Laboratory experiments to understand the molecular diversity of astrophysical environments

Grégoire DANGER

L. Honold, A. Ruf, T. Javelle, A. Garcia, P. Schmitt-Kopplin, and V. Vinogradoff

[1] Université d'Aix-Marseille, CNRS, Laboratoire PIIM, France

[2] Institut Universitaire de France

gregoire.danger@univ-amu.fr

https://sites.google.com/view/gregoire-danger

Meteorites : Key pieces of evidence in Astrobiology

Reservoir of carbonaceous matter

Meteorites : reservoir of carbonaceous matter

25% of soluble organic matter

75% of insoluble organic matter

Soluble organic matter carbonaceous chondrites

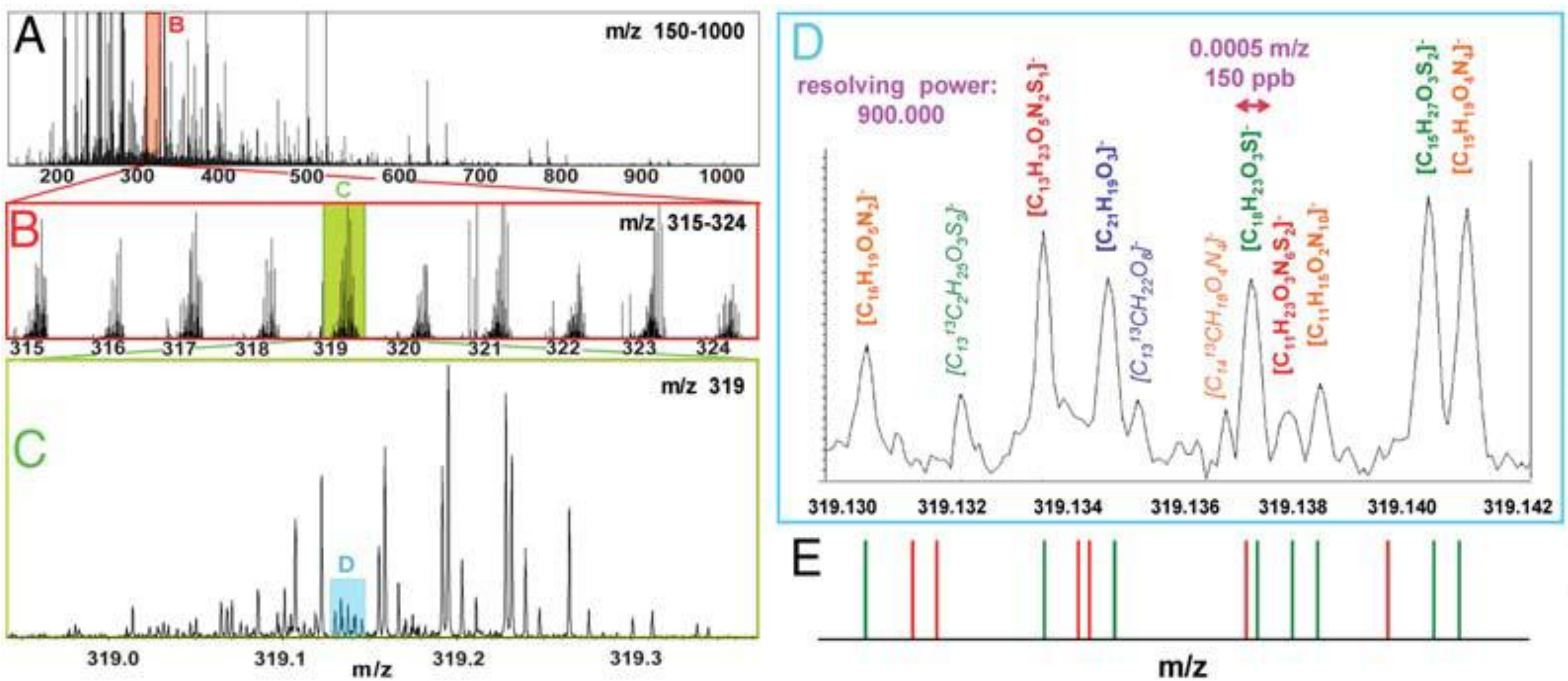
Objectif : Comprehensive image of their molecular content

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*

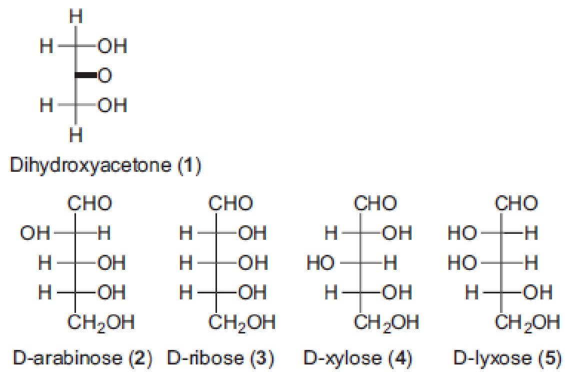


Thousand of different molecular ions observed in the range m/z=150 à 1000

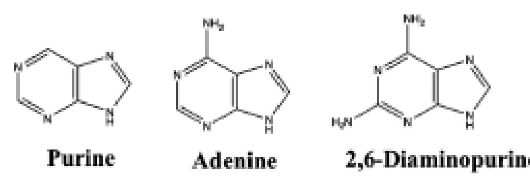
unprecedented molecular diversity

Soluble organic matter carbonaceous chondrites

More than 500 structures identified



Furukawa et al., PNAS, 2019



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

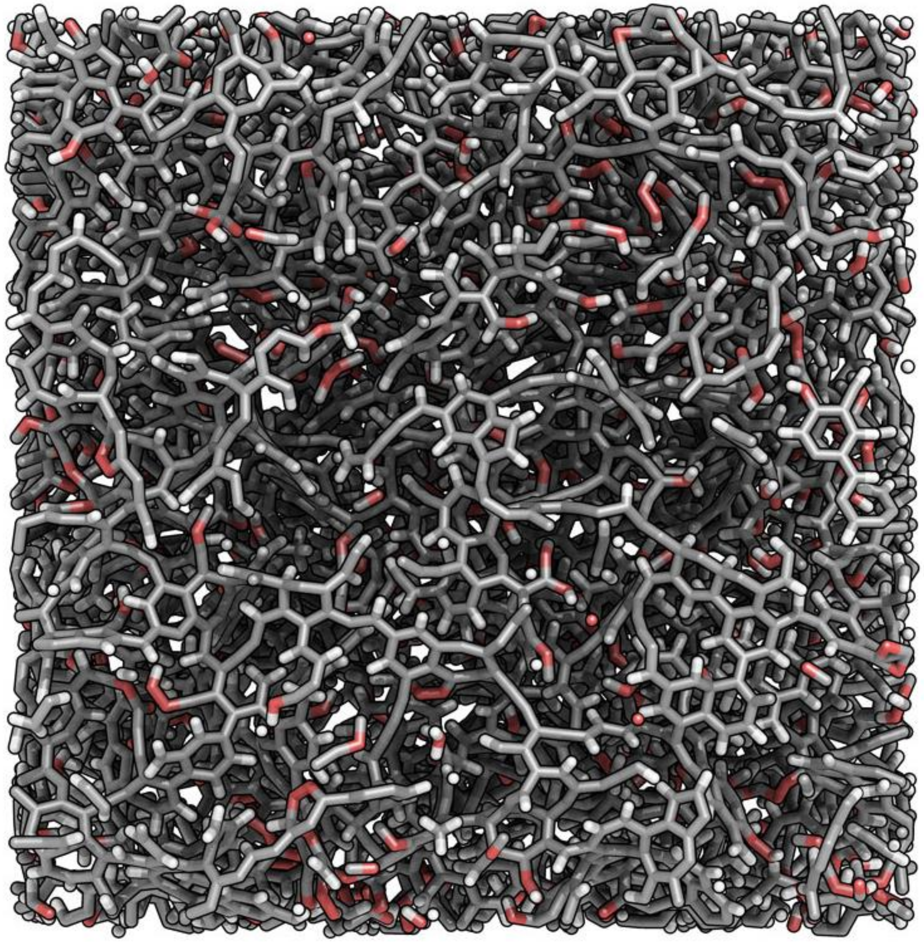
Reservoir of organic matter

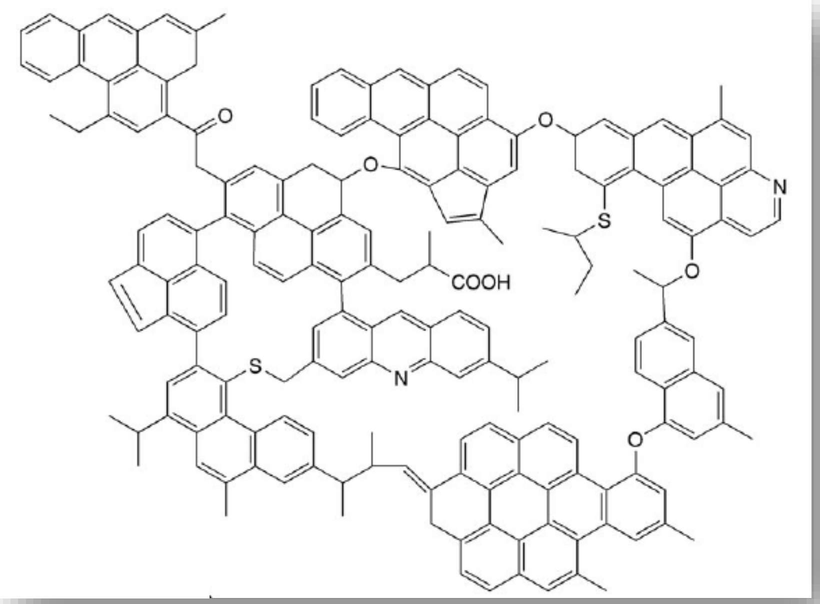
Insoluble organic matter
carbonaceous chondrites

IOM

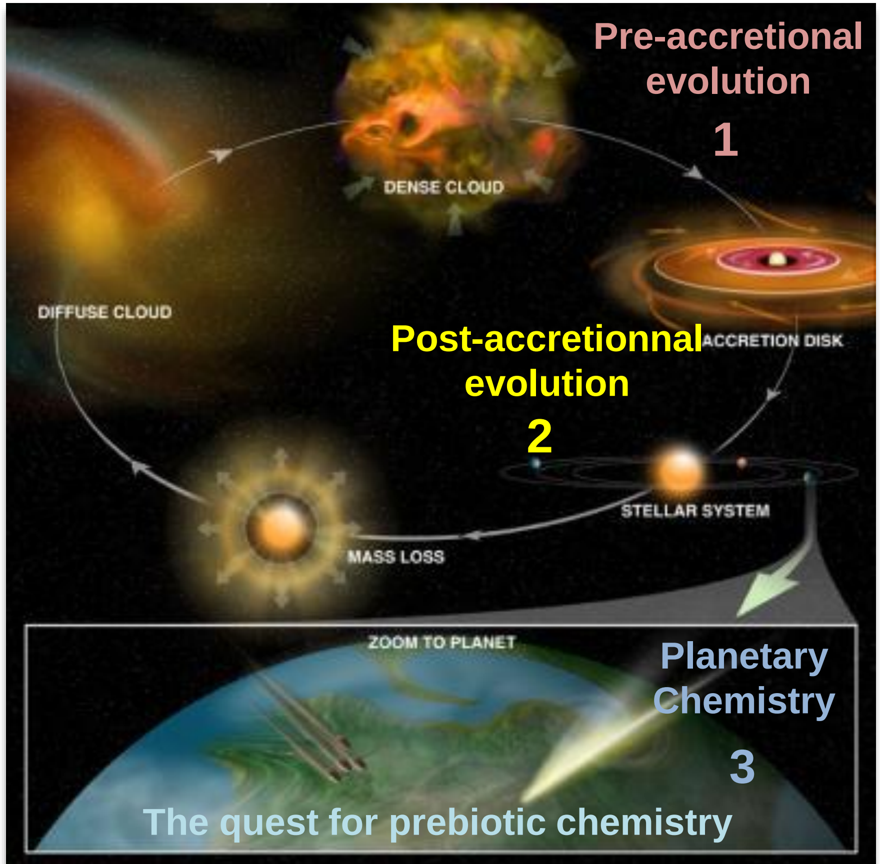
$C_{100}H_{70}O_{12}N_3S_2$

H/C=0.7;O/C=0.12;N/C=0.03;S/C=0.02



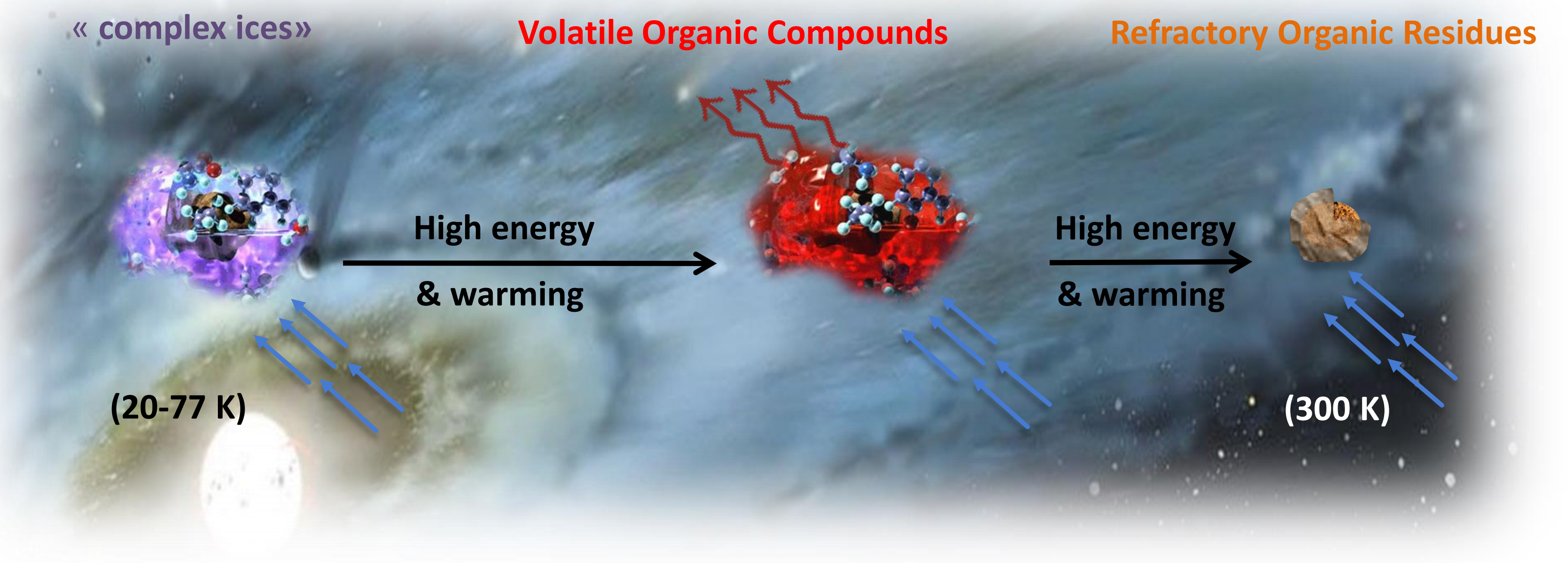


From Astrochemistry to Prebiotic Chemistry: Organic Matter Evolution

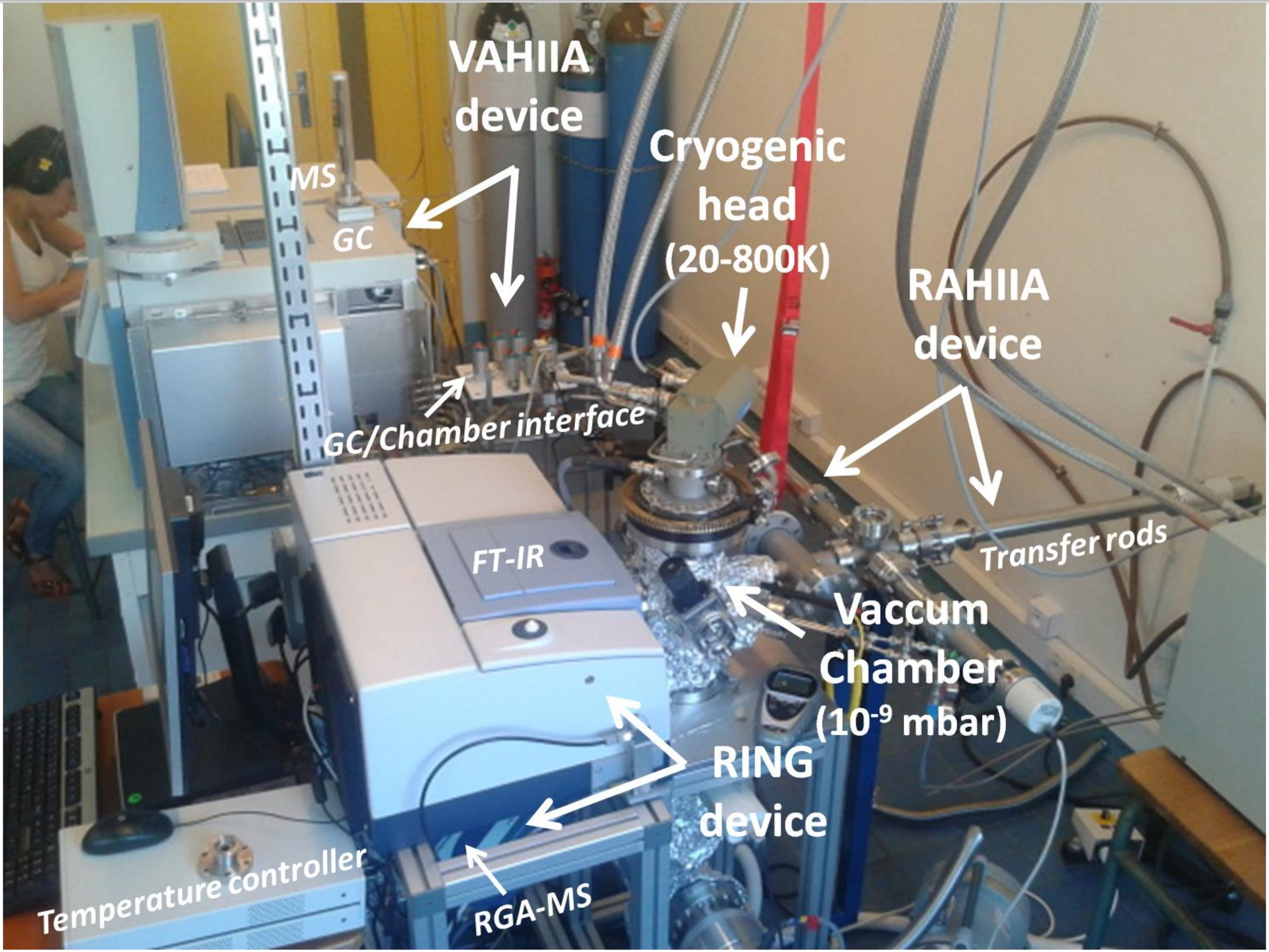


- ***Pre-accretional process: What sort of organic matter is generated***
- ***Post-accretional process: How the pre-accrational organic matter evolved***
- ***Planeraty Chemistry: what conditions for a prebiotic chemistry***

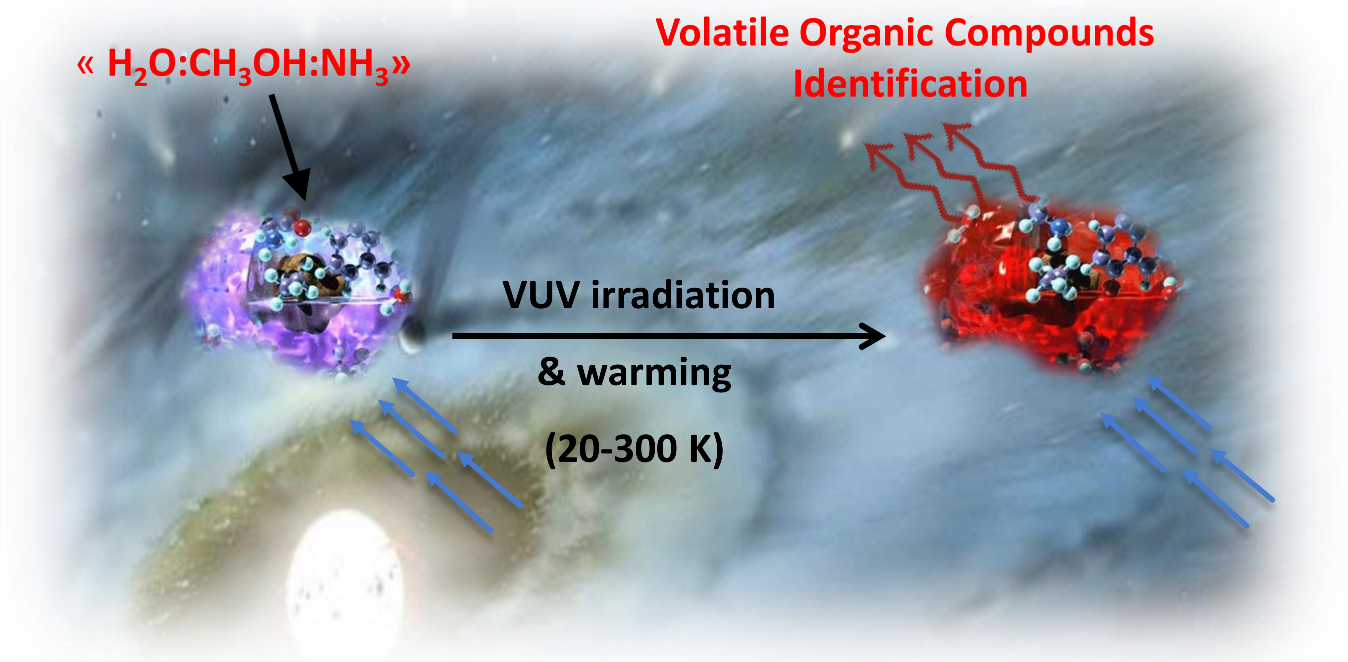
Astrophysical ices as a source of molecular diversity



Laboratory experiments: Simulate Pre-accretional processes



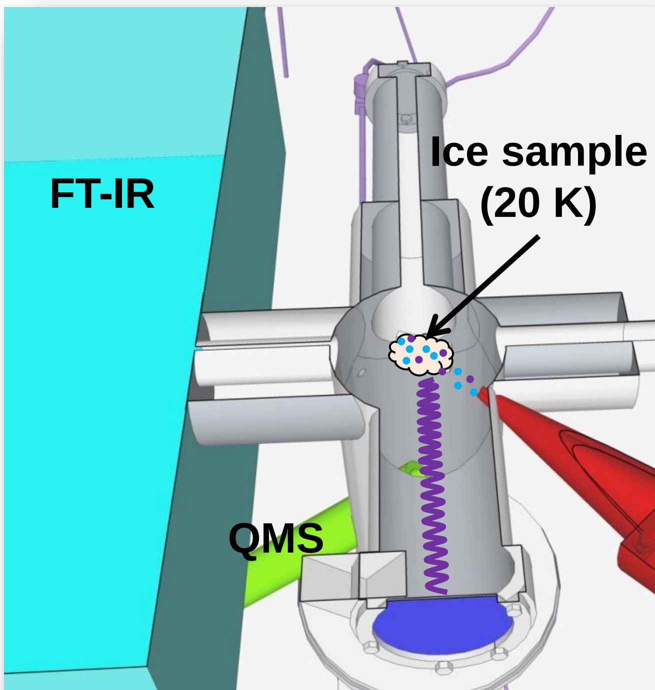
Astrophysical ices
A source of VOCs in astrophysical environments

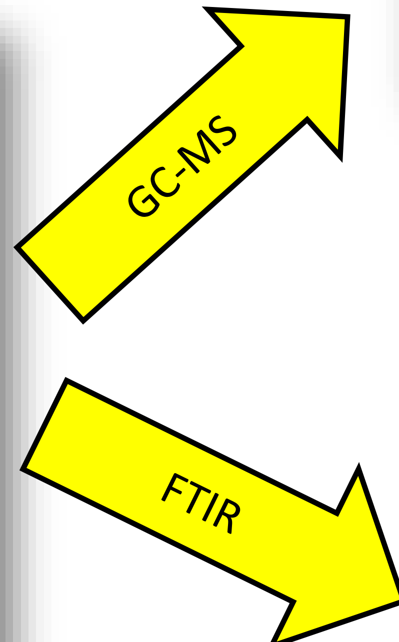


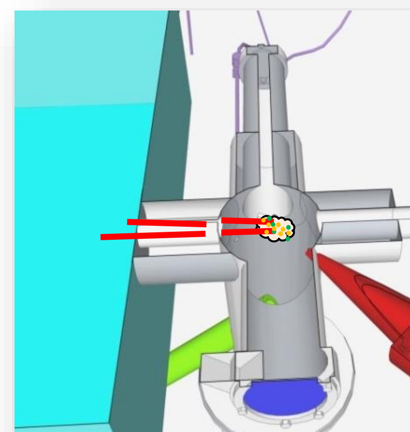
Principle of the VAHIIA device
Recovery and analysis of VOC by GC-MS

ANR-12-JS08-0001
2012-2015

Vacuum chamber (10^{-9} mbar)



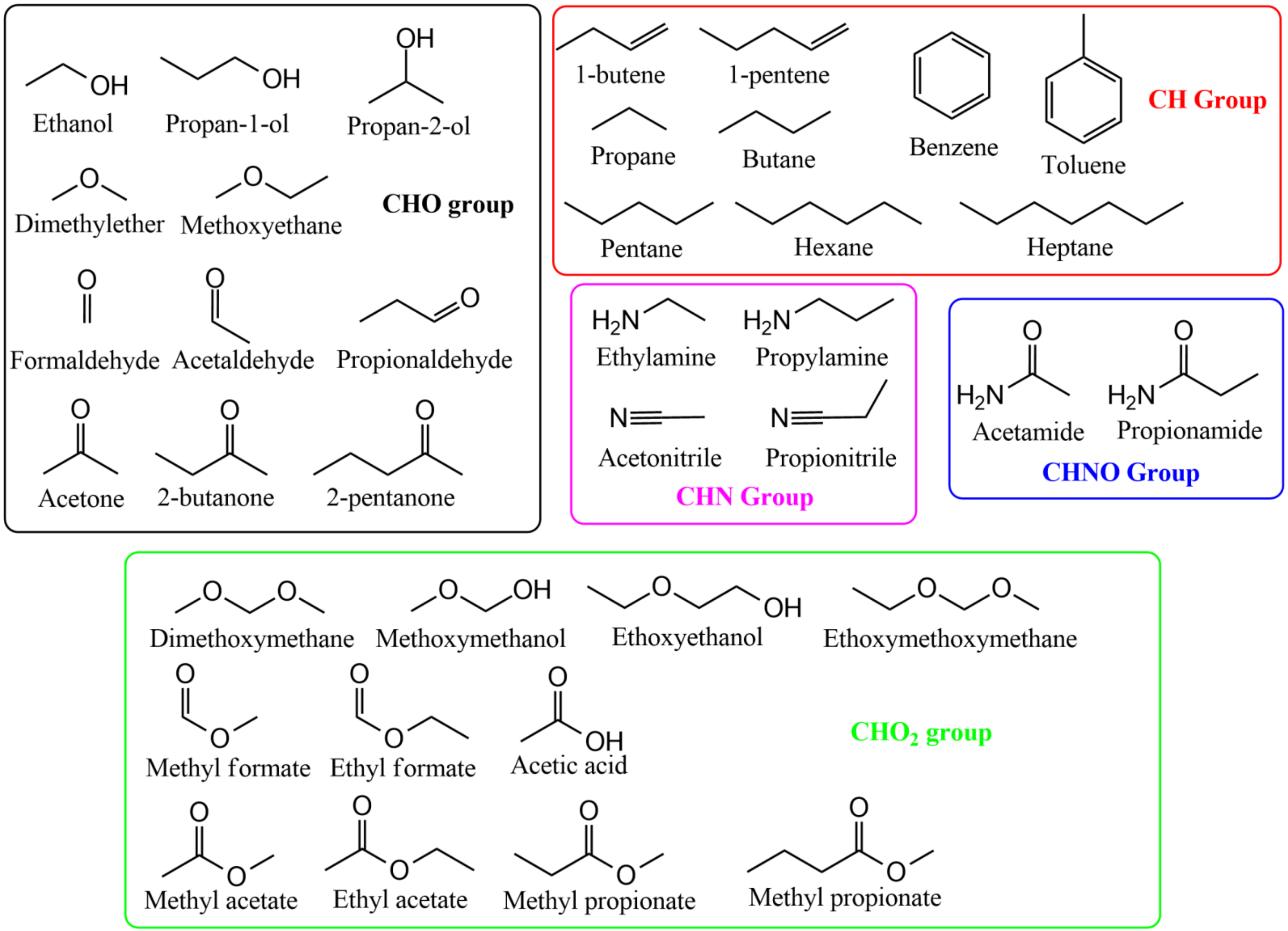




Ice formation in simulated conditions

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

Ice $H_2O:CH_3OH:NH_3$
Analysis with the VAHIIA system – products identified



Javelle et al., 2024

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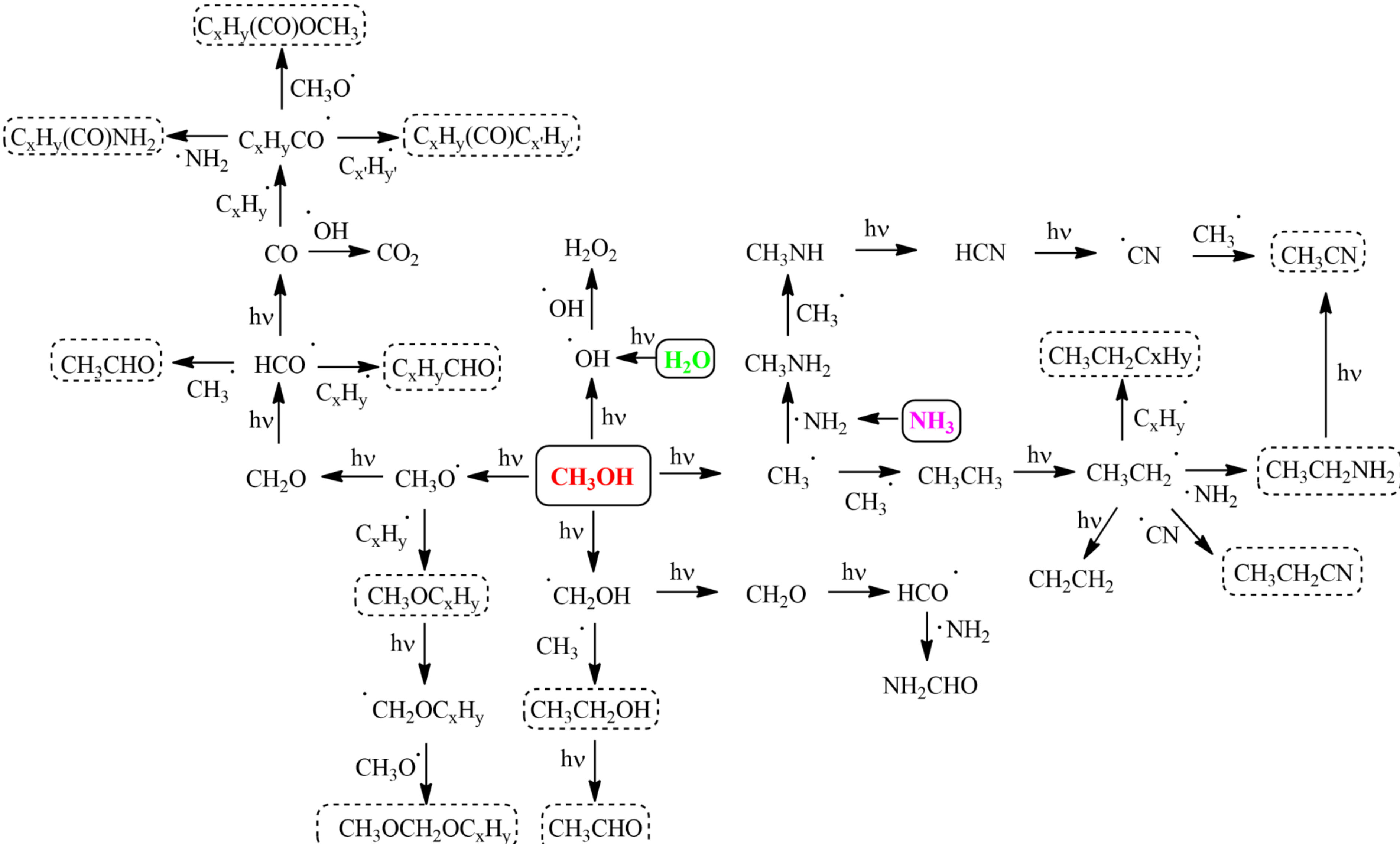
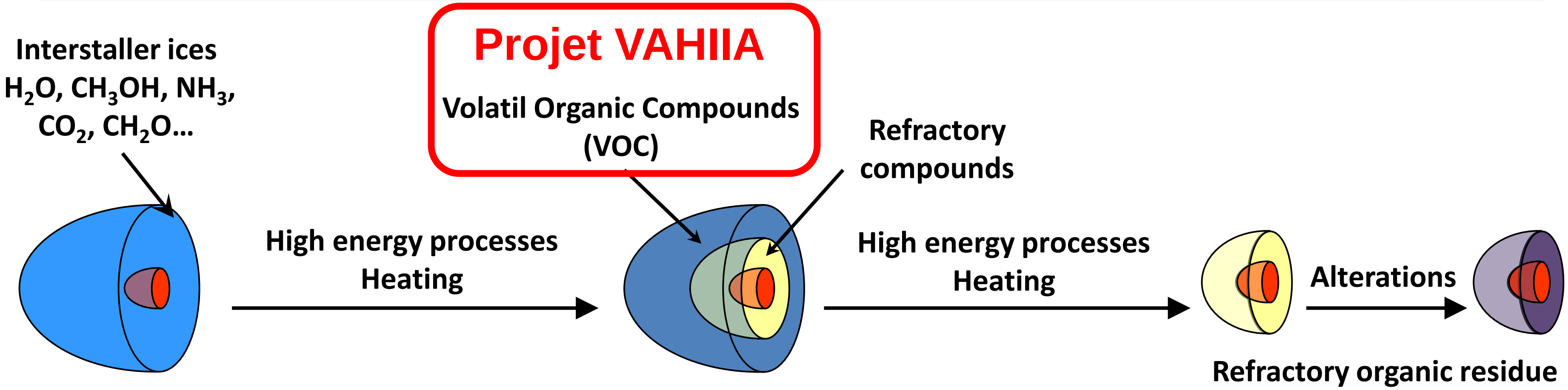


Javelle et al., 2024

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



Chemistry in diluted environment
20 K – 150 K

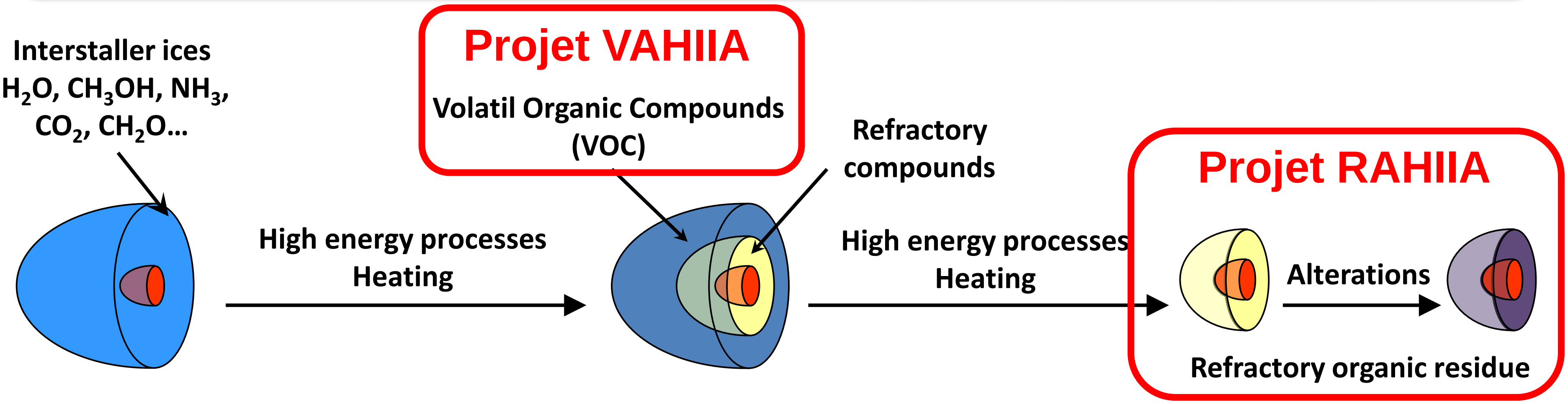
Radical and Thermal reactivities in water ice

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



ANR RAHIIA_SSOM (2016-2021)

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

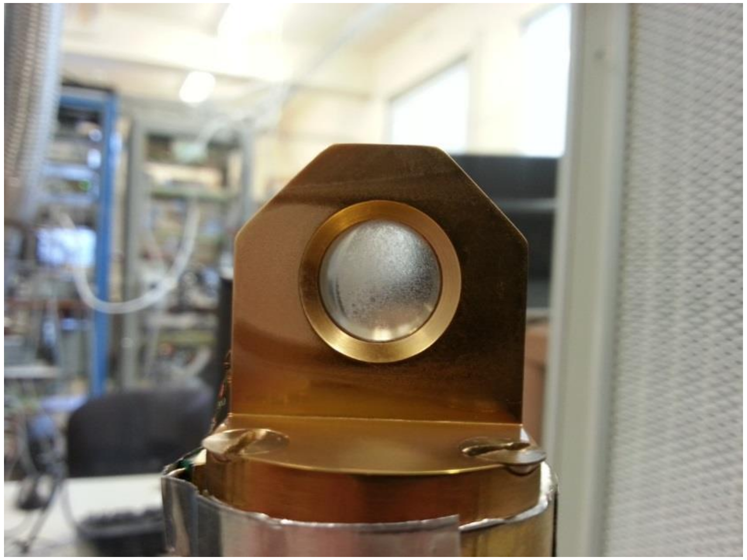
Chemistry in concentrated environment
> 185 K

Reactivity in absence of water

Formation of « macromolecules »

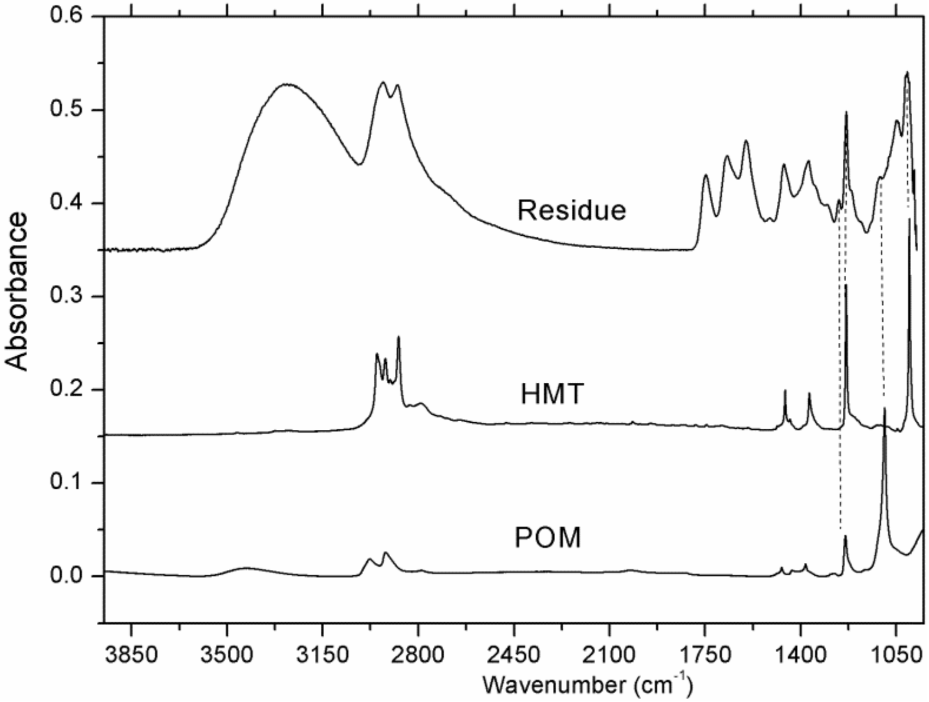
Soluble organic residue from ice processing

ANR-16-CE29-0015
2016-2021



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

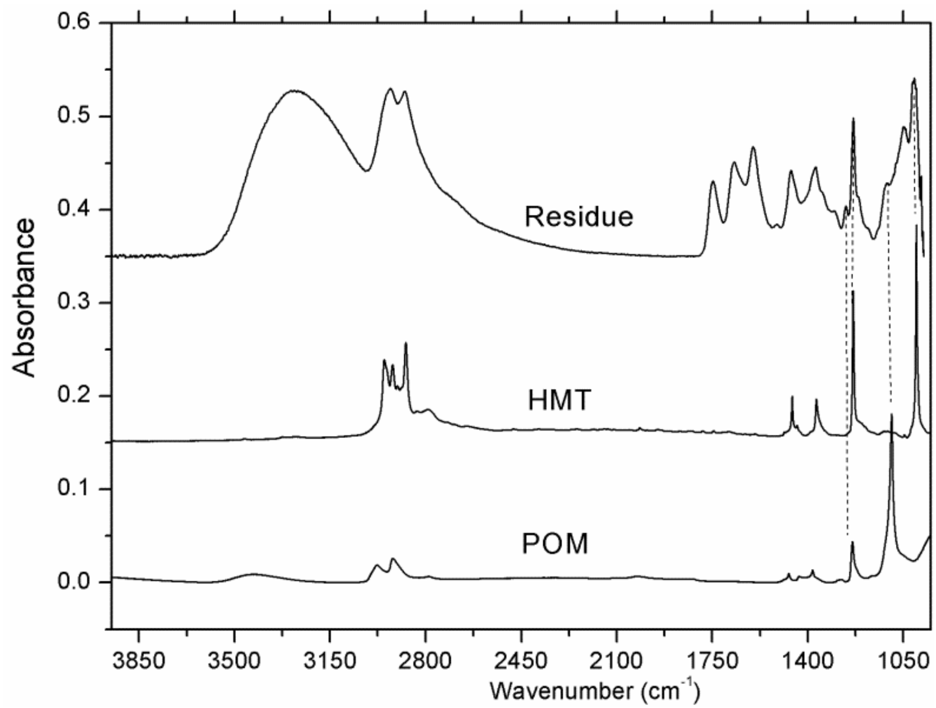
Most abundant molecules



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

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

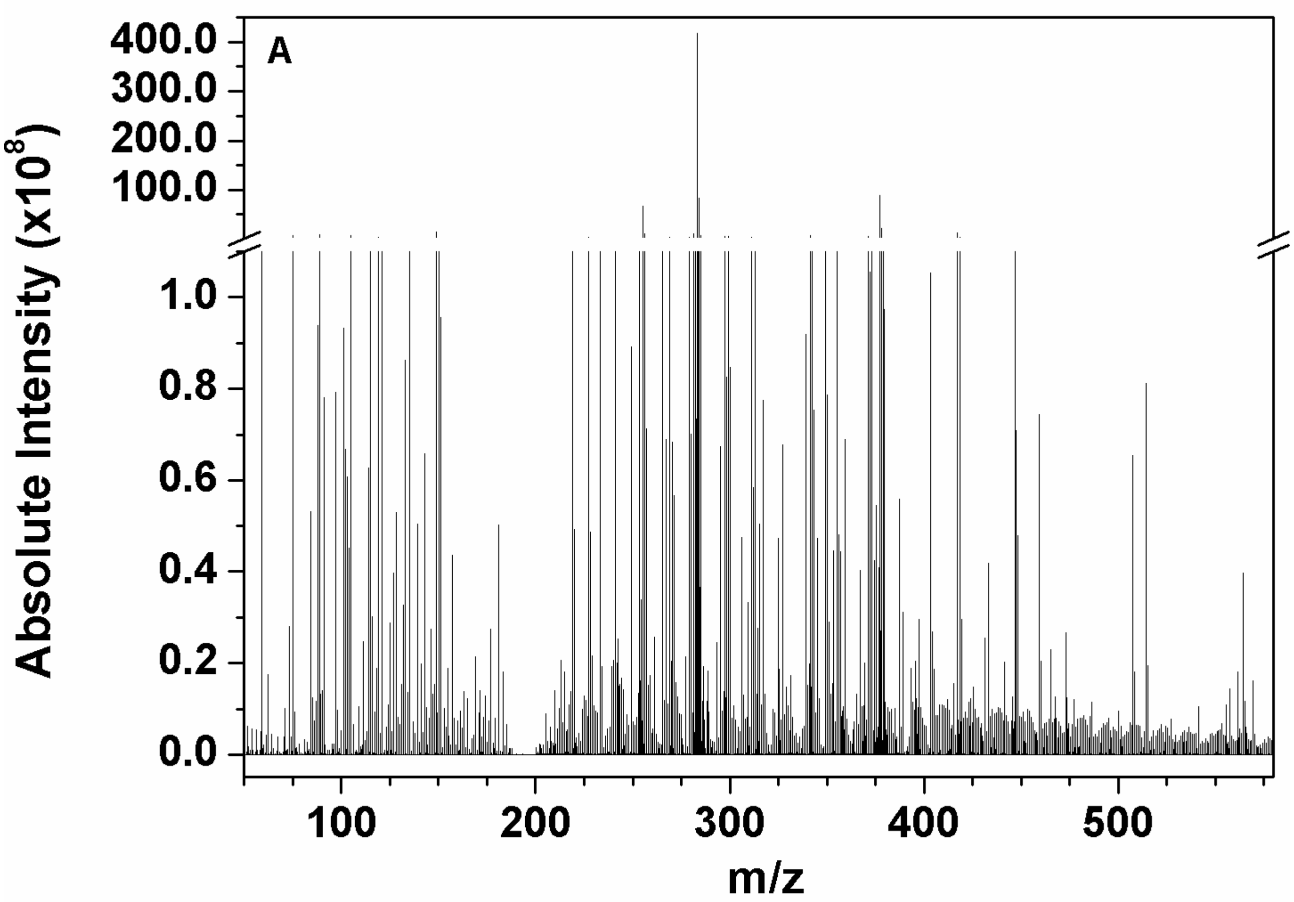
Position cm^{-1}	Carrier	Vibration mode
3500–2300	R–COOH, alcohols, NH_4^+	OH str., NH str.
3165	NH_4^+[a]	$\nu_1+\nu_5$[a]
3035	NH_4^+[a]	$\nu_2+\nu_4$
2926	HMT[b]	$2\nu_{19}$, $\nu_2+\nu_{19}$
2876	HMT[b], NH_4^+[a]	ν_{18} sym. CH_2 str., $2\nu_4$ of NH_4^+[a]
1742	Esters	C=O str.
1680	Amides	C=O str.
1586	COO^- in carboxylic acid salts	COO^- antisym. str.
1463	NH_4^+[a]	ν_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

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



UHRMS FT-Orbitrap Analysis in Negative ESI mode = $[M\text{-}H]^-$ 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

Soluble organic residue from ice processing: untargeted analyses

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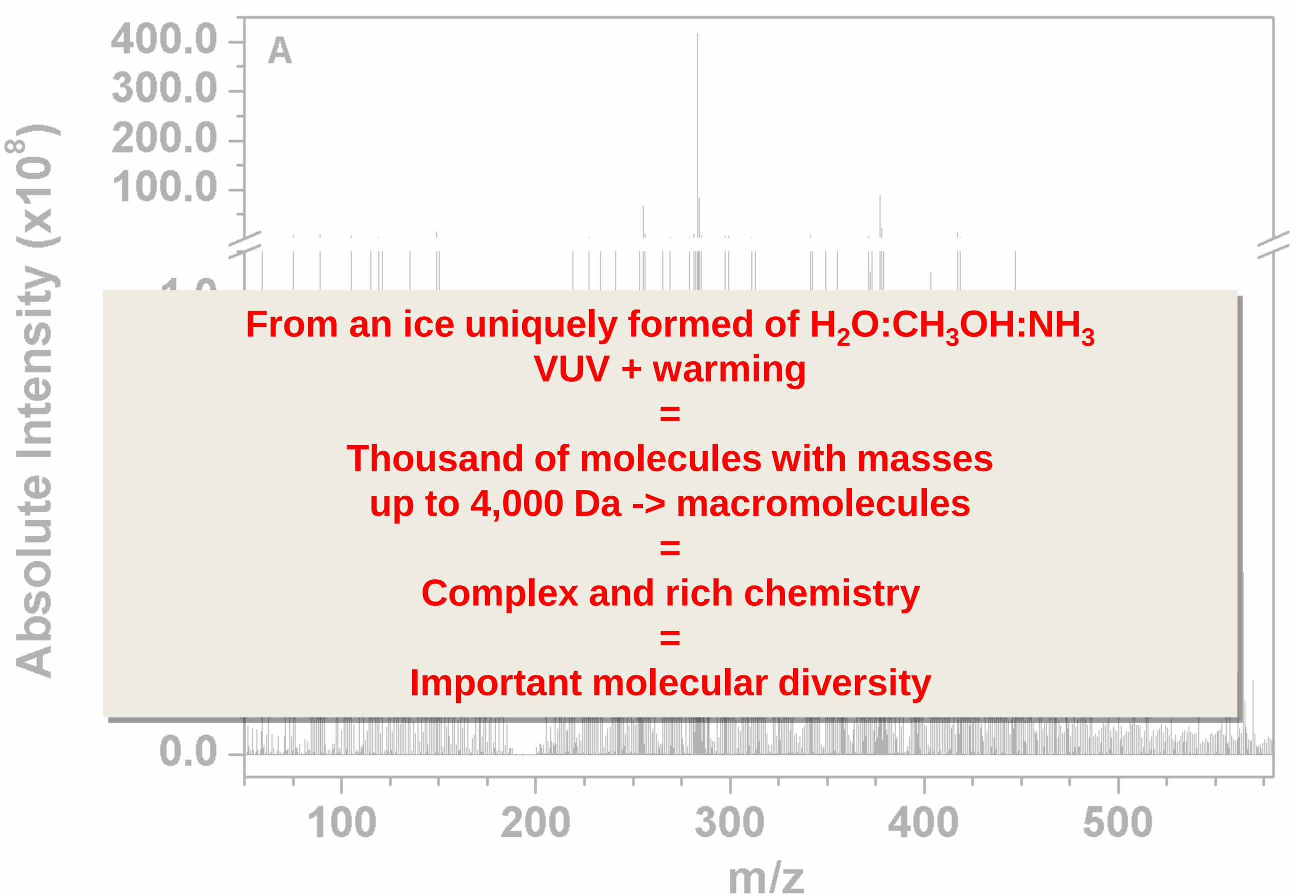


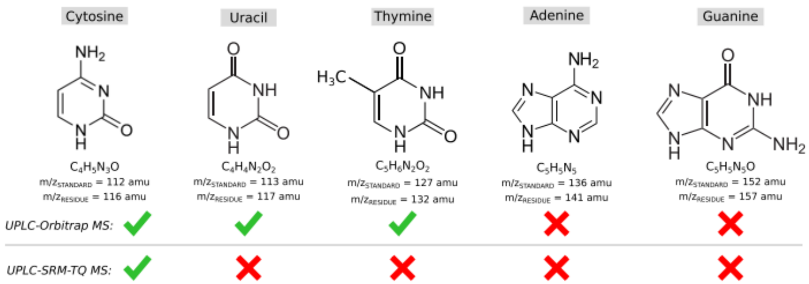
From an ice uniquely formed of H_2O:CH_3OH:NH_3
VUV + warming
=
Thousand of molecules with masses
up to 4,000 Da -> macromolecules
=
Complex and rich chemistry
=
Important molecular diversity

UHRMS FT-Orbitrap Analysis in Negative ESI mode = $[M\text{-}H]^-$ 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

Targeted analyses of soluble organic residues ($H_2O/NH_3/CH_3OH/\ldots$)

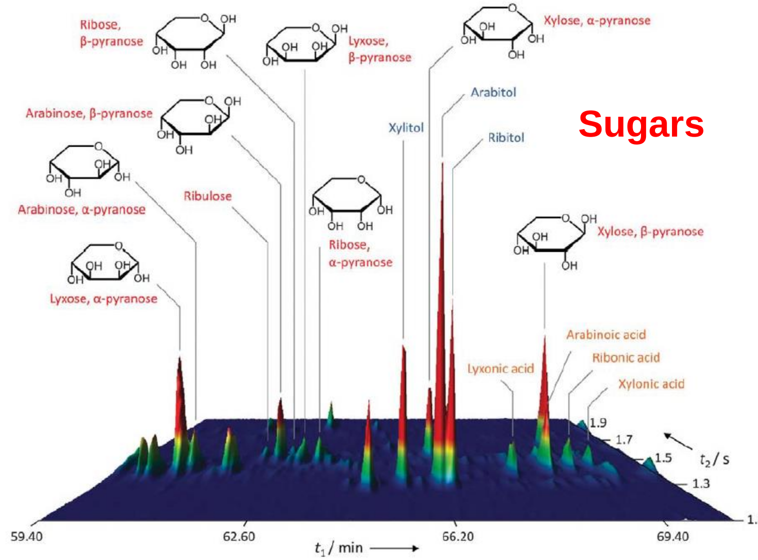
Nucleobases



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

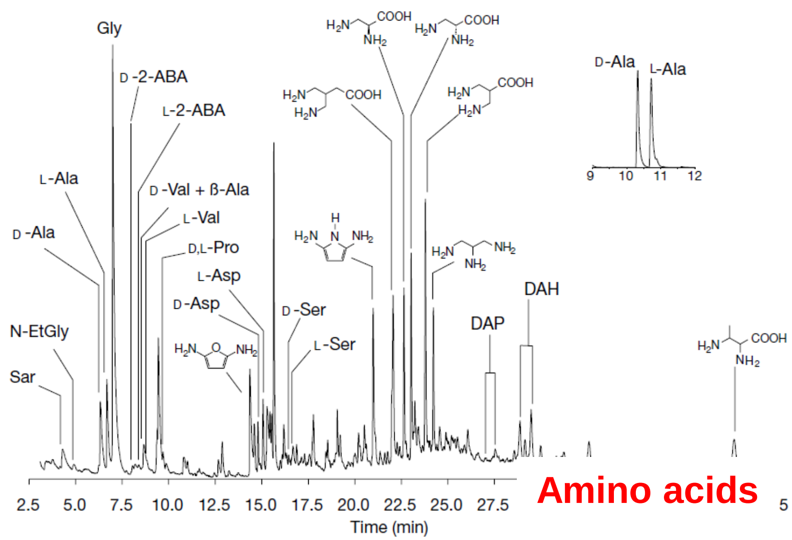
Oba et al., 2019, NatCom, 10, 4413

Sugars



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

Amino acids



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

Dipeptides

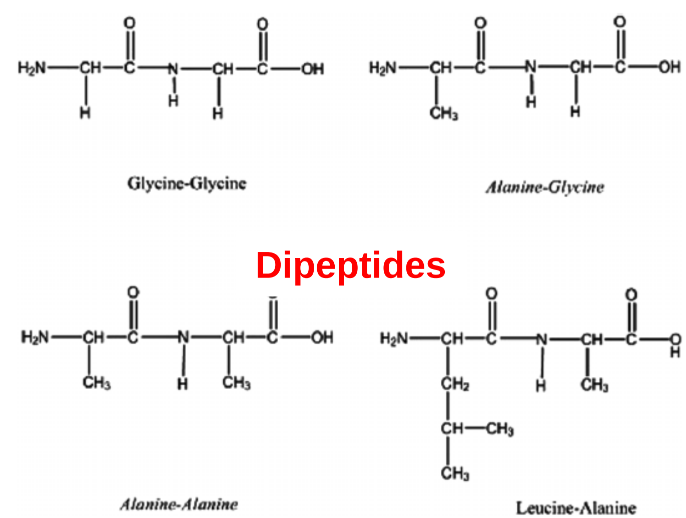


Figure 3. Dipeptides characterized via microchip capillary electrophoresis.

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

Meteorites : reservoir of carbonaceous matter

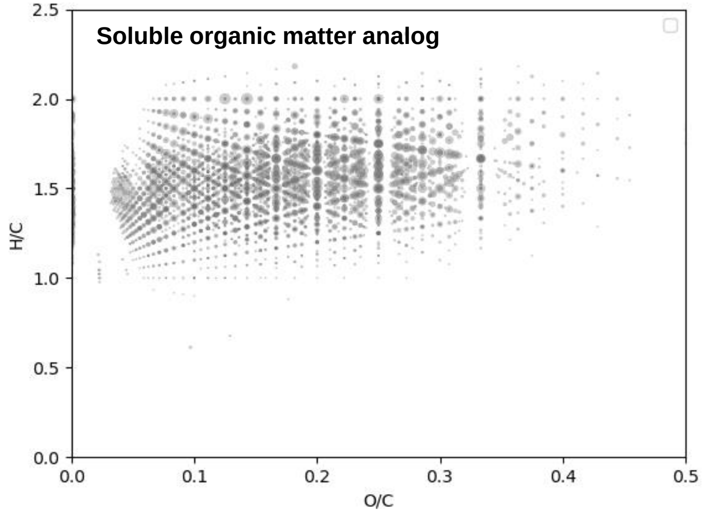
25% of soluble organic matter
75% of insoluble organic matter

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

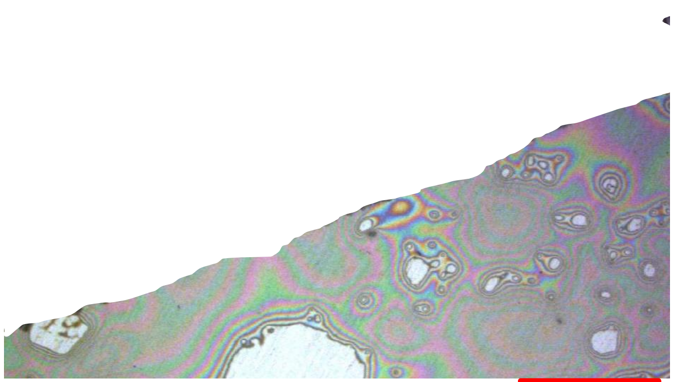
A scenario from extraterrestrial ices to soluble and insoluble materials

Residue (soluble)

300 K, 10^{-8} mbar



Laser desorption/ionization FT-ICR-MS



residue

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

Danger et al., A&A, 2022, 667, A120

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)

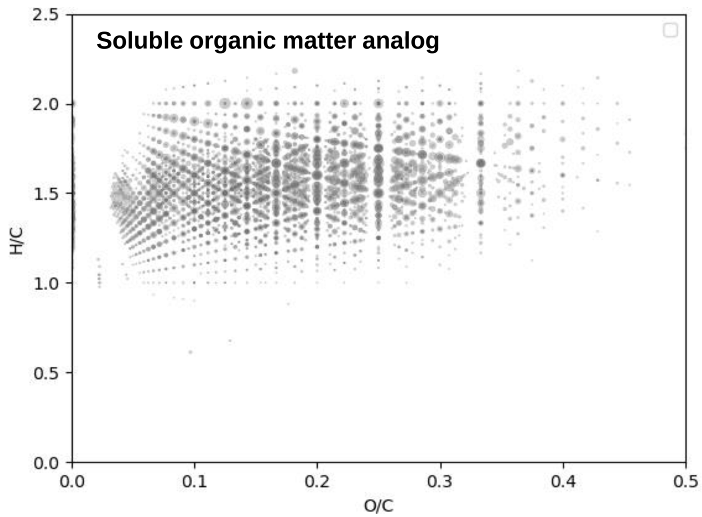
300 K, 10^{-8} mbar

UV →

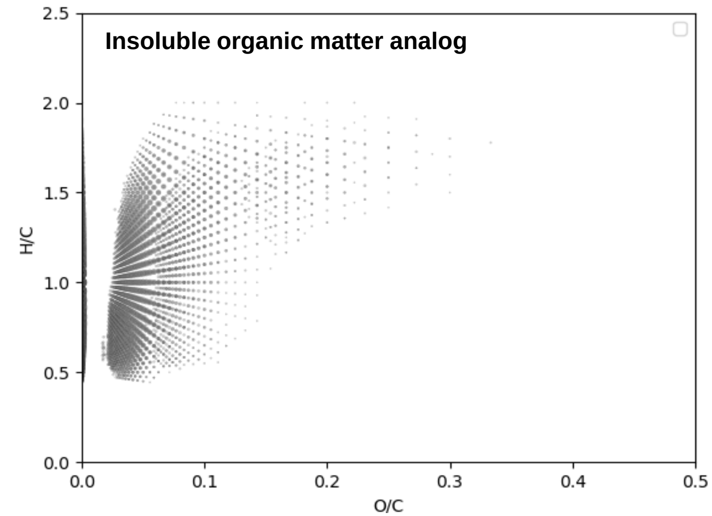
Residue irradiated (insoluble)

Residue (soluble)

300 K, 10^{-8} mbar

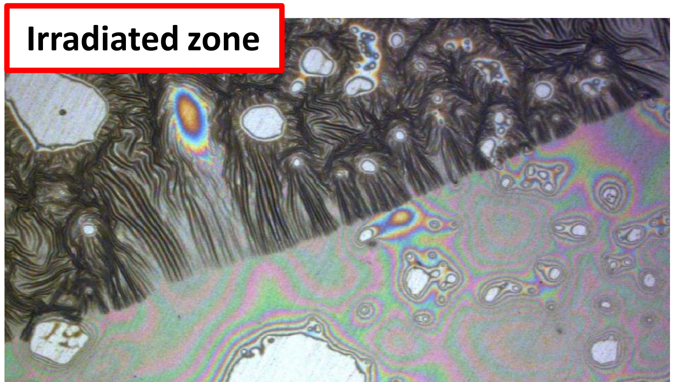


Laser desorption/ionization FT-ICR-MS



Laser desorption/ionization FT-ICR-MS

Irradiated zone



unirradiated zone

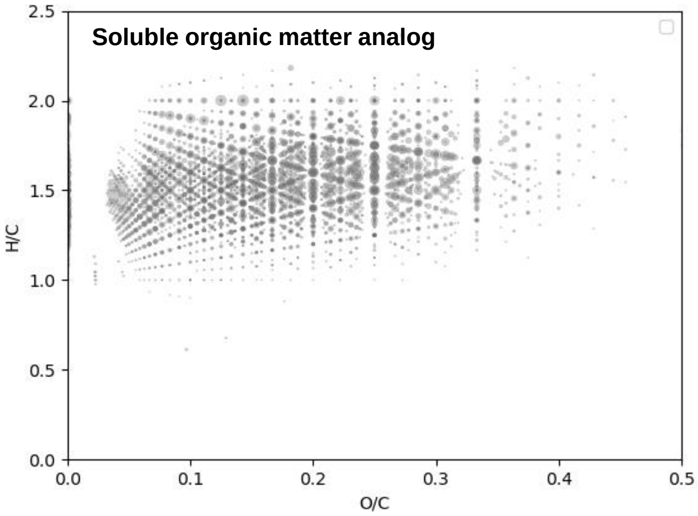
de Marcellus et al., MNRAS, 2017, 464, 114

Danger et al., A&A, 2022, 667, A120

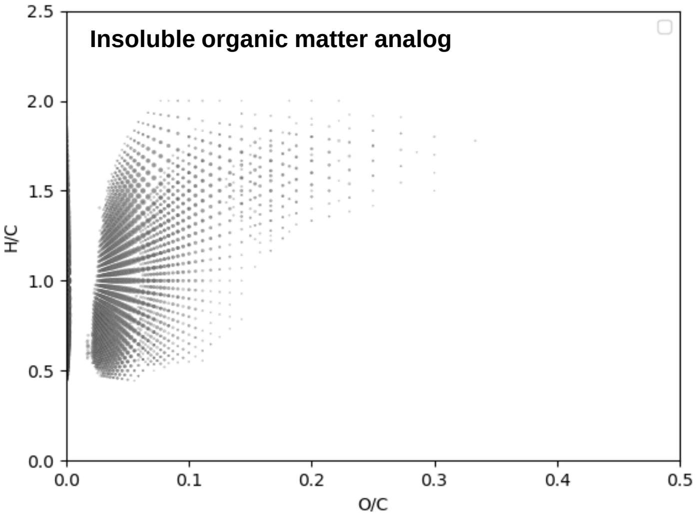
From soluble organic residues to insoluble ($H_2O/NH_3/CH_3OH$ =3/1/1)

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

A scenario from extraterrestrial ices to soluble and insoluble materials



UV, Electron, ion



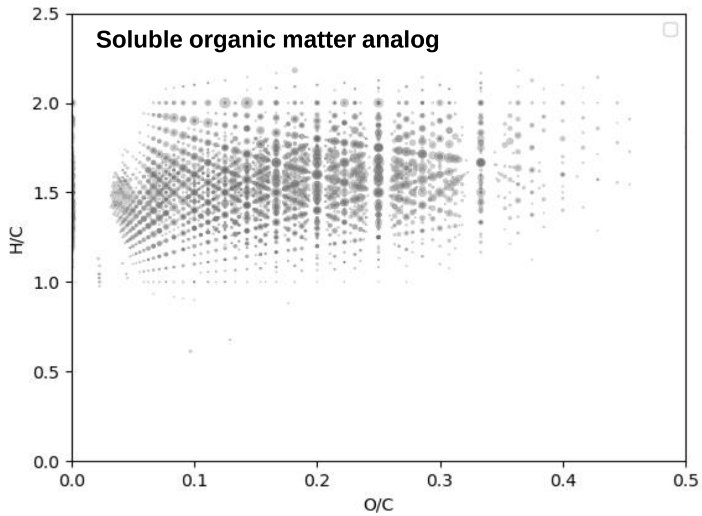
Laser desorption/ionization FT-ICR-MS **Laser desorption/ionization FT-ICR-MS**

Danger et al., A&A, 2022, 667, A120

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

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

A scenario from extraterrestrial ices to soluble and insoluble materials



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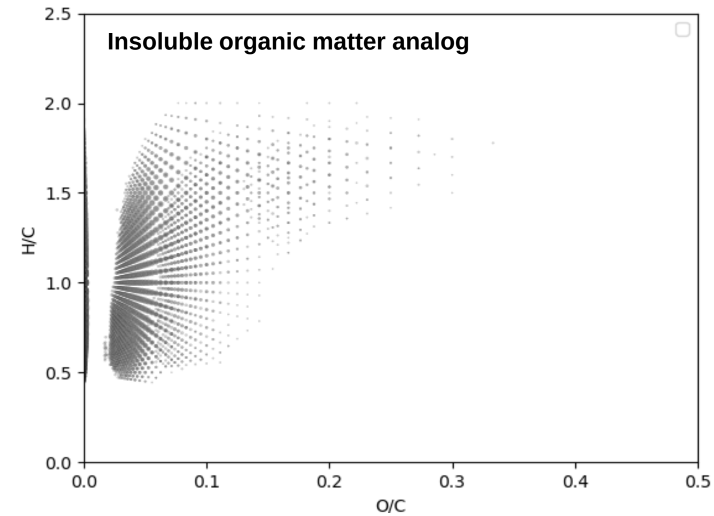

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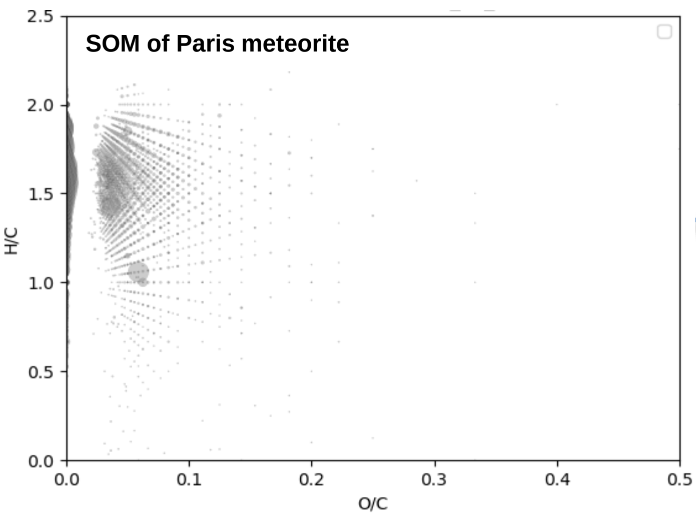
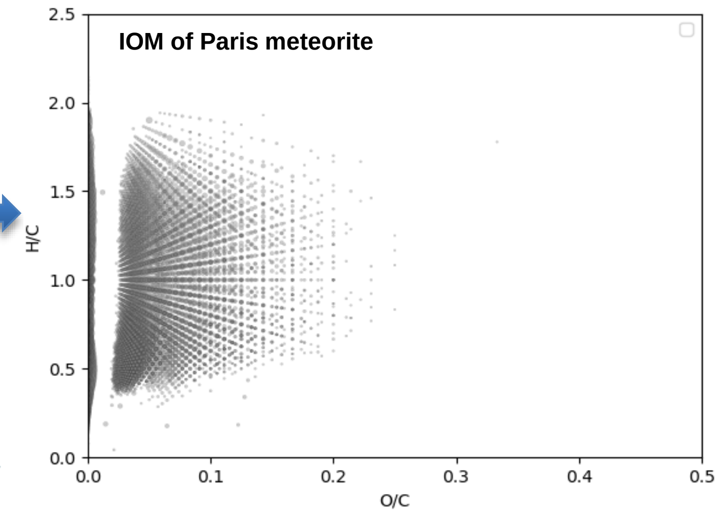


Meteorites



links
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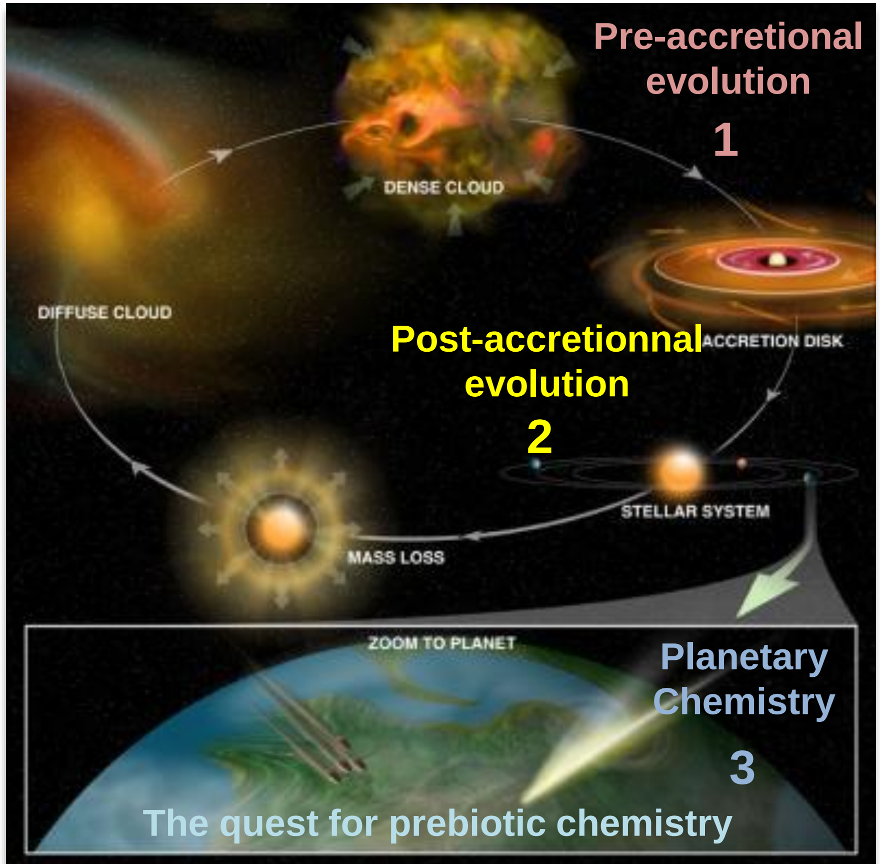
Danger et al., A&A, 2022, 667, A120

From Astrochemistry to Prebiotic Chemistry: Organic Matter Evolution

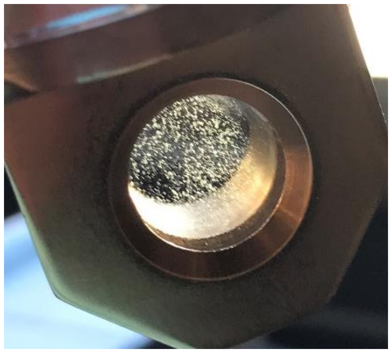


- ***Pre-accretional process: an important molecular diversity is formed from soluble to insoluble***
- ***Post-accretional process: How the pre-accrational organic matter evolved***
- ***Planeraty Chemistry: what conditions for a prebiotic chemistry***

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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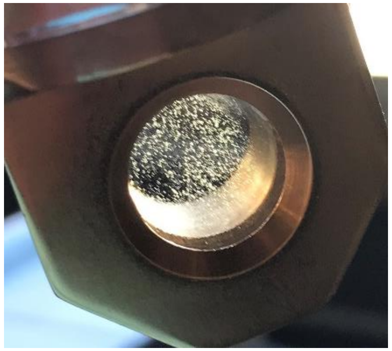
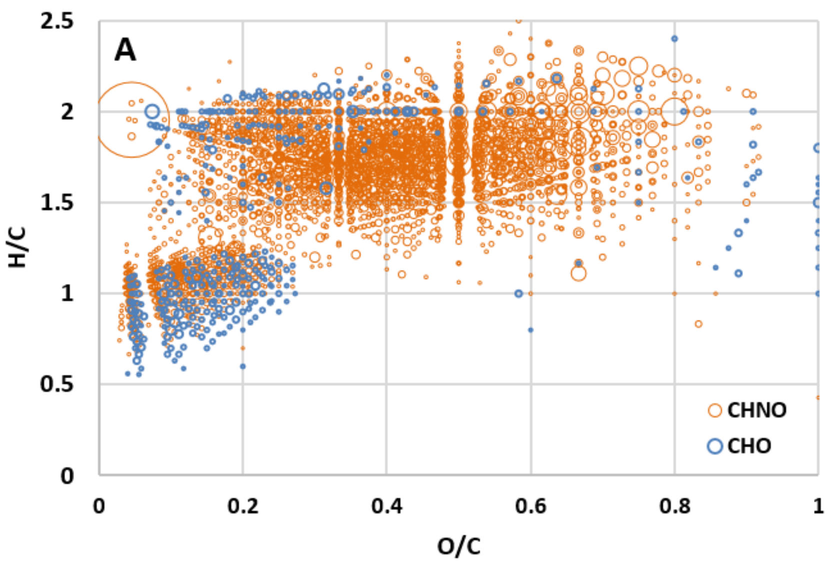
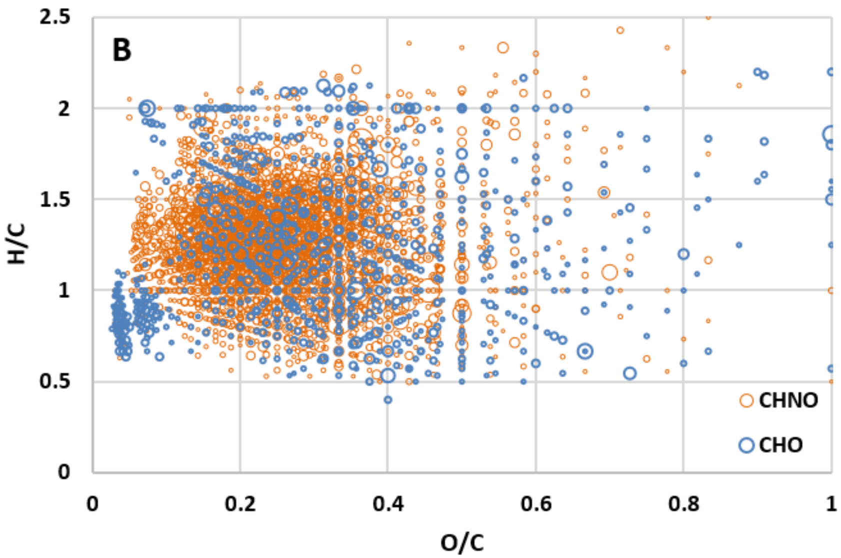




Fresh residue t_0



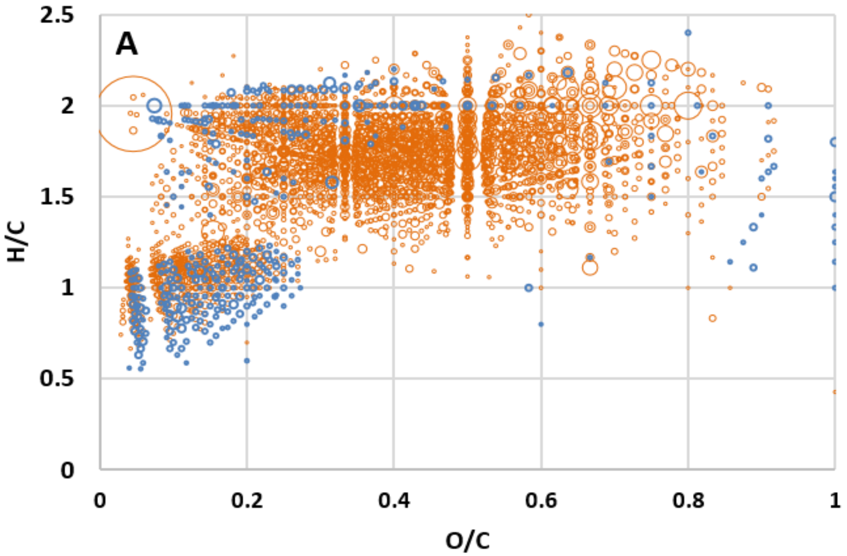
Residue after 100 days at 150°C

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

Laboratory experiments: Simulate post-accretional processes

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

Comparison to Soluble Organic Matter
Murchison meteorite



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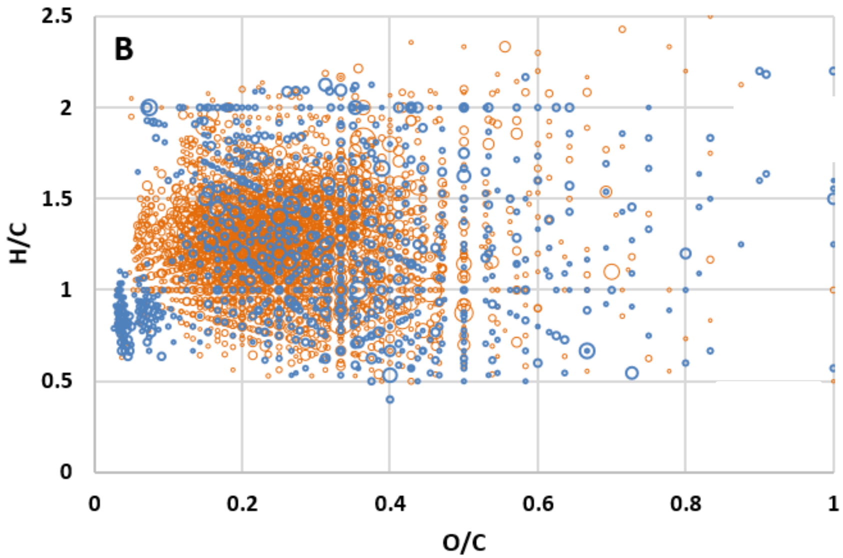

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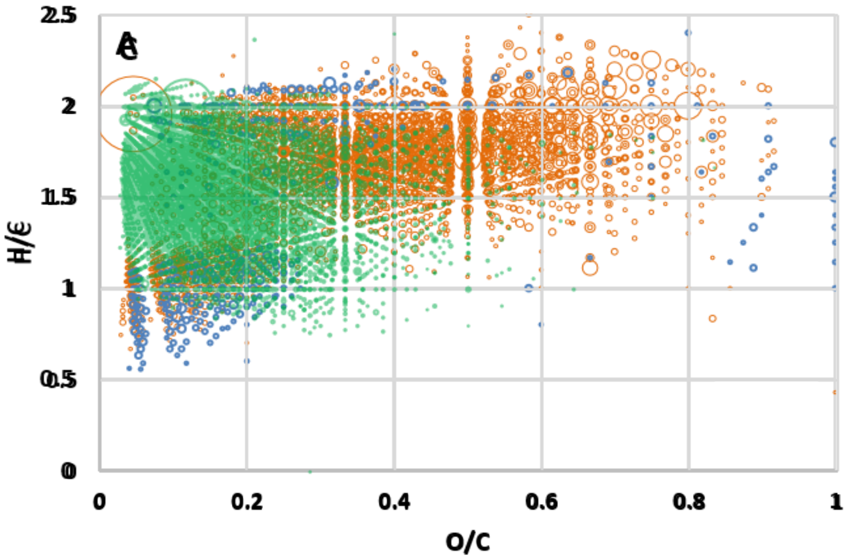

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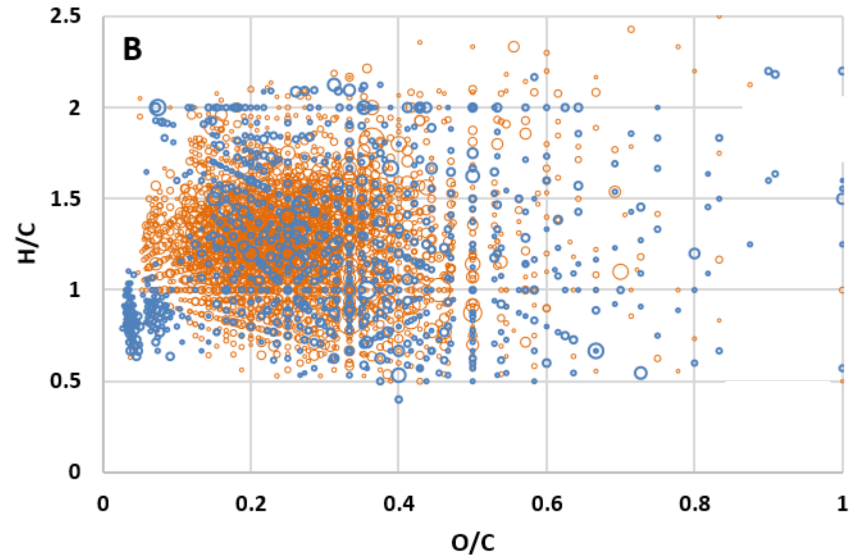

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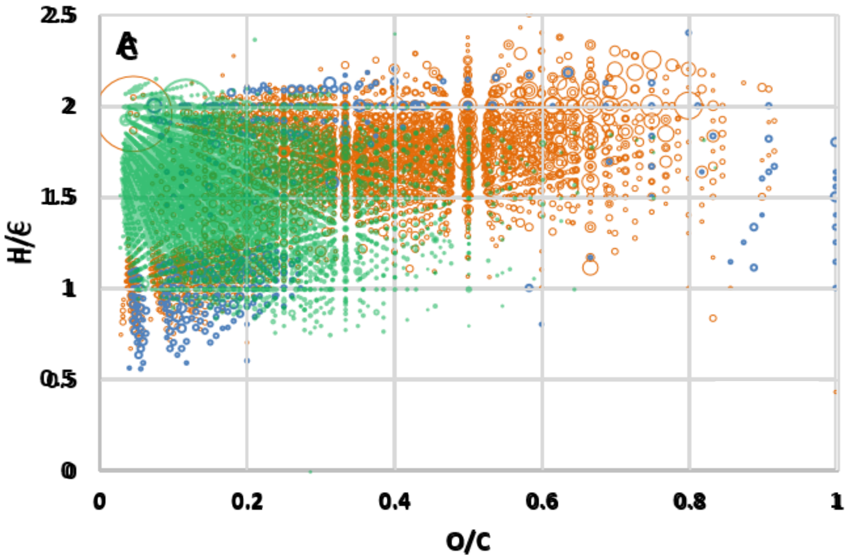
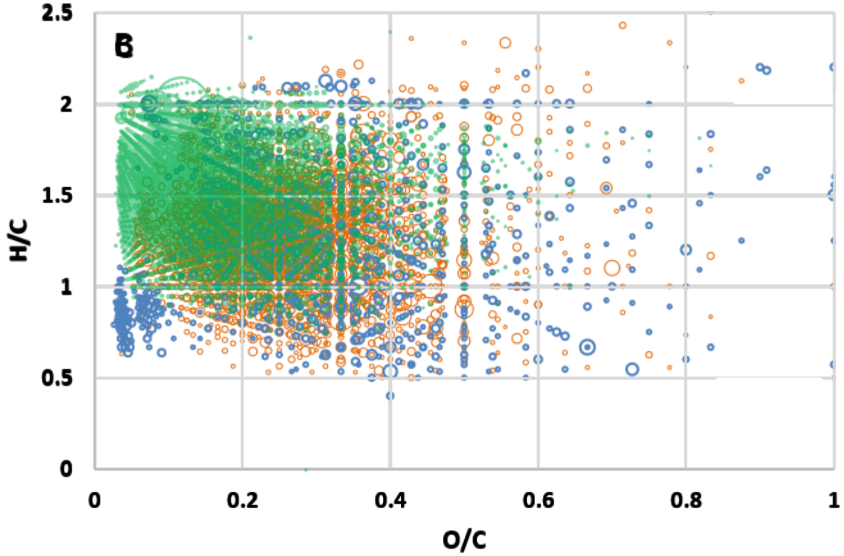
Comparison to Soluble Organic Matter
Murchison meteorite



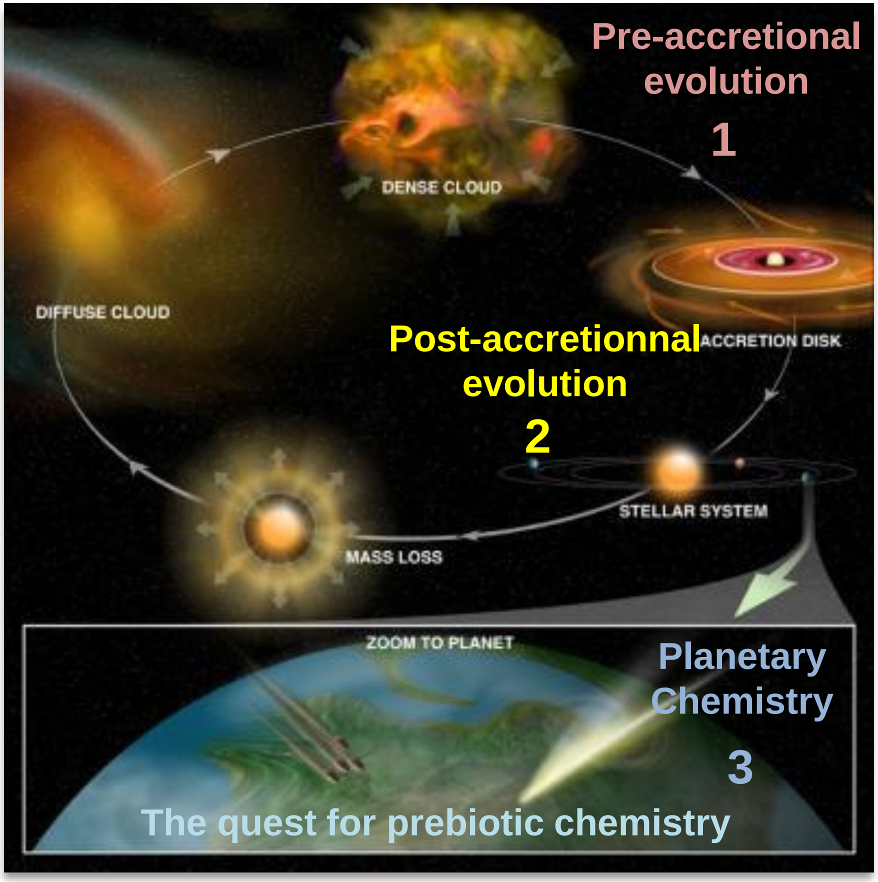
Fresh residue t_0



Residue after 100 days at 150°C

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

From Astrochemistry to Prebiotic Chemistry: Organic Matter Evolution



- ***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***

Collaborations and Funding

Collaborations:

Funding: