

Ion irradiation affects the composition of frozen surfaces in space

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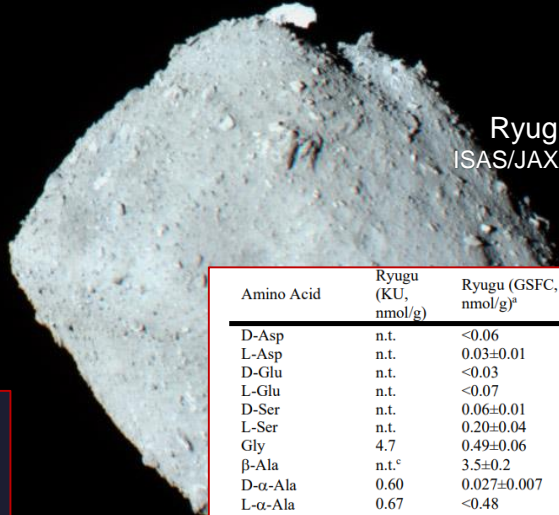


Astrophysical context

Atmosphere-less surfaces in the Solar System



67P/C-G
ESA/Rosetta/MPS



Ryugu
ISAS/JAXA



Arrokoth
NASA/J. Hopkins Univ. R. Tkachenko

→ THE COMETARY ZOO: GASES DETECTED BY ROSETTA

esa

THE LONG CARBON CHAINS: Methane, Ethane, Propane, Butane, Pentane, Hexane, Heptane

THE AROMATIC RING COMPOUNDS: Benzene, Toluene, Xylene, Benzoic acid, Naphtalene

THE KING OF THE ZOO: Glycine (amino acid)

THE "MANURE SMELL" MOLECULES: Ammonia, Methylamine, Ethylamine

THE "POISONOUS" MOLECULES: Acetylene, Hydrogen cyanide, Acetonitrile, Formaldehyde

THE VOLATILES: Nitrogen, Oxygen, Hydrogen peroxide, Carbon monoxide, Carbon dioxide

THE "SMELLY" MOLECULES: Hydrogensulphide, Carbonylsulphide, Sulphur monoxide, Sulphur dioxide, Carbon disulphide

THE "SMELLY AND COLOURFUL" MOLECULES: Sulphur, Disulphur, Trisulphur, Tetrasulphur, Methanethiole, Ethanethiole, Thioformaldehyde

THE ALCOHOLS: Methanol, Ethanol, Propanol, Butanol, Pentanol

THE "SALTY" BEASTS: Hydrogen fluoride, Hydrogen chloride, Hydrogen bromide, Phosphorus, Chloromethane

THE BEAUTIFUL AND SOLITARY: Argon, Krypton, Xenon

THE "EXOTIC" MOLECULES: Formic acid, Acetic acid, Acetaldehyde, Ethylenglycol, Propylenglycol, Butanamide

THE TREASURES WITH A HARD CRUST: Sodium, Potassium, Silicon, Magnesium

THE MOLECULE IN DISGUISE: Cyanogen

www.esa.int
Credits: Based on data from ROSINA
European Space Agency

Credits ESA

Amino Acid	Ryugu (KU, nmol/g)	Ryugu (GSFC, nmol/g) ^a	C11 Orgueil ^b (GSFC, nmol/g)
D-Asp	n.t.	<0.06	0.41±0.23
L-Asp	n.t.	0.03±0.01	0.14±0.21
D-Glu	n.t.	<0.03	0.32±0.11
L-Glu	n.t.	<0.07	0.56±0.15
D-Ser	n.t.	0.06±0.01	<0.01
L-Ser	n.t.	0.20±0.04	<0.01
Gly	4.7	0.49±0.06	11.5±6.0
β-Ala	n.t. ^c	3.5±0.2	30.6±7.6
D-α-Ala	0.60	0.027±0.007	0.90±0.19
L-α-Ala	0.67	<0.48	1.1±0.25
γ-ABA	n.t.	3.8±0.2	2.7±1.3
D-β-AIB	n.t.	0.22±0.02	^d
L-β-AIB	n.t.	0.18±0.02	
D-β-ABA	n.t.	0.35±0.01 ^e	2.1±1.1
L-β-ABA	n.t.	0.35±0.01 ^e	1.8±0.6
α-AIB	n.t.	0.41±0.03	3.3±1.4
D-α-ABA	0.091	<0.01	0.69±0.48 ^d
L-α-ABA	0.095	<0.01	
D-Val	0.022	<0.08	0.19±0.05
L-Val	0.047	<0.07	0.48±0.02
D-Nva	0.014	<0.04 ^e	
L-Nva	0.014	<0.04 ^e	
D-Iva	0.044	<0.06	0.31±0.03
L-Iva	0.039	<0.05	0.42±0.02
D,L-β-APA	n.t.	<0.15	1.6±0.1
δ-AVA	n.t.	1.3±0.1 ^e	1.2±0.2
D,L-3-A-2-MBA	n.t.	c	0.55±0.03
3-A-3-MBA	n.t.	c	<0.26
3-A-2,2-DMBA	n.t.	0.060±0.002 ^e	0.59±0.03
D,L-3-A-2-EPA	n.t.	c	1.5±0.1
D,L-γ-APA	n.t.	c	2.4±0.2
D,L-4-A-2-MBA	n.t.	<0.19	1.5±0.1
D,L-4-A-3-MBA	n.t.	c	2.8±0.1

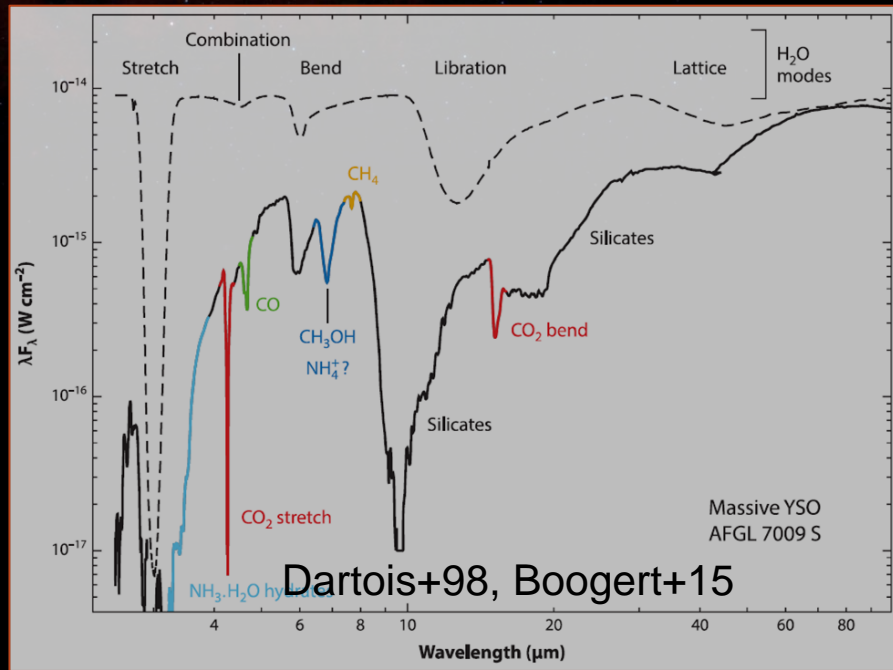
Parker et al. LPSC 2022

Astrophysical context

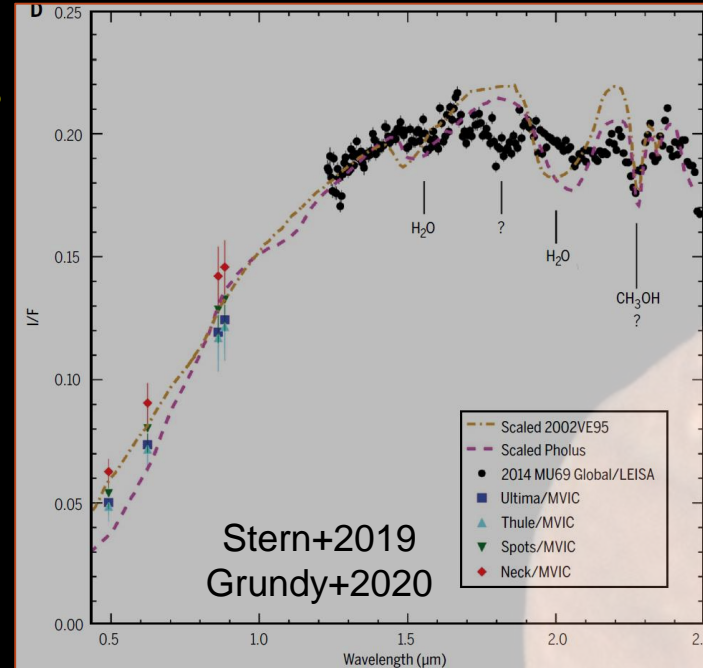
- Icy grain mantles in the interstellar medium

Simple frozen volatile compounds

e.g., H_2O , CH_3OH , NH_3 (e.g. Barucci + 2011)

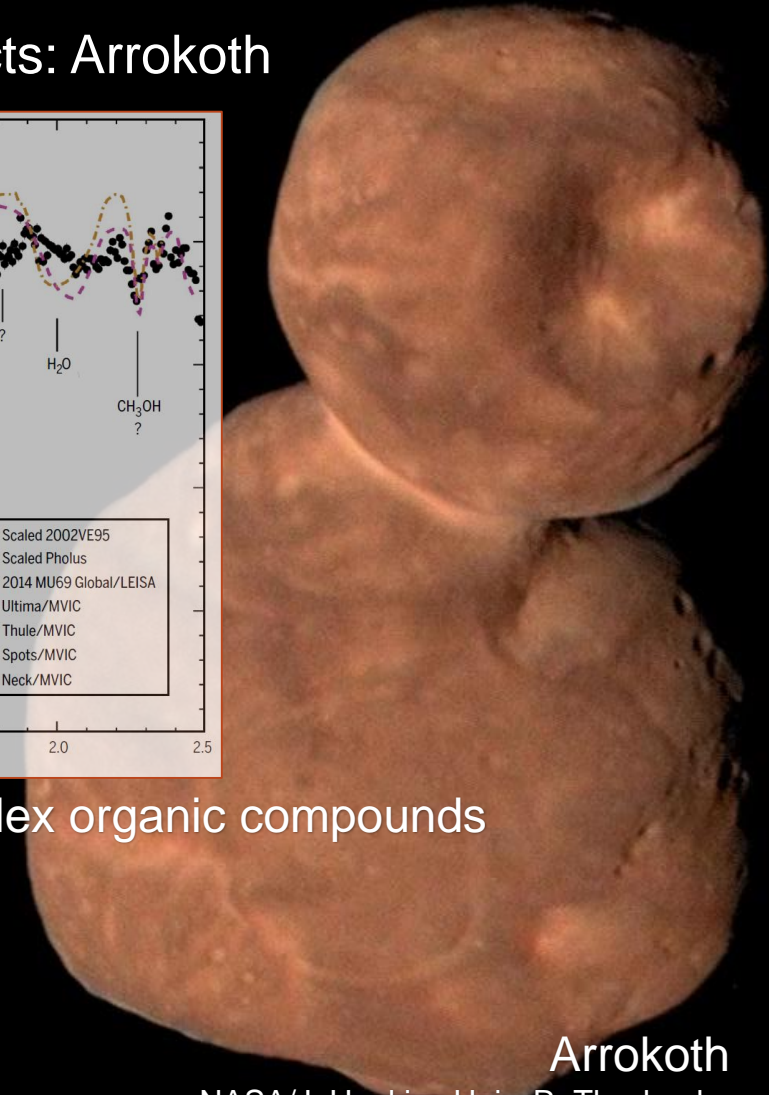


- Kuiper-belt objects: Arrokoth



VIS-NIR red slopes: complex organic compounds

(e.g. Dalle Ore + 2011)

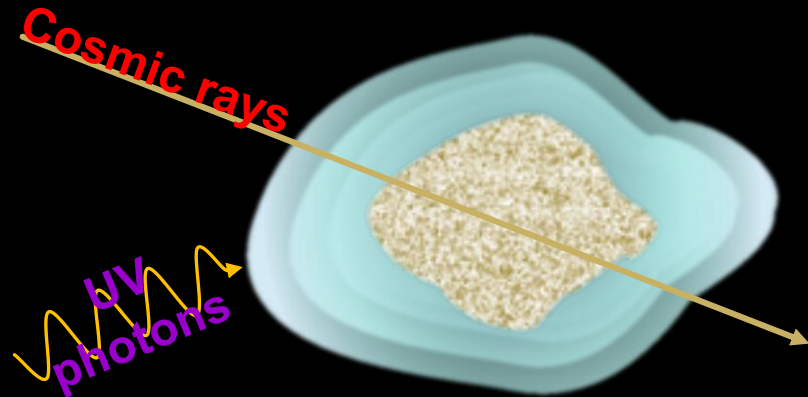


Arrokoth

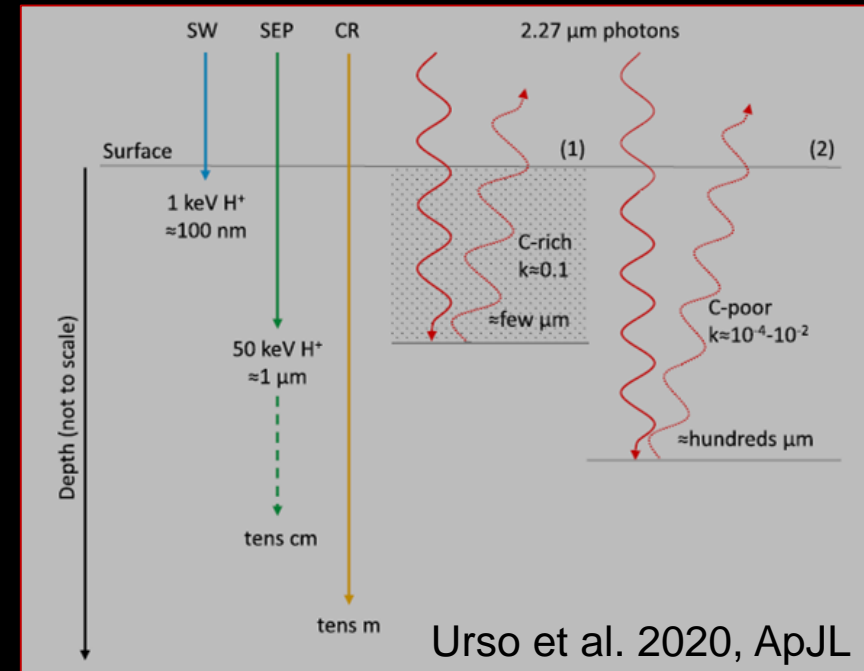
NASA/J. Hopkins Univ. R. Tkachenko

Ion irradiation in space

Icy grain mantles
In young star-forming regions

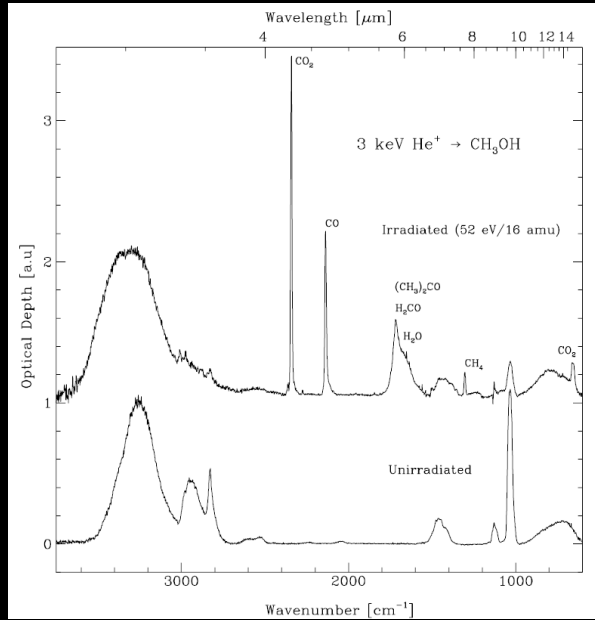


Atmosphere-less surfaces
in the outer Solar System

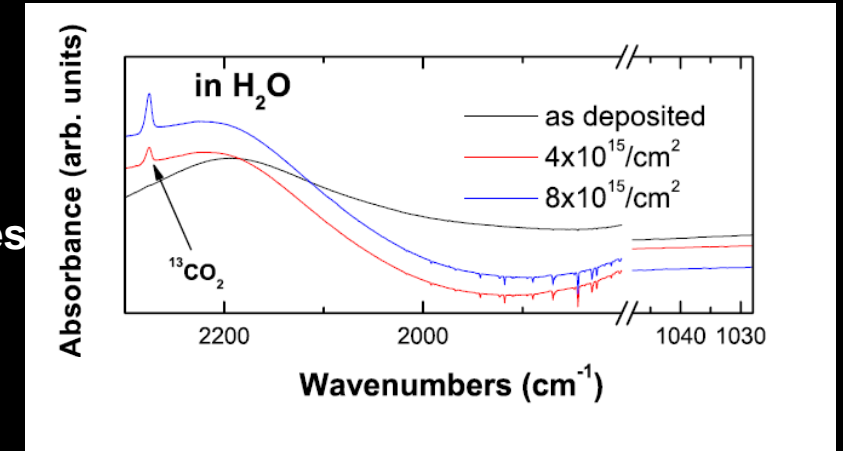


Ion irradiation in space

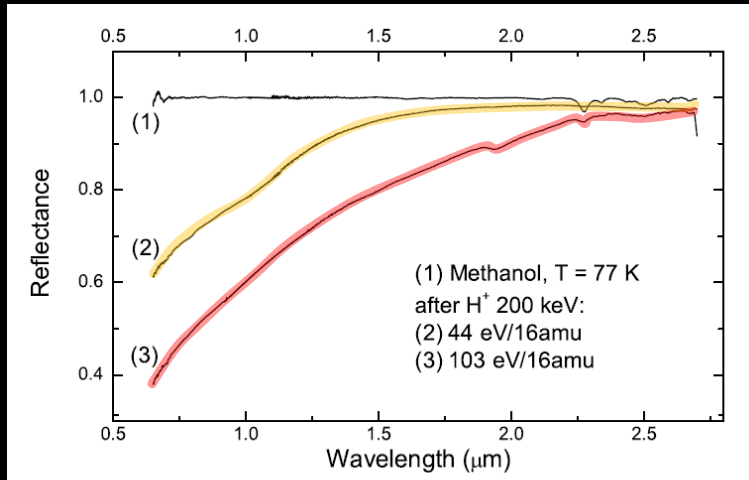
chemical changes
energy transfer
Palumbo+99



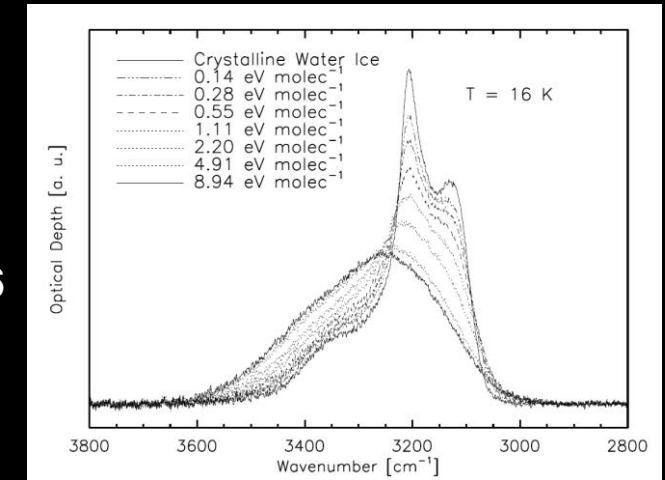
chemical changes
implantation
Boduch+13



Reddening
Brunetto+06
Poston+18
Hénault+in prep.

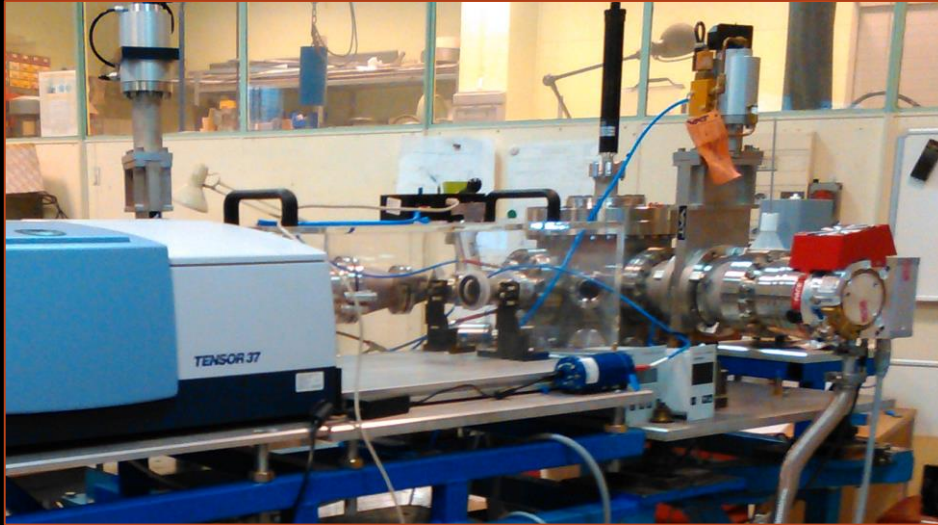


Structural changes
Leto & Baratta 03
Mastrapa & Brown 06
Dartois+15

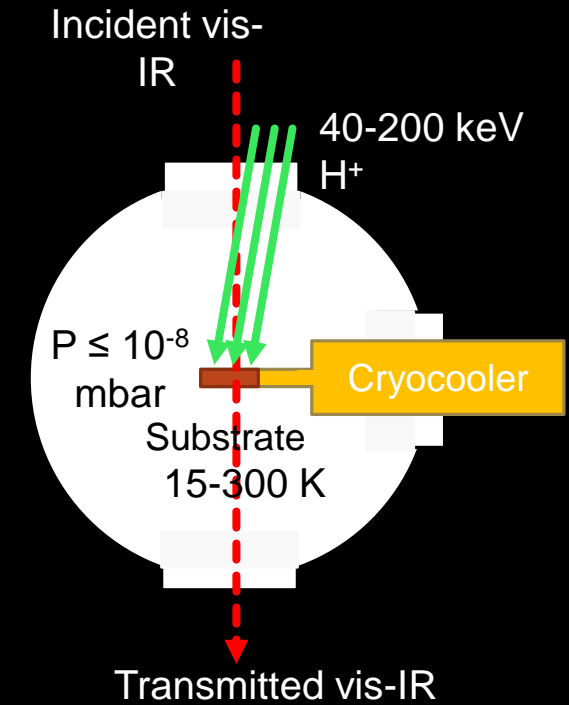
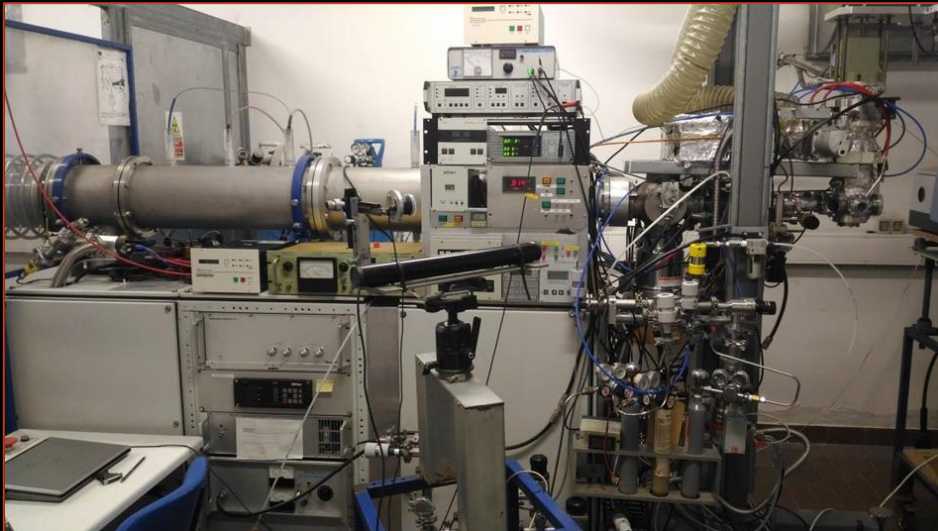


Laboratory experiments

INGMAR-T
IAS-IJCLab,
Orsay, France



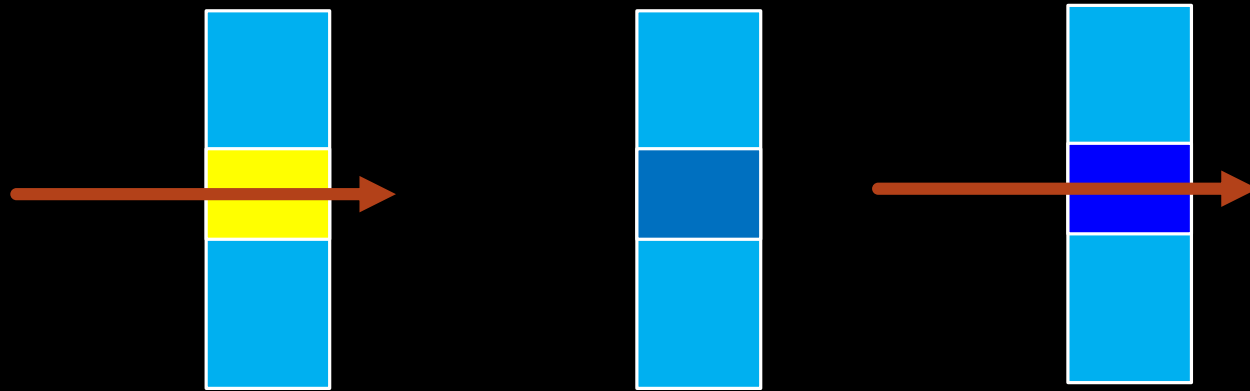
LASp
INAF-OACT,
Catania, Italy



1. H₂O:CH₃OH:NH₃ ices
2. Irradiation with 40-200 keV H⁺
3. in-situ infrared spectroscopy
4. warm-up to 300 K

Laboratory Experiments

- **Temperature:** ≥ 10 K, 40 K, heating possible
- **Pressure:** $10^{-9} - 10^{-8}$ mbar
- **Ion source:** 40 keV – 200 keV H^+ \rightarrow High energy loss in the sample thicknesses
- **Low ion-beam current:** hundreds of nA to 1 μ A

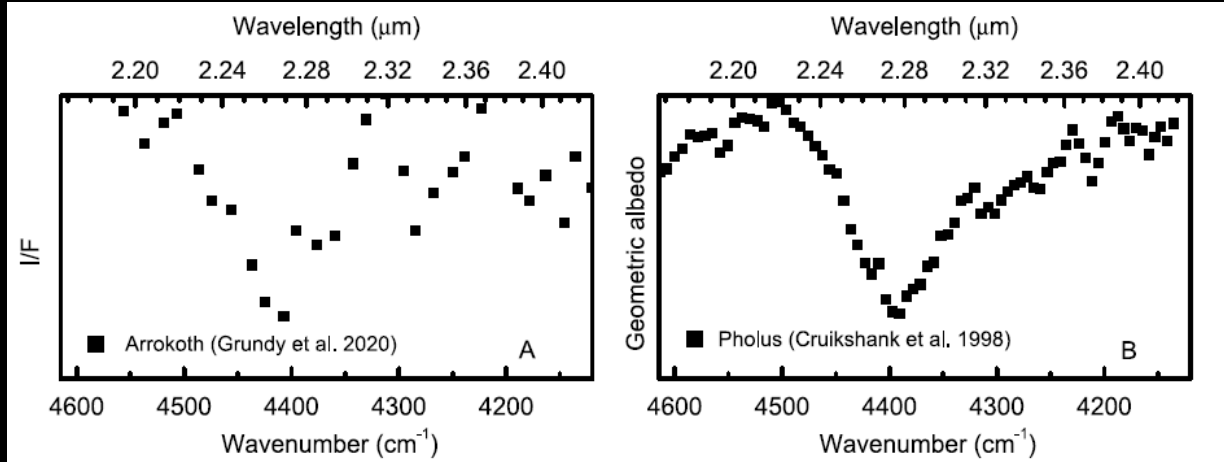


Excitation and recombination along the ion track: $\leq 10^{-12}$ s (1 picosecond)

Time needed for another ion to hit the same spot: 1.6×10^{-2} s

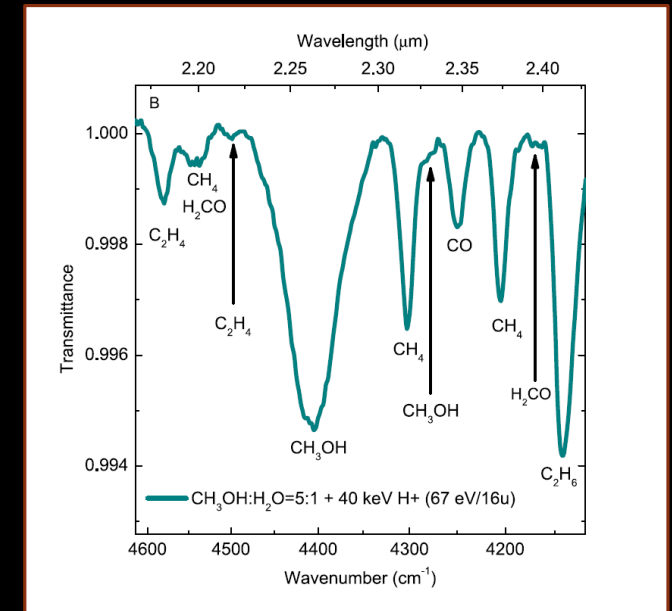
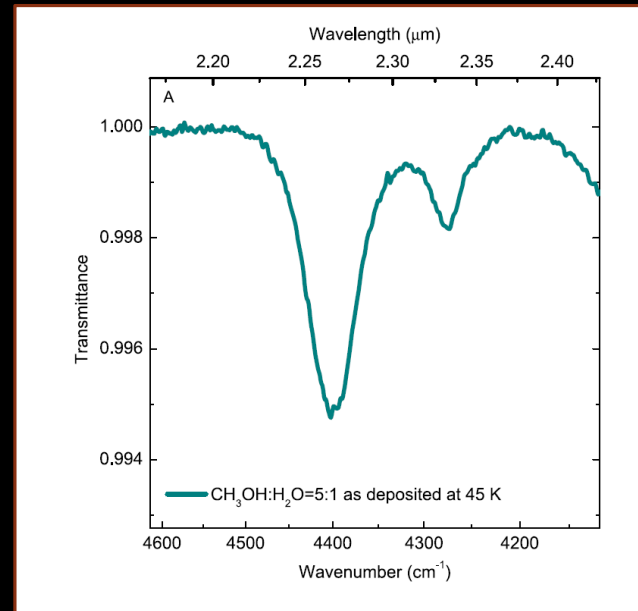
ions travel in non-excited volumes of target ice

Spectral changes induced by irradiation



Production of new compounds
(e.g. Palumbo+1999, Hudson & Moore 2000)
Decrease of the 2.34 μm band (Brunetto+2005)

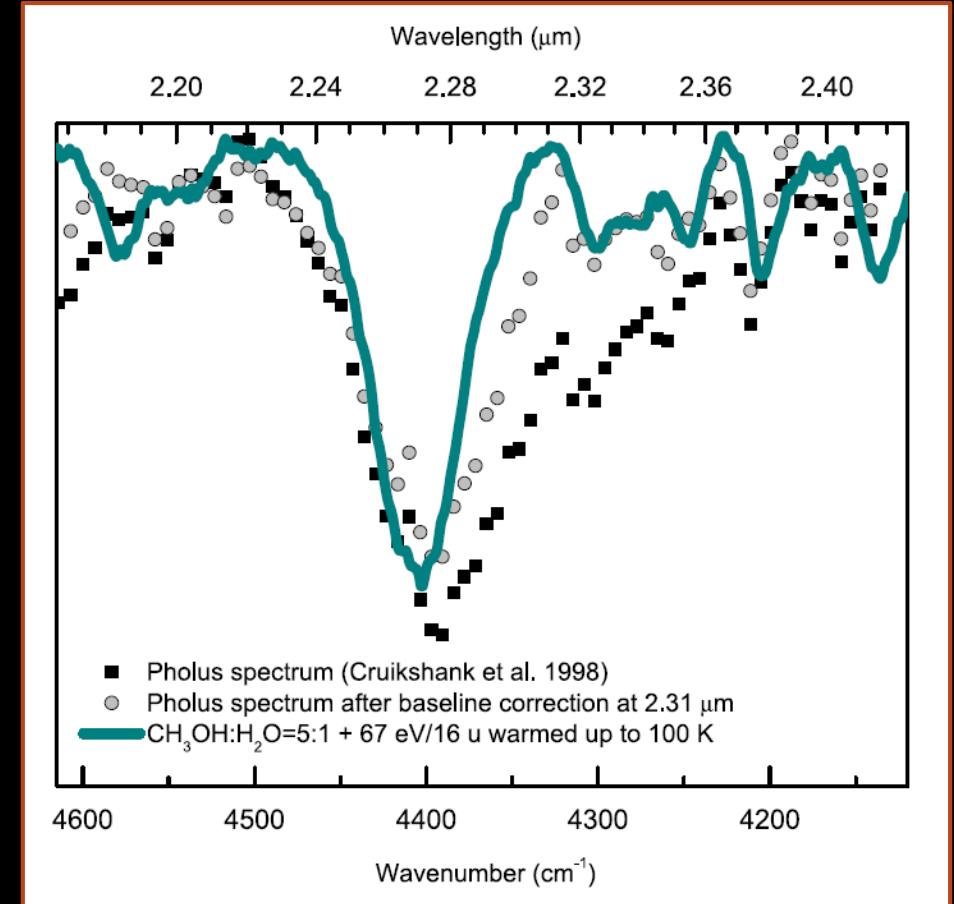
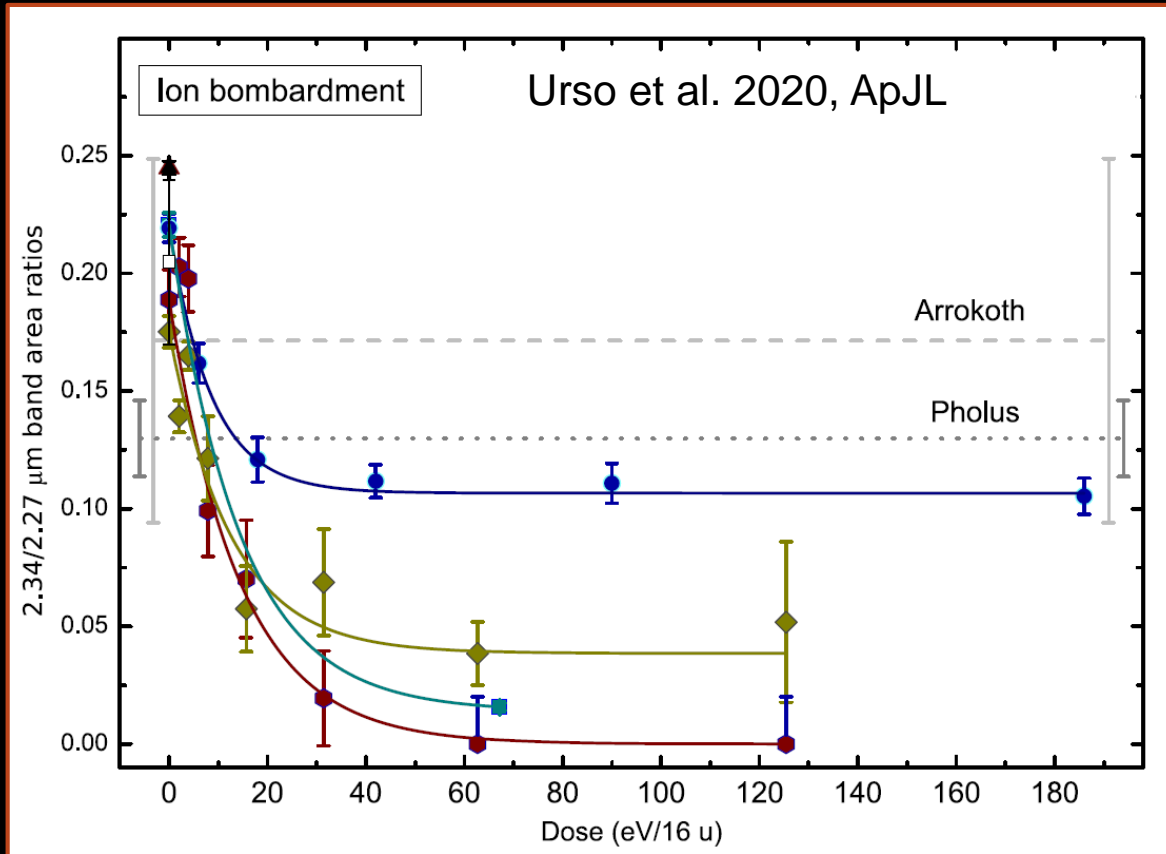
NIR methanol bands
2.27, 2.34 μm



Urso et al. 2020, ApJL

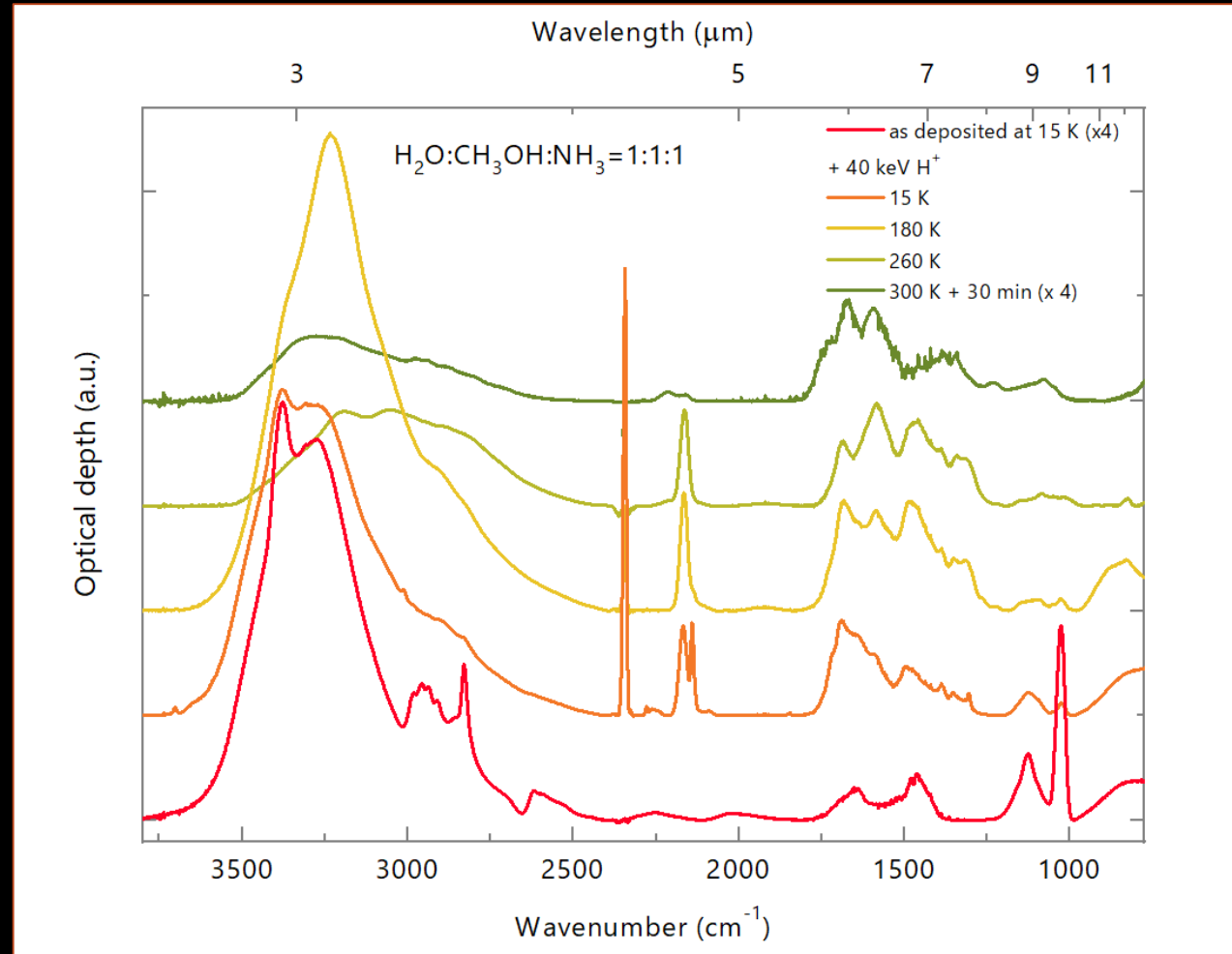
Spectral changes induced by irradiation

Testing the 2.34/2.27 μm band ratio as a probe of irradiation



Timescales of irradiation at 20-40 AU: $4-8 \times 10^9$ years by CR
 $6-30 \times 10^6$ years by SEP

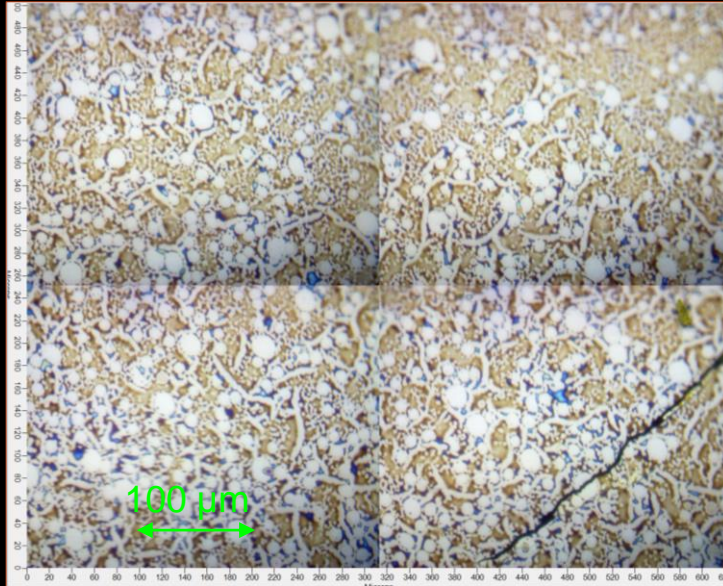
Formation of complex organics



Ion irradiation
+
Heating

sublimation of volatiles and
diffusion

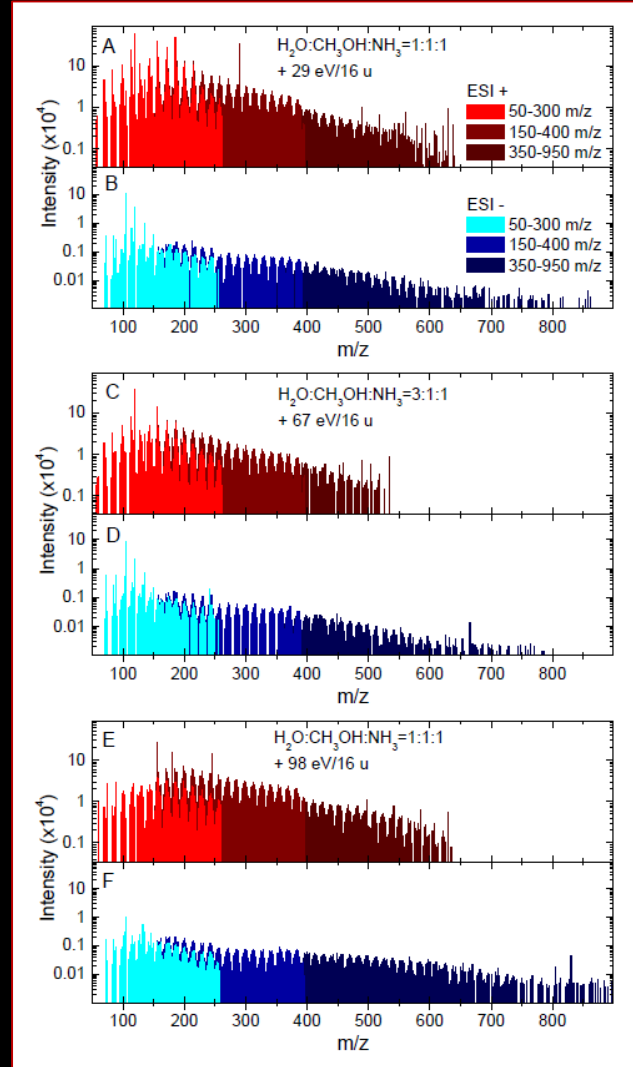
Formation of complex organics



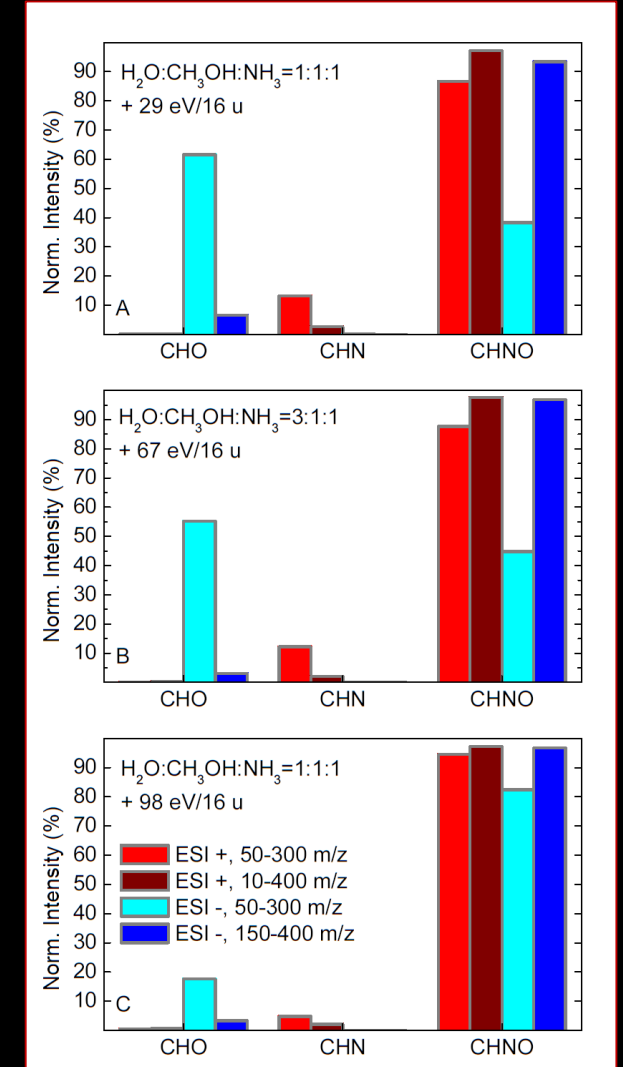
LTQ-Orbitrap
IPAG (Grenoble, France)

More than 3000 molecular fragments
in each sample

Urso, R. G. et al. 2020, A&A



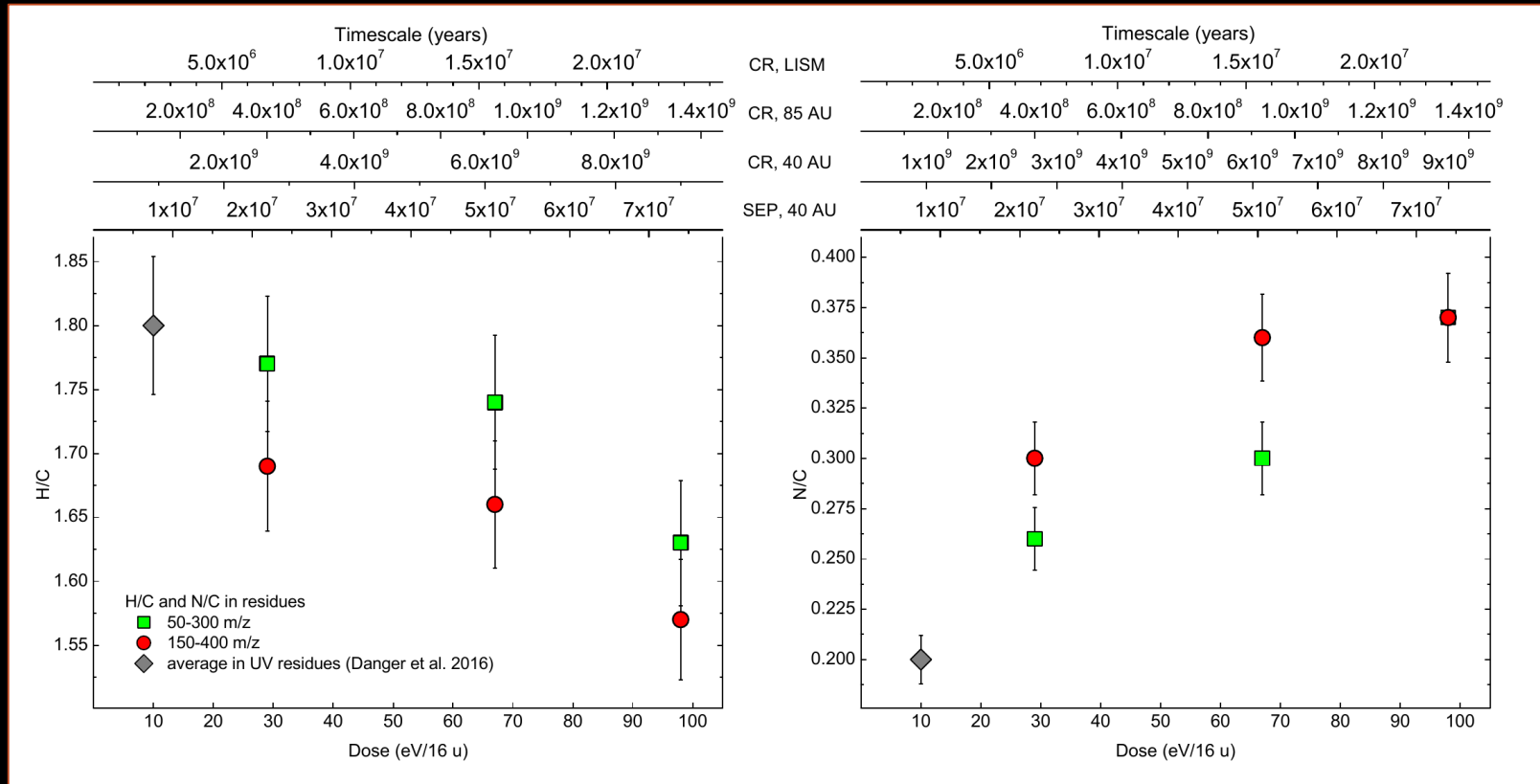
Mass spectra 50-950 m/z



Abundance of molecular groups

Cosmic rays 2: the salt of the star formation recipe

Formation of complex organics



Urso, R. G. et al. 2020, A&A

Isomers of amino acids:

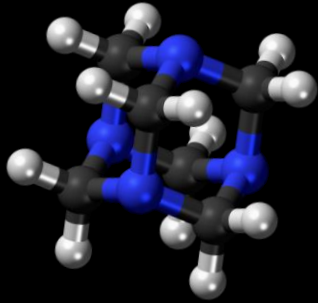
Histidine, Glutamine, Threonine, Proline, Amino isobut. Acid, Alanine, Glycine

Isomers of nucleobases:

Thymine, Cytosine, Uracil

Formation of complex organics

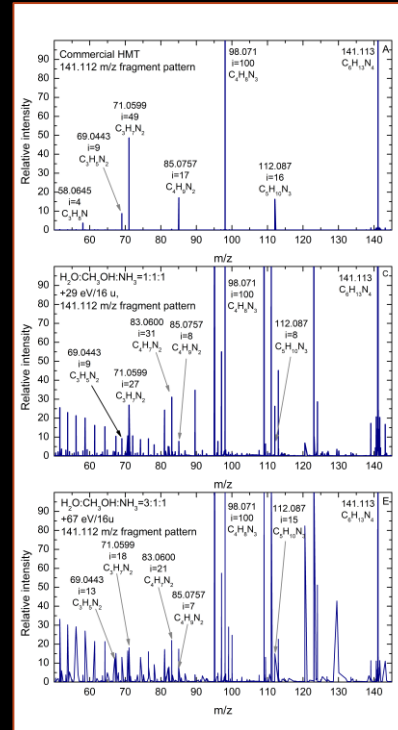
Hexamethylenetetramine (HMT)
precursor of amino acids and
N-heterocycles



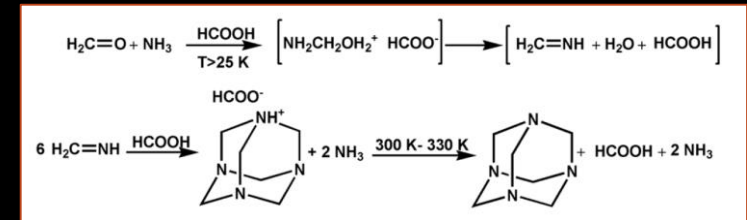
Revealed in carbonaceous chondrites (Oba+2020)

Revealed in laboratory samples

HMT decreases with increasing dose

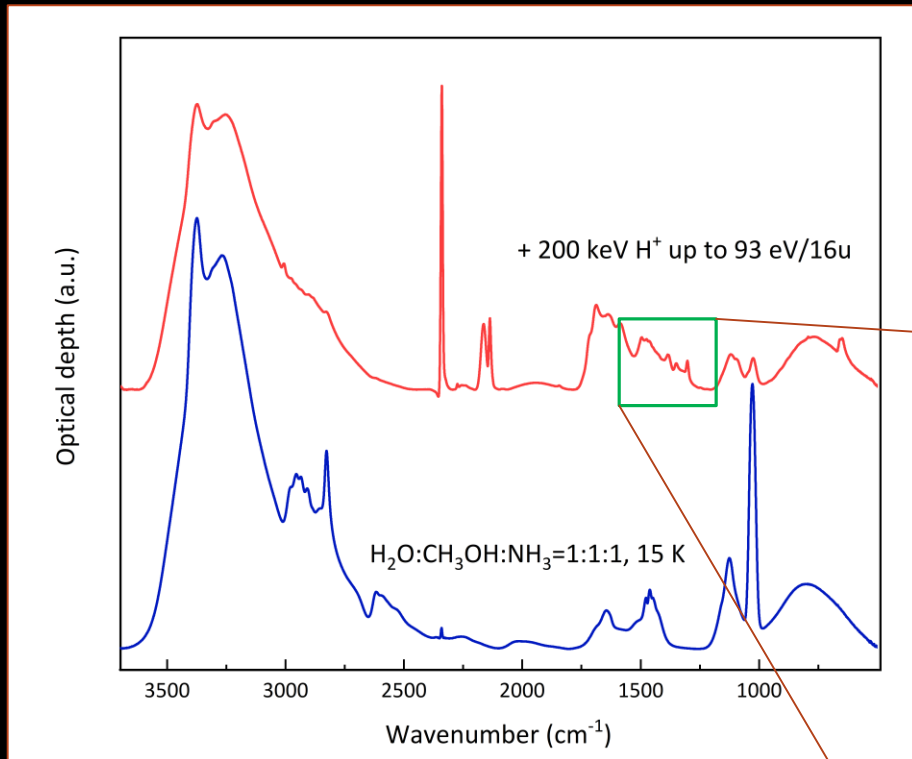


Urso+20, A&A



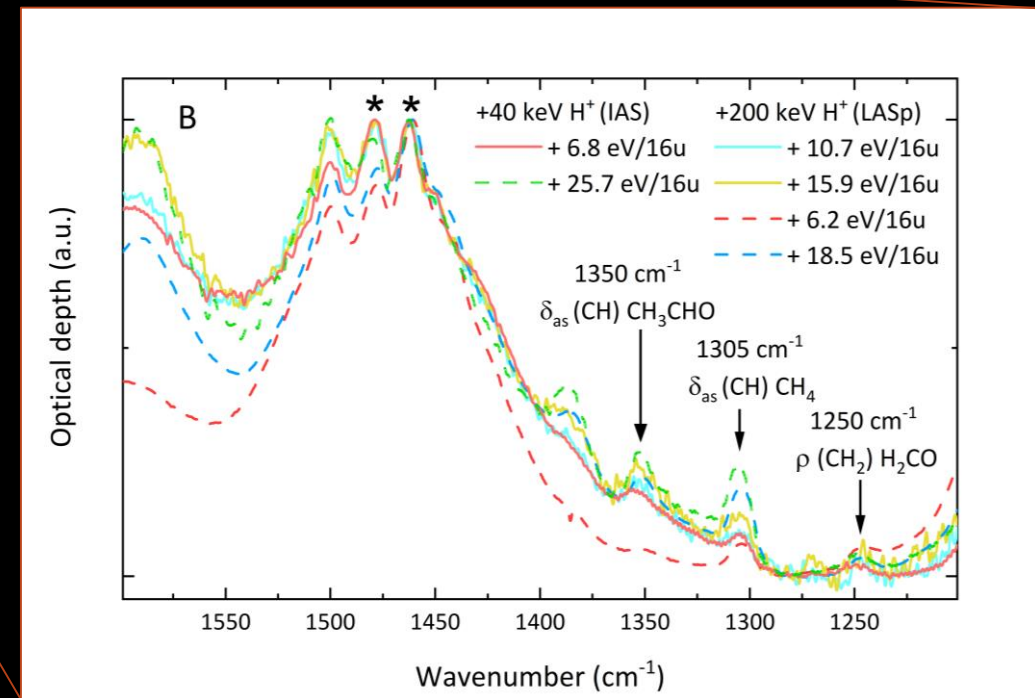
(Vinogradoff + 2012)

Precursors of complex organics in ices



Cosmic rays and solar/stellar particles trigger the formation of H₂CO, CH₃CHO, CH₄

Urso et al. 2022



Precursors of complex organics in irradiated ices

Why does the composition of refractory organics depend on the irradiation dose?

Formation/destruction of complex organic precursors in the ice

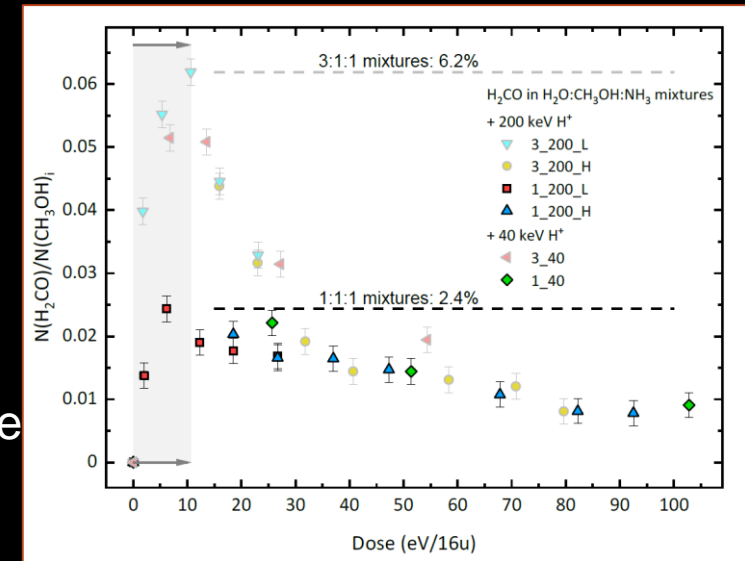
Timescales of formation: $10^6 - 10^8$

Doses > 10 eV/molecule determine H_2CO destruction

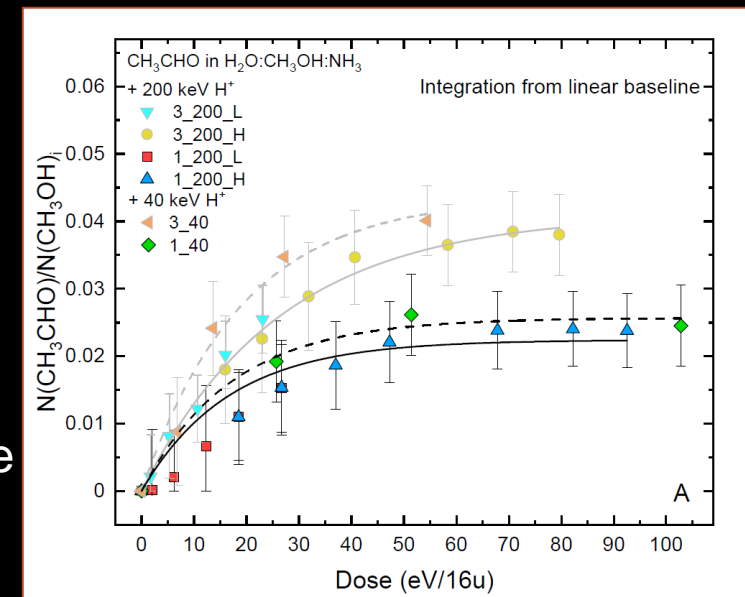
- Lower quantities of Hexamethylenetetramine can form

Urso et al. 2022

Formaldehyde

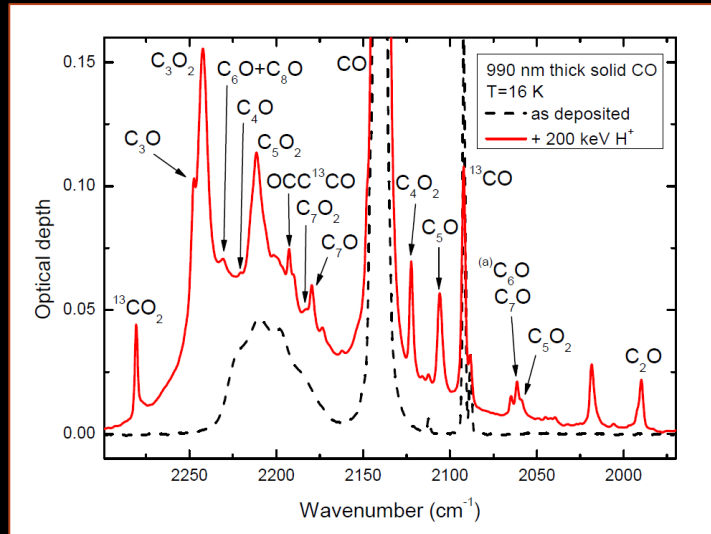


Acetaldehyde

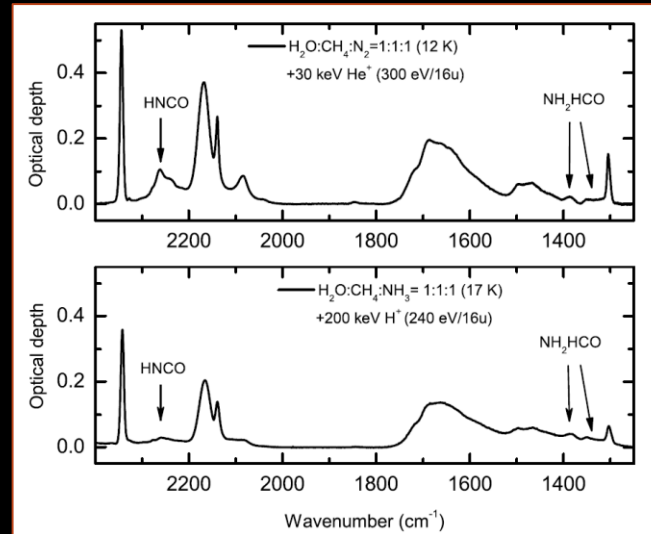


Other species in irradiated ices

C_2O and C_3O
Palumbo+08, Urso+19



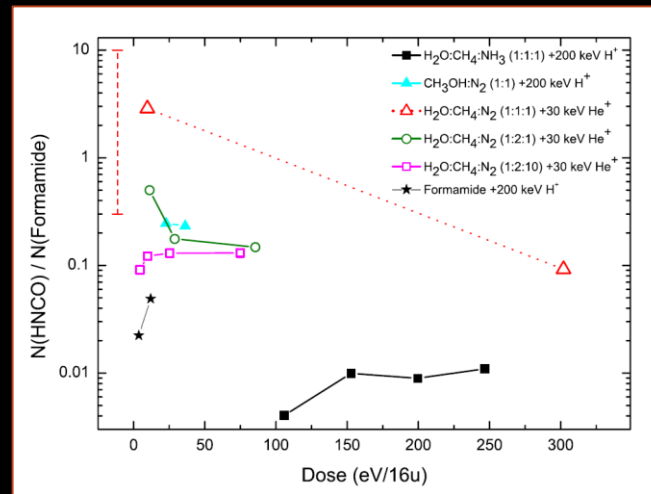
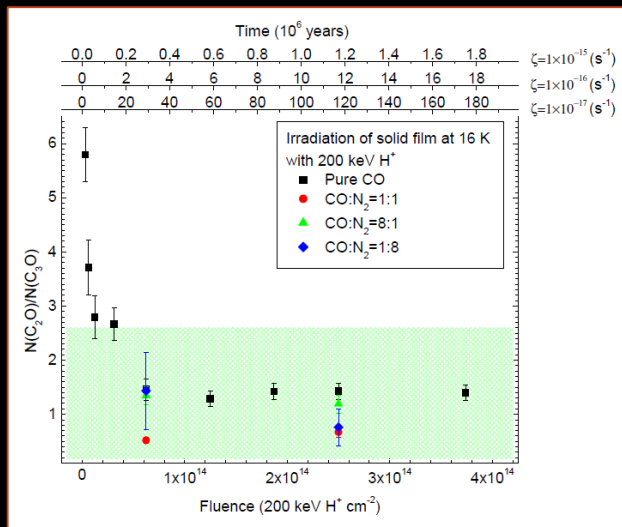
Formamide Kanuchova+16, Urso+17



Many other
compounds could
be present

!!!
Intrinsic limits of IR
spectroscopy

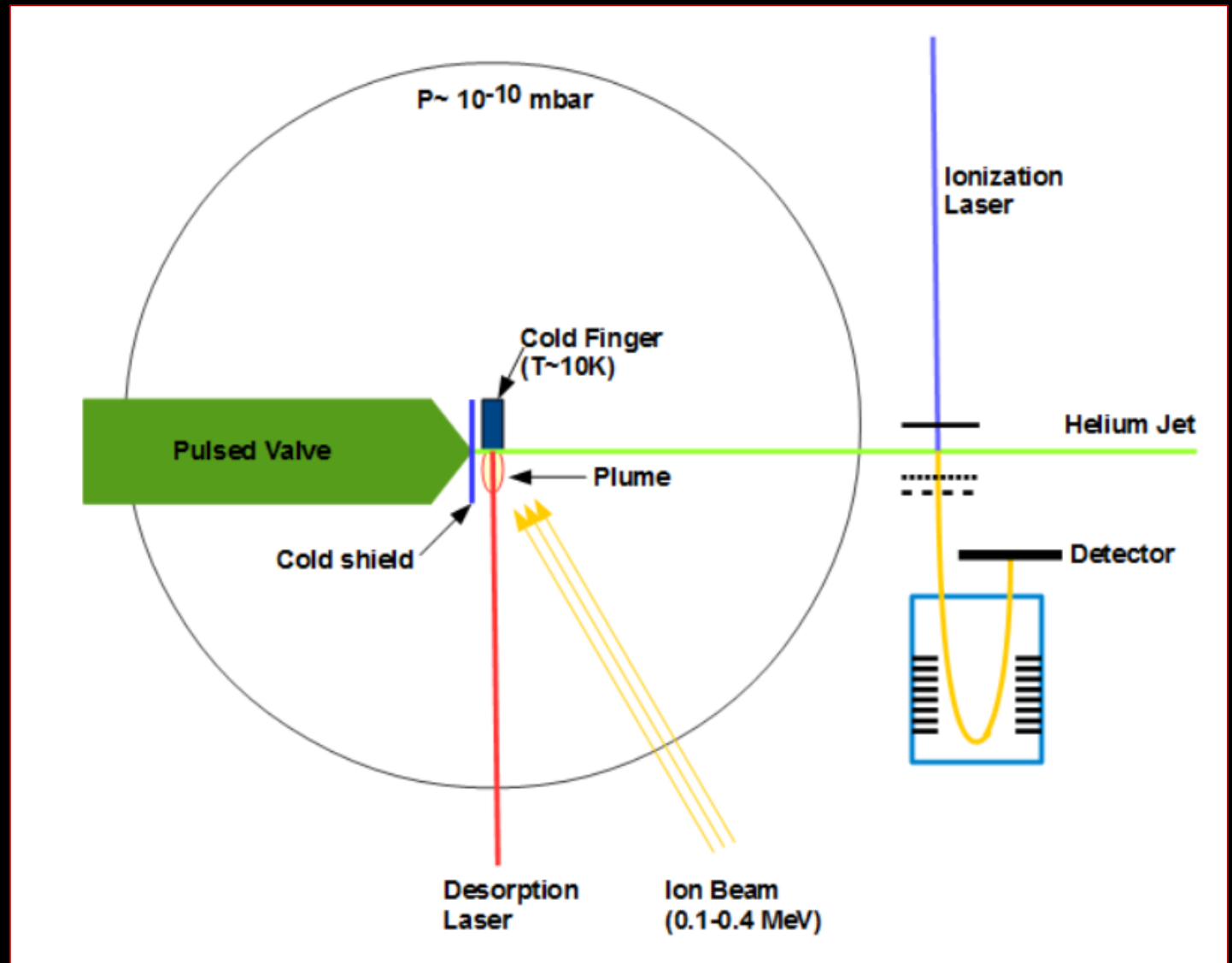
Combining different
techniques



Perspectives and conclusions

Need for more sensitive techniques to detect molecules formed after ion irradiation of ices

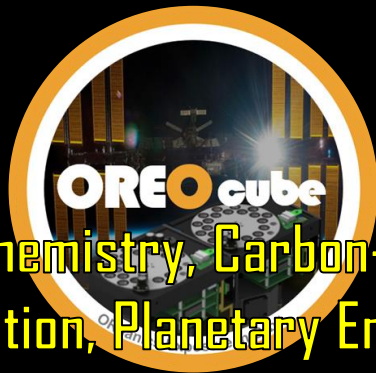
In-situ mass spectrometry at INAF-OACT



Irradiation-induced alteration of complex organics



He Cryocooler (10-350 K)
5 keV electron gun
Mid-IR, Uv-vis spectroscopy
TPD



Astrochemistry, Carbon- and Photochemistry, Life
Detection, Planetary Environments, Meteoritics



Astrobiology, Radiation Biology, Extreme Life, Life
Support, Biocontamination

P.I. A. Elsaesser (FUB, Berlin)

Conclusions

- Cosmic rays and solar ions alter frozen surfaces
- NIR methanol band ratio as a spectroscopic probe of irradiation
- Formation of complex organics: dependence on the irradiation dose
- Astrobiologically-relevant compounds: HMT, isomers of amino acids, and nucleobases
- High doses destroy the precursors of complex organics

Thank you!