Formation and evolution of organic matter in the solar system

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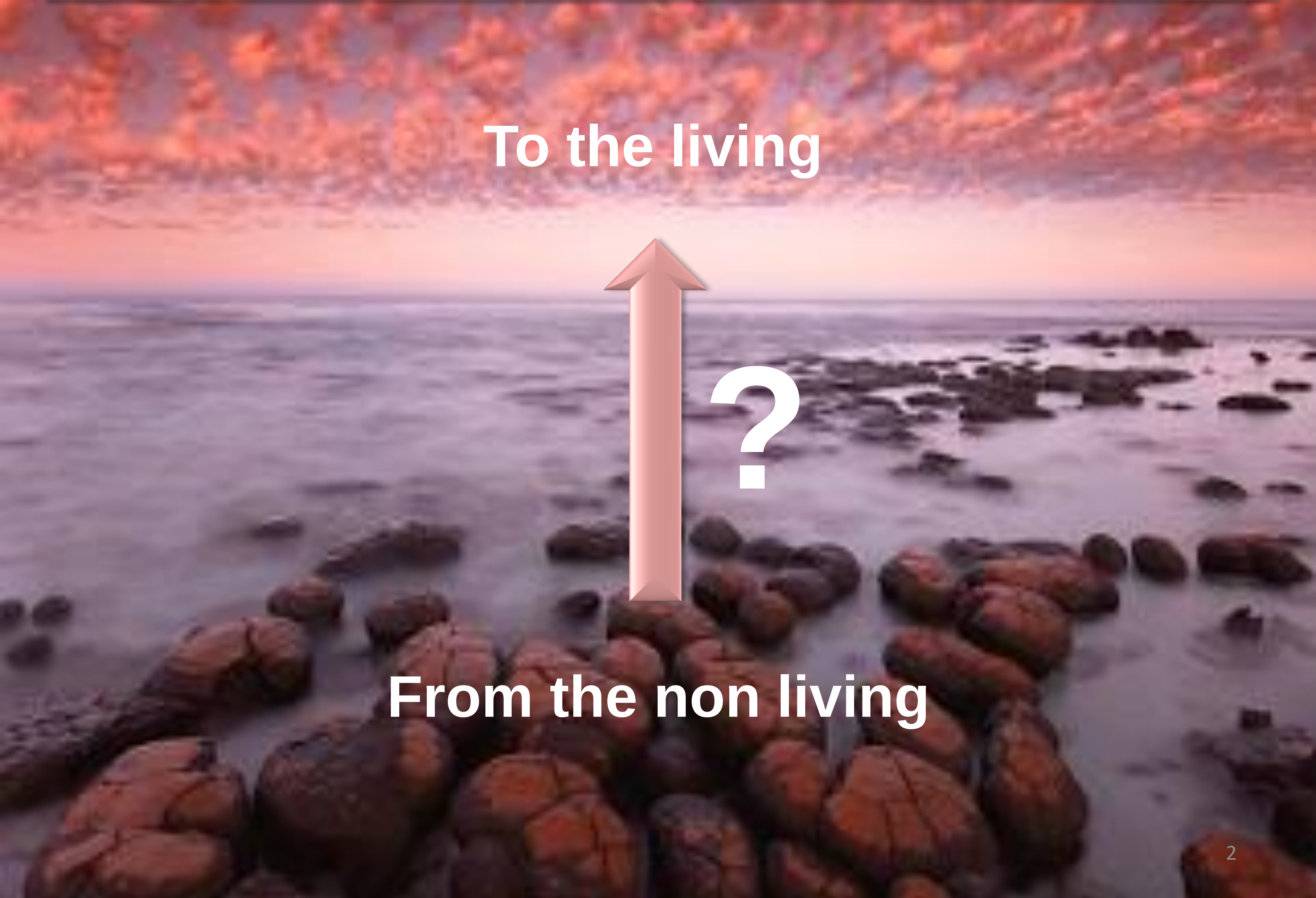
The aim : answer the question of the transition

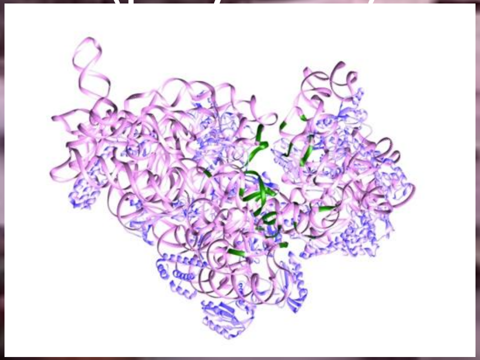


Chemical evolution on the early Earth
A bottom-up approach

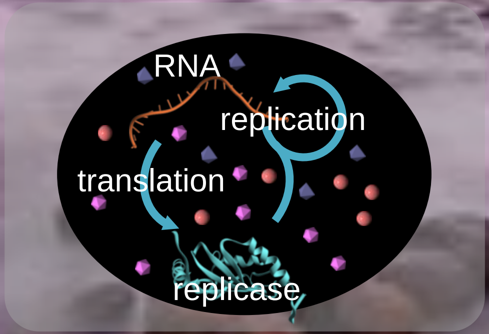
small molecules
(*i.e.* ammonia, CO_2, methane)

building blocks

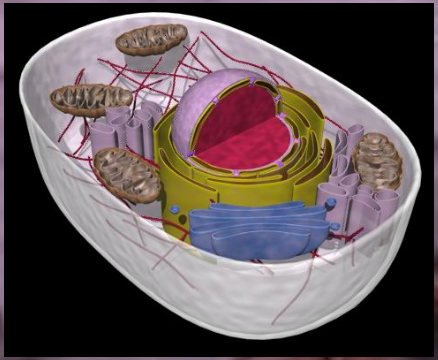
macromolecule
(polymers)



primitive cell

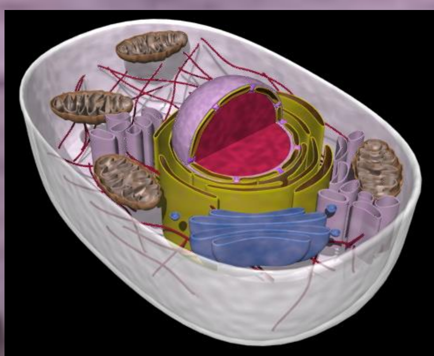


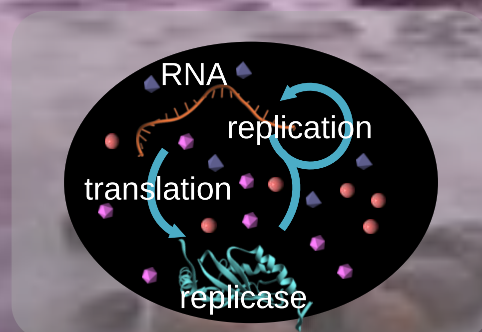
Living cell

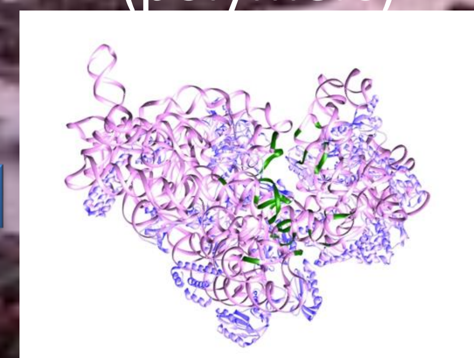


Chemical evolution on the early Earth
A bottom-up approach

small molecules (*i.e.* ammonia, CO_2, methane) → building blocks → macromolecule (polymers) → primitive cell → Living cell





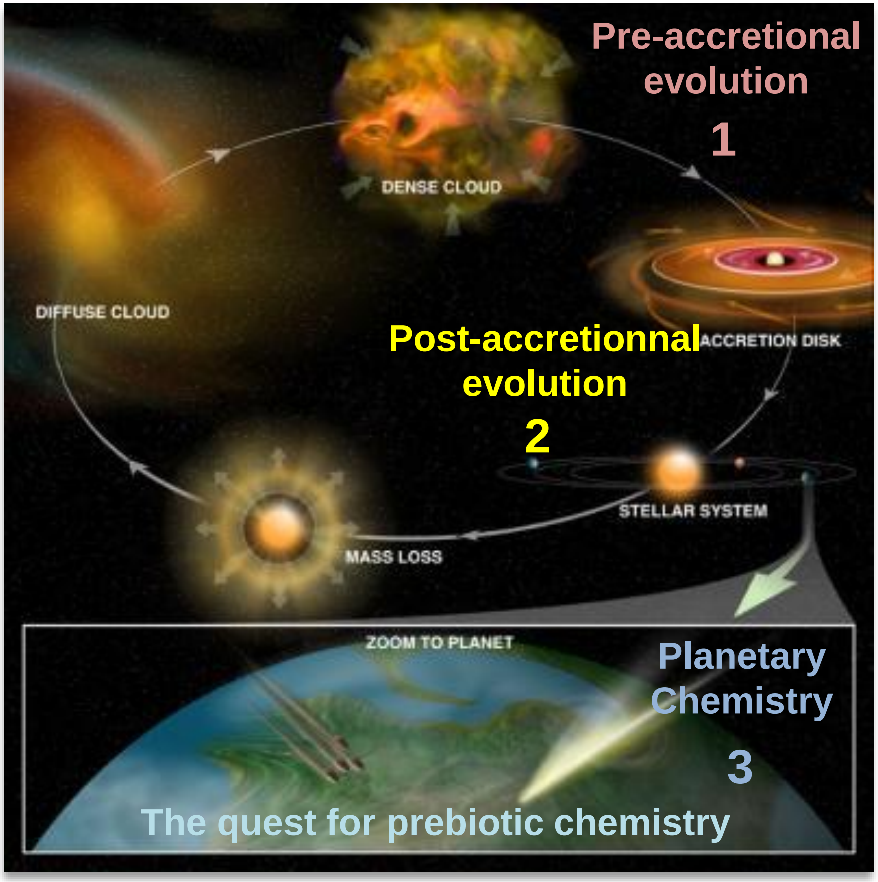


Building blocks (organics) on Early Earth: where could they come from?

Meteorites : Key pieces of evidence in Astrobiology

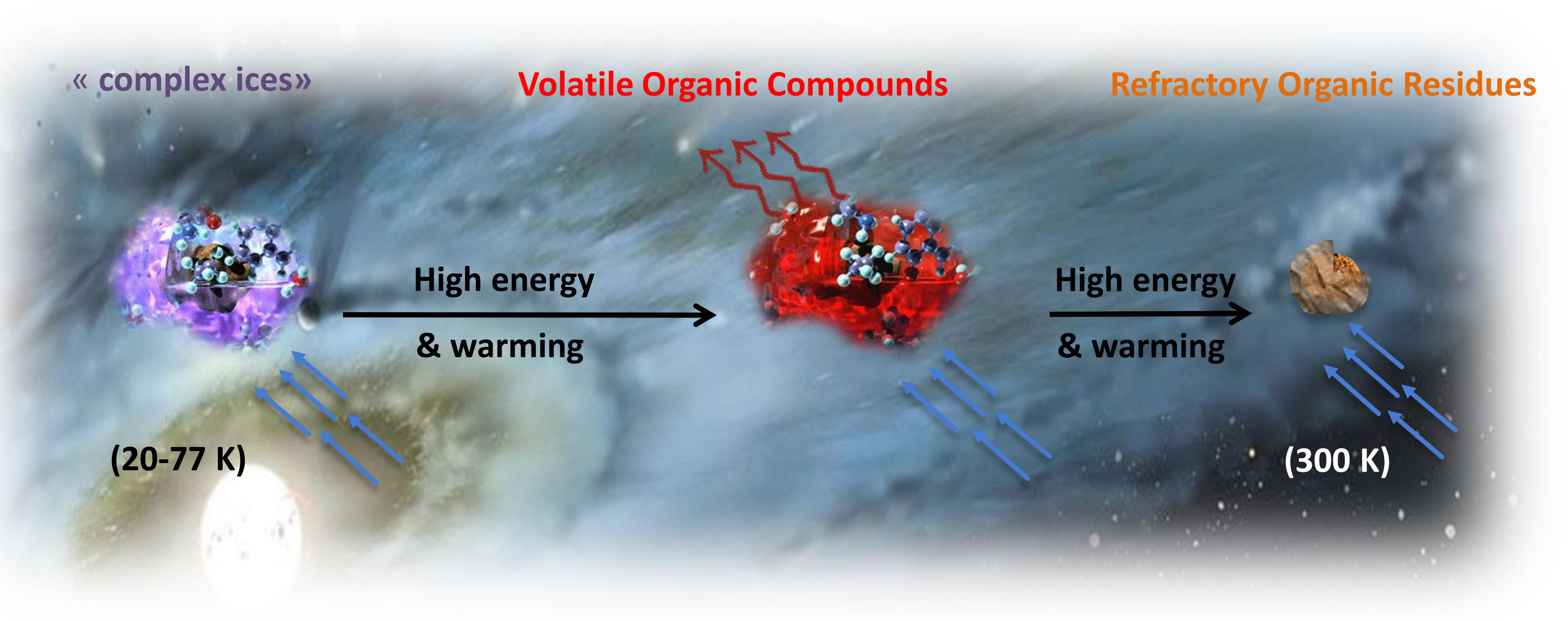
Reservoir of carbonaceous matter

From Astrochemistry to Prebiotic Chemistry: Organic Matter Evolution

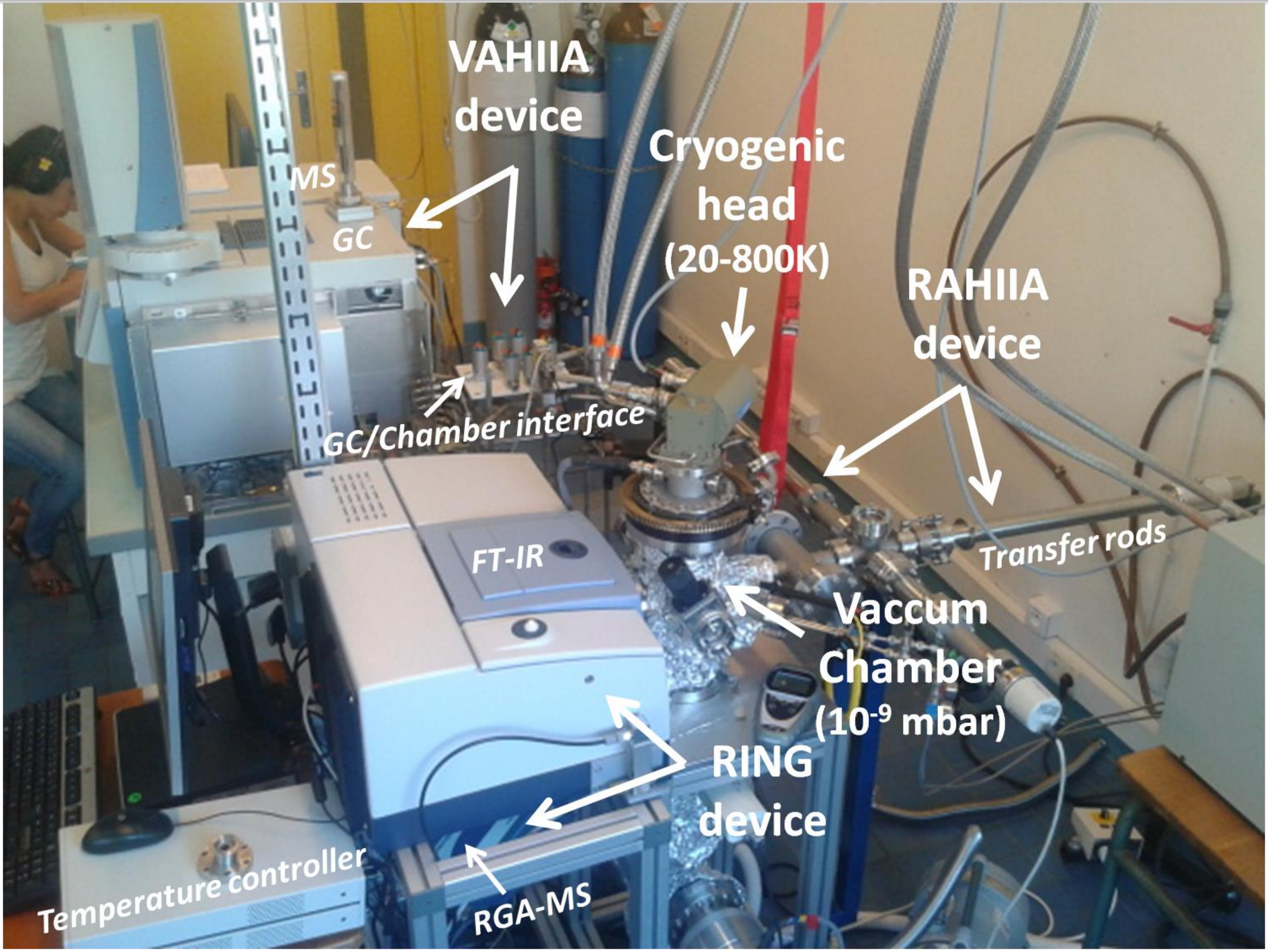


- ***Pre-accretional process: What sort of organic matter is generated***
- ***Post-accretional process: How the pre-accrational organic matter evolved***
- ***Planeraty Chemistry: what conditions for a prebiotic chemistry***

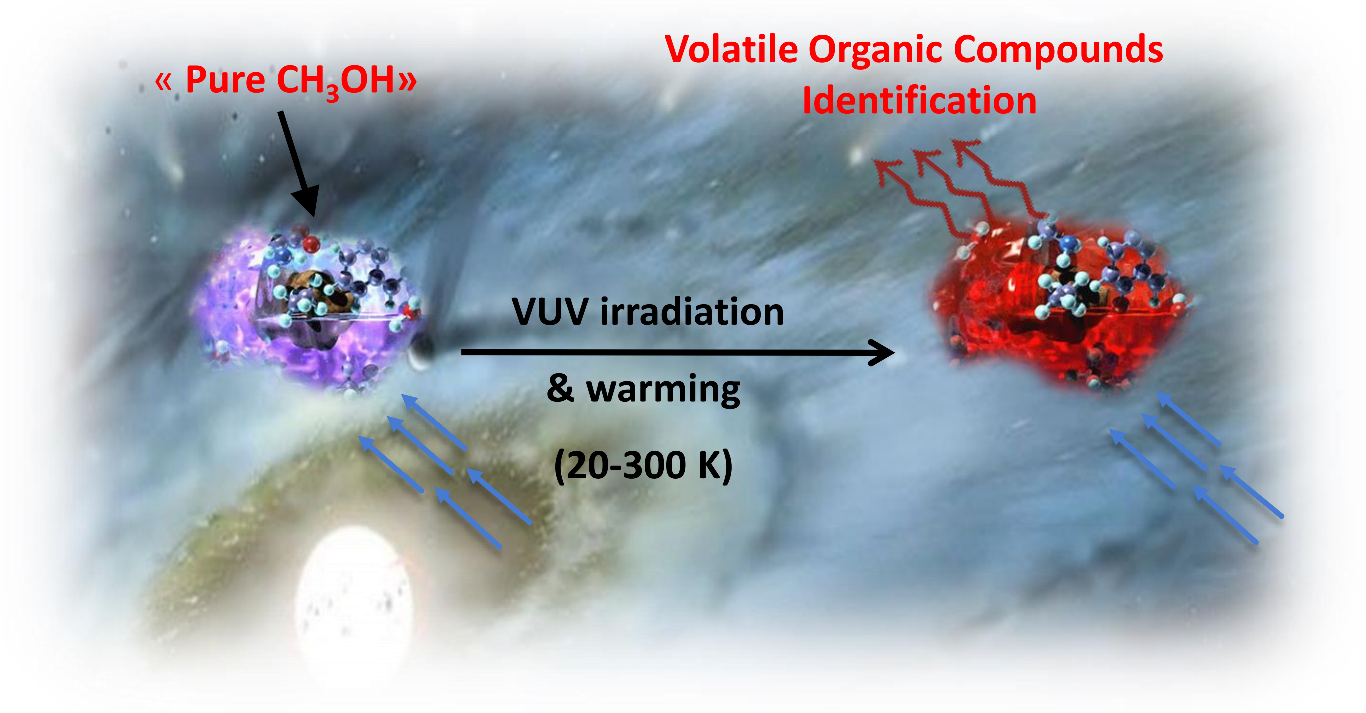
Astrophysical ices as a source of molecular diversity



Laboratory experiments: Simulate Pre-accretional processes



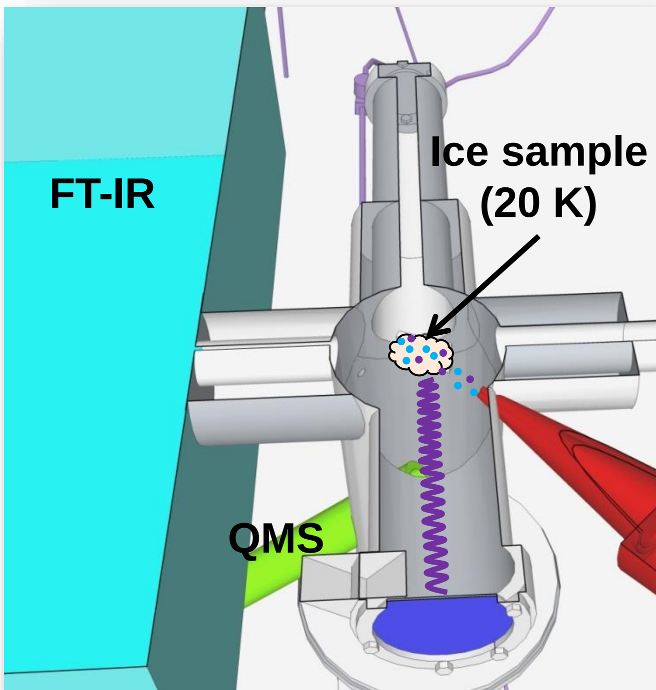
Methanol CH_3OH
An abondant source of reduces carbon in interstellar and cometary ices



Principle of the VAHIIA device
Recovery and analysis of VOC by GC-MS

ANR-12-JS08-0001
2012-2015

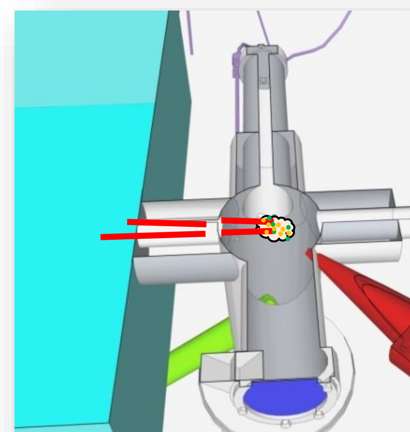
Vacuum chamber (10^{-9} mbar)



Ice formation in simulated conditions

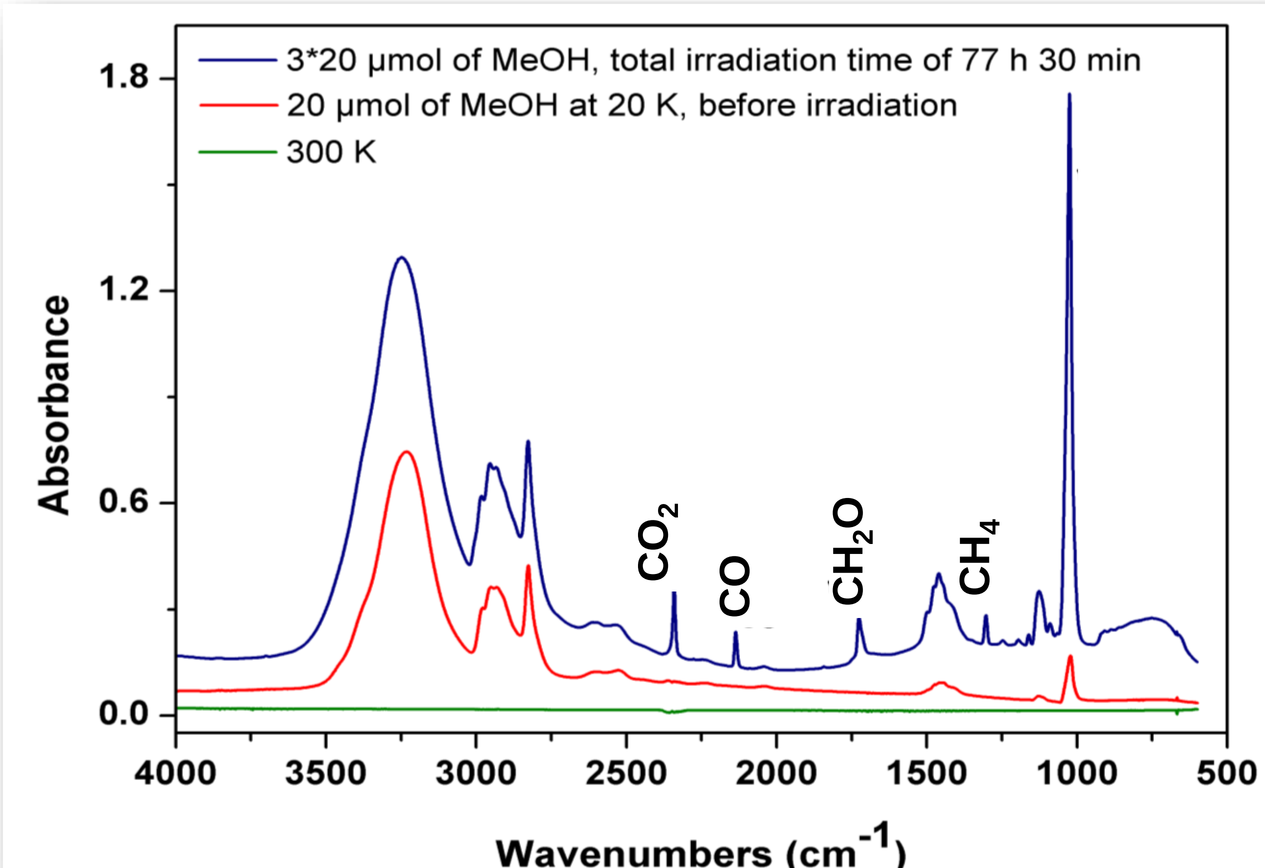
GC-MS

FTIR



Abou Mrad et al., Anal. Chem., 2014, 86, 8391

Methanol CH_3OH
Analysis with the VAHIIA system

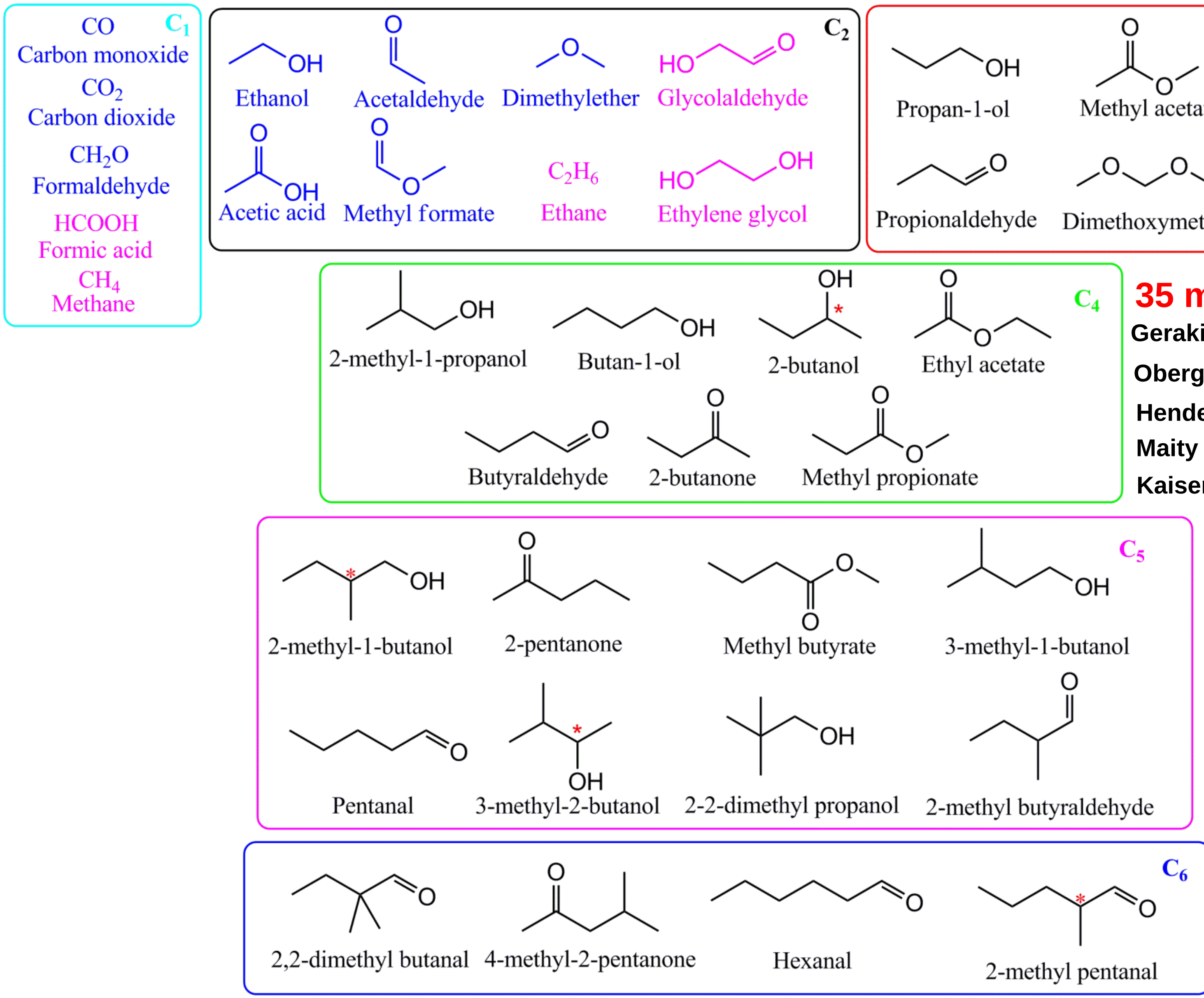


Infrared spectroscopy at 20K:

Non ambiguous Identification of CH_4, CO, CO_2 & formaldehyde

Abou Mrad et al., MNRAS, 2016, 458,1234

Methanol CH_3OH
Analysis with the VAHIIA system – products identified



35 molecules identified

Gerakines et al., A&A, 1996, 312, 289

Oberg et al., A&A, 2009, 504, 891

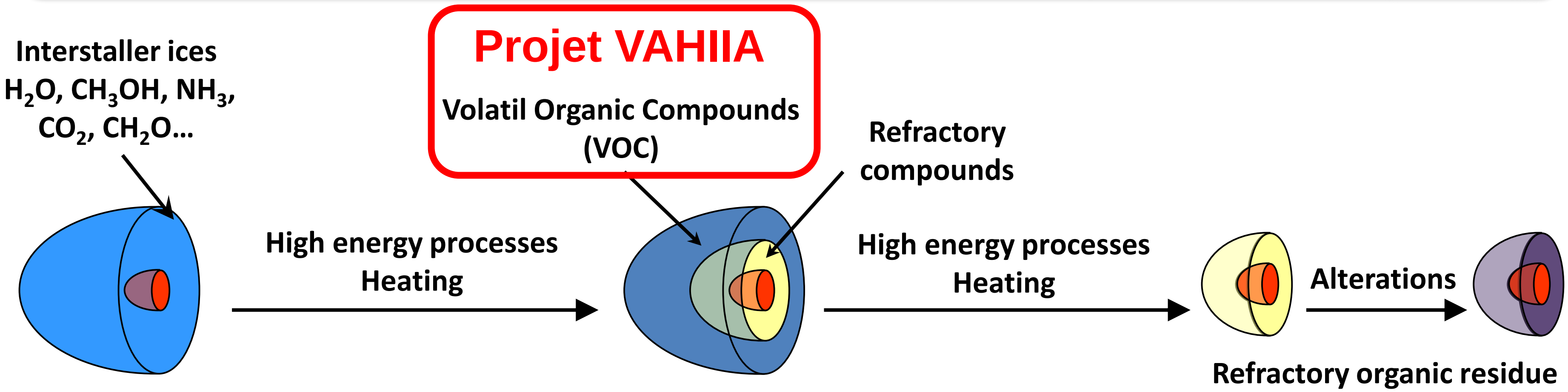
Henderson et al., ApJ, 2015, 800, 66

Maity et al., PCCP, 2015, 17, 3081

Kaiser, Angew. Chem., 2015, 54, 195

Abou Mrad et al., MNRAS, 2016, 458,1234

Evolution of interstellar icy grains
Toward the formation of complex organic matter in interplanetary bodies



Chemistry in diluted environment
20 K – 150 K

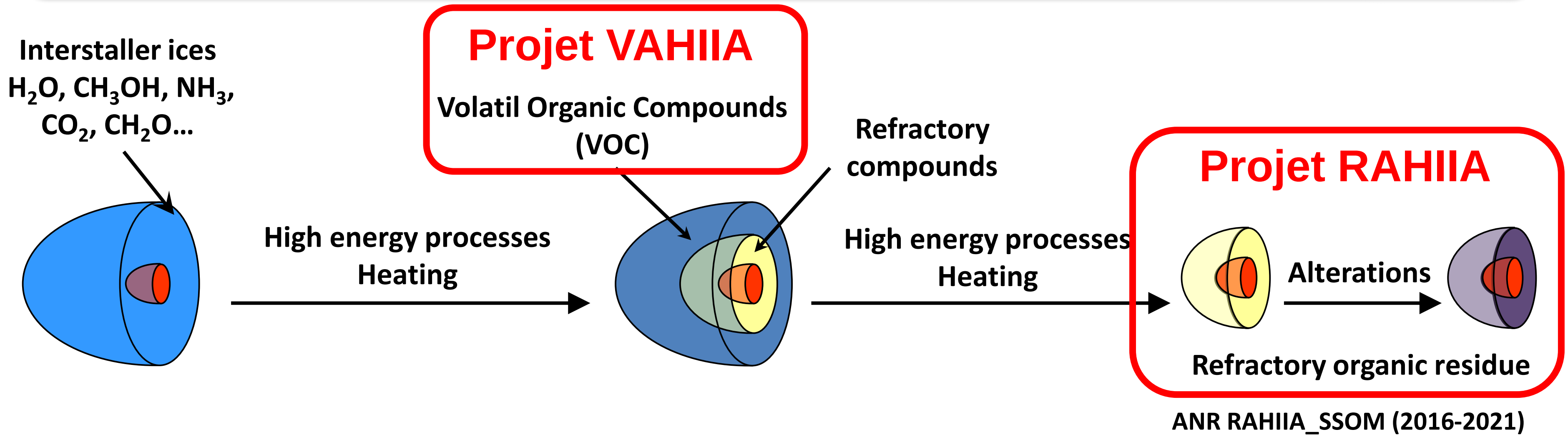
Radical and Thermal reactivities in water ice

Formation of small complex organic molecules

Water matrix restructuration and water desorption
150 K – 185 K

① Main desorption of VOCs

Evolution of interstellar icy grains
Toward the formation of complex organic matter in interplanetary bodies



Chemistry in diluted environment
20 K – 150 K

Radical and Thermal reactivities in water ice

Formation of small complex organic molecules

Water matrix restructuration and water desorption
150 K – 185 K

① Main desorption of VOCs

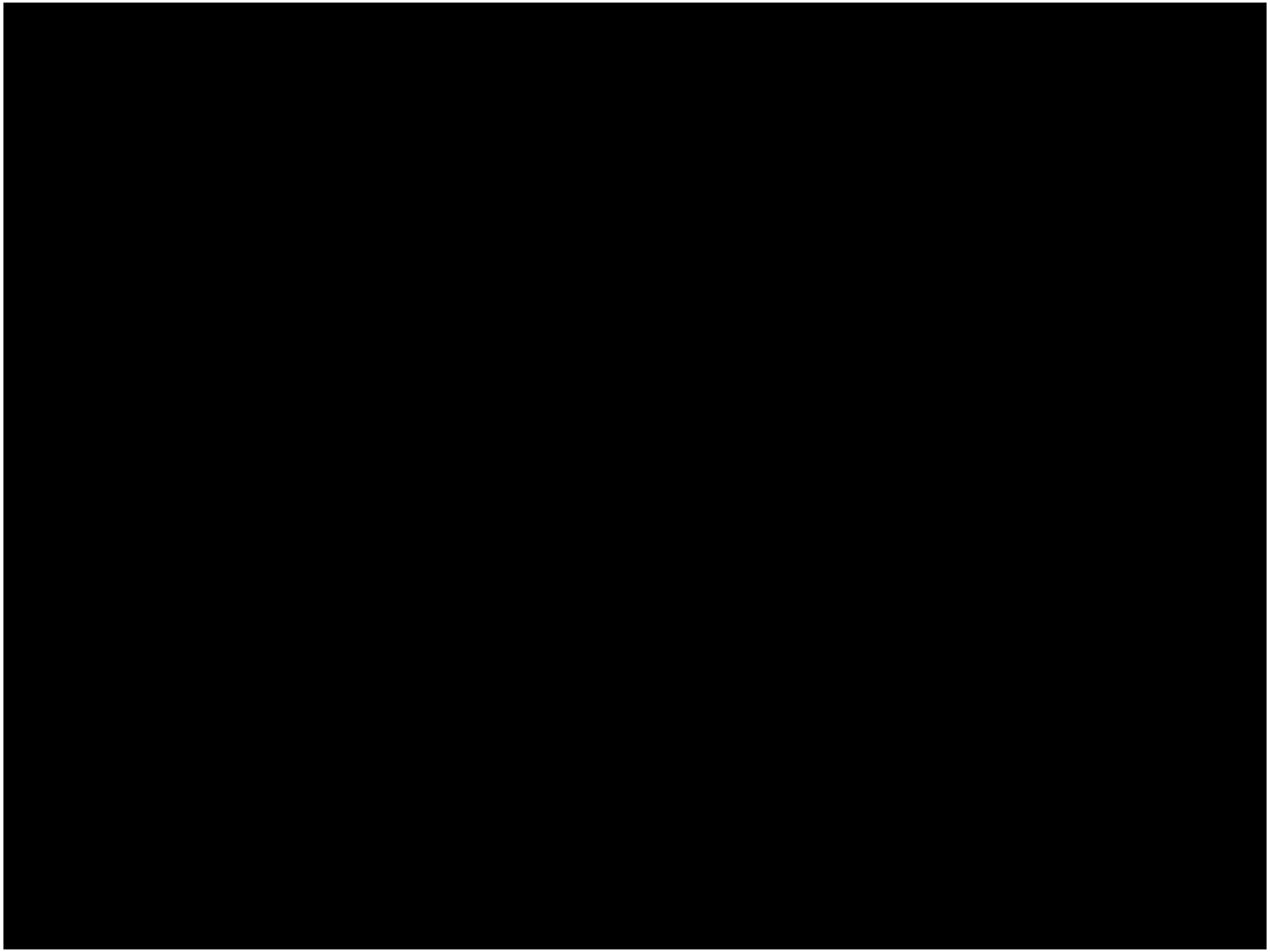
② Some VOCs trapped and react in the water matrix

Chemistry in concentrated environment
> 185 K

Reactivity in absence of water

Formation of « macromolecules »

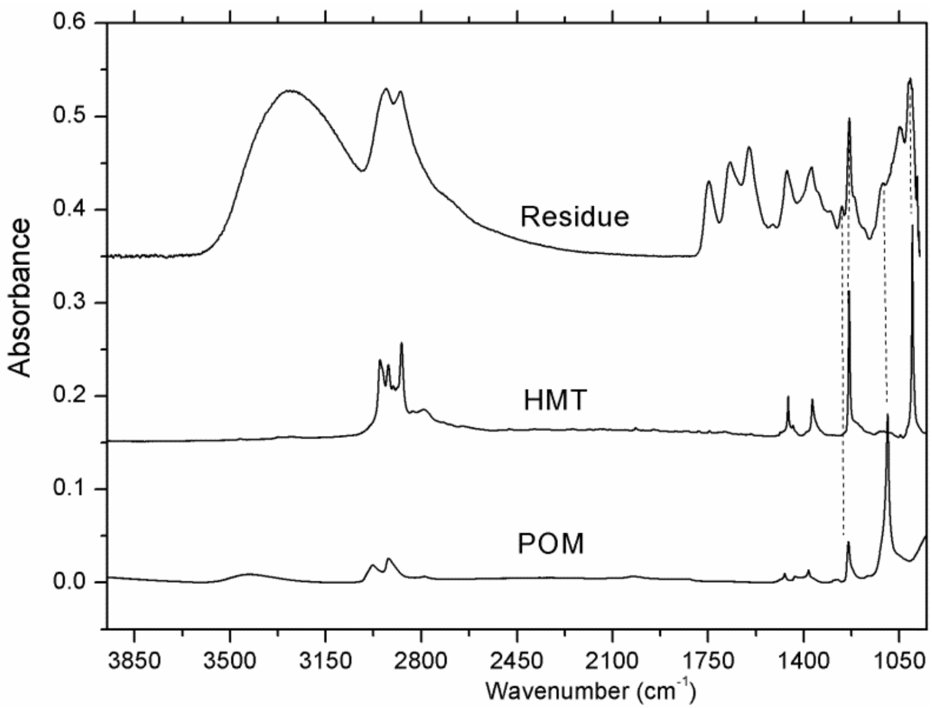
Evolution of interstellar icy grains
Toward the formation of complex organic matter in interplanetary bodies



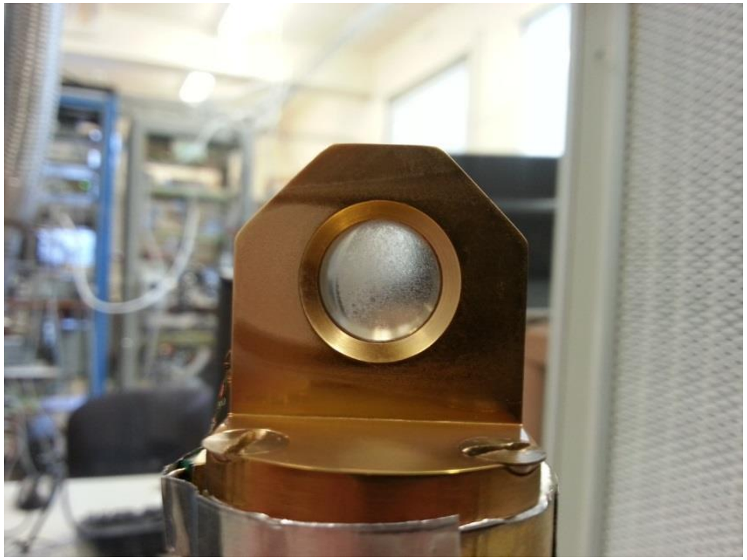
Soluble organic residue from ice processing

ANR
ANR-16-CE29-0015
2016-2021

Most abundant molecules



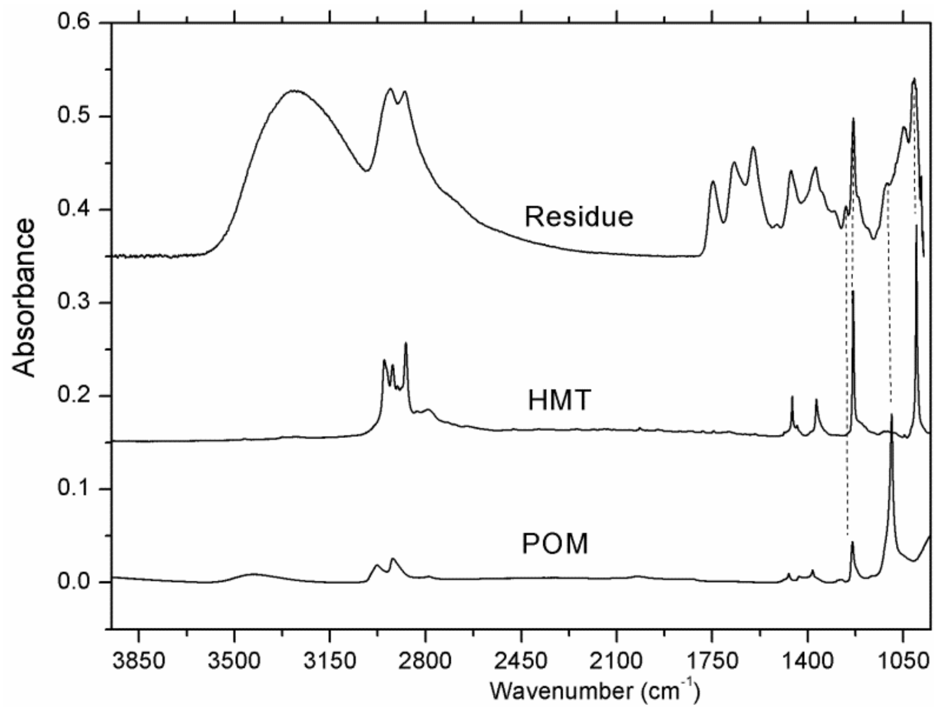
FT-IR analysis of an organic residue coming from a H_2O:CH_3OH:NH_3 ice



Images from Louis d'Hendecourt, IAS, Paris Orsay XI

Soluble organic residue from ice processing

Most abundant molecules



FT-IR analysis of an organic residue coming from a $H_2O:CH_3OH:NH_3$ ice

Gudipati, Abou Mrad et al., 2015, Space Science Review,197,101-150

Chemical functions identified

Position cm^{-1}	Carrier	Vibration mode
3500–2300	R–COOH, alcohols, NH_4^+	OH str., NH str.
3165	NH_4^{+a}	$\nu_1+\nu_5{}^a$
3035	NH_4^{+a}	$\nu_2+\nu_4$
2926	HMT^b	$2\nu_{19}$, $\nu_2+\nu_{19}$
2876	HMT^b, NH_4^{+a}	ν_{18} sym. CH_2 str., $2\nu_4$ of NH_4^{+a}
1742	Esters	C=O str.
1680	Amides	C=O str.
1586	COO^- in carboxylic acid salts	COO^- antisym. str.
1463	NH_4^{+a}	$\nu_4{}^a$
1375	HMT^b	CH scissoring ^{a}
1320	COO^- in carboxylic acid salts	COO^- sym. str.
1236	HMT^b	ν_{21} CN str.
1085	$HOCH_2COO^-$	
1007	HMT^b	ν_{22} CN str.
918	carboxylic acid dimers	OH def.
820	HMT^b	NH_2 wag
765	Ammonium formate?	
678	HMT^b, ammonium glycolate	ν_{24} CNC def. (for HMT)

FT-IR analyses of an organic residue coming from a $H_2O:CH_3OH:CO:CO_2:NH_3$

Muñoz-Caro et al., 2003,A&A, 412, 121-132

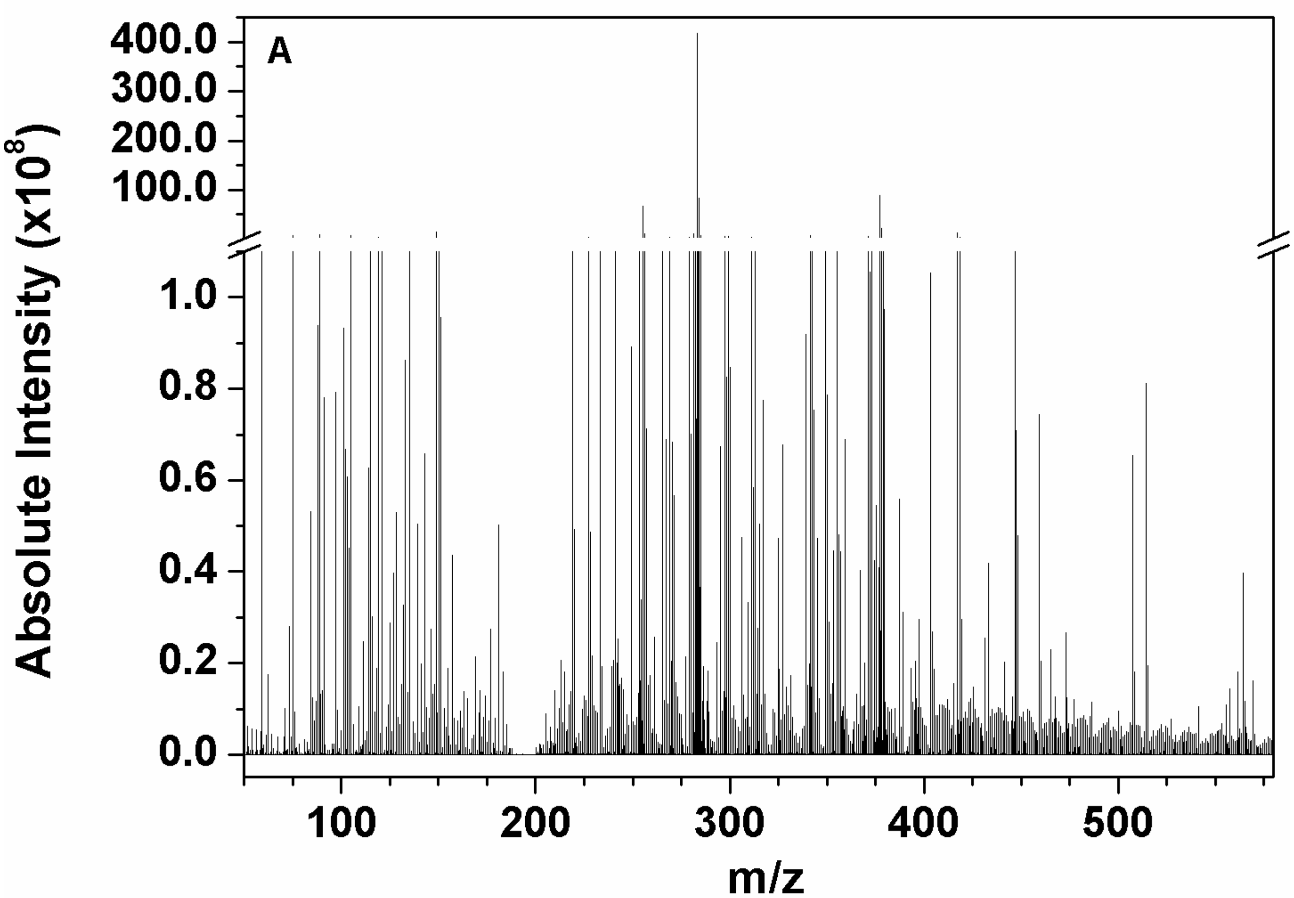
Soluble organic residue from ice processing: untargeted analyses

Samples (<100 µg) recovered with methanol: no sample degradation

Electro-spray ionization: soft ionization minimizing fragmentations

Soluble organic residue from ice processing: untargeted analyses

Collaboration with R. Thissen (IPAG, Grenoble, France)



UHRMS FT-Orbitrap Analysis in Negative ESI mode = [M-H]$^-$ analysis

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

($H_2O/NH_3/CH_3OH$ =3/1/1)

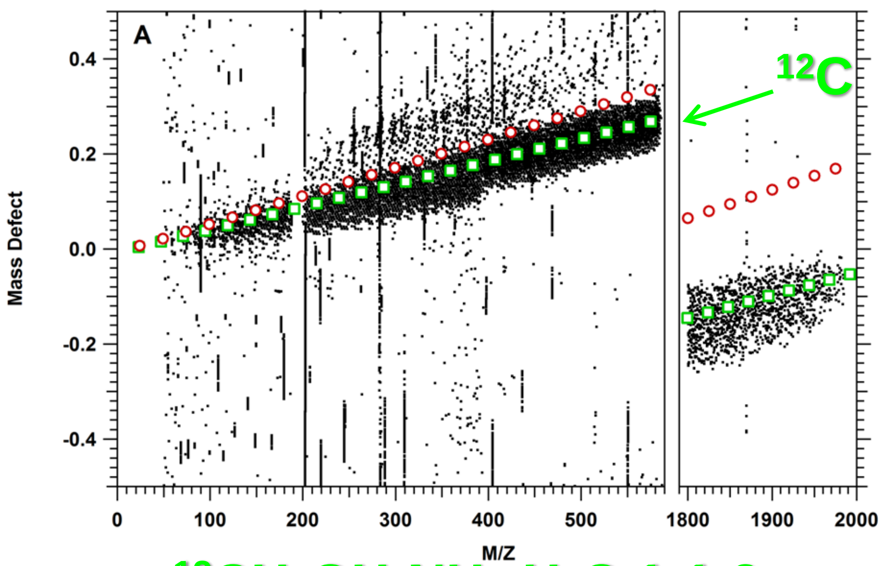
Danger et al., Geochim.Cosmochim.Acta, 2013, 118 , 184-201

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

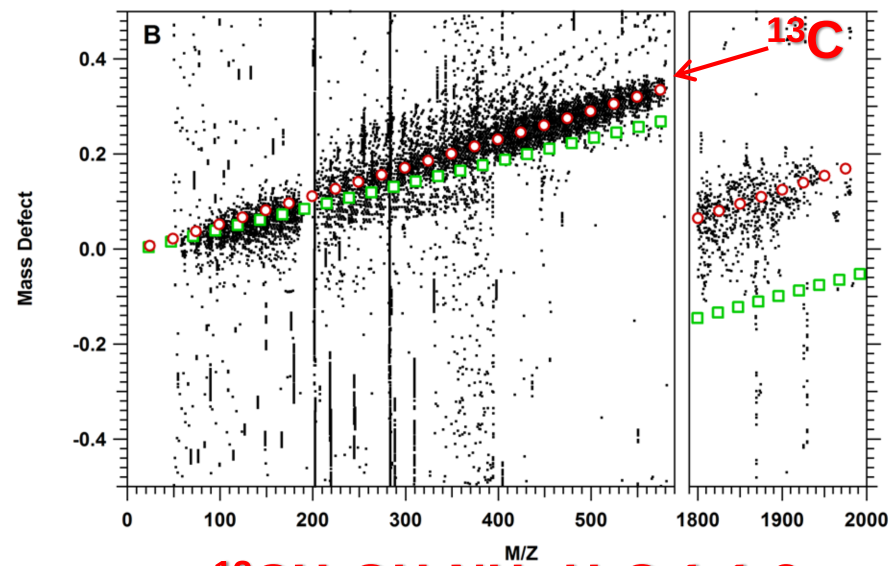
Collaboration with R. Thissen (IPAG, Grenoble, France)

Mass Defect vs Exact Mass (MDvM)

Exact mass: 141.1128
Mass Defect: 141.1128-141= 0.1128



$^{12}CH_3OH:NH_3:H_2O$ 1:1:3

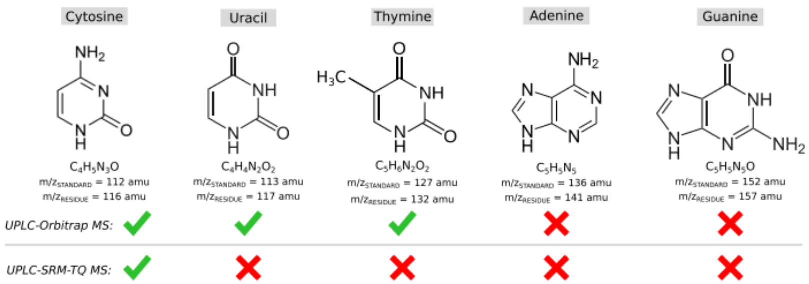


$^{13}CH_3OH:NH_3:H_2O$ 1:1:3

From an ice uniquely formed of $H_2O:CH_3OH:NH_3$
VUV + warming
=
Thousand of molecules with masses
up to 4,000 Da -> macromolecules
=
Complex and rich chemistry
=
Important molecular diversity

Danger et al., Geochim.Cosmochim.Acta, 2013, 118 , 184-201

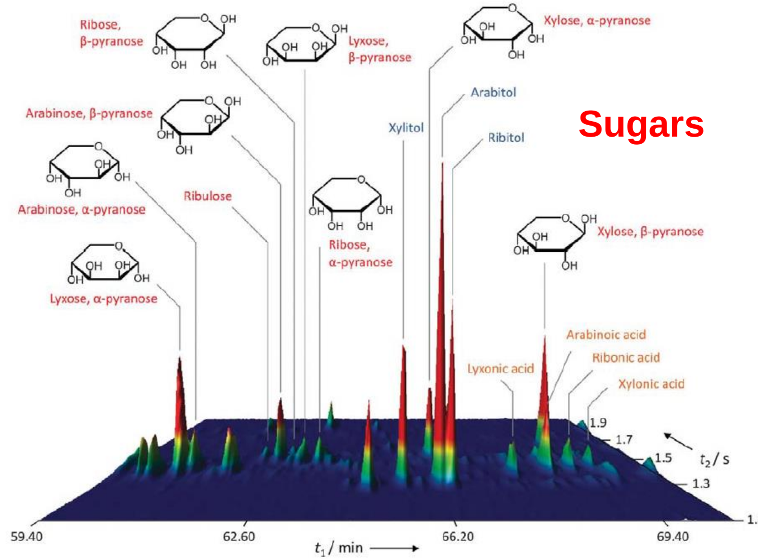
Nucleobases



Ruf et al., 2019, AJ, 887, L31

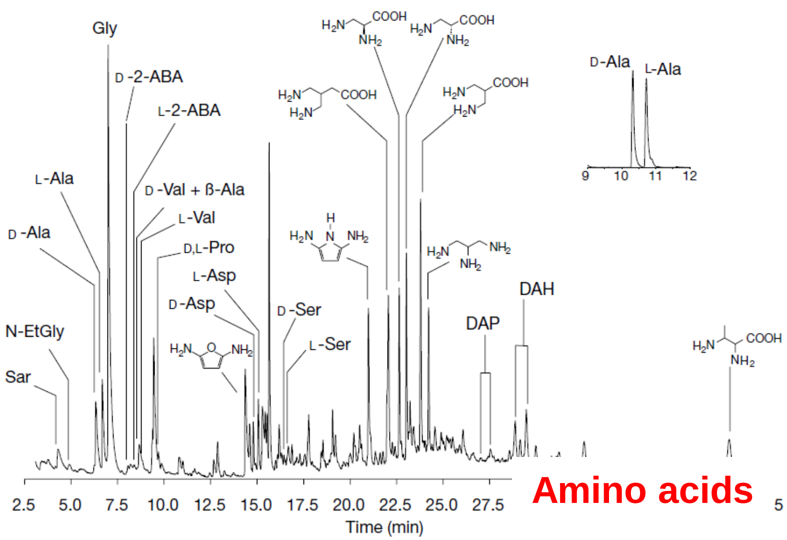
Oba et al., 2019, NatCom, 10, 4413

Sugars



Meinert et al., 2016, Science, 352,208

Amino acids



Munoz-Caro et al., 2002, Nature, 416, 403

Dipeptides

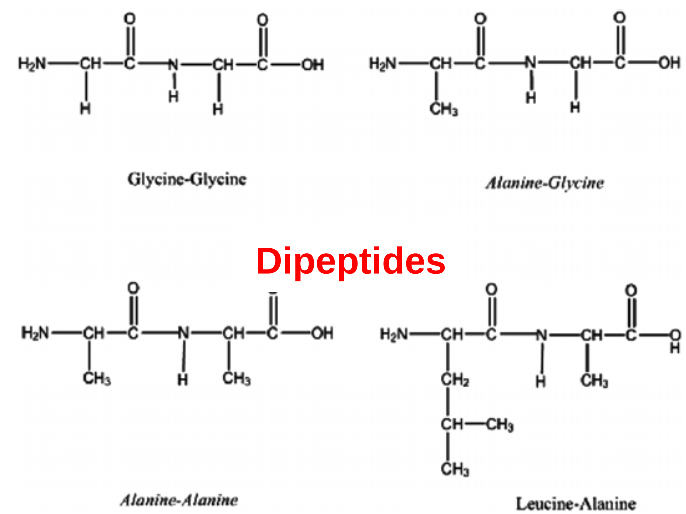


Figure 3. Dipeptides characterized via microchip capillary electrophoresis.

Kaiser et al., 2013, ApJ, 765, 111

Meteorites : reservoir of carbonaceous matter

25% of soluble organic matter

Untargeted analysis of soluble organic matter of carbonaceous chondrites using HRMS

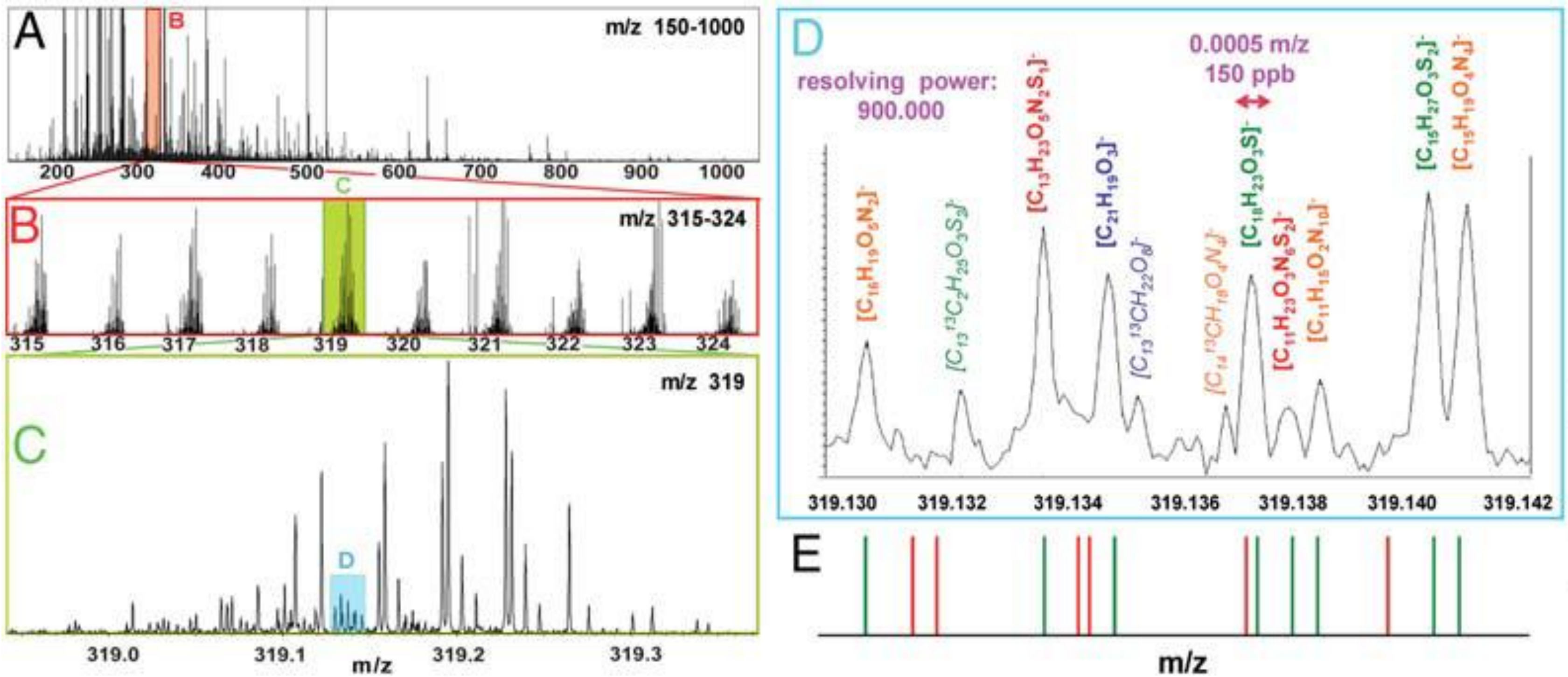
Objectif : Comprehensive image of their molecular content

SOM

$C_{100}H_{155}O_{20}N_3S_3$

H/C=1.55;O/C=0.2;N/C=0.03;S/C=0.03

Schmitt-Koplin et al., *PNAS*, ***107*** *(2010) 2763-2768*

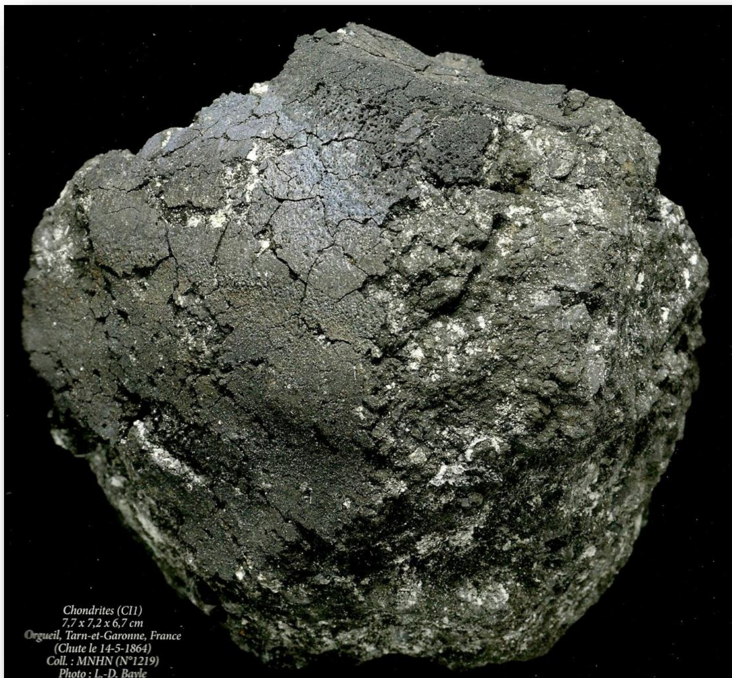


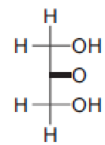
Thousand of different molecular ions observed in the range m/z=150 à 1000

unprecedented molecular diversity

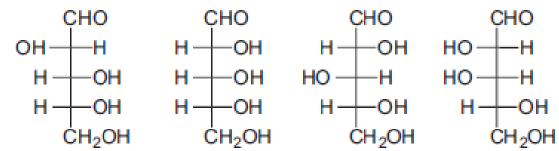
Targeted analyses of soluble organic matter of carbonaceous chondrites

More than 500 structures identified



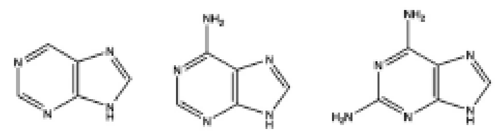


Dihydroxyacetone (1)



D-arabinose (2) D-ribose (3) D-xylose (4) D-lyxose (5)

Furukawa et al., PNAS, 2019



Purine **Adenine** **2,6-Diaminopurine**

Callahan et al., PNAS, 2011

Oba et al., NatCom, 2022

Peak #	Amino acid
1	α-AIB
2	L-Isovaline[a]
3	D-Isovaline[a]
4	D-Alanine
5	L-Alanine
6	D-α-ABA[b]
7	L-α-ABA[b]
8	D-Valine
9	L-Valine
10	Glycine
11	D,L-β-AIB[b,c]
12	D-Norvaline
13	L-Norvaline
14	β-Alanine
15	D-β-ABA[b]
16	L-β-ABA[b]
17	D-Leucine
18	L-Leucine
19	D-Norleucine
20	L-Norleucine
21	γ-ABA
22	D-Aspartic acid
23	L-Aspartic acid
24	EACA
25	D-Glutamic acid
26	L-Glutamic acid

Martins et al., MPS, 2015

Reservoir of organic matter

Meteorites : reservoir of carbonaceous matter

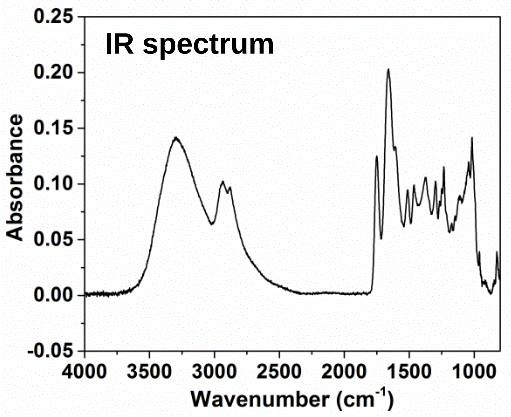
25% of soluble organic matter
75% of insoluble organic matter

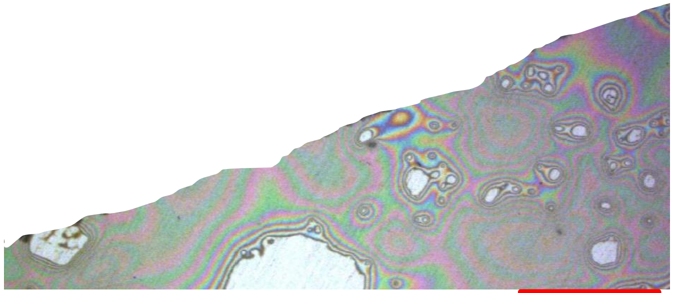
From soluble organic residues to unsoluble ($H_2O/NH_3/CH_3OH$ =3/1/1)

A scenario from extraterrestrial ices to soluble and insoluble materials

Residue (soluble)

300 K





residue

de Marcellus et al., MNRAS, 2017, 464, 114

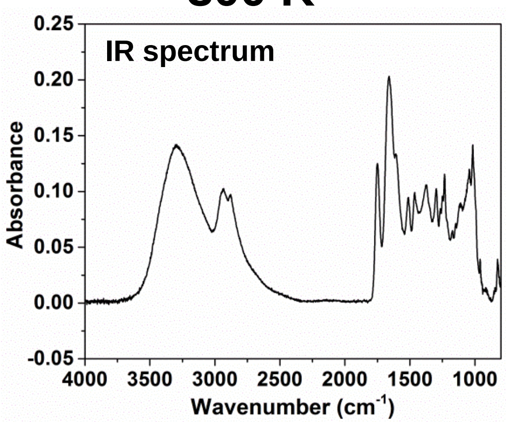
From soluble organic residues to unsoluble ($H_2O/NH_3/CH_3OH$ =3/1/1)

A scenario from extraterrestrial ices to soluble and insoluble materials

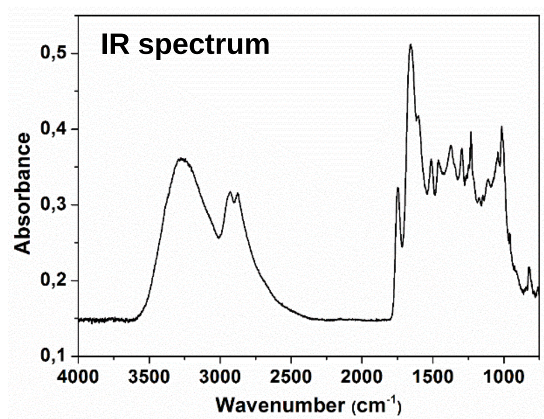
UV

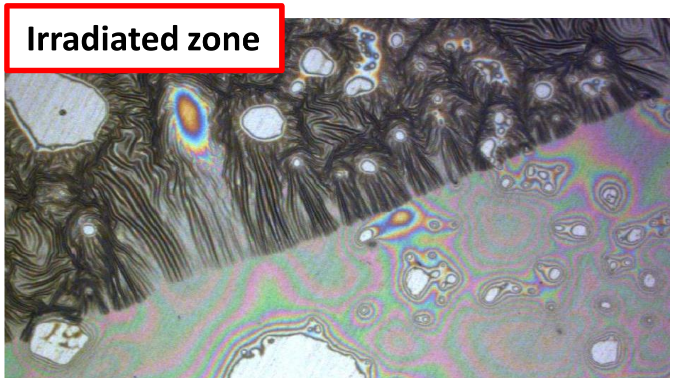
Residue (soluble) → Residue irradiated (insoluble) / Residue (soluble)

300 K



300 K





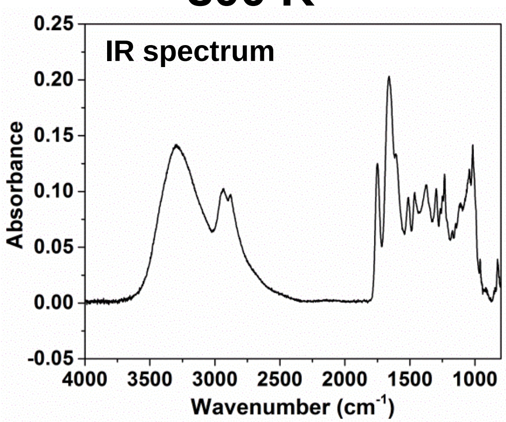
de Marcellus et al., MNRAS, 2017, 464, 114

From soluble organic residues to unsoluble ($H_2O/NH_3/CH_3OH$ =3/1/1)

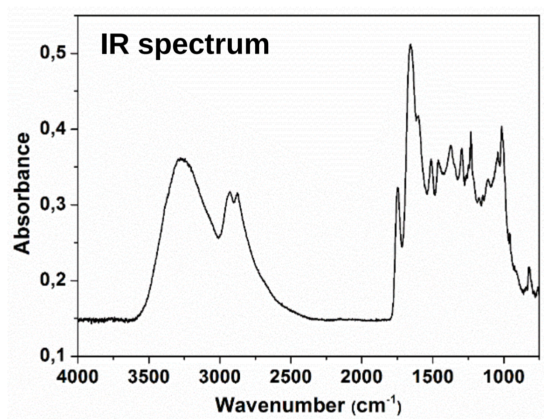
A scenario from extraterrestrial ices to soluble and insoluble materials

Residue (soluble) → UV → Residue irradiated (insoluble) / Residue (soluble) → H_2O 14h → Irradiated residue (insoluble)

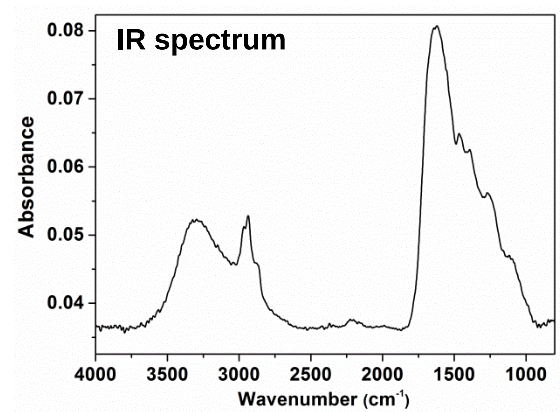
300 K



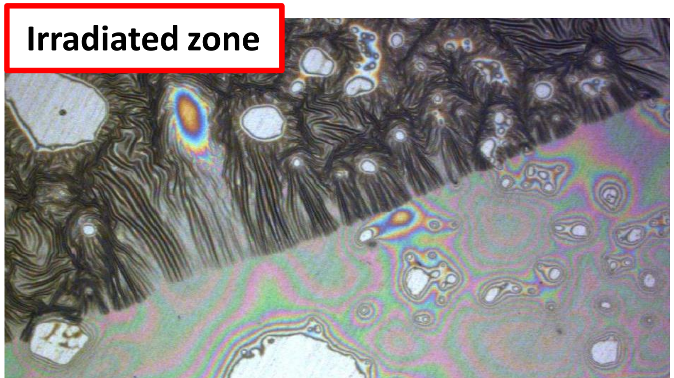
300 K



300 K



Irradiated zone



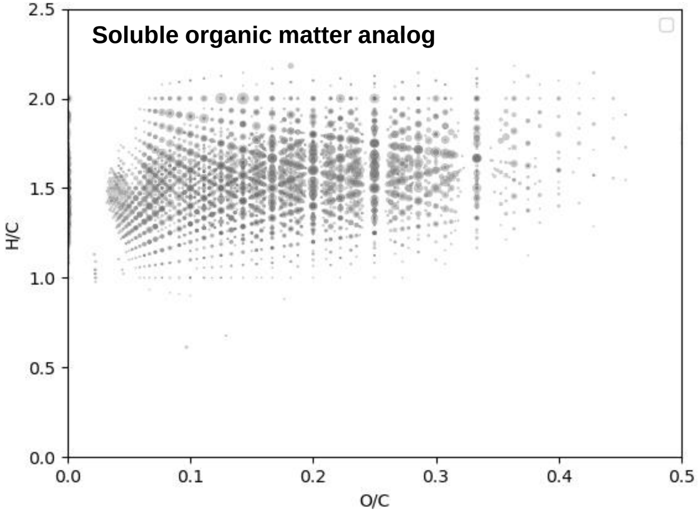
unirradiated zone

de Marcellus et al., MNRAS, 2017, 464, 114

From soluble organic residues to insoluble ($H_2O/NH_3/CH_3OH$ =3/1/1)

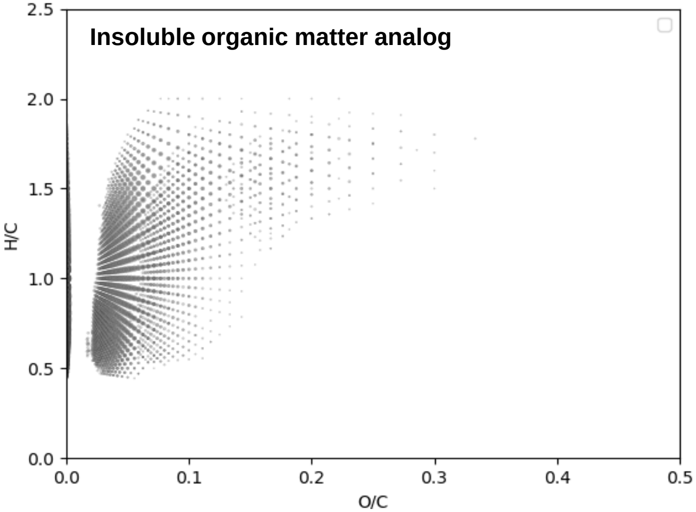
Collaboration with C. Afonso (COBRA, Rouen, France)

A scenario from extraterrestrial ices to soluble and insoluble materials



Laser desorption/ionization FT-ICR-MS

UV, Electron, ion



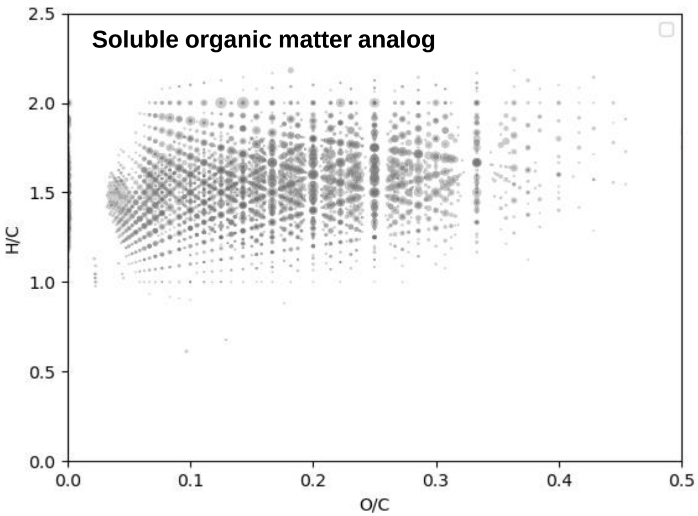
Laser desorption/ionization FT-ICR-MS

Danger et al., A&A, 2022, submitted

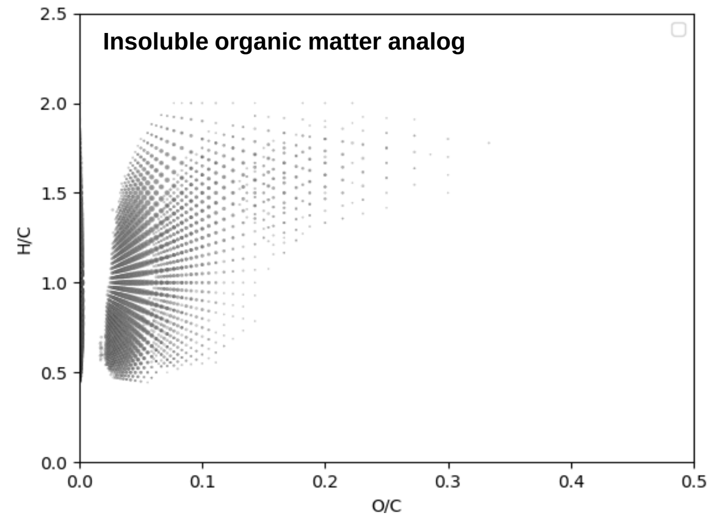
From soluble organic residues to insoluble ($H_2O/NH_3/CH_3OH$ =3/1/1)

Collaboration with C. Afonso (COBRA, Rouen, France) and L. Rémusat (IMPMC, Paris, France)

A scenario from extraterrestrial ices to soluble and insoluble materials



UV, Electron, ion



Laser desorption/ionization FT-ICR-MS

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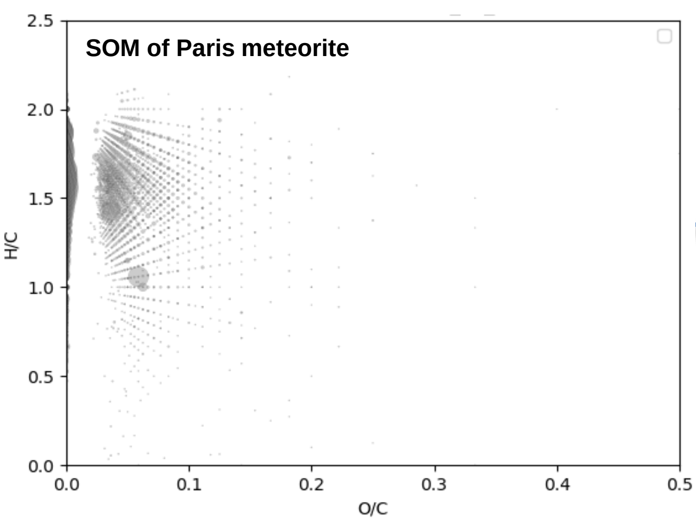
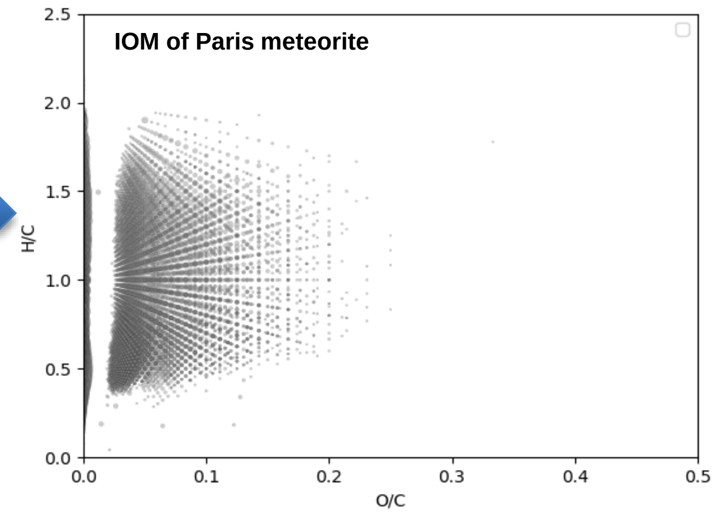


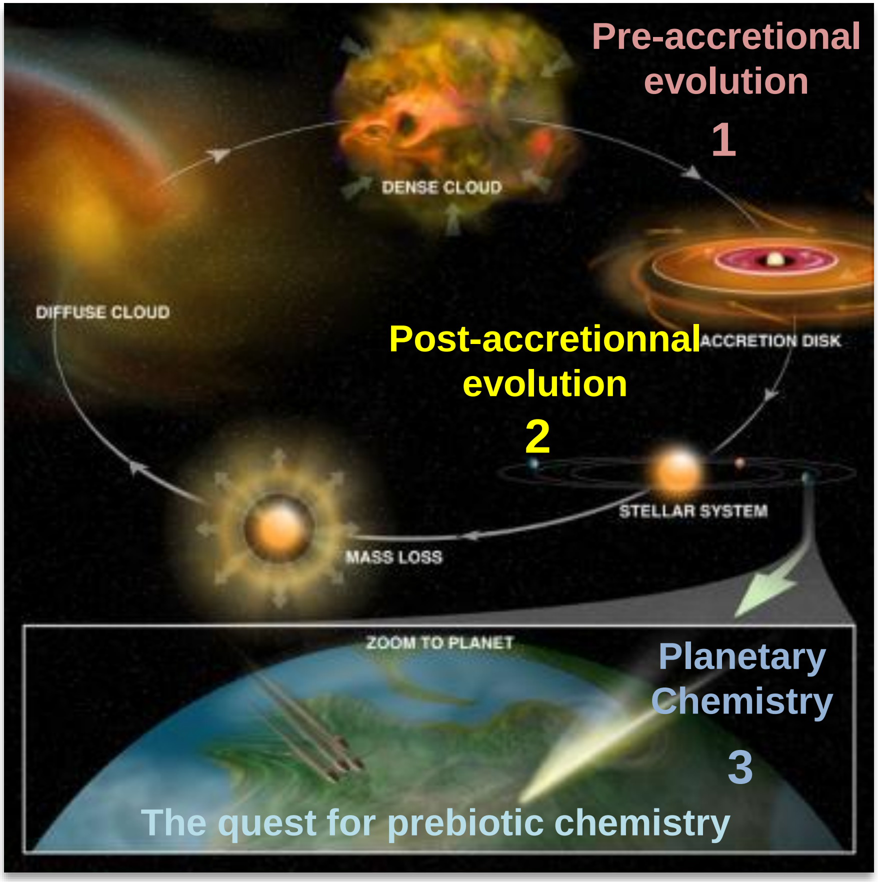
Météorites



liens
?

Danger et al., A&A, 2022, submitted

From Astrochemistry to Prebiotic Chemistry: Organic Matter Evolution

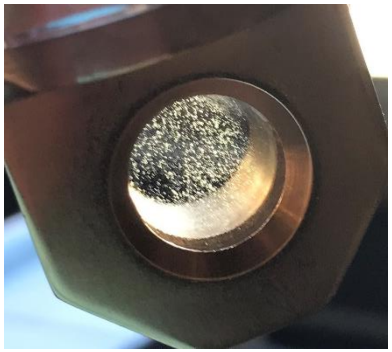


- ***Pre-accretional process: an important molecular diversity is formed from soluble to insoluble***
- ***Post-accretional process: How the pre-accrational organic matter evolved***
- ***Planeraty Chemistry: what conditions for a prebiotic chemistry***

Laboratory experiments: Simulate post-accretional processes

Collaboration with L. Remusat (MNHM, Paris, France) et P. Schmitt-Kopplin (HelmholtzZentrum, Munich, Germany)

Aqueous alteration: soluble fraction analysis by ESI FT-ICR-MS



H_2O

150°C

under water pressure (6 bar)

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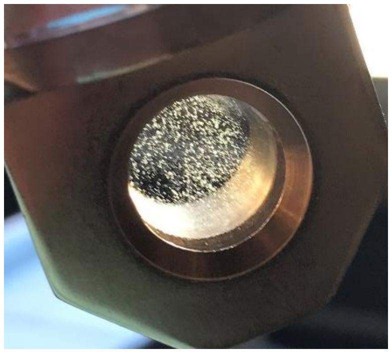

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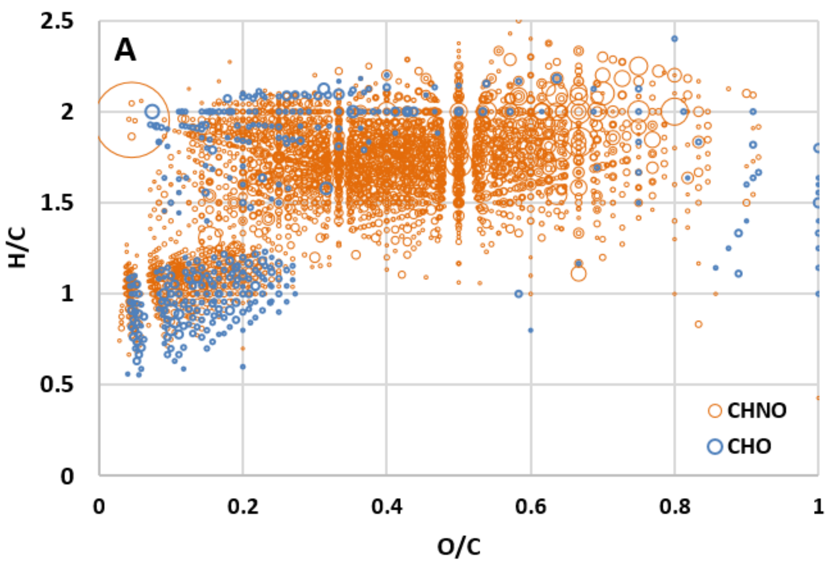
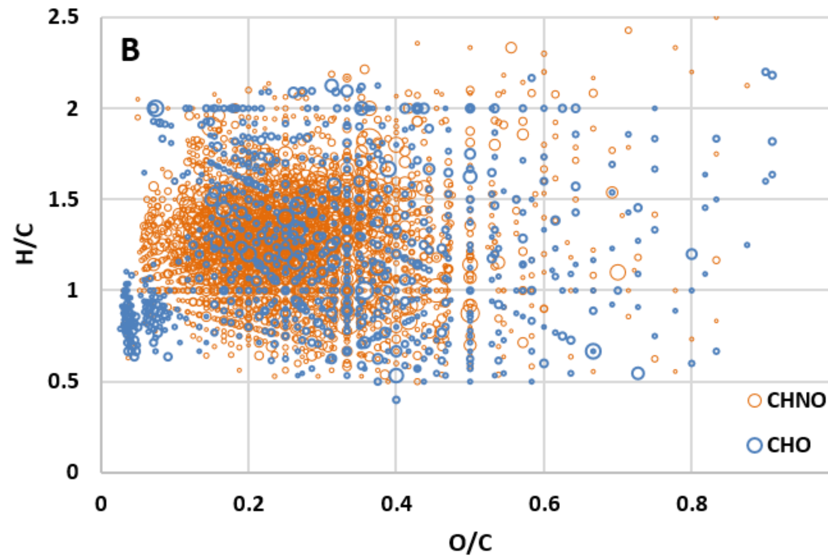


Fresh residue t_0



Residue after 100 days at 150°C

Danger et al., NatComm, 2021, 12, 3538

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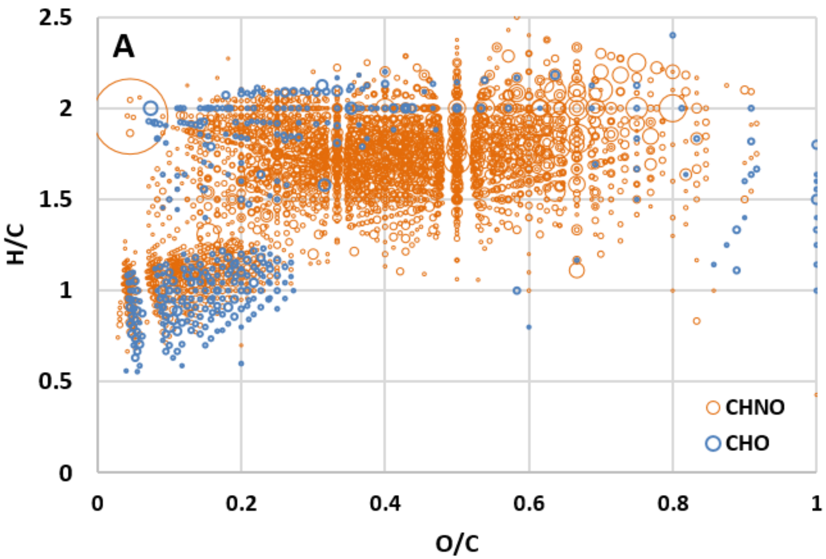

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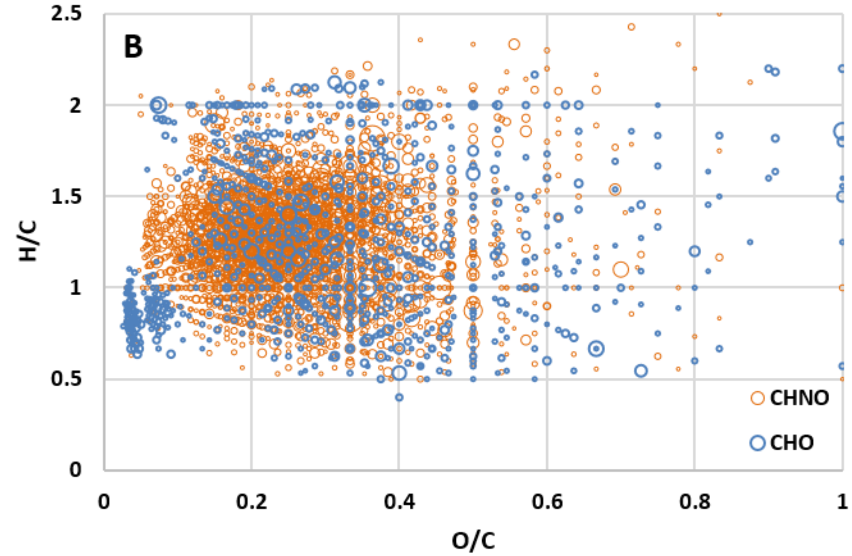

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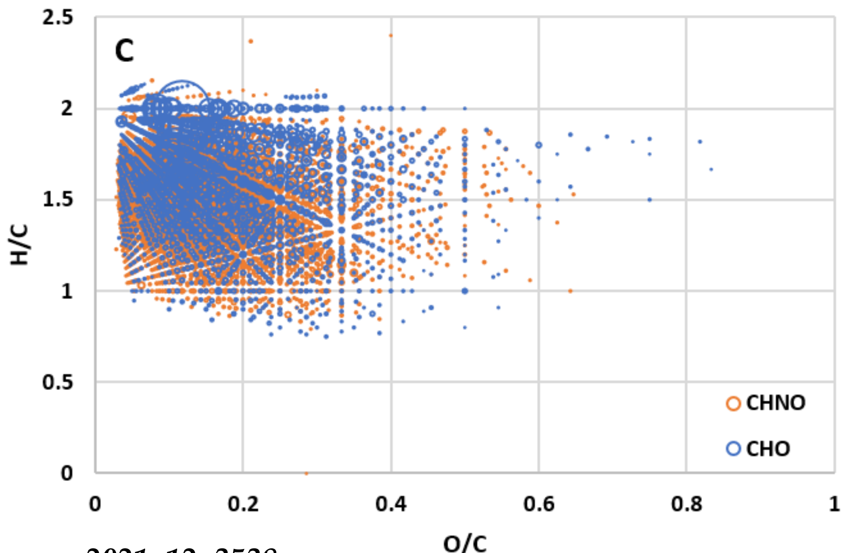

Soluble Organic Matter
Murchison meteorite

Danger et al., NatComm, 2021, 12, 3538

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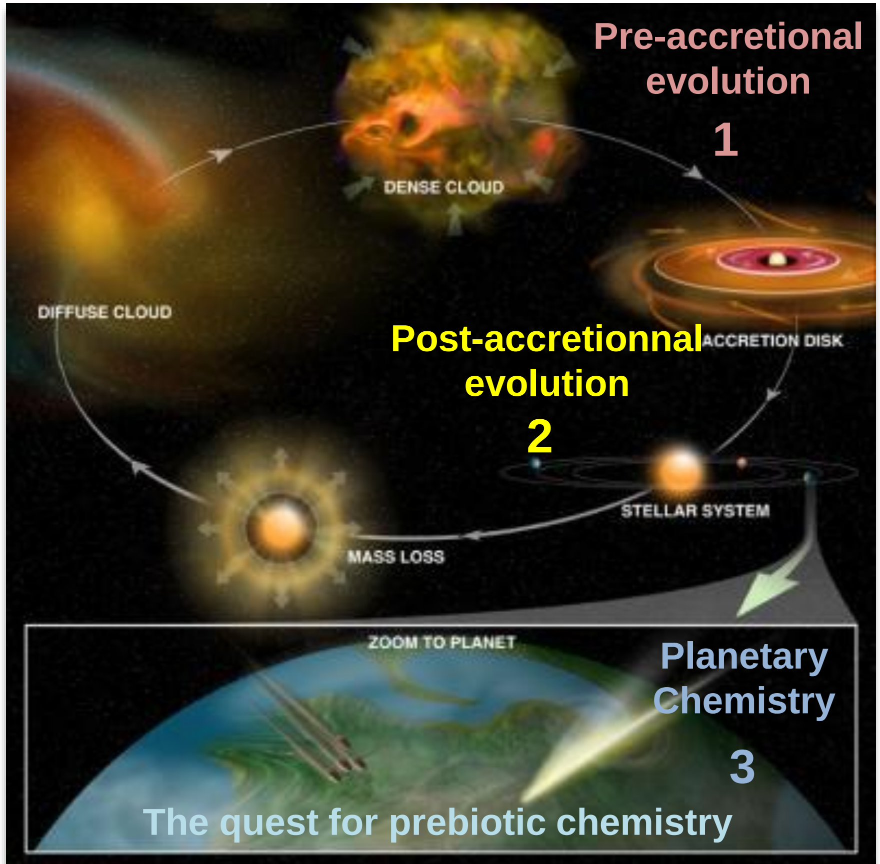


- ***Pre-accretional process: an important molecular diversity is formed from soluble to insoluble***
- ***Post-accretional process: secondary evolution occurs***
- ***Planeraty Chemistry: what conditions for a prebiotic chemistry***

Role of exogenous organics in the emergence of life

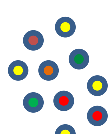
ANR-14-CE33-0020-0001 2014-2018

exogeneous
organic matter

Abiotic
chemistry

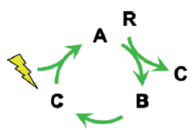
Early Earth
aqueous environments

Molecular diversity



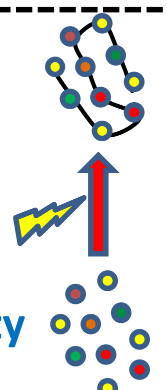
Danger et al., Nature Review Chemistry, 2020, 4, 102-109

Role of exogenous organics in the emergence of life



Emergence of Replicators

Self-organization



Molecular diversity

exogeneous organic matter

Early Earth aqueous environments

Abiotic chemistry

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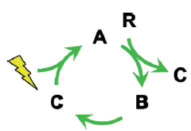
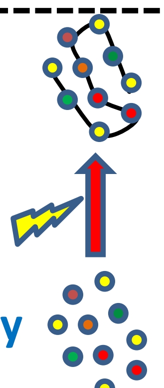


Emergence of Replicators

Determined by energy available in the environment

Prebiotic Chemistry

Self-organization



Molecular diversity

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Early Earth aqueous environments

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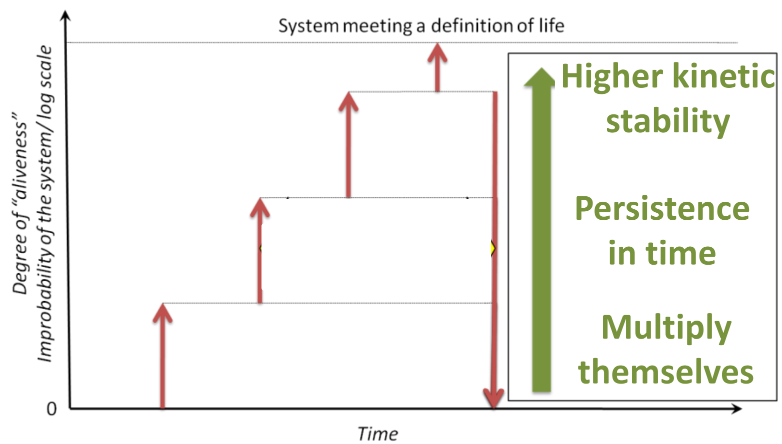

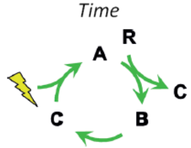

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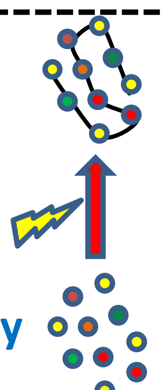


exogeneous organic matter

Abiotic chemistry

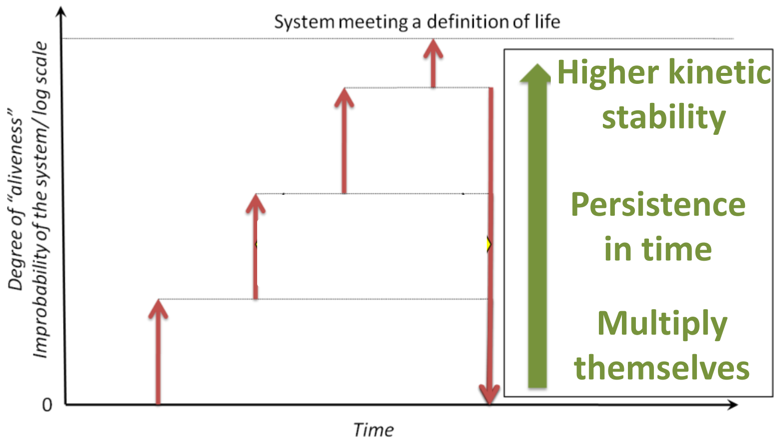
Early Earth aqueous environments

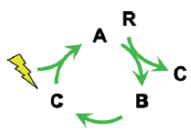
Molecular diversity

Danger et al., *Nature Review Chemistry*, 2020, 4, 102-109

Role of exogenous organics in the emergence of life

Biochemical systems





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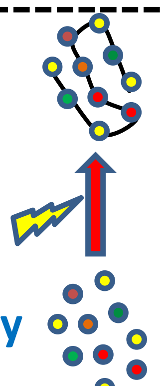
Prebiotic Chemistry

Self-organization



Molecular diversity

exogeneous organic matter

Early Earth aqueous environments

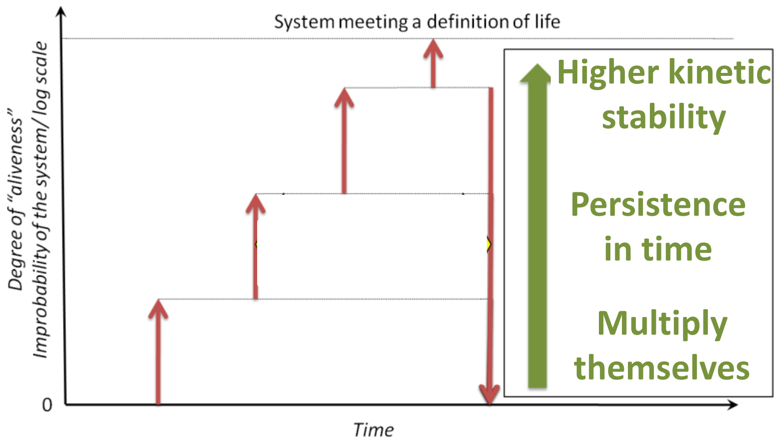
Abiotic chemistry

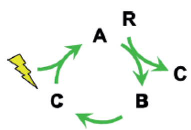
Danger et al., Nature Review Chemistry, 2020, 4, 102-109

Role of exogenous organics in the emergence of life

Increasing in organization complexity

Biochemical systems





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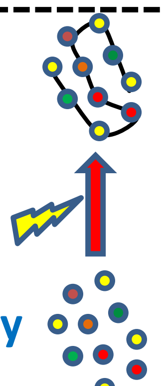

Molecular diversity

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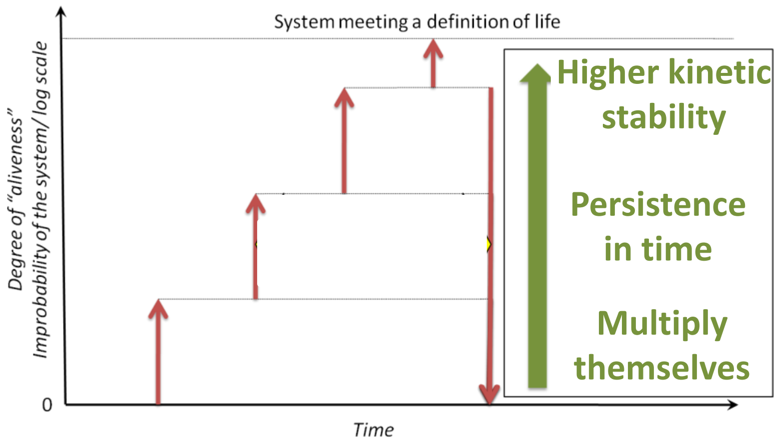
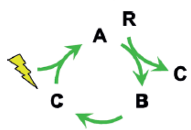




Emergence of Replicators

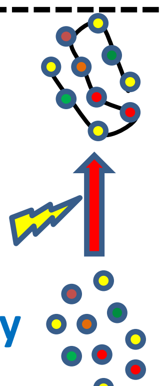
Biochemistry

Continuous Evolution under DKS

Prebiotic Chemistry

Determined by energy available in the environment

Self-organization



Molecular diversity

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Early Earth aqueous environments

Abiotic chemistry

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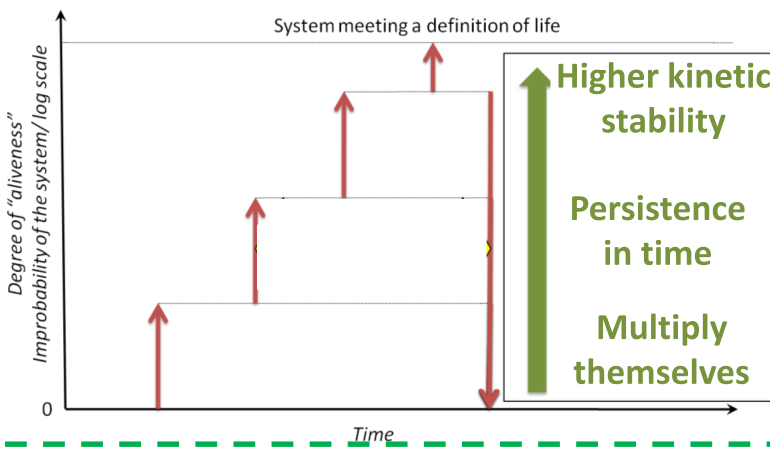

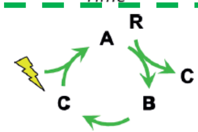

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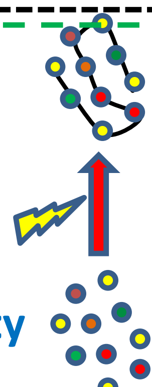

Molecular diversity

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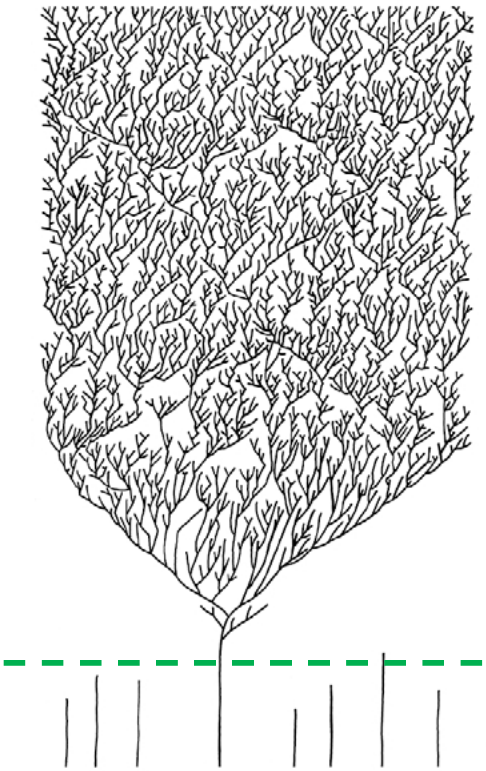

Roots of the tree of life

Prebiotic Chemistry

exogeneous organic matter

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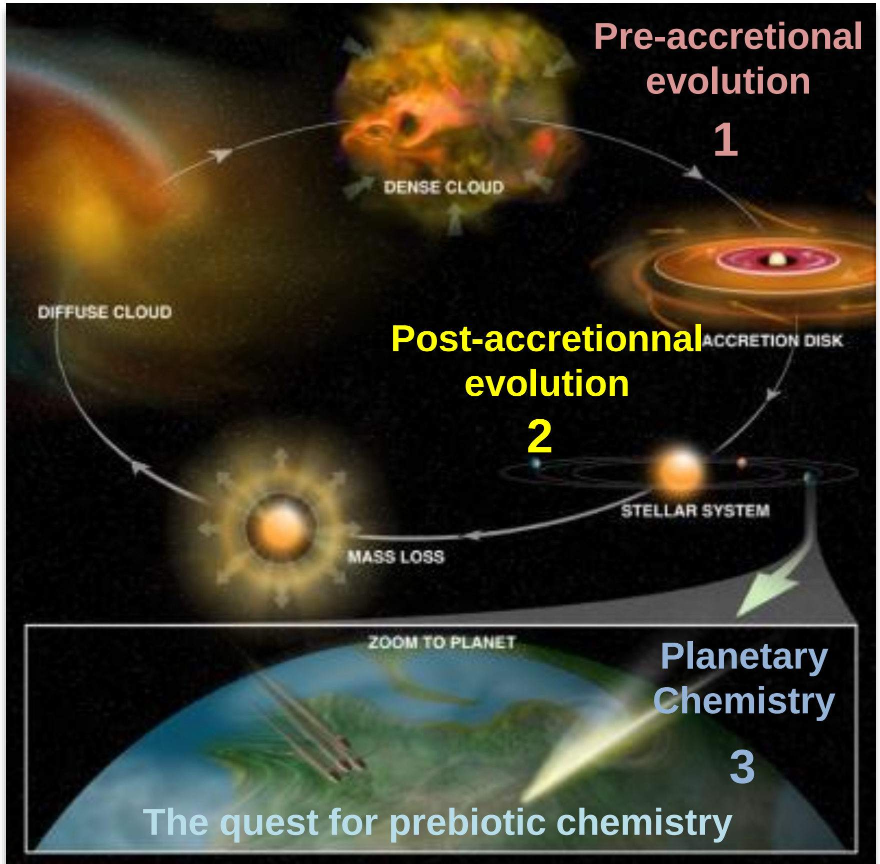

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- ***Post-accretional process: secondary evolution occurs***
- ***Planeraty Chemistry: specific environment for a prebiotic chemistry, the chemistry of systems***