

Formation and evolution of a complex organic molecule : from interstellar ices to asteroids



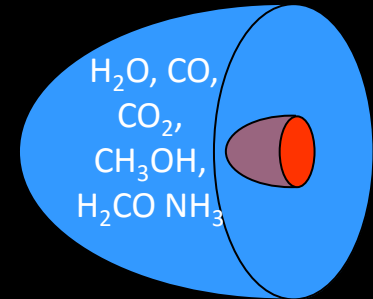
V. Vinogradoff,

S. Bernard, Duvernay F., C. Le Guillou,
Chiavassa T., L. Remusat

Molecules in Interstellar ices

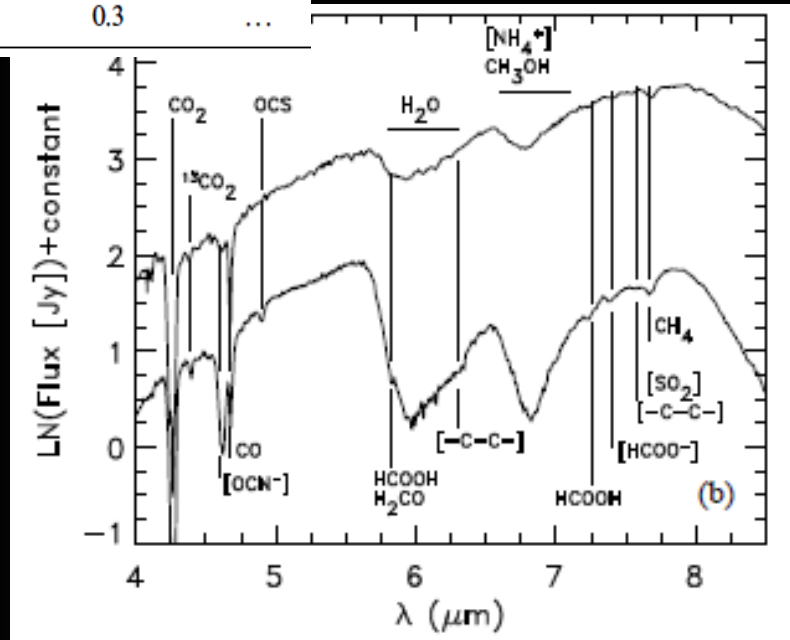
ICE ABUNDANCES TOWARD INFRARED SOURCES AND COMETS^a

Species	Elias 16 ^b	NGC 7538 IRS 9 ^c	GL 7009S ^d	W33A ^e	GL 2136 ^f	Sgr A* ^g
H ₂ O	100	100	100	100	100	100
CO (total)	25	16	15	8	2	<12
CO (polar)	3	2	...	6	2	...
CO (nonpolar)	22	14	...	2
CO ₂ (total)	18	22	21	13	16	14
CO ₂ (polar)	18	14	...	11	13	14
CO ₂ (nonpolar)	<1	8	...	2	3	<1
CH ₄	2	4	1.5	...	2
CH ₃ OH	<3	5	30	18	6	<4
H ₂ CO	4	3	6	3	<3
HCOOH	3	...	7	...	3
OCS	<0.2	...	0.2	0.2
NH ₃	≲9	13	...	15	...	20-30
XCN ⁱ	<0.5	1	1.5	3.5	0.3	...



Gibb et al. , The Astrophysical Journal, 2000.

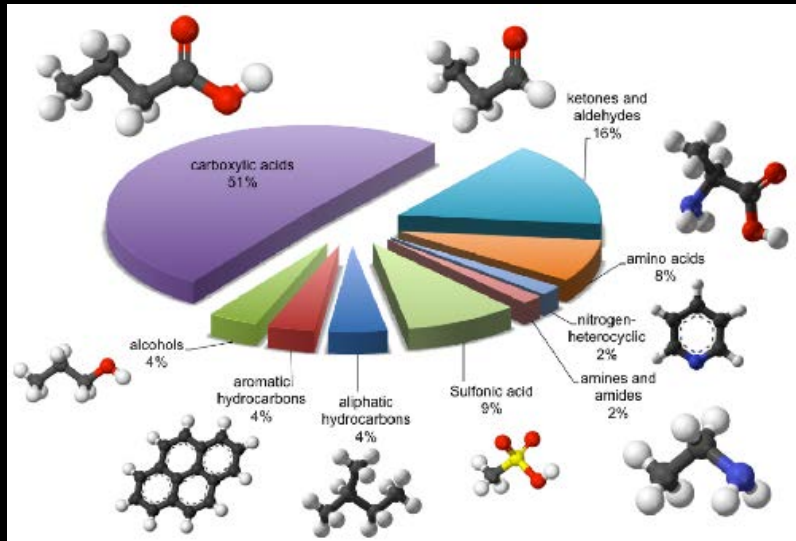
Simple molecules observed in interstellar ices



Organic matter in chondrites

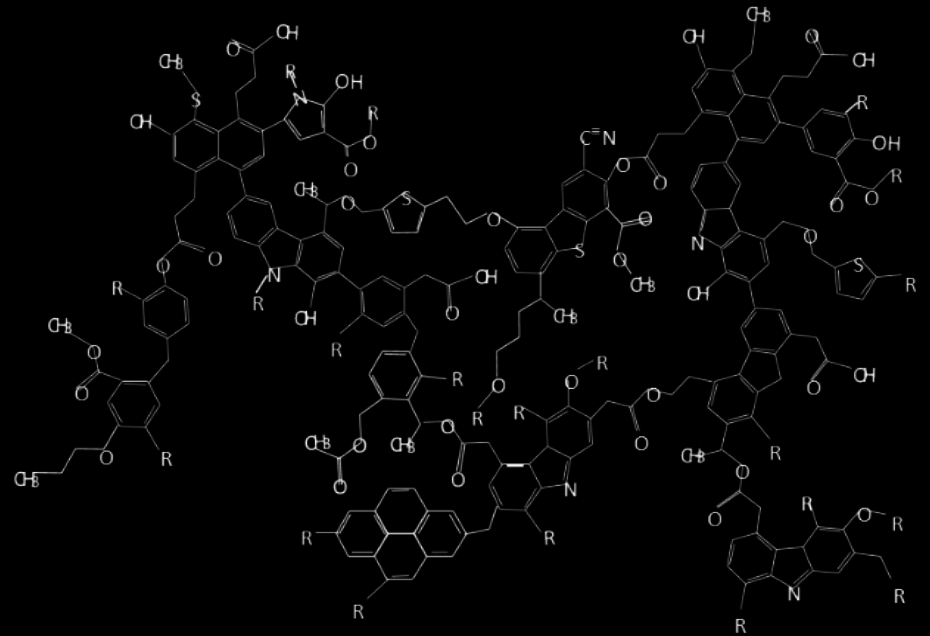


SOM (10-25%)

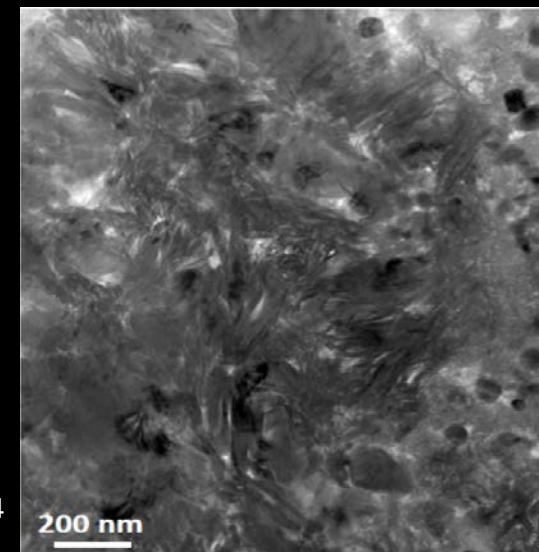


Remusat, 2015

IOM (75-90%)



Derenne & Robert, 2010

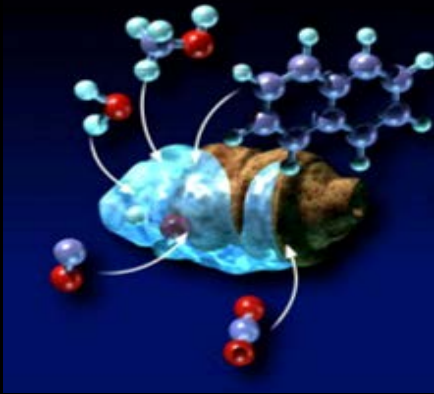


Le Guillou et al., 2014

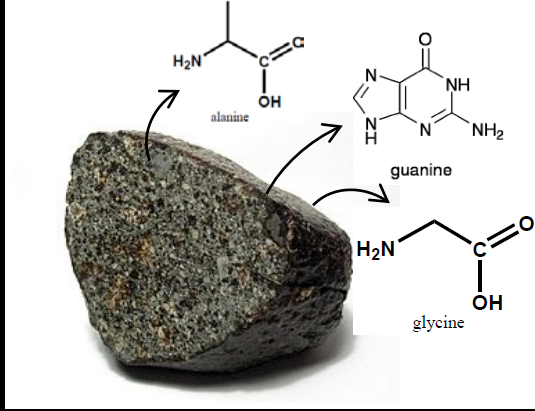
200 nm

➔ Evidence of hydrothermal alteration in chondrites : modification of the organic matter ?

Goal

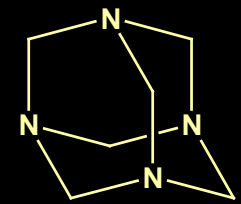


?



Relationship between ices and asteroids ?

The HMT molecule

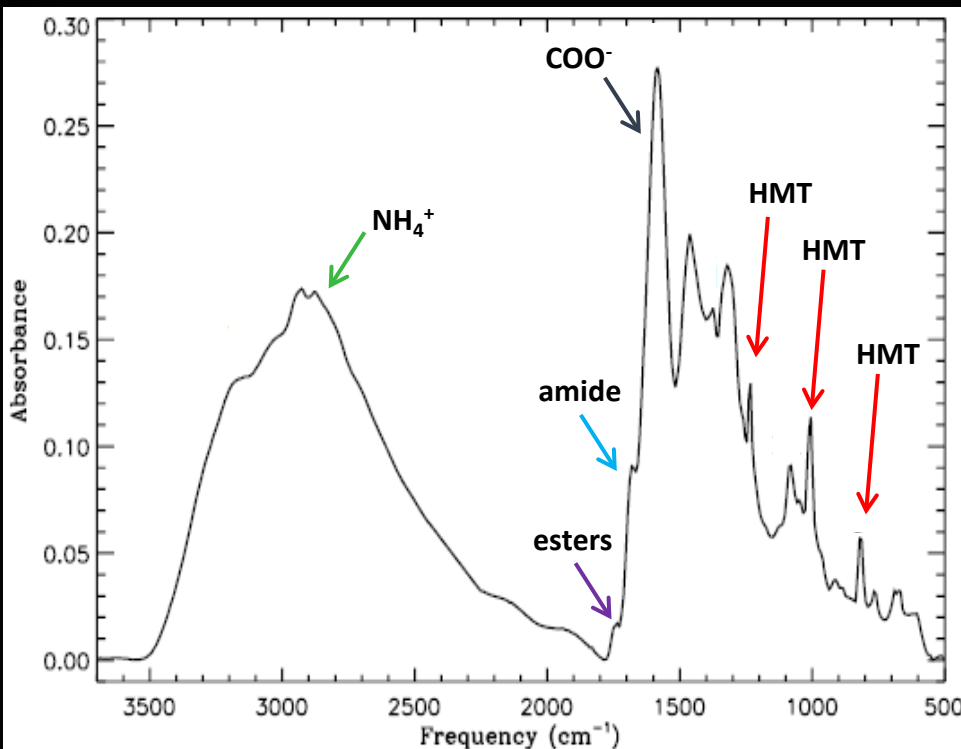


Hexamethyltetramine
(HMT)

✓ Characterized in interstellar ice analogue residues

Up to 60%wt of the residue

H₂O / CH₃OH / NH₃ / CO / CO₂ ice analogue:
photolysed at 20 K and warmed to room temperature



☐ never observed in the ISM,
nor in meteorites

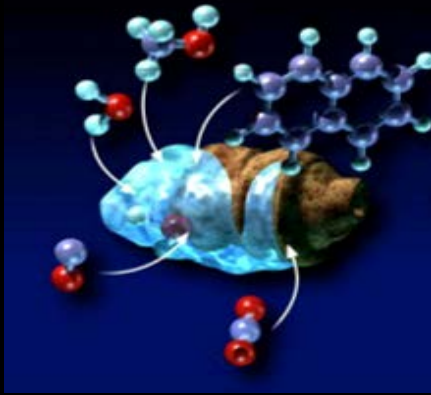
J.E. Bowey, MNRAS, 298, 1998

**-initial molecule in the OM in
meteorites ? What is its
modifications during hydrothermal
alteration ?**

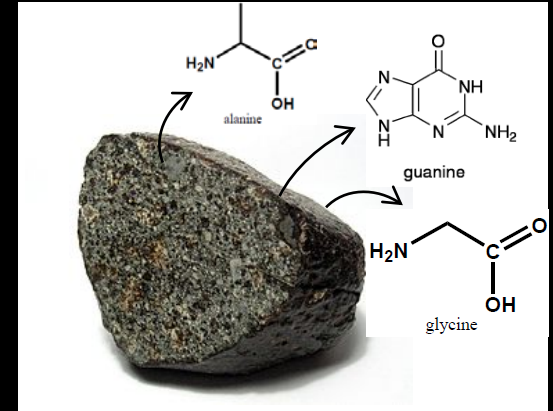
- mechanism formation in ices ?

G.M. Muñoz-Caro et al., Nature, 2002, 416, 403-406
M.P. Bernstein et al., Nature, 2002, 416, 401-403

Experimental investigations



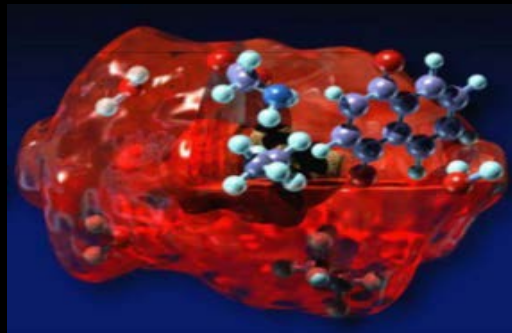
?

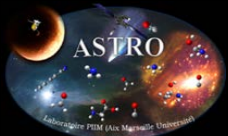


Interstellar ice evolution:

Formation of complex organic molecules in ices

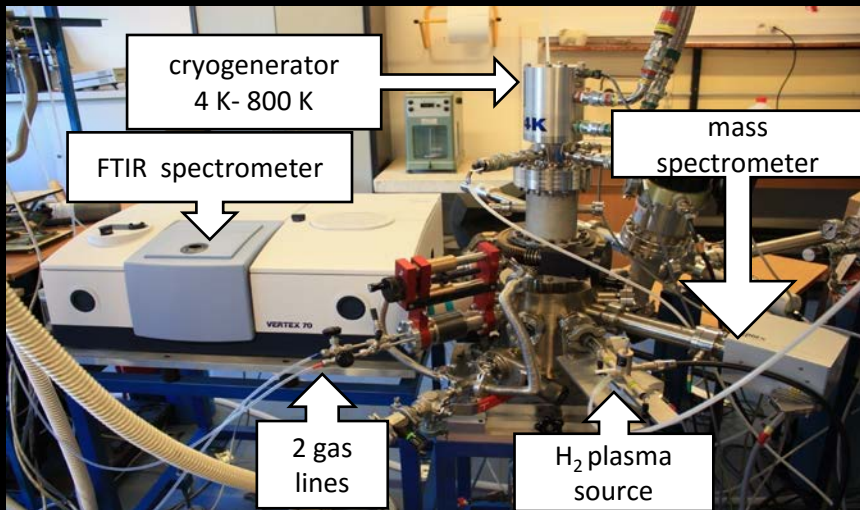
From simple molecules
(3-5 atoms)
to HMT (22 atoms)





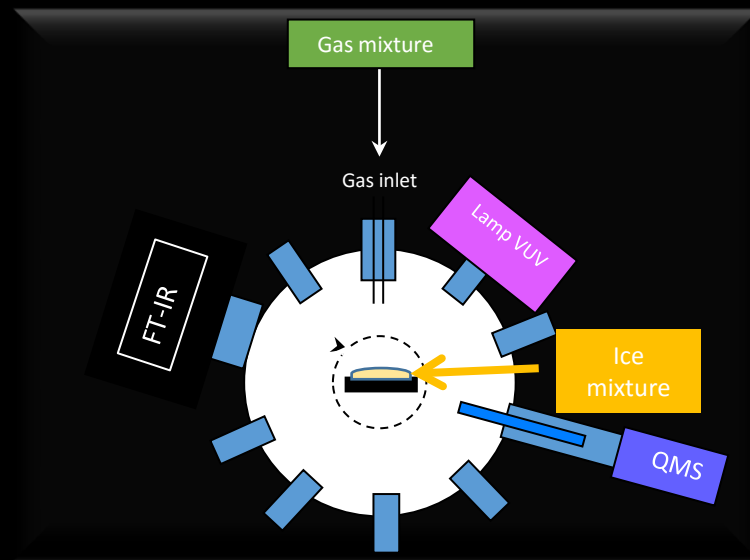
Interstellar ice evolution

(Reactivity in INTERstellar Grains)

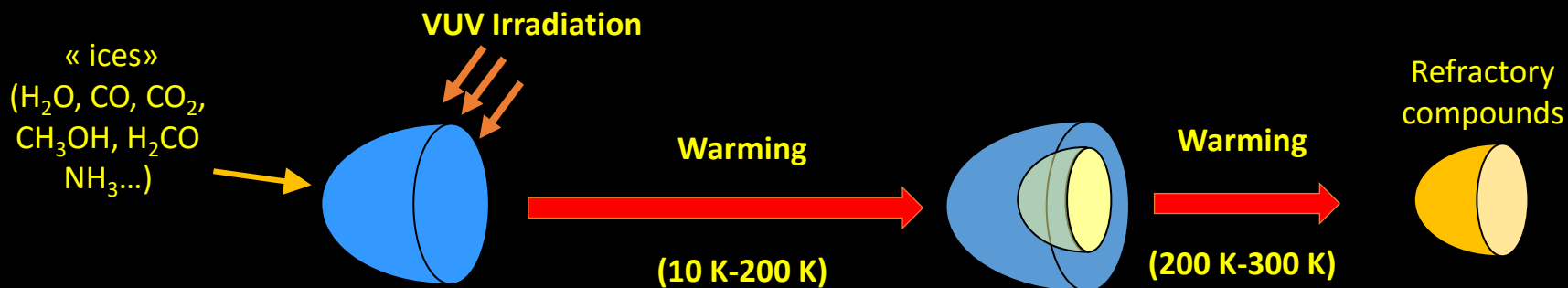


Pressure inside $\approx 10^{-9}$ mbar

Simulation of ISM energetic processes



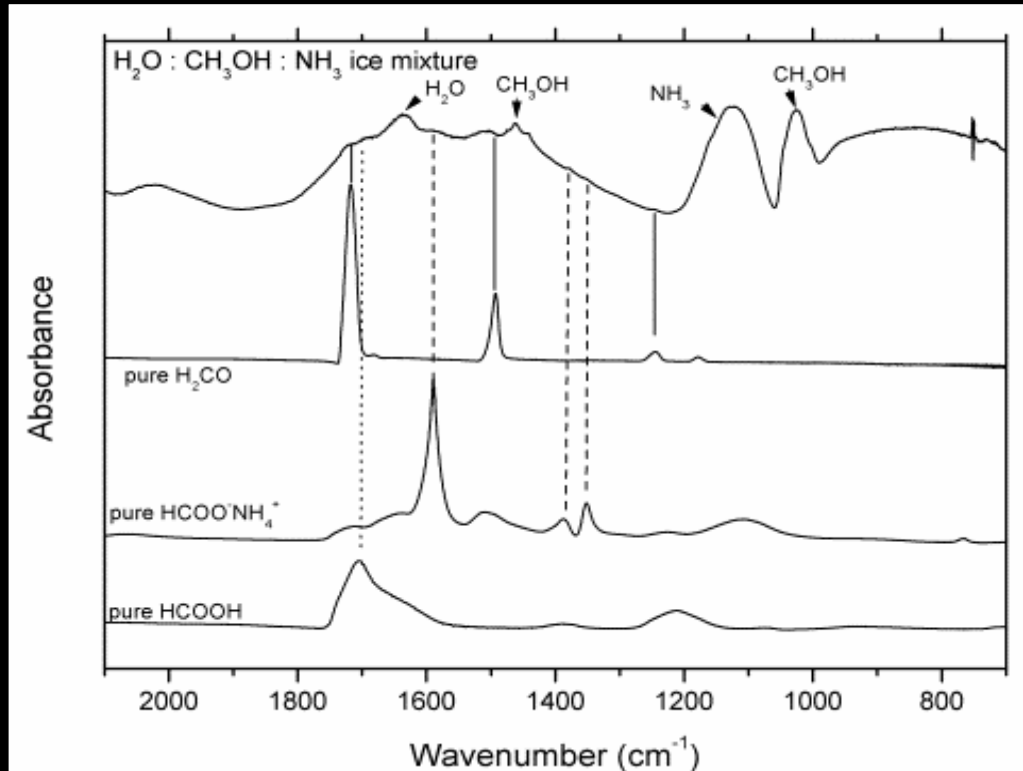
Experiments and detection of products followed by **infrared** and **mass spectrometers**



Interstellar ice evolution: the case of HMT

UV irradiation process: 25 K

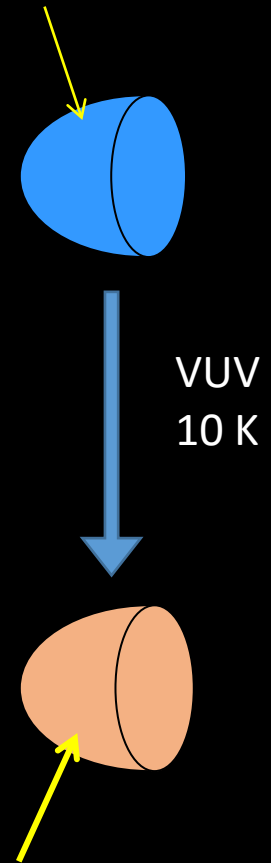
$\text{H}_2\text{O} / \text{CH}_3\text{OH} / \text{NH}_3$ 10:1:1 $h\nu$ 25 K



After warming, HMT is observed in the residue

HMT is not formed after the irradiation process
Thermal process ?

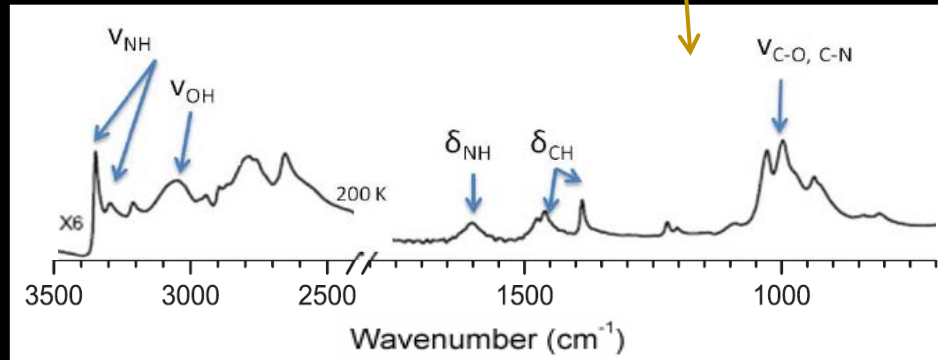
$\text{CH}_3\text{OH} + \text{NH}_3 + \text{H}_2\text{O}$



Main Products
H₂CO,
HCOOH

Interstellar ice evolution: the case of HMT

□ Thermal process: 10 K to 210 K



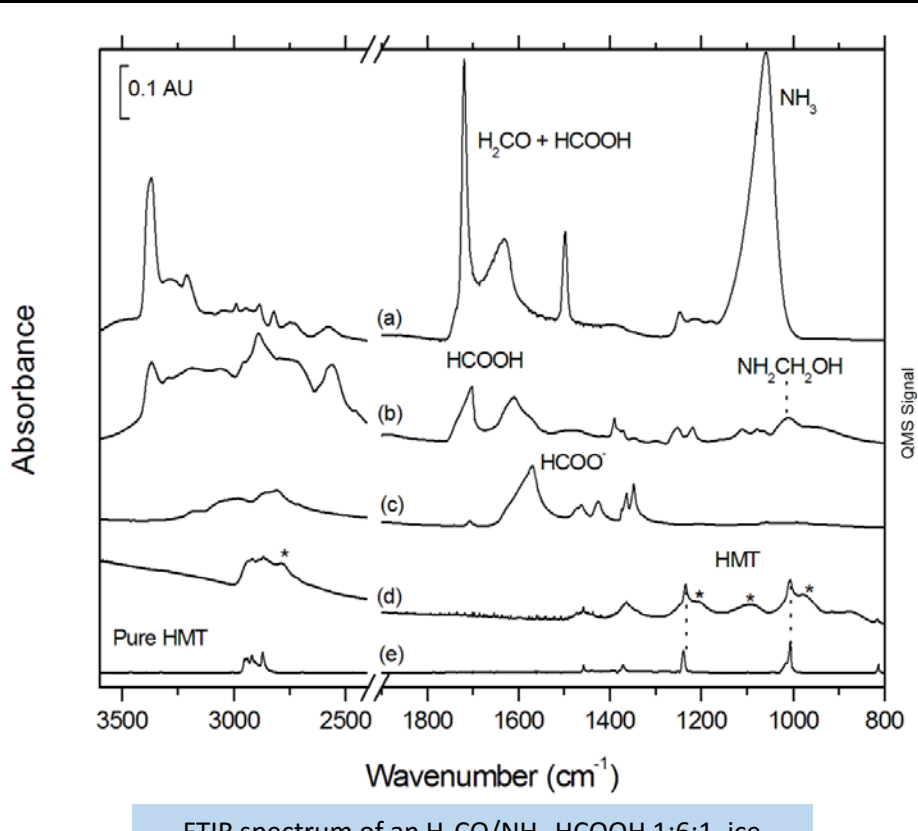
Bossa et al. The Astrophysical Journal, 707, 2009

**Is formic acid key molecule ?
(main product of the irradiation process)**

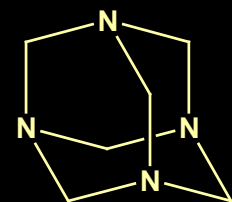
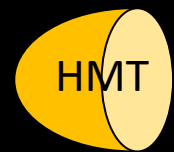
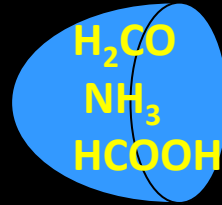
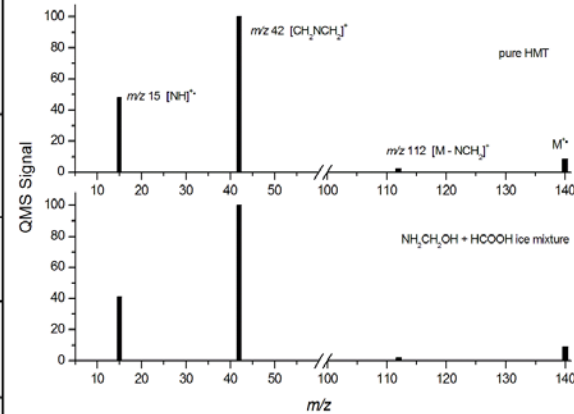
Interstellar ice evolution: the case of HMT

☐ Thermal process: 10 K to 330 K

$\text{H}_2\text{CO}/\text{NH}_3/\text{HCOOH}$ 1:6:1



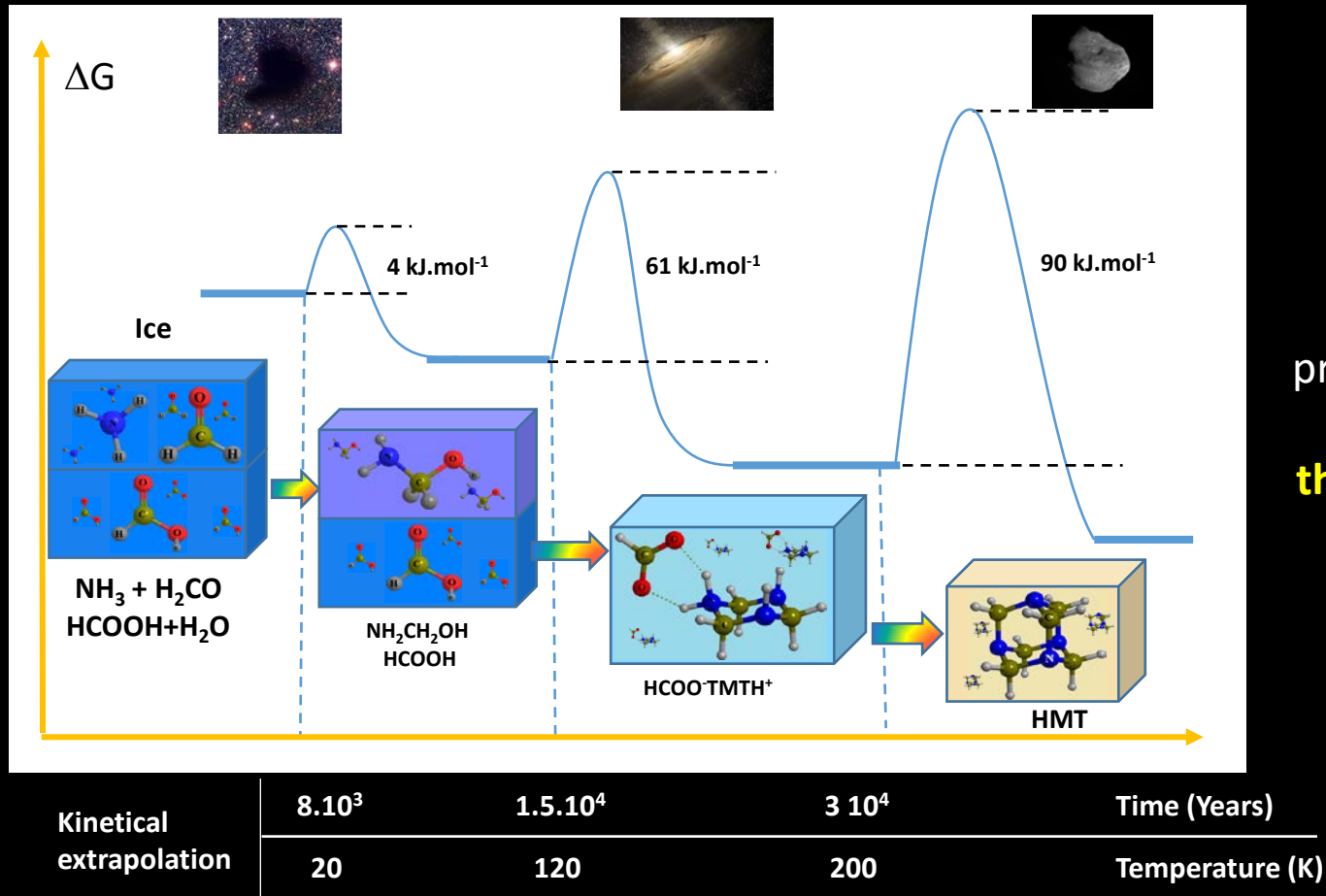
FTIR spectrum of an $\text{H}_2\text{CO}/\text{NH}_3/\text{HCOOH}$ 1:6:1, ice mixture 10 K (a), 170 K (b), 240 K (c) and 330 K (d).



HMT is formed only by thermal process

Interstellar ice evolution: the case of HMT

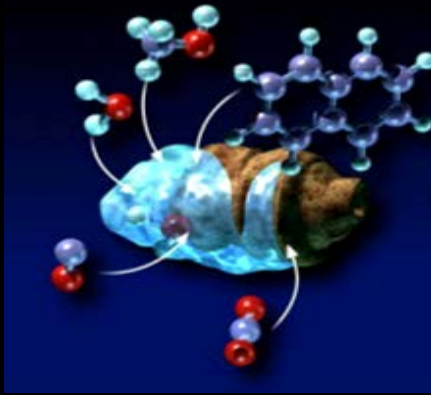
Importance of the thermal processes



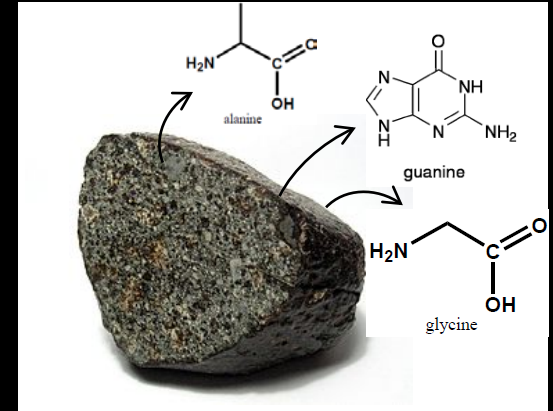
↓
HMT and precursors could be used as **thermometer** in ISM

HMT is likely a molecule accreted in asteroids

Experimental investigations

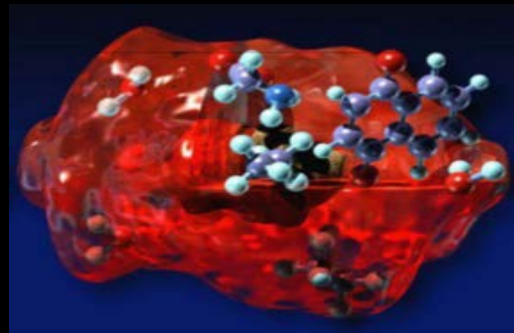


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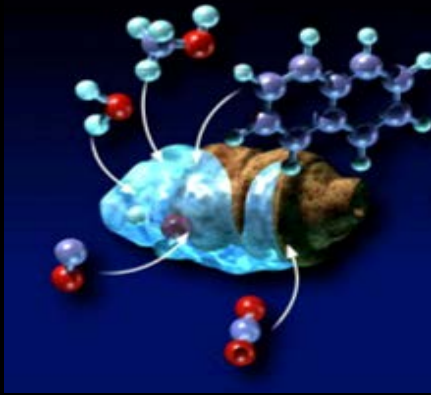


Interstellar ice evolution:

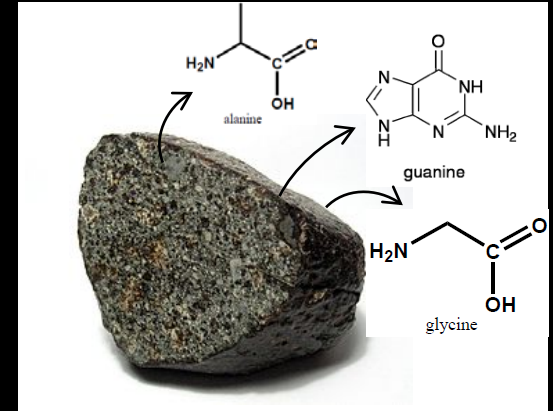
Formation of complex
organic molecules in ices



Experimental investigations



?



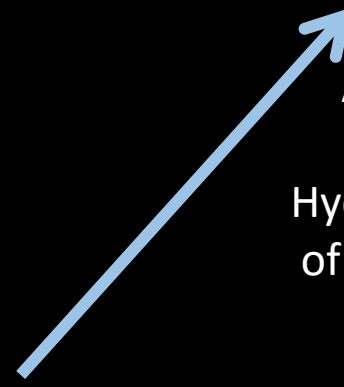
Interstellar ice evolution:

Formation of complex organic molecules in ices

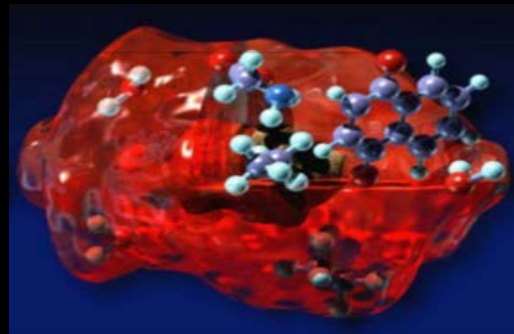


Asteroid evolution:

Hydrothermal alteration of interstellar molecule



The case of HMT



Asteroids evolution: the case of HMT

Hydrothermal alteration experiments

1) Product



+ Water pH 10

2) autoclave



3) Glove box under N₂



4) Stove at 150 °C



→ After different duration, up to 31 days

5) Treatment for analysis

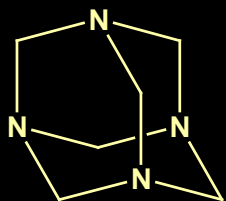


6) Analyses

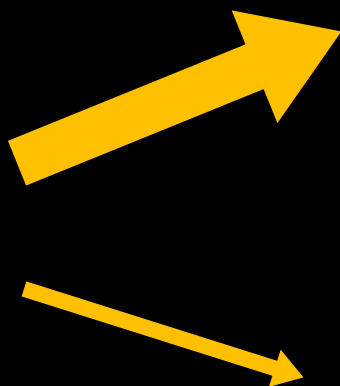
- GC-MS
- FTIR
- XANES-STXM (synchrotron based)

Asteroids evolution: the case of HMT

Hydrothermal alteration experiments



22 atoms



**99 %wt of
soluble
compounds**



**Mainly nitrogen aromatic
compounds
> 10-50 atomes**

**1%wt of
insoluble
compound**



**Macromolecule
> 100 atomes**

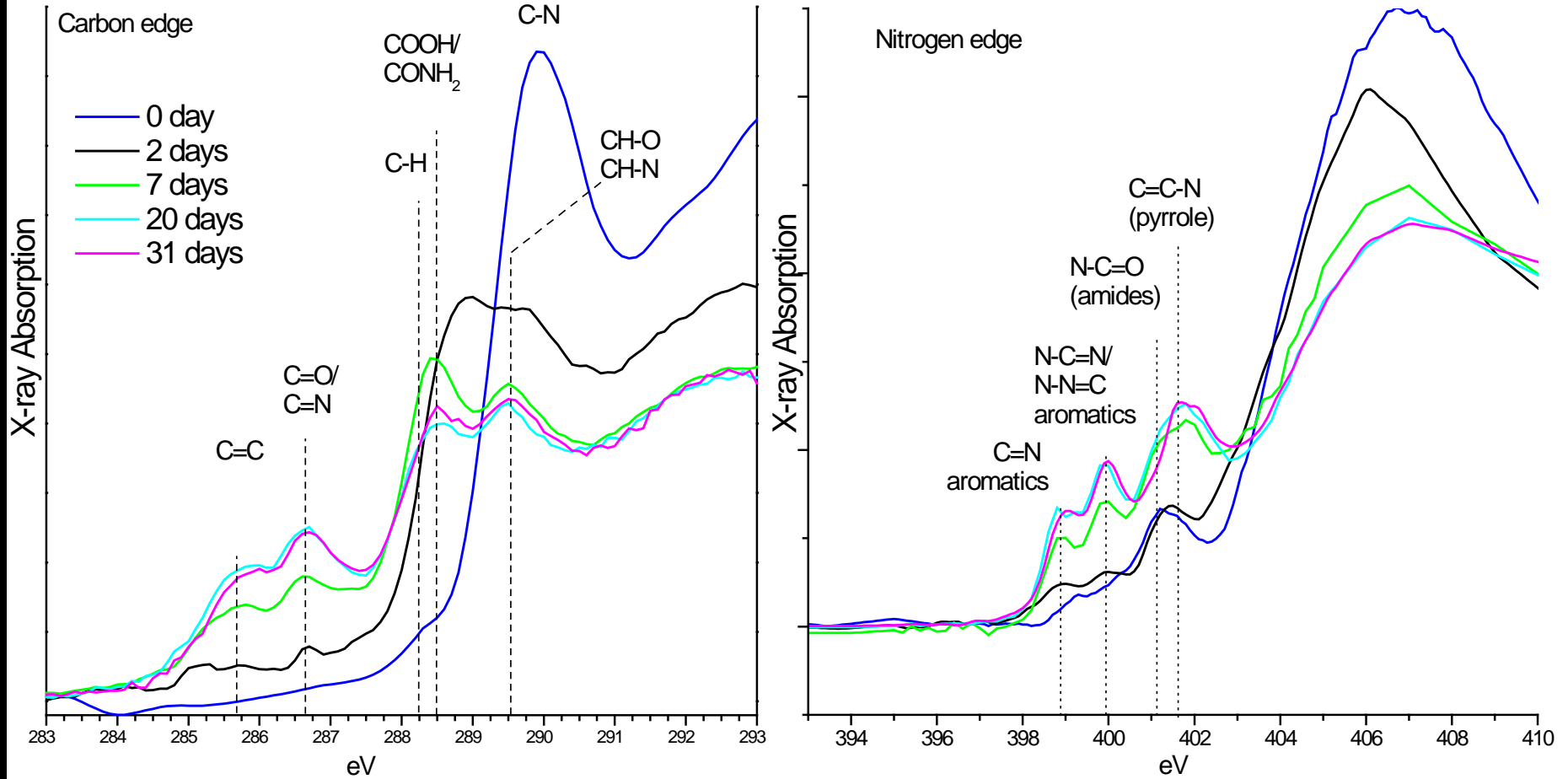
Asteroids evolution: the case of HMT

XANES analysis of organic compounds in the solution

Liquide phase

HMT under hydrothermal alteration, 150 °C, pH 10

0,7 M

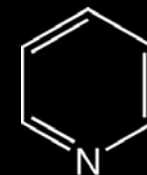
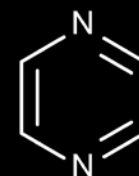
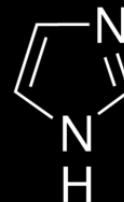


Fast transformation of HMT

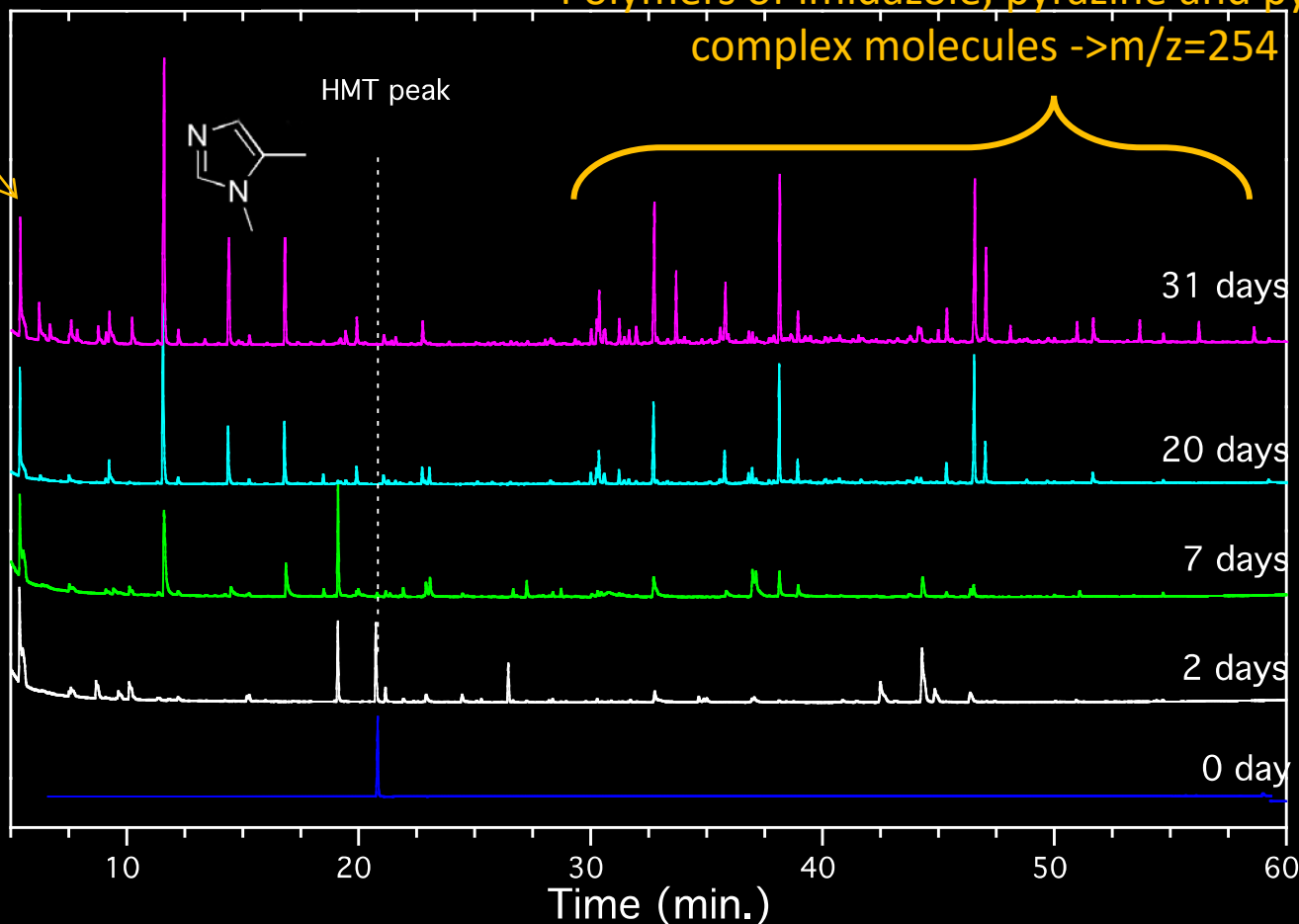
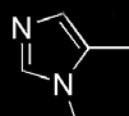
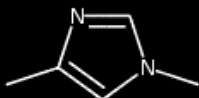
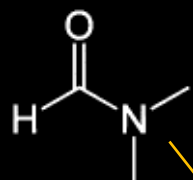
No more evolution after 20 days

Asteroids evolution: the case of HMT

GC-MS analysis Diversity of soluble compounds



Polymers of imidazole, pyrazine and pyridine
complex molecules $\rightarrow m/z=254$



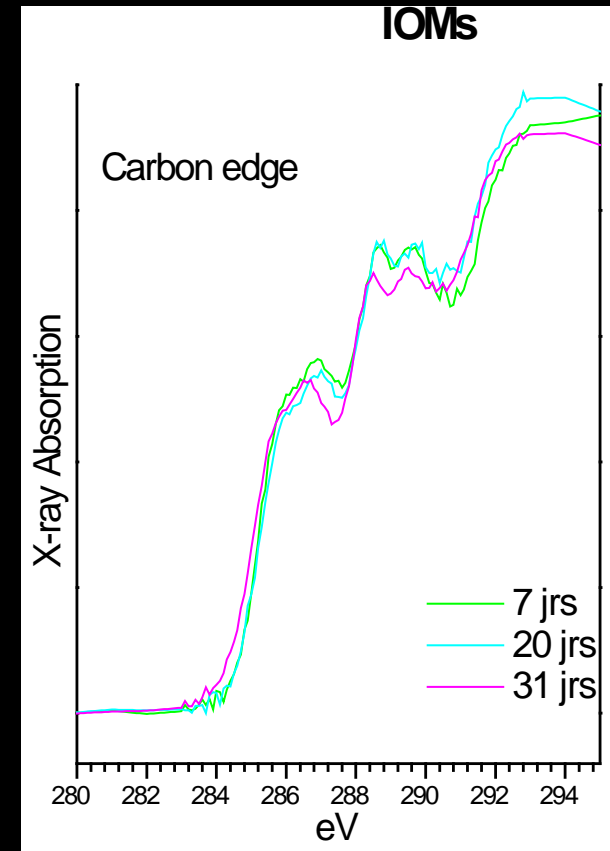
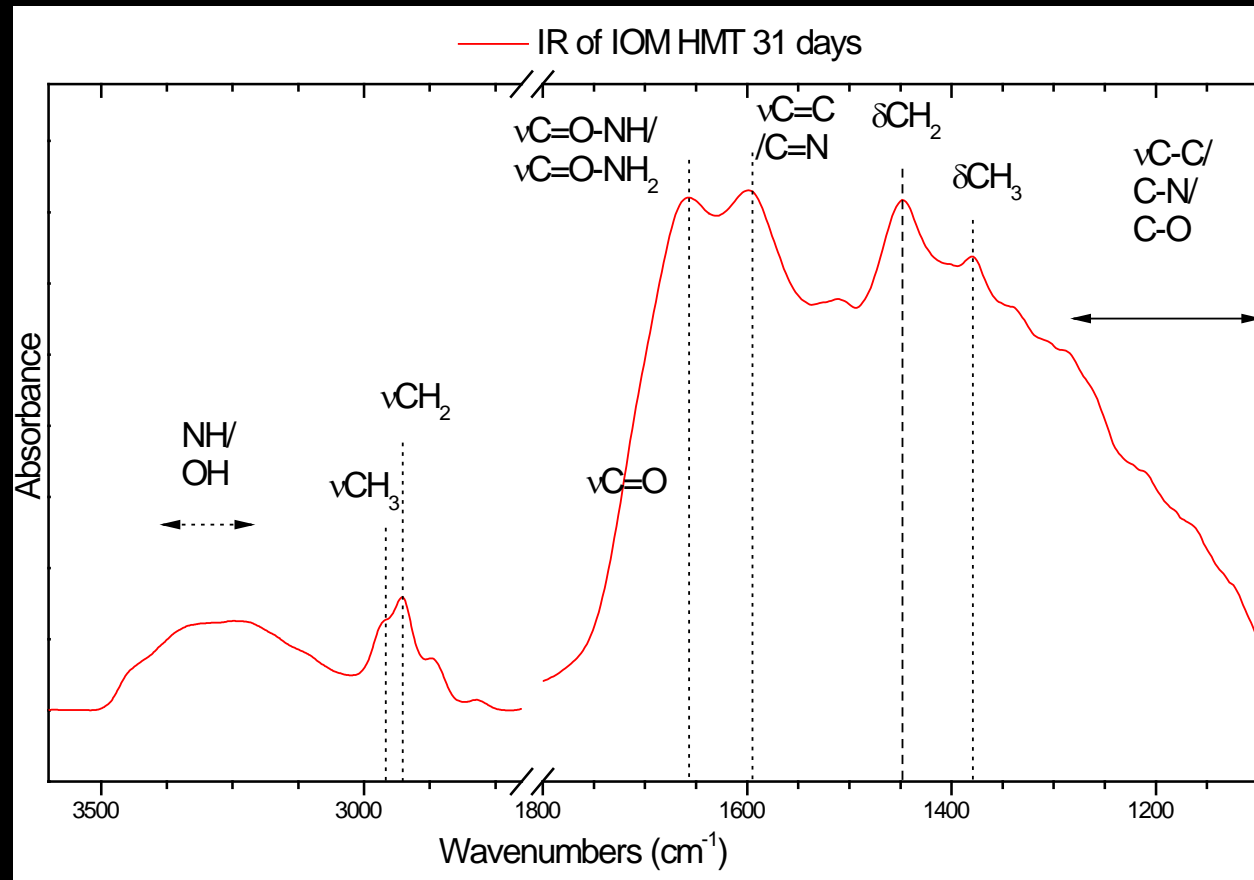
Large diversity of soluble organic molecules formed, No more HMT after 20 days

Asteroids evolution: the case of HMT

The Insoluble organic matter formed from HMT (<1 wt.%),
formed from 7 days

FTIR

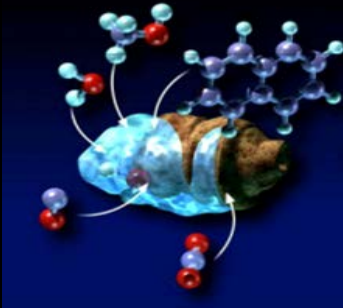
XANES-carbon edge



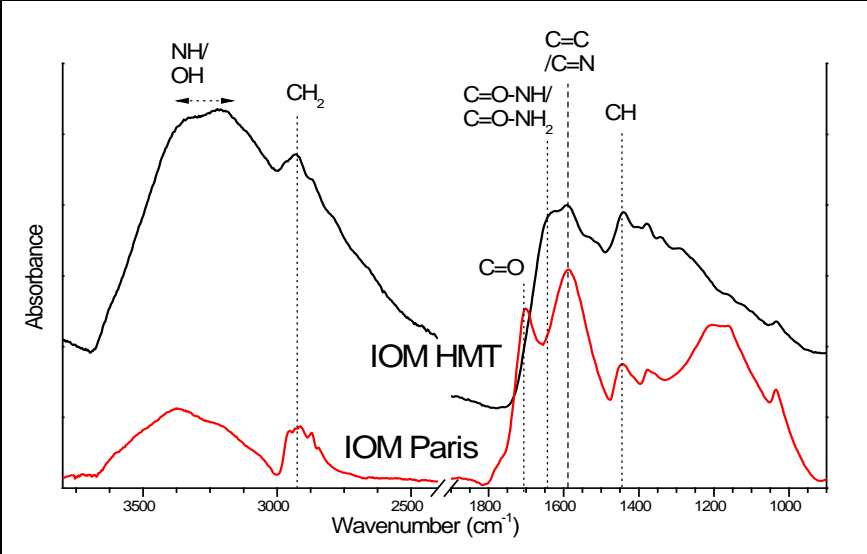
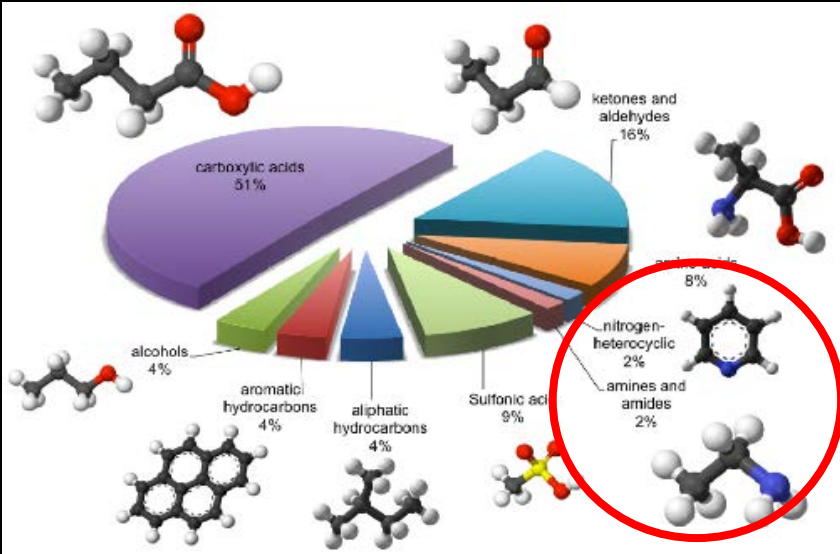
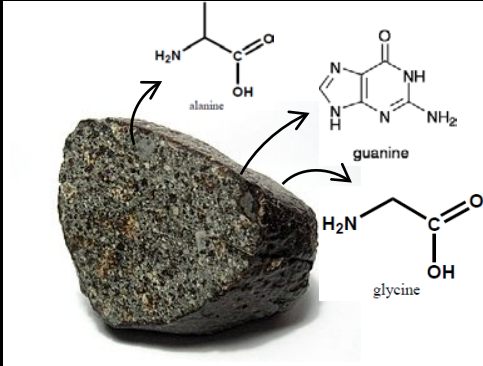
-Complex macromolecule

-no evolution once formed

Where do we stand ?



?



Similar molecules from meteorites
 2% nitrogen aromatic cycles
 2% amides/amines

HMT IOM compared to Paris IOM,
 similar features but not all

SO....

Ices to Asteroids: take home message



-Organic evolution in ices is the first stage to form complex organic molecules

→ Thermal process has to be closely investigated

Potential link between organic in ices and organic in Asteroids, but :

-High impact of hydrothermal alteration in organics

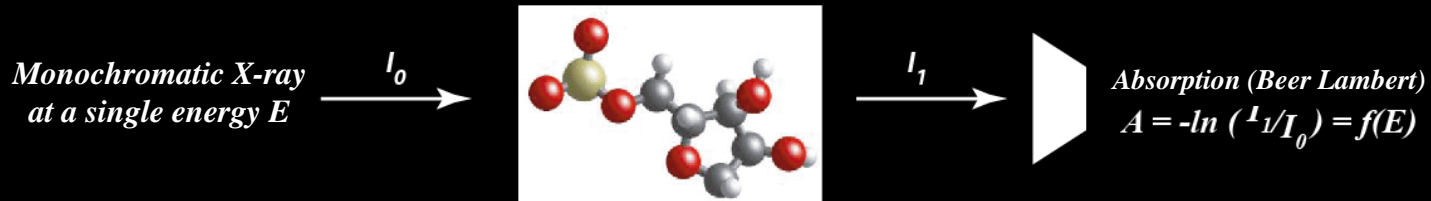
→ HMT totally decomposed in less than 20 days

→ Formation of a IOM (clues for SOM and IOM origins in Meteorites)

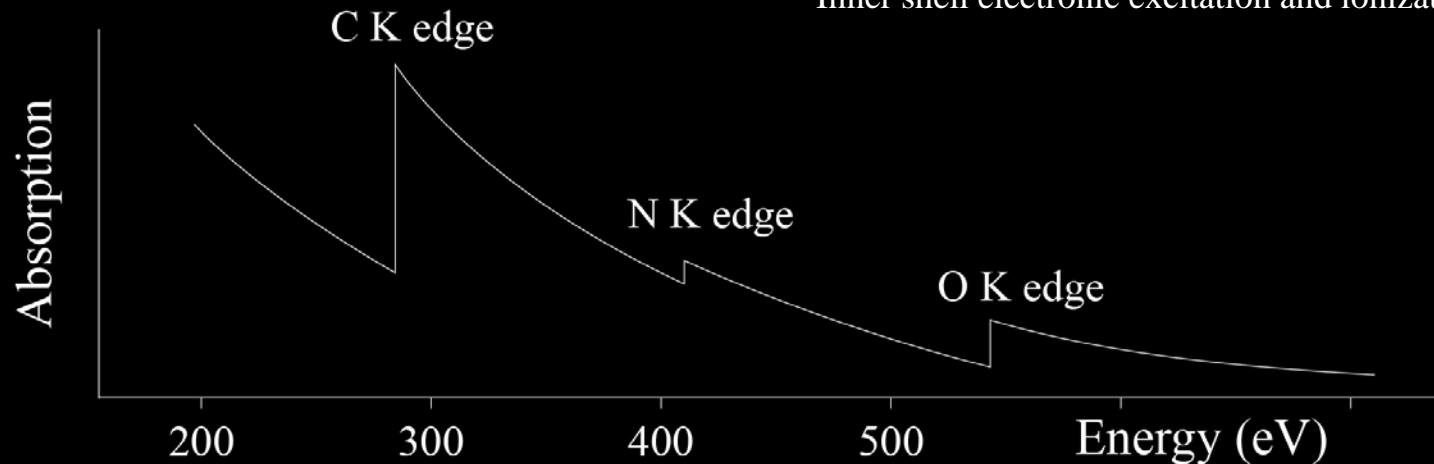


STXM = Scanning Transmission X-ray Microscopy

Synchrotron radiation - Spatial Resolution: ~25 nm - Spectral Resolution: 0.1eV



Inner shell electronic excitation and ionization (K-edge)



The energy of the edge is specific of the chemical element

STXM = Scanning Transmission X-ray *MICROSCOPY*

Synchrotron radiation - Spatial Resolution: ~25 nm - Spectral Resolution: 0.1 eV

Spectromicroscopy = Both spectroscopy and MICROSCOPY at high spatial resolution 20 nm

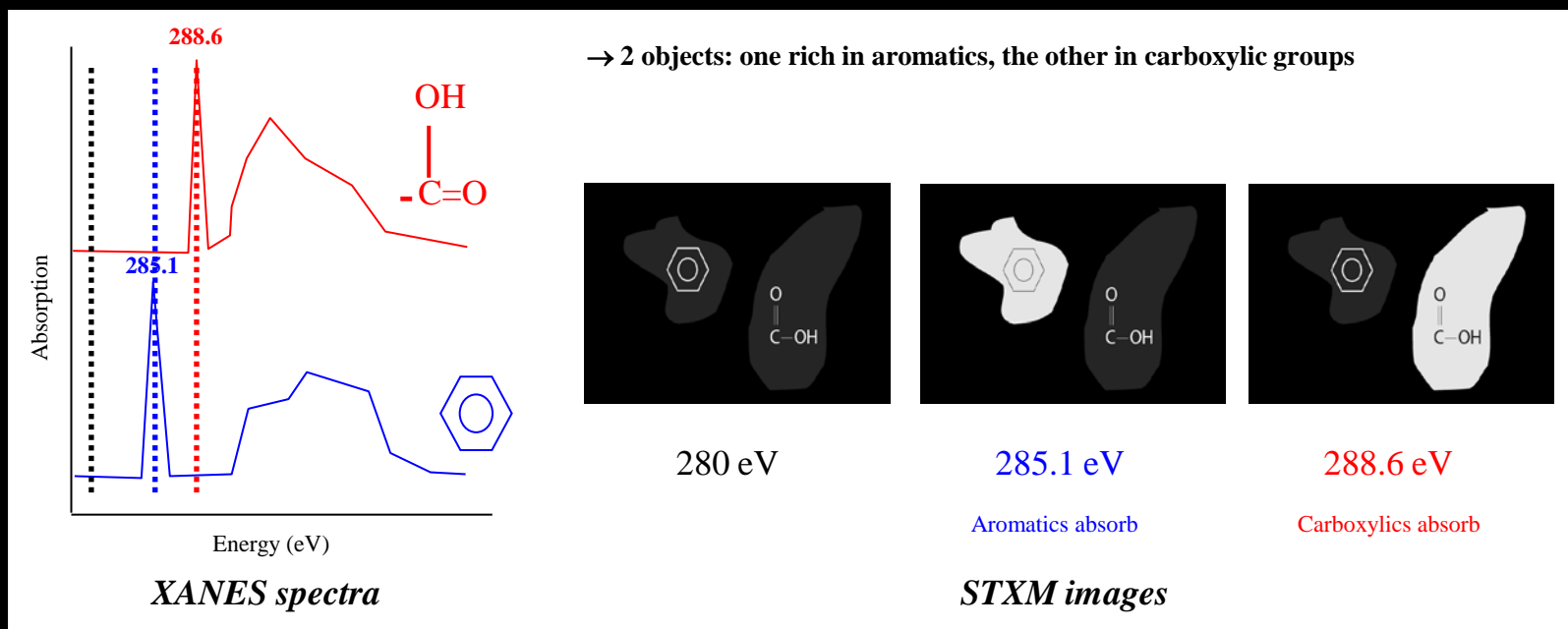


Image contrast = Differential absorption of X-rays depending on speciation

STXM = Organic Geochemistry at the nanoscale

