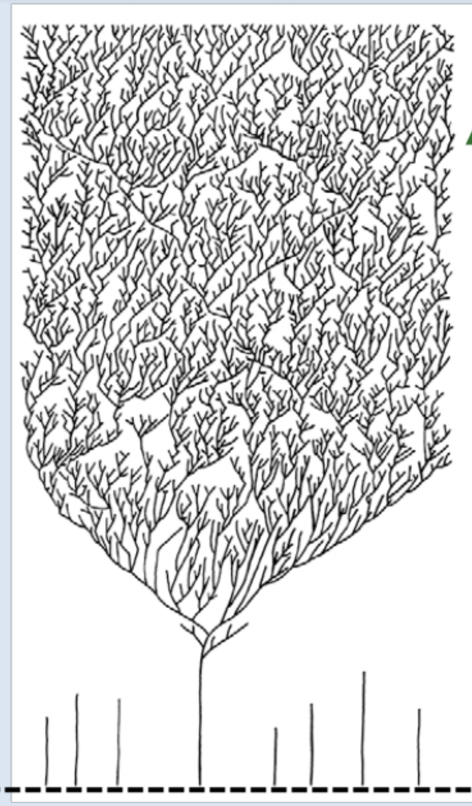
Pross et al., *Open Biology*, **3** (2013) 120190

FAPCOME project: From Astrochemistry to Prebiotic Chemistry: Organic Matter Evolution

G. Danger

R. Pascal

Only in specific environment



Continuous Evolution under DKS

Biochemistry

A. Pross

Prebiotic Chemistry

Emergence of REPLICATORS

MILLER [2.0]

exogeneous environments

Molecular threshold

Thermodynamic equilibrium

Abiotic chemistry

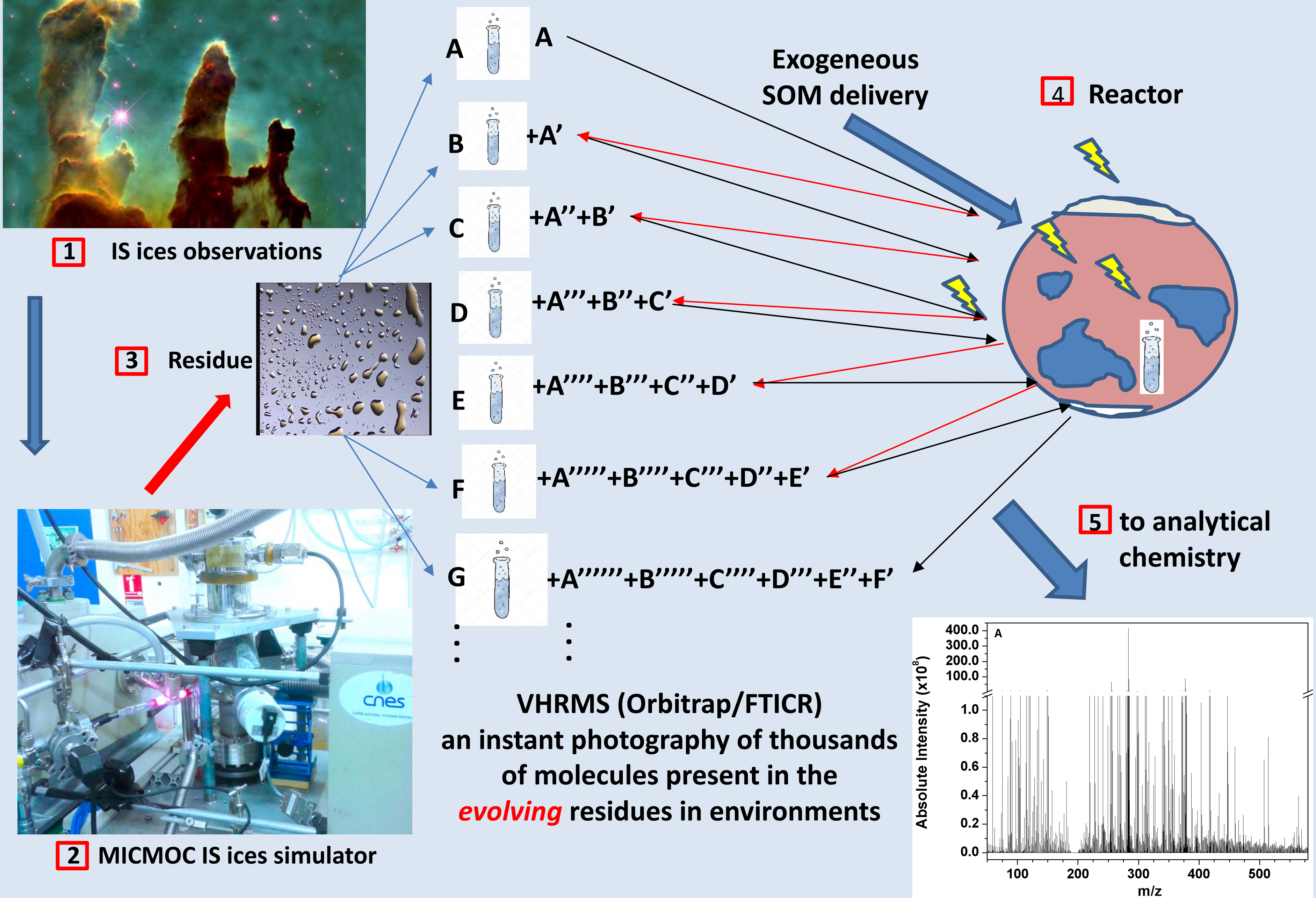
L. d'Hendecourt

Present-day MICMOC

MILLER [2.0]

**A semi-open
reactor for prebiotic chemical evolution
in a « natural » environment**

MILLER [2.0] ?


1 IS ices observations
2 MICMOC IS ices simulator
3 Residue
A A
B +A'
C +A''+B'
D +A'''+B''+C'
E +A''''+B'''+C''+D'
F +A'''''+B''''+C'''+D''+E'
G +A''''''+B'''''+C''''+D'''+E''+F'
Exogeneous SOM delivery
4 Reactor
5 to analytical chemistry
VHRMS (Orbitrap/FTICR)
an instant photography of thousands of molecules present in the *evolving* residues in environments
A
Absolute Intensity (x10^8)
400.0
300.0
200.0
100.0
1.0
0.8
0.6
0.4
0.2
0.0
100
200
300
400
500
m/z

Conclusions

Astrophysical and cosmochemical relevance

- molecules of the ISM (ices around protostars, hot cores)
- extraterrestrial organic matter (soluble part (SOM) from primitive meteorites, comets…
- *enantiomeric excesses* in synthetized amino acids with UV-CPL in star forming regions (de Marcellus et al, 2011; Modica et al, 2014)

Astrobiological relevance (exogenous delivery scenario)

- formation in the same samples (via the same processes) of various molecules of "prebiotic" interest: amino acids, sugars, urea, hydantoin, etc.
- Delivery on telluric planets in once, at *the same time*

- *need for far from equilibrium non directed experiments-MILLER [2.0] in planetary environments*

Acknoweldgments to many collaborators

P. de Marcellus (2011), P. Modica (2014), I. Mygodorska (2016) – PhD's

Uwe Meierhenrich, ICN
Conny Meinert, ICN
University of Nice, France

Analytical Chemistry
GCxGC-MS as a « chemical telescope »

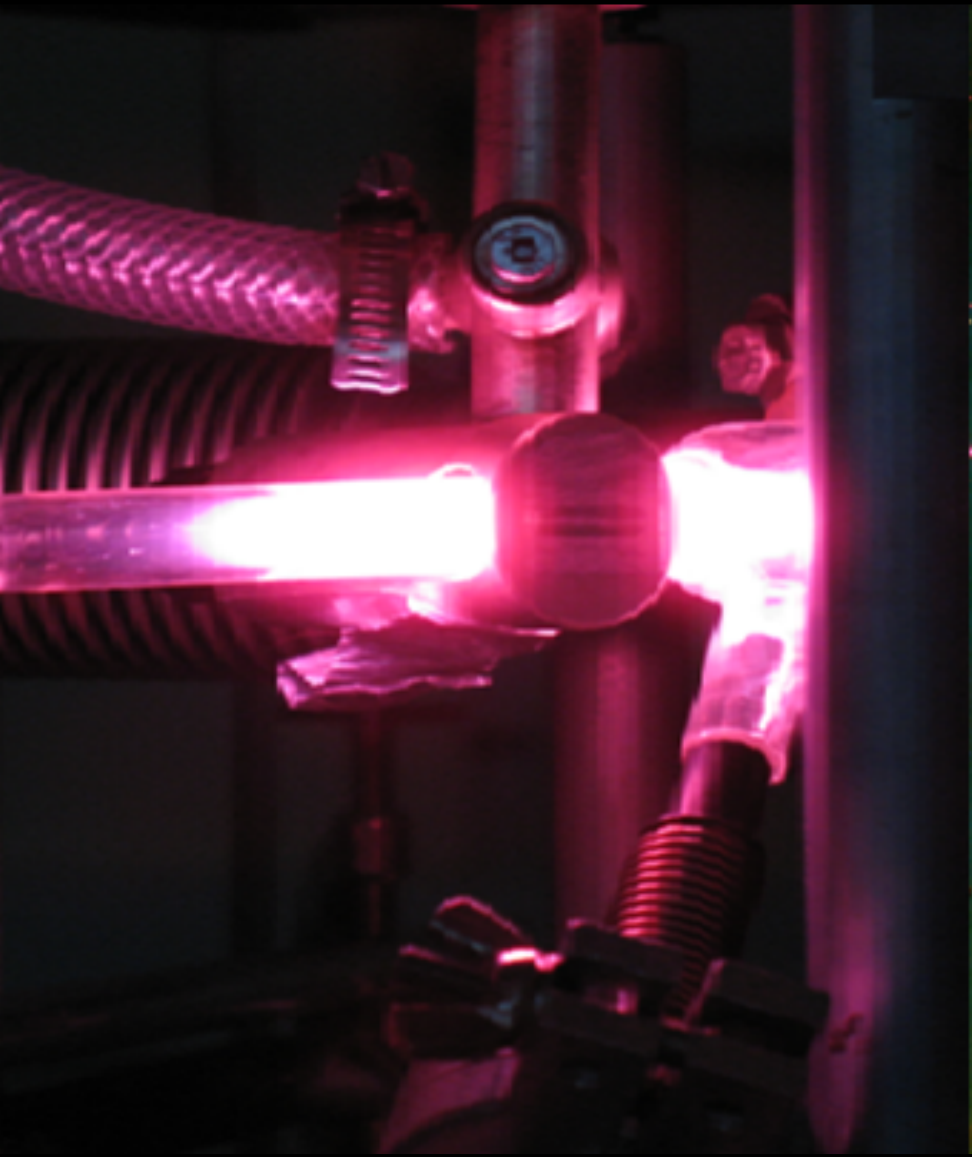
Zita Martins (UCL) **Meteorites - GCMS**

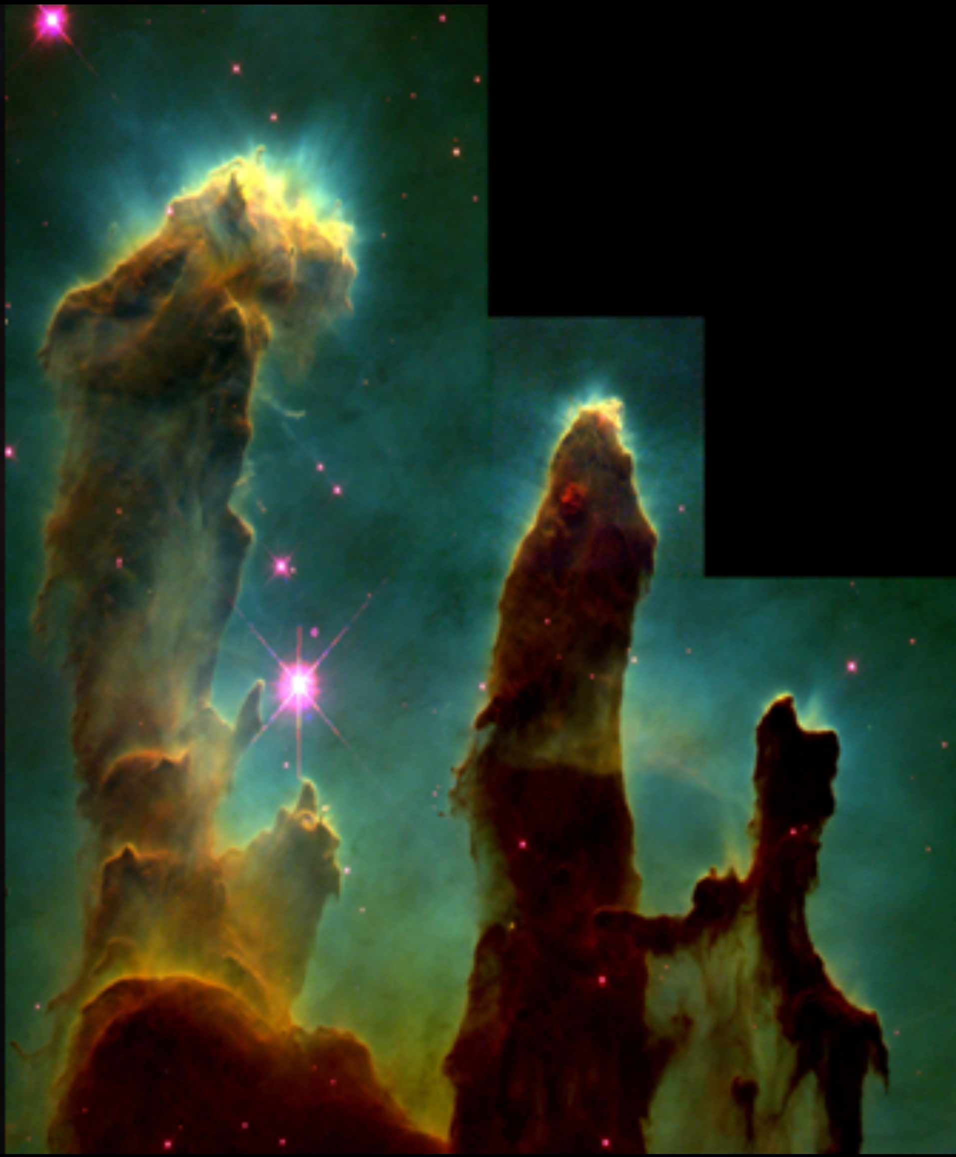
Laurent Nahon (SOLEIL synchrotron) **Chirality and enantiomeric e.e's**

Grégoire Danger, PIIM, Marseille, France
Robert Pascal, IMMBC, Montpellier, France
MILLER[2.0]

cnes for financial support

FULLY INTERDISCIPLINARY FIELD





Thank you!