Cosmic Ray effects in astrophysical ices and complex organic molecules

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Topical Review:
H. Rothard, A. Domaracka, Ph. Boduch, M. E. Palumbo, G. Strazzulla, E. F. da Silveira, E. Dartois
Modification of ices by cosmic rays and solar wind
J. Phys. B: At. Mol. Opt. Phys. 50 (2017) 062001

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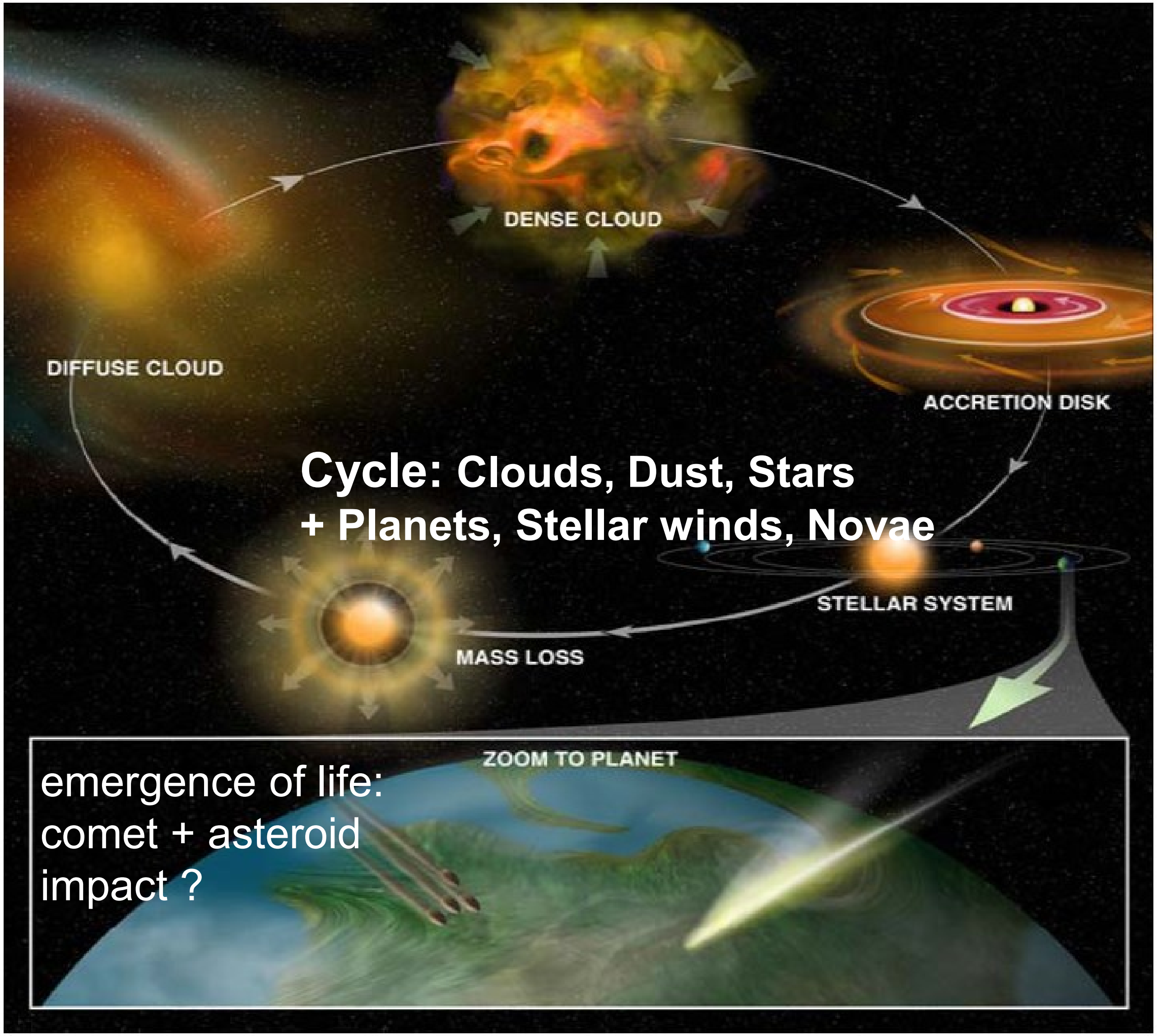
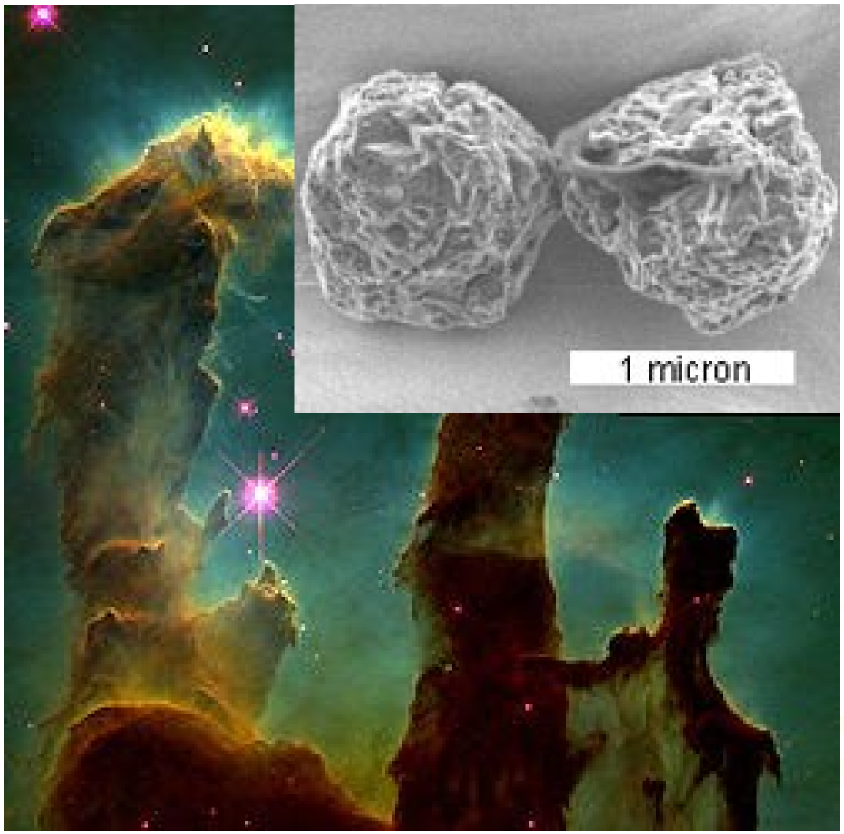
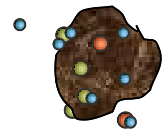
Astrochemistry and Astrobiology



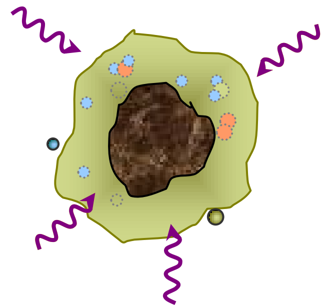
Credit: Bill Saxton, NRAO/AUI/NSF

Interstellar dust grains in dense molecular clouds

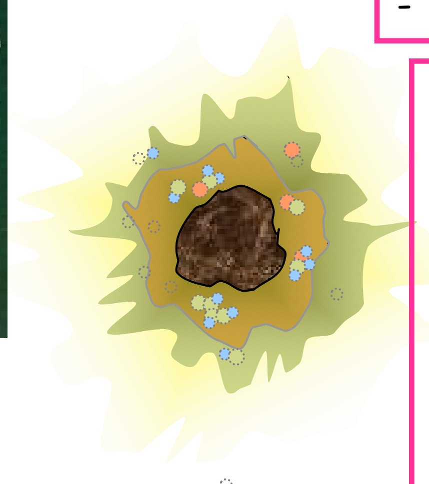




... covered with thin layers of ices (H_2O, CO, NH_3, ...)



are exposed to
- cosmic rays;
  (protons, helium, heavy ions)
- solar/stellar wind
  (H, He, C, O, S ...)
- UV photons
- electrons



irradiation leads to ...

Radiolysis

fragmentation/destruction

formation of molecules
(radiation chemistry)

Desorption / Sputtering

Compactation / Amorphization

Astrophysics + Chemistry @ CIMAP-GANIL

Why?

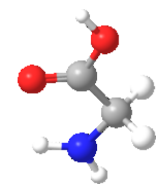
Astrophysical materials:
Carbon containing, **Silcates, ices**

Ices ubiquitous in space (dust grains, molecular clouds, icy satellites, comets, Trans Neptunian Objects, …)

Physico-chemical evolution of icy bodies in space exposed to **cosmic rays**, **solar wind**, magnetosphere ions

Space weathering

Structure: amorphous vs. cristalline, porous vs. compact



Radiolysis: radiation **resistance** and **survival times** of molecules in space (destruction cross sections)

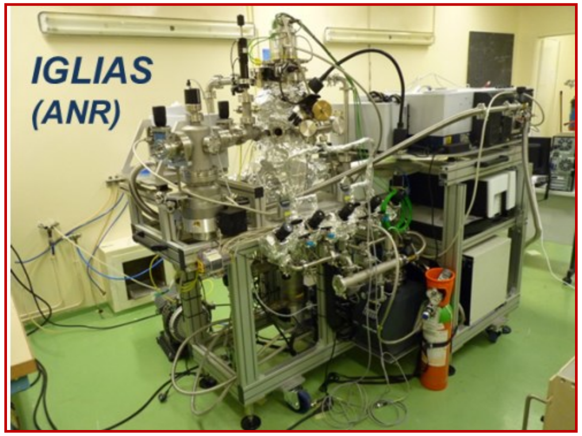
Formation of **new** molecular **species** (cross sections)

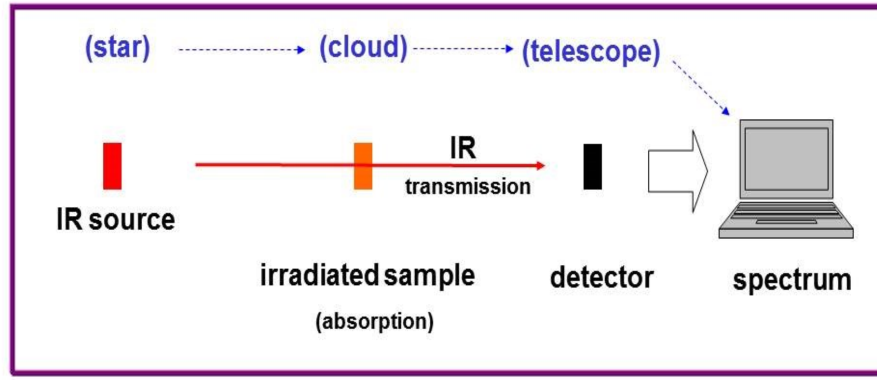
Increasing chemical complexity: **organics emergence of life?**

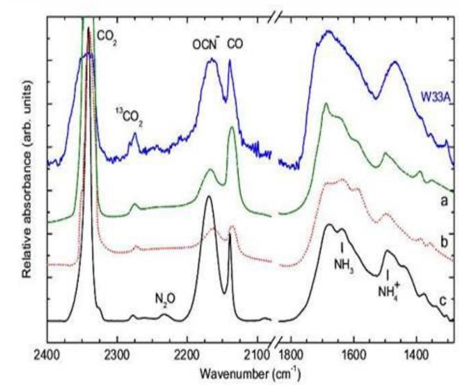
Astrophysics + Chemistry @ CIMAP-GANIL

How?

laboratory simulation: irradiation of Ices, silicates, carbon containing molecules







Space observation:

ISO Infrared Space Observatory, protostellar source W33a

Laboratory simulation:

UV photons

protons

heavy ions

S. Pilling et al. Astronomy & Astrophysics 509 (2010) A87

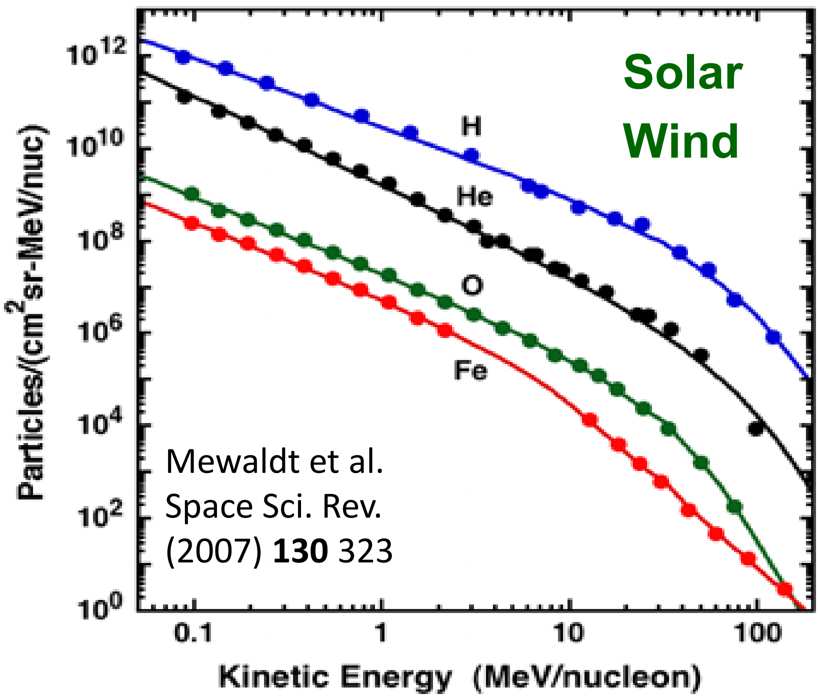
Infrared Absorption Spectroscopy FTIR
+ TOF-SIMS, QMS, QMB,
UV-vis, Chromatography, Nano-SIMS

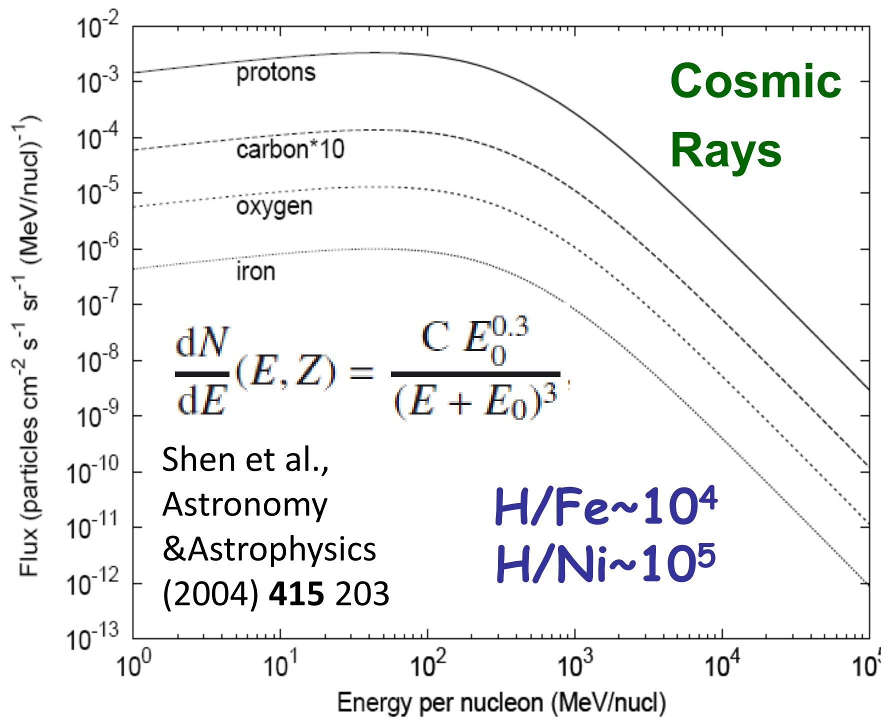
Comparison to space observations

Input to astrochemical models
(cross sections: scaling laws)

Topical Review: H. Rothard, A. Domaracka, Ph. Boduch, M. E. Palumbo, G. Strazzulla, E. F. da Silveira, E. Dartois
Modification of ices by cosmic rays and solar wind, J. Phys. B: At. Mol. Opt. Phys. 50 (2017) 062001

Radiation Field in Space : complex ! (UV, e-, x-rays, ions)



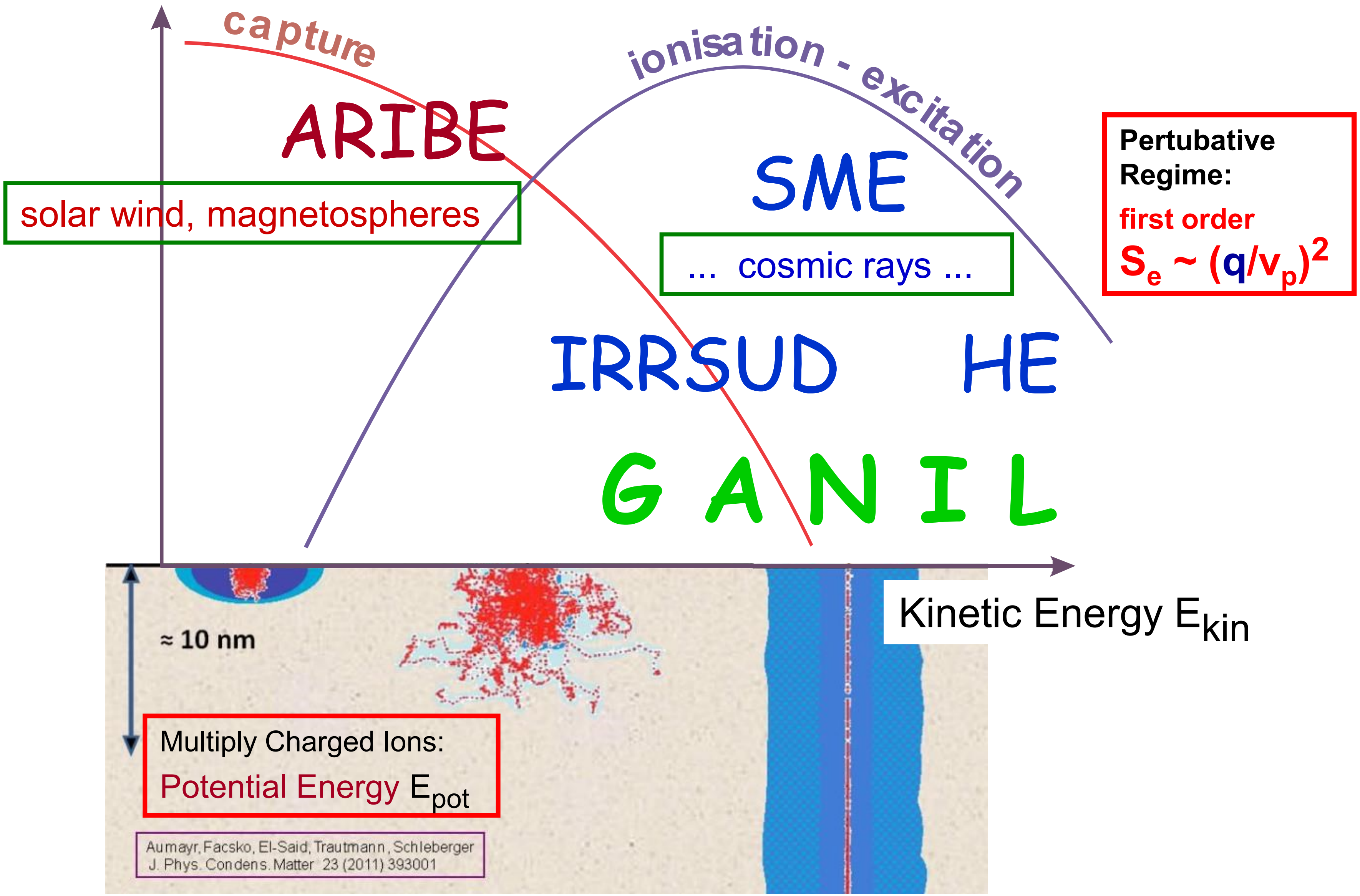


Heavy Ions: why? - large electronic energy loss S_e

- Scaling laws: S_e^n with n ≈ ½,1,$^3/_2$,**2**, ... 4)
- Unexplained findings (gas phase molecules in dense clouds...), few data
- Astrochemistry: origin of CO_2 and H_2SO_4 on Europe, emergence of life?

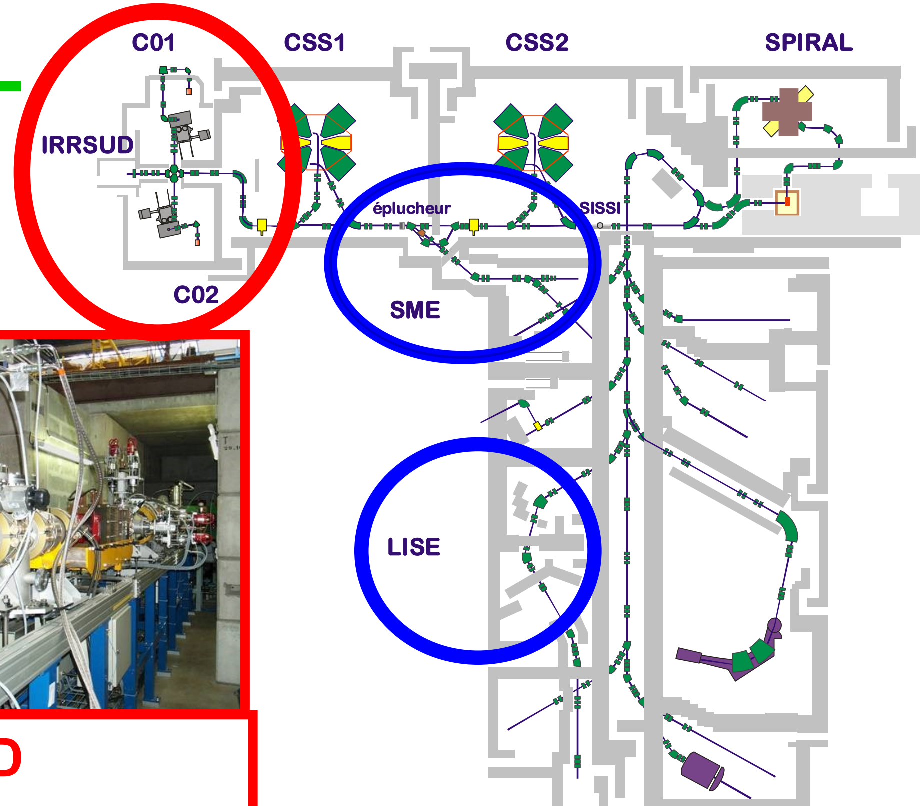
Elastic Collisions:
ion - (screened) nucleus
"nuclear stopping"

Inelastic Collisions: ion – target electron
"electronic stopping" S_e



Astromaterials @G A N I L

HE, SME, IRRSUD



+ARIBE low energy multiply charged ions

He, C, O, S, Ar, Xe:
q keV

IRRSUD

O, Ni, Xe, Ta, Pb:

0.5 to 1 MeV/u

High Energy: LISE

Fe: 70 MeV/u

Medium Energy: SME

O, Fe, Ni, Kr: 5-13 MeV/u

Water ice:

Sputtering,
Compaction,
Amorphization

Centre de Recherche sur les Ions,
les MAtériaux et la Photonique

Astrophysics + Chemistry @ CIMAP-GANIL

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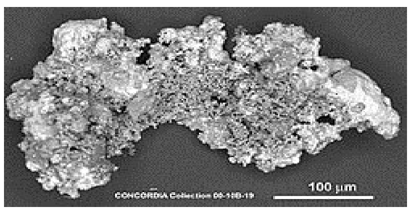
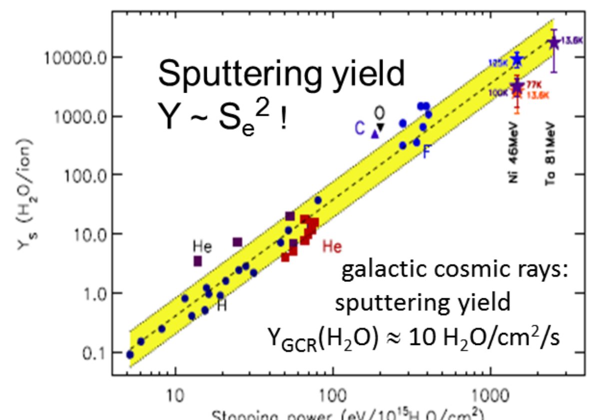
Recent Highlights @ GANIL (LISE + IRRSUD)

B. Augé, E. Dartois, C. Engrand, J. Duprat, M. Godard, L. Delauche, N. Bardin, C. Mejía, R. Martinez, G. Muniz, A. Domaracka, P. Boduch, H. Rothard
Irradiation of nitrogen-rich ices by swift heavy ions - Clues for the formation of ultracarbonaceous micrometeorites
Astronomy and Astrophysics 592 (2016) A99



French-Italian Station
Concordia (Antarctica)

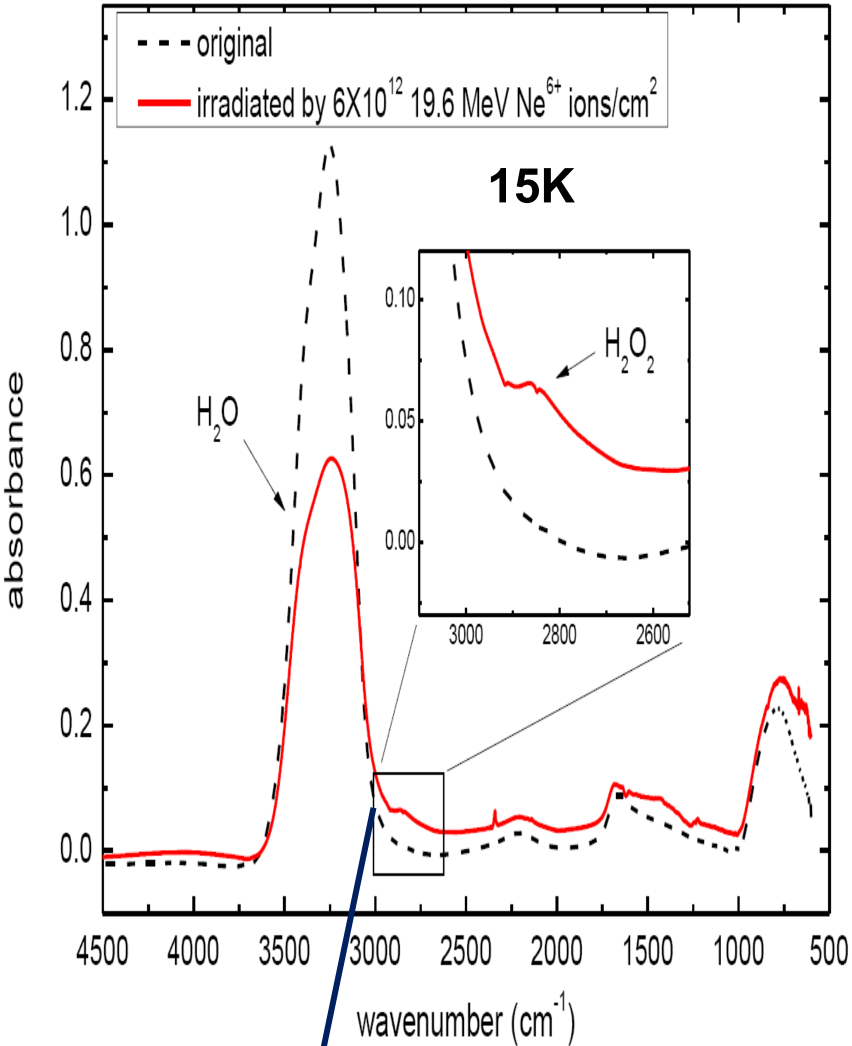
E. Dartois, B. Augé, P. Boduch, R. Brunetto, M. Chabot, A. Domaracka, J.J. Ding, O. Kamalou, X.Y .Lv, H. Rothard, E.F. da Silveira, J.C. Thomas
Heavy ion irradiation of crystalline water ice -Cosmic ray amorphization cross-section and sputtering yield
Astronomy & Astrophysics 576 (2015) A126



http://www.ganil-spiral2.eu/science/actualites/influence-des-ions-lourds-composant-le-rayonnement-cosmique-sur-la-glace-interstellaire

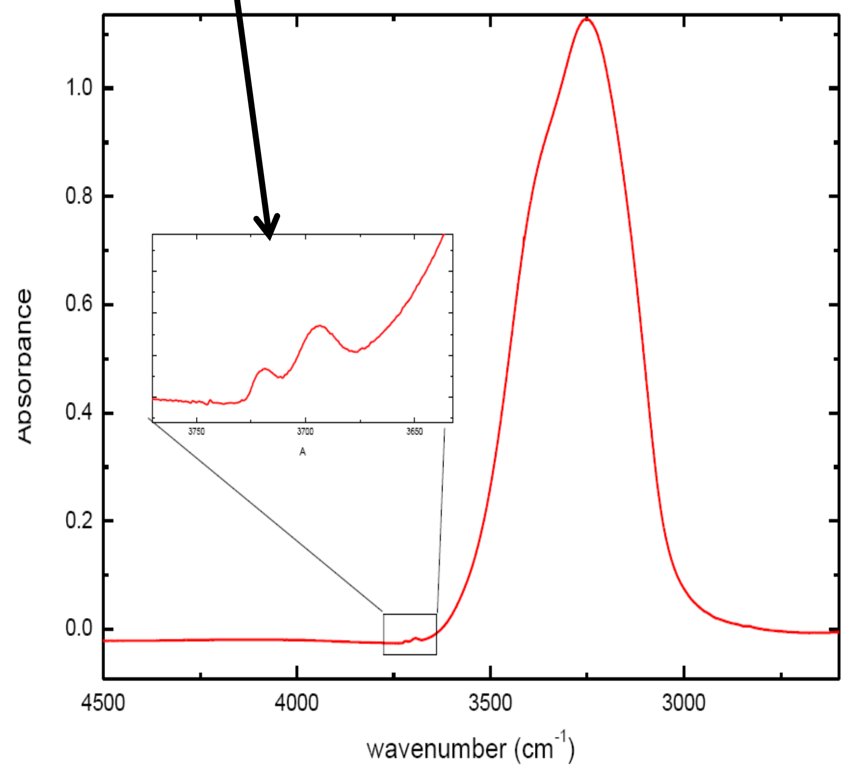
The most abundant molecule in interstellar ices:

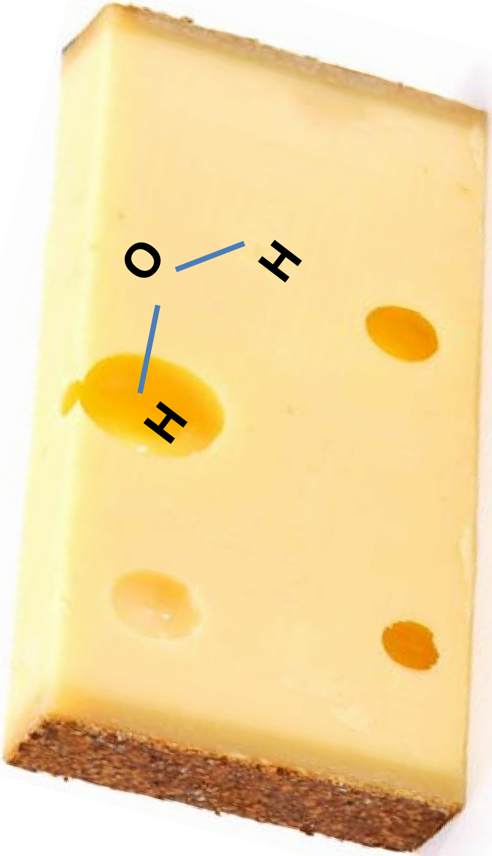
Water H_2O

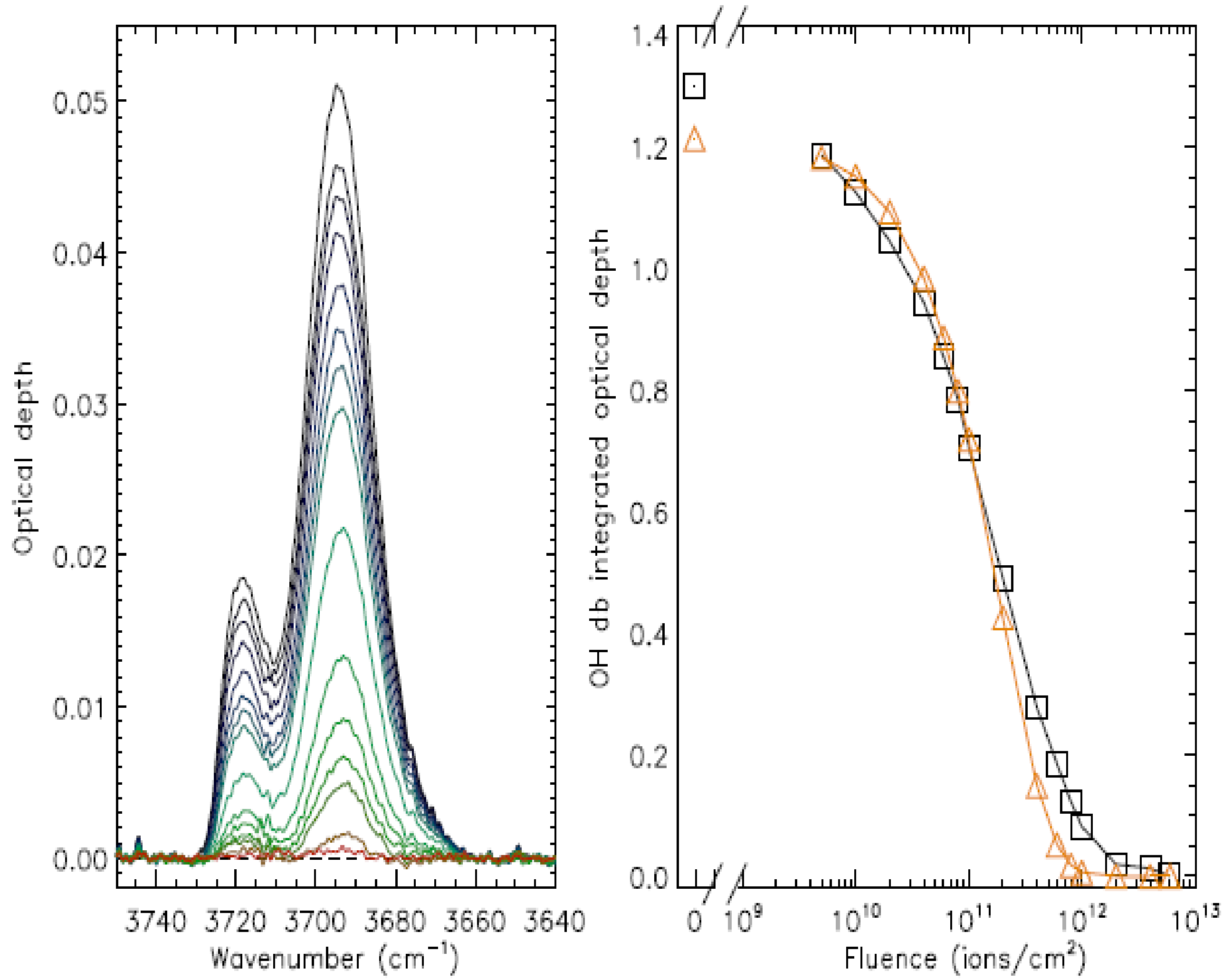


Irradiation of H_2O ice: formation of H_2O_2

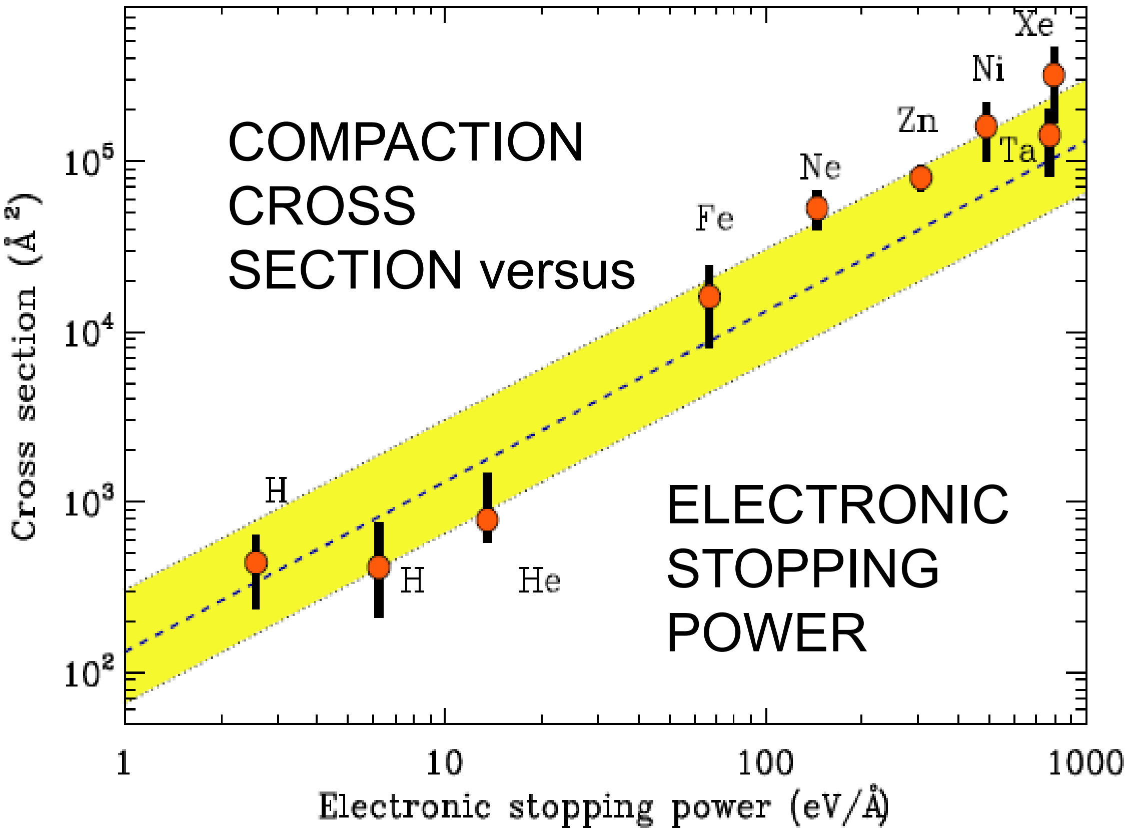
Porosity: OH dangling bonds







compaction "dose": 1 eV/molecule



t_{comp} = 1 $\times 10^5$ to 2 $\times 10^6$ years

small compared to cloud lifetimes

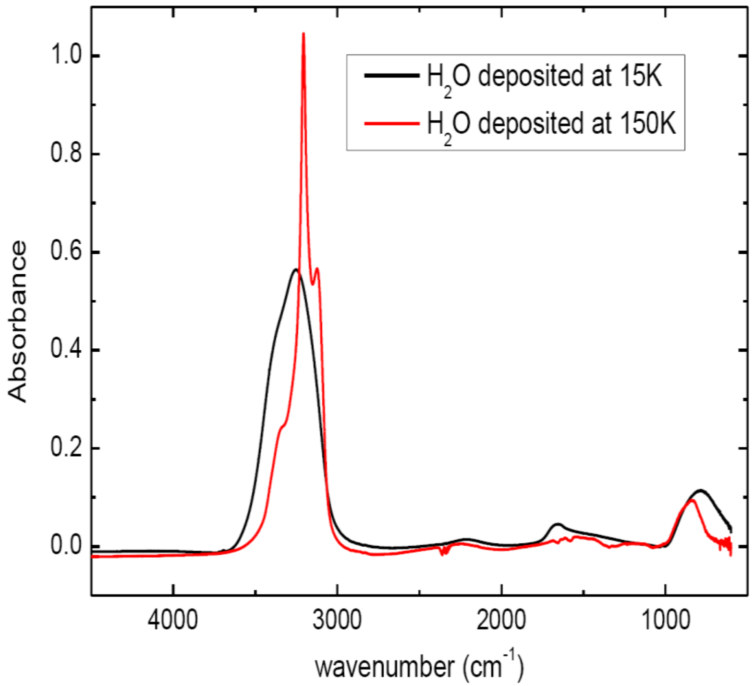
Indeed **no** OH dangling bonds observed by ISO in ISM

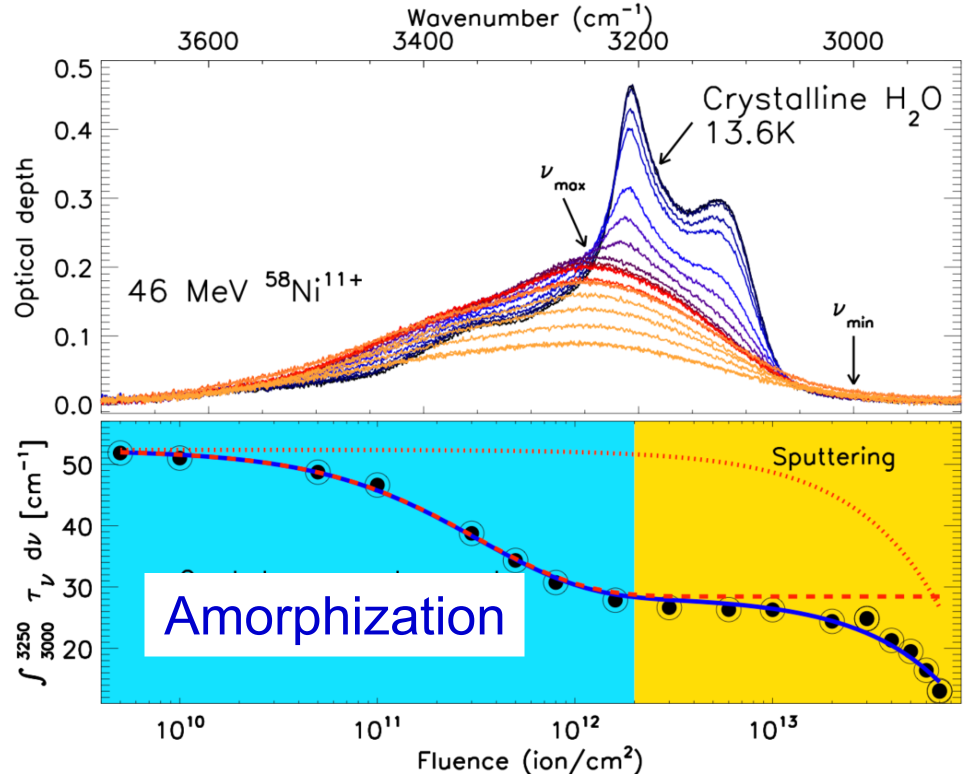
Compaction of Water Ice by Cosmic Rays: Experiment 2012 GANIL-LISE

E. Dartois, J.J. Ding, A.L.F. de Barros, P. Boduch, R. Brunetto, M. Chabot, A. Domaracka, M. Godard, X.Y. Lv, C.F. Mejia Guaman, T. Pino, H. Rothard, E.F. da Silveira, J.C. Thomas

Swift heavy ion irradiation of water ice at MeV to GeV energies: approaching true cosmic ray compaction

Astronomy & Astrophysics <u>557</u> (2013) A97





Amorphization "dose" 3 eV/molecule

Ion irradiation 3 times more efficient for compaction vs. amorphization
Water ice resilient to phase transition

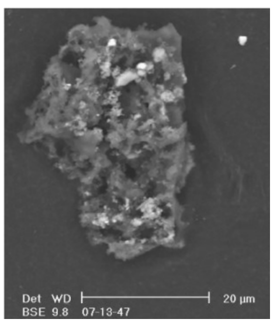
→ End point:
amorphous compact ice

E. Dartois, B. Augé, P. Boduch, R. Brunetto, M. Chabot, A. Domaracka, J.J. Ding, O. Kamalou, X.Y .Lv, H. Rothard, E.F. da Silveira, J.C. Thomas
Heavy ion irradiation of crystalline water ice -Cosmic ray amorphization cross-section and sputtering yield
Astronomy & Astrophysics 576 (2015) A126

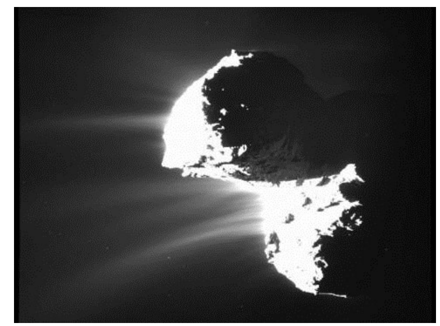
Formation and radioresistance of COMs

Complex organic molecules **COMs**

- In Astrophysics: at least 6 atomes, at least 1 C
- CH_3OH, amino-acids, nucleo-bases, proteins…
- Essential bricks for the emergence of life
- In dense clouds, in comets (Rosetta: amino acids)

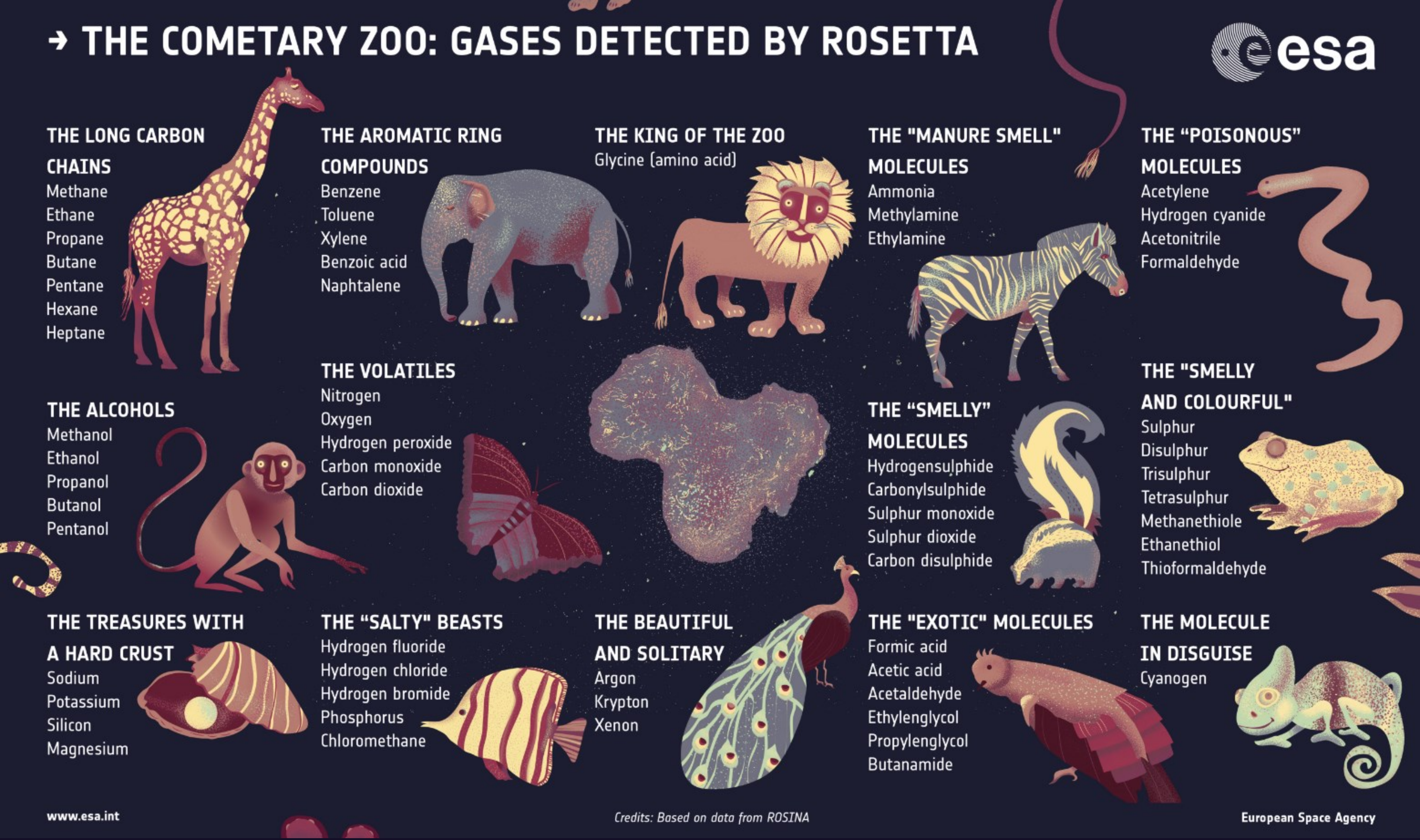


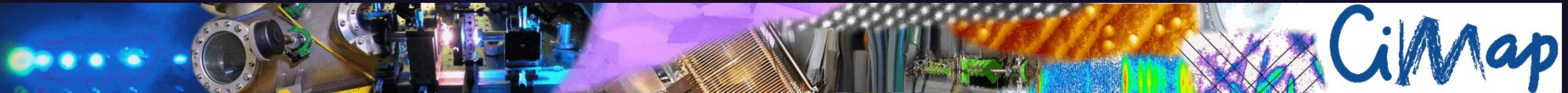
Formation in ice?



Surface (catalytic reaction)

Ion (Cosmic rays) and UV irradiation


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 ALCOHOLS
Methanol
Ethanol
Propanol
Butanol
Pentanol
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"
Sulphur
Disulphur
Trisulphur
Tetrasulphur
Methanethiole
Ethanethiol
Thioformaldehyde
THE TREASURES WITH A HARD CRUST
Sodium
Potassium
Silicon
Magnesium
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 MOLECULE IN DISGUISE
Cyanogen
www.esa.int
Credits: Based on data from ROSINA
European Space Agency

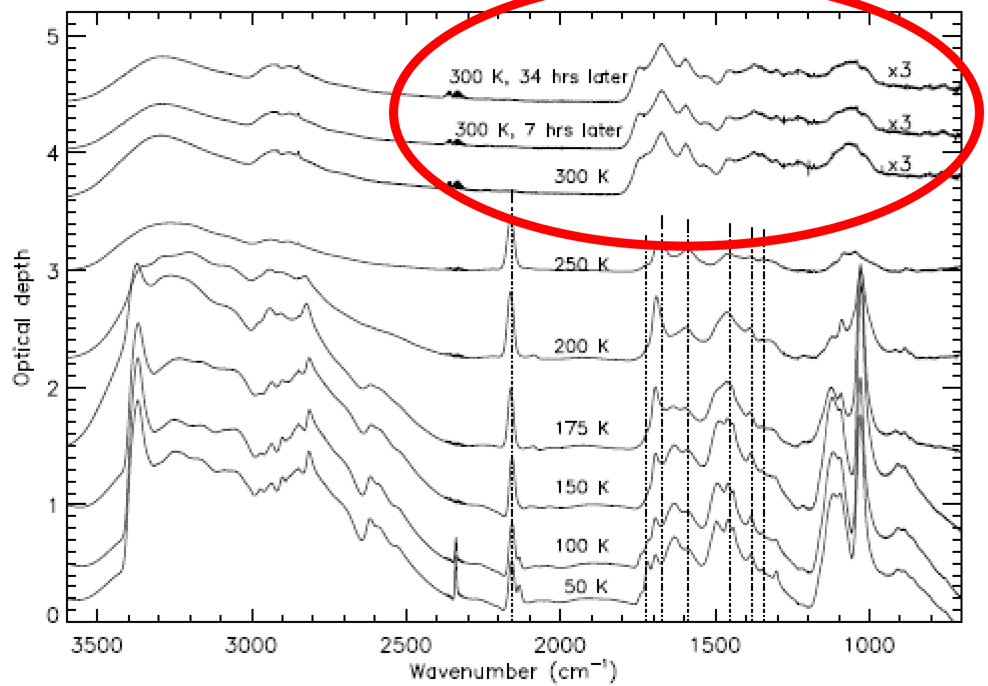

CiMap

Radiolysis: formation of prebiotic molecules ?

G. M. Muňoz Caro, E. Dartois,
P. Boduch, H. Rothard,
A. Domaracka, A. Jiménez-Escobar
Comparison of UV and high-energy ion irradiationof methanol:ammonia ice
Astron. & Astrophys. 566 (2014) A93

NH_3:CH_3OH ice

CASIMIR@GANIL:
Zn (SME), Ne (IRRSUD)



New bands attributed to irradiation products

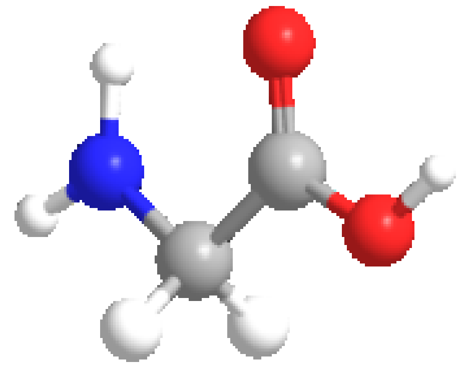
position[a] (cm^{-1})	Assignment	vibration mode
2340	CO_2	CO str.
2160	OCN^-	CN str.
2138	CO	CO str.
1740	C=O ester/aldehyde	CO str.
1720	H_2CO	CO str.
1694	$HCONH_2$?	CO str.
1587	COO^- in carb. ac. salts[b,c]	COO^- asym. str.
1498	H_2CO	CH_2 scis.
1385	CH_3 groups	CH_3 sym. def.
1347	COO^- in carb. ac. salts[b,c]	COO^- sym. str.
1303	CH_4	def.

at 300K: stable organic Residues!

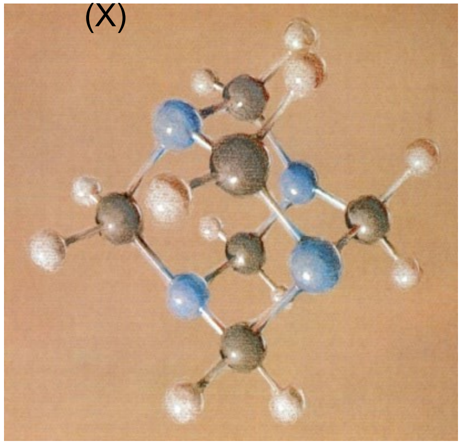
Frequency (cm^{-1})	Wavelength (μm)	Temp. (K)	Molecule
2233	4.48	13	N_2O
2218–2200	4.51-4.54	300	nitriles†
2168	4.61	13, 300	OCN^-
2147	4.66	300	aliph. isocyanide†
~2112	4.73	300	$NCO_2^\dagger$
1725	5.80	300	ester†
1683	5.94	300	amides†
1652	6.05	300	asym-$N_2O_3^\dagger$
1637	6.11	13	?
1593	6.28	300	$NH_3^+CH_2COO^{-\dagger}$
1558	6.42	300	?
1533	6.52	300	?
1506	6.64	300	$NH_3^+CH_2COO^{-\dagger}$
~1490	6.71	13	NH_4^+
1474	6.78	13	$NO_3^\dagger$
1440	6.94	13	$NH_3^+CH_2COO^{-\dagger}$
1415	7.07	300	$NH_3^+CH_2COO^{-\dagger}$
~1370	7.30	13, 300	HMT†
			$HCOO^-$
~1338	7.47	13, 300	$NH_3^+CH_2COO^{-\dagger}$
			$NH_2CH_2COO^{-\dagger}$
			$HCOO^-$
1305	7.66	13	$N_2O_3^\dagger$; $N_2O_4^\dagger$
1283	7.80	300	$N_2O^\dagger$

H_2O - CO - NH_3 ice

⇒ glycine (amino acid)



$C_2H_5NO_2$



hexamethylene-tetramine HMT

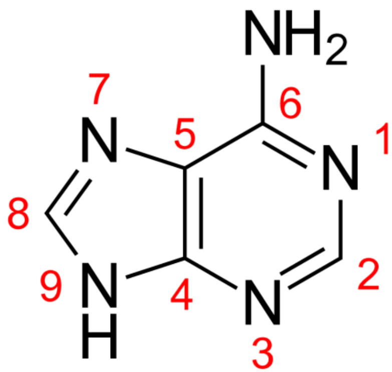
S. Pilling, E. Seperuelo Duarte, E. F. da Silveira, E. Balanzat, H. Rothard, A. Domaracka, P. Boduch
Radiolysis of ammonia-containing ices by energetic, heavy and highly charged ions inside dense astrophysical environments,
Astronomy & Astrophysics 509 (2010) A87

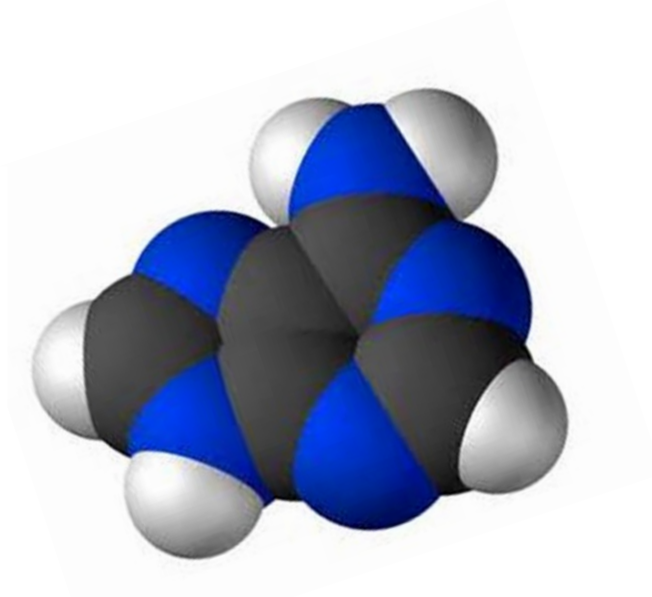
(X) http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/index.html

Radiation resistance of complex organic molecules

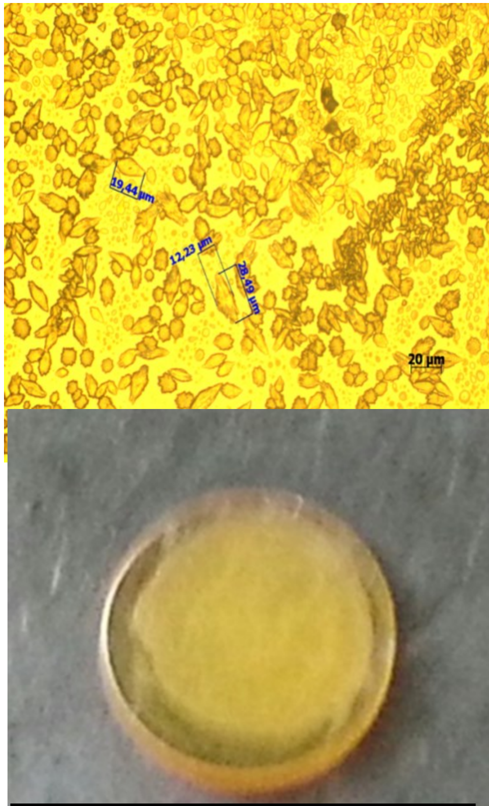
irradiation with swift heavy ions at GANIL and GSI
Laboratory simulation of cosmic ray effects

First results: **adenine**





9*H*-purin-6-amine $C_5H_5N_5$



sample on ZnSe

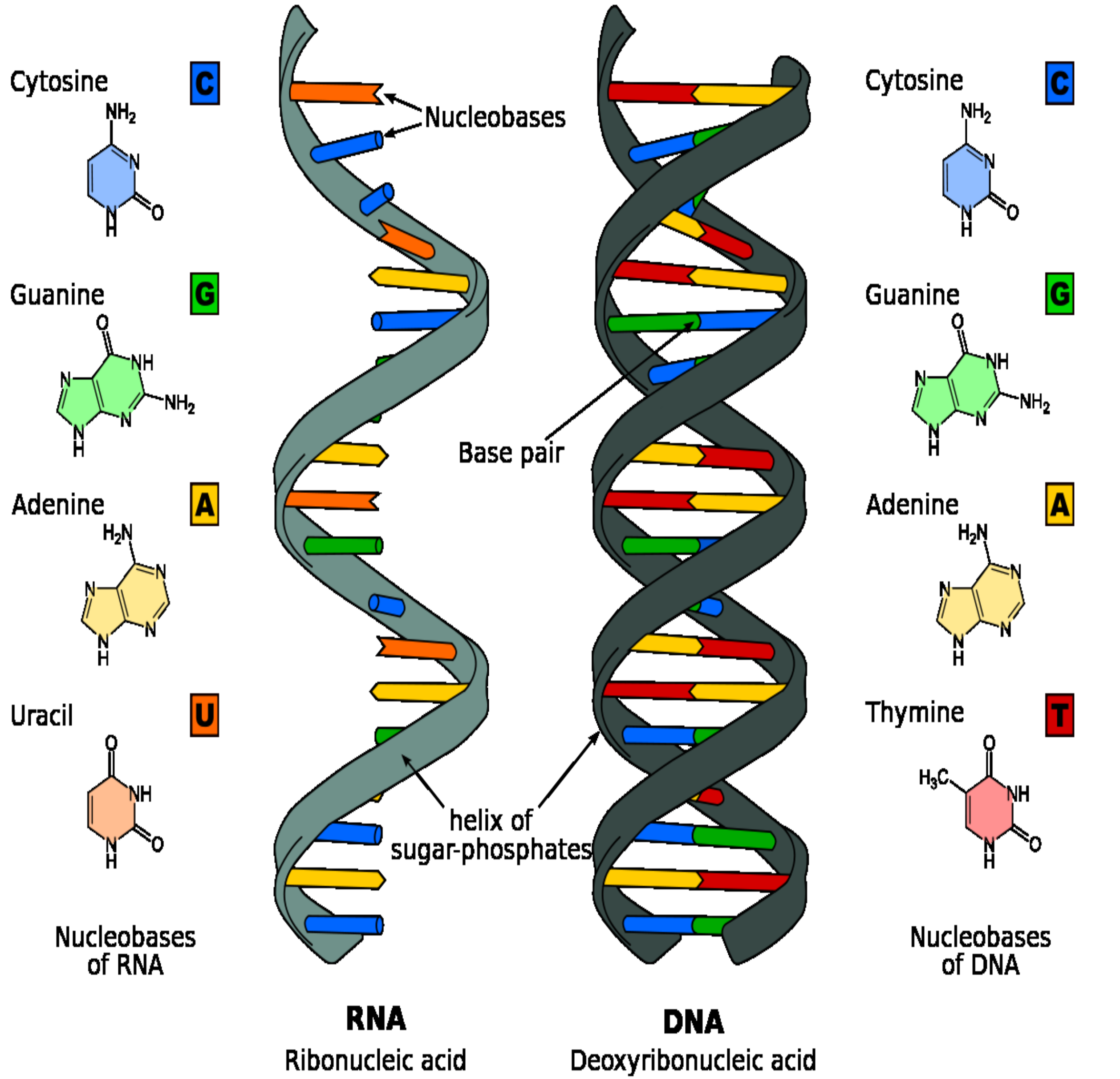
Adenine

$C_5H_5N_5$

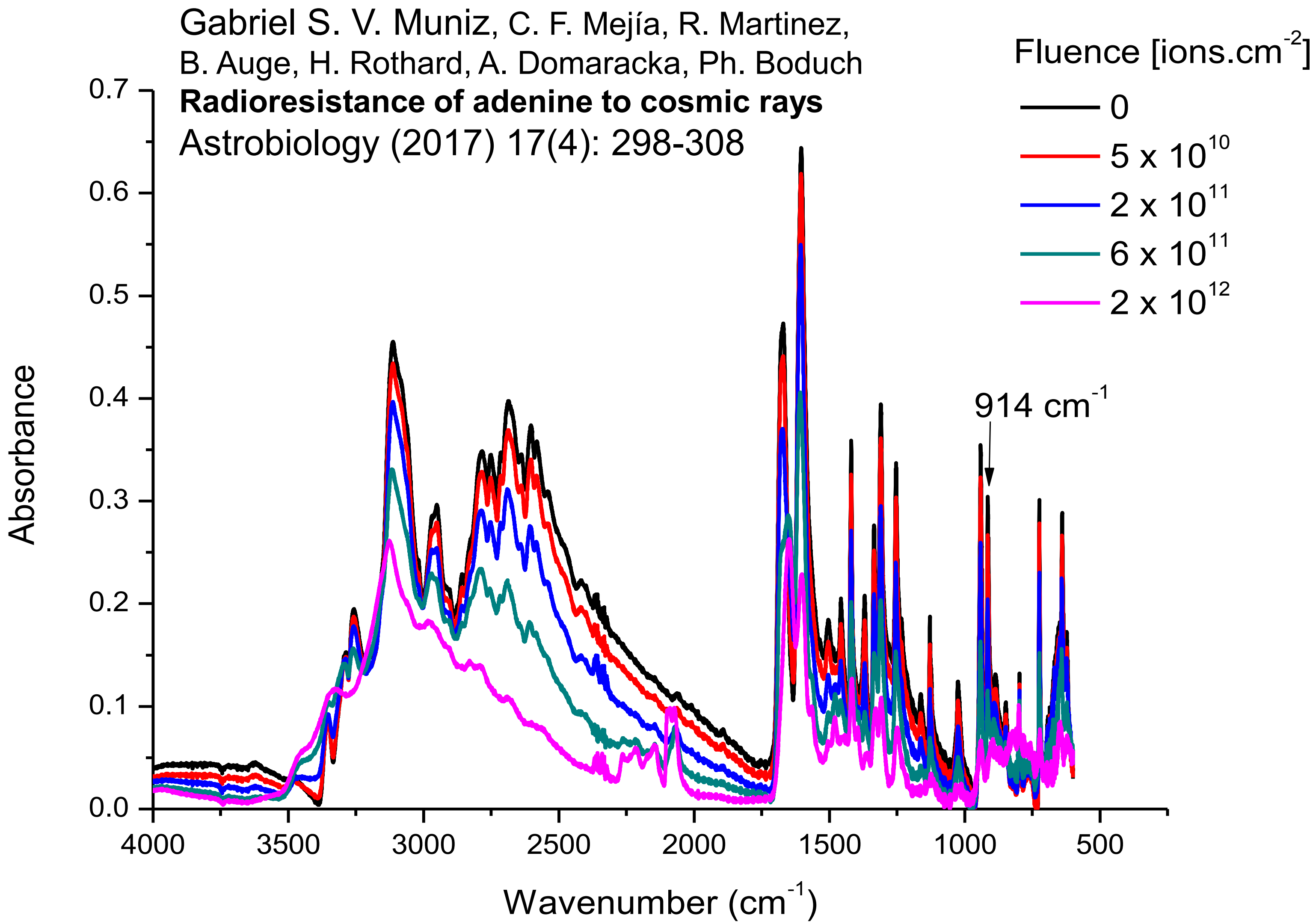
purine nucleobase

Part of biomole-
cules of unique
importance
(ATP, DNA, RNA)

evolutionarily
preserved in all
living beings,
including viruses.



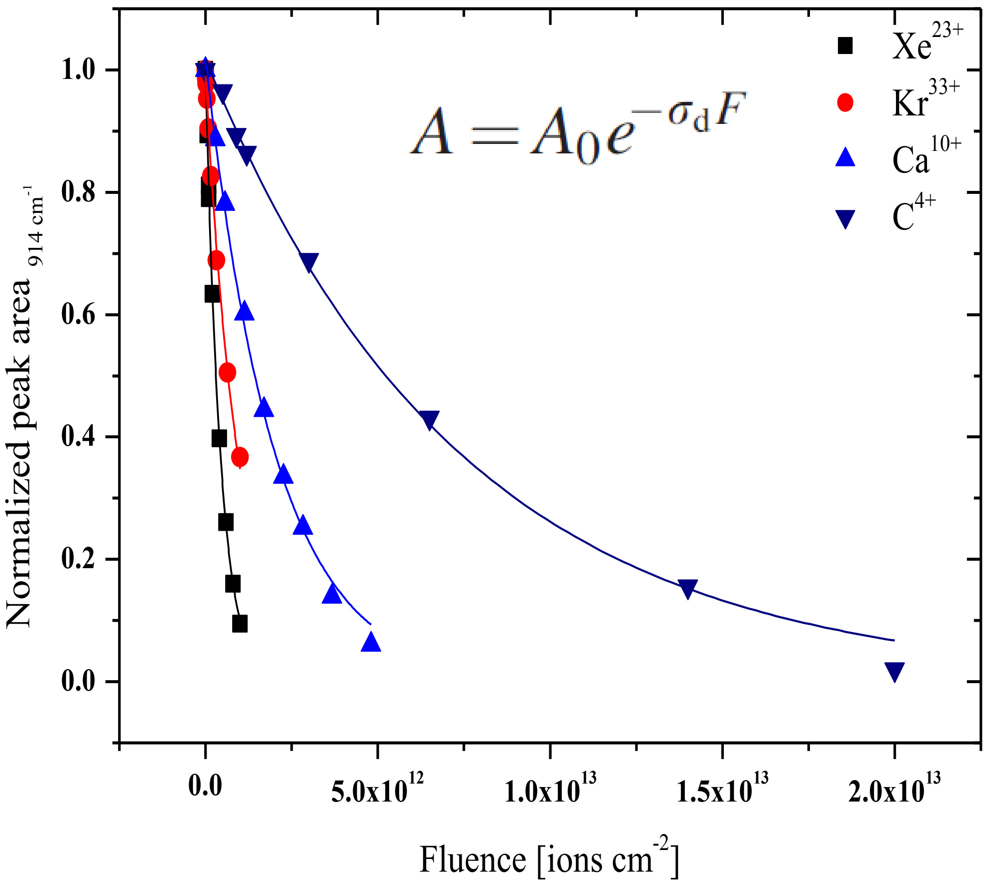
IR spectra: Evolution with projectile fluence



Adenine irradiation experiments at Ganil (IRRSUD, SME) and GSI (Unilac M-Branch)

Ion Beam	Energy (MeV/u)	Electronic stopping power (keV.µm^{-1})	Nuclear stopping power (keV.µm^{-1})	Thickness (µm)	Penetration depth (µm)
Xe^{+23}	0.7	1.12×10^4	6.95×10^1	0.29	16
Kr^{33+}	10.5	5.80×10^3	3.6	0.50	120
Ca^{10+}	4.8	3.3×10^3	2.22	0.35	50
C^{4+}	0.98	$1{,}00 \times 10^3$	0.9	0.25	12

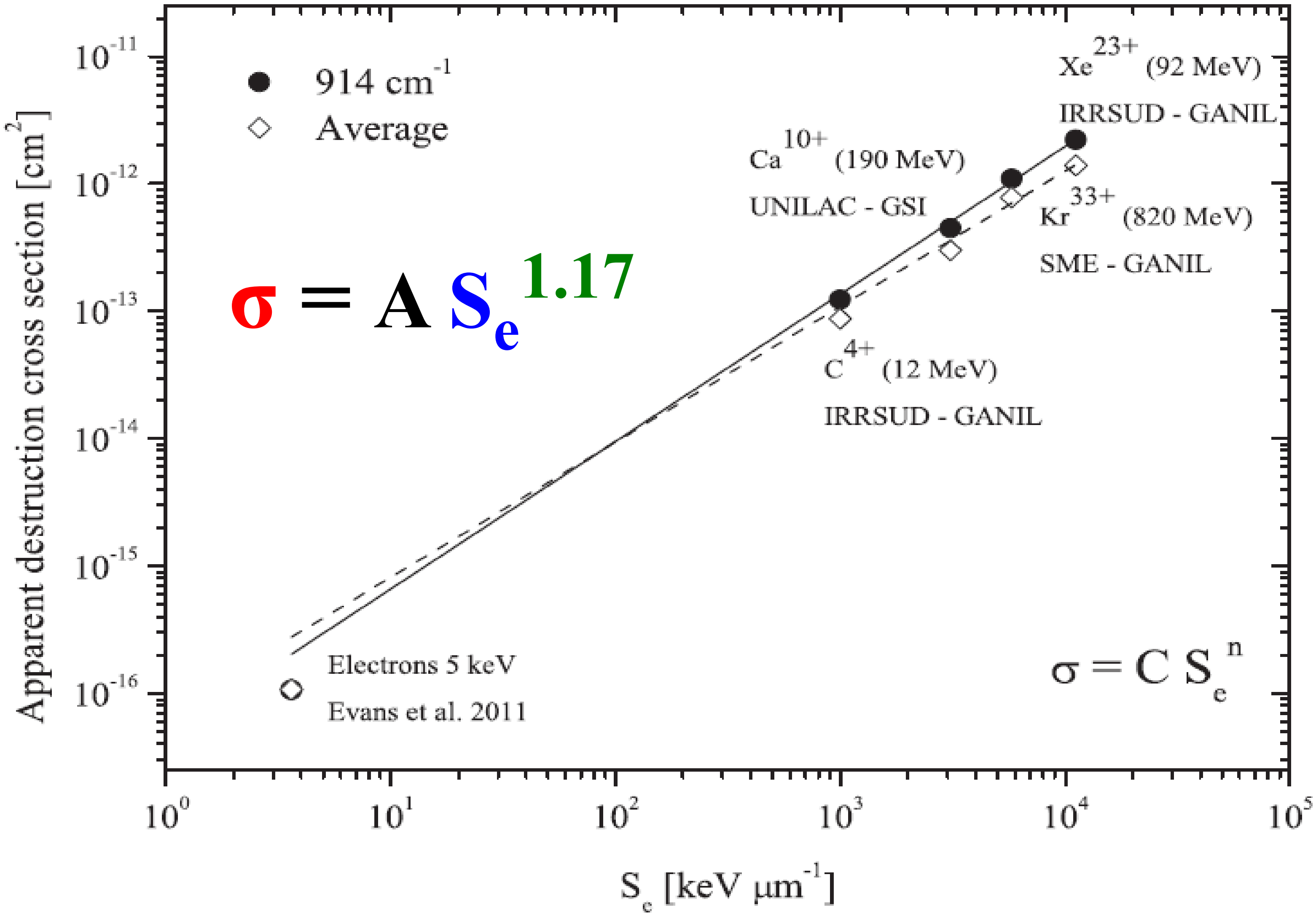
Evolution with projectile fluence: peak intensity (914 cm^{-1})



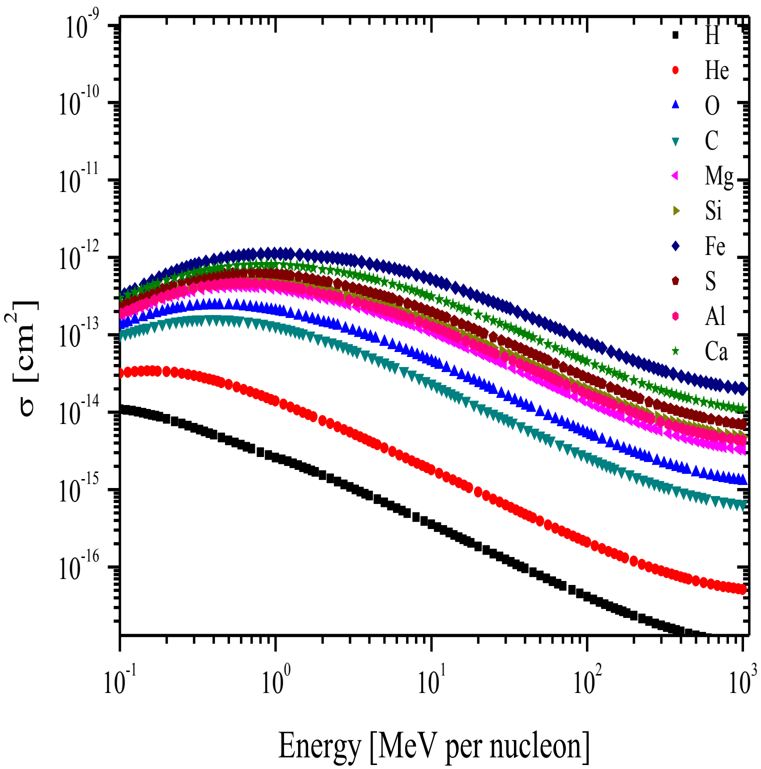
Projectile	Destruction cross section (x10^{-13} cm^2)
Xe^{23+}	22.1 ± 0.1
Kr^{33+}	11.4 ± 0.3
Ca^{10+}	4.5 ± 0.2
C^{4+}	1.24 ± 0.06

Cross section as a function of the **stopping power**:

$$\sigma = A\, S_e^{1.17}$$

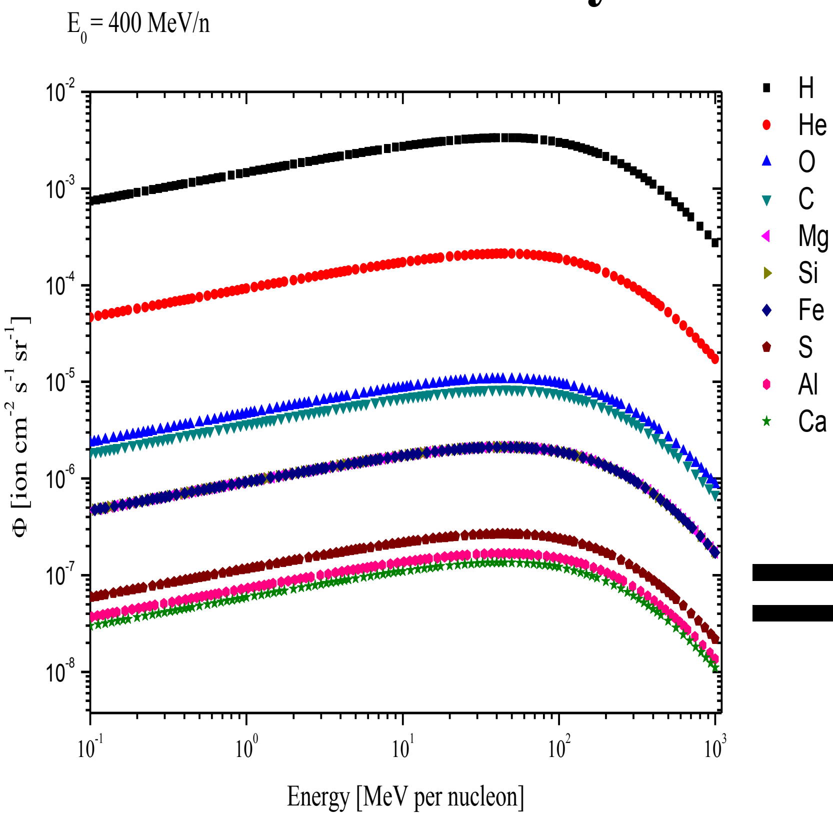


Destruction cross section



X

Cosmic Ray Flux

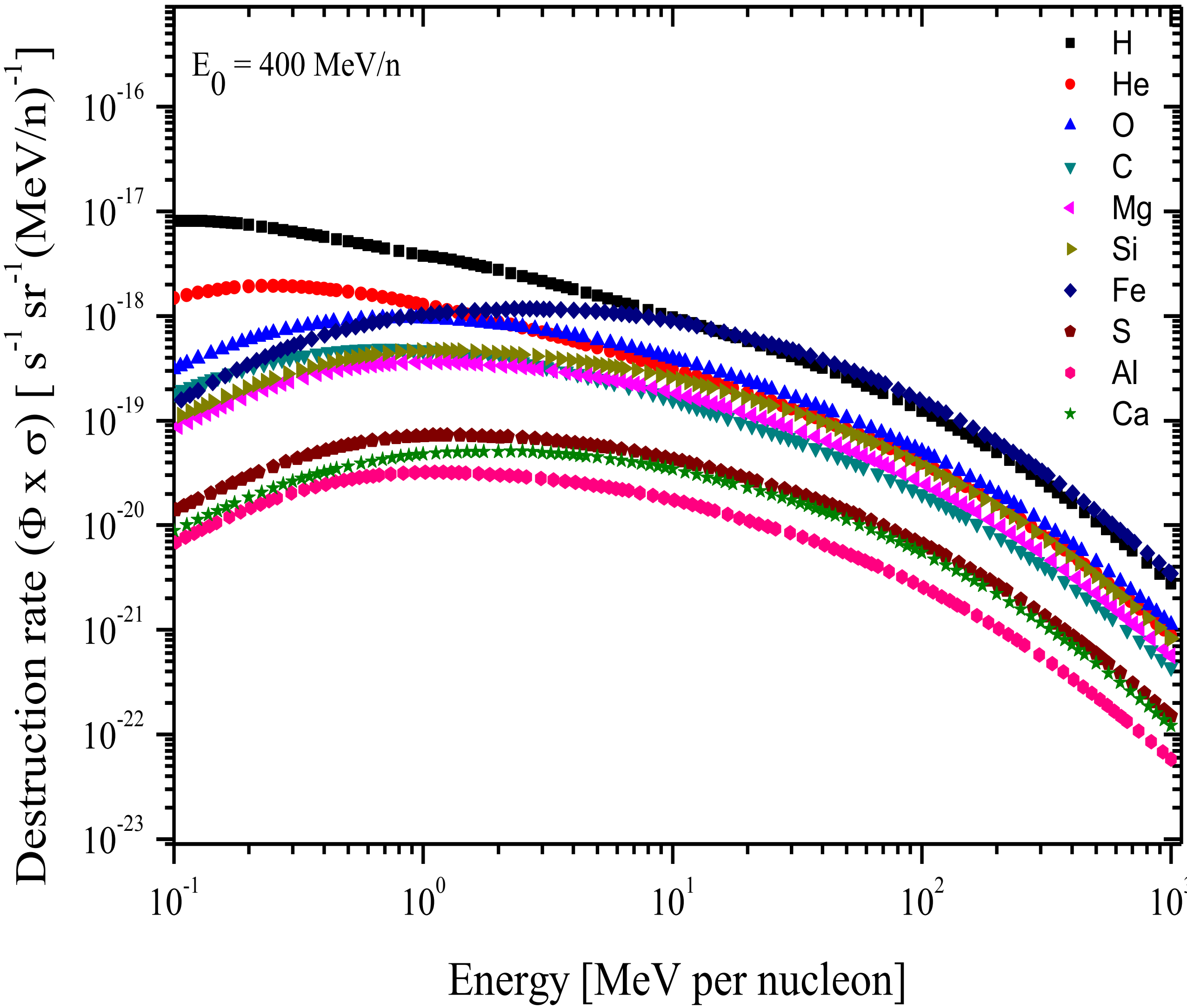


=

$$\phi(Z,E) = \frac{C\,(Z)\,E^{0.3}}{(E + E_0)^3}$$

W. R. Webber, S. M. Yushak, Astrophys. J. (1983) 275:391

Destruction rate



H and Fe (heavy ion component!) **dominant**

Astrophysical implications?

Half-life of solid adenine exposed to cosmic rays in the ISM

$$\tau_{1/2} = \ln 2 \left(4\pi \sum_Z \int_{10^{-1}}^{10^3} \sigma(Z,E)\Phi(Z,E)dE \right)^{-1}$$ = 10 ± 8 x 10^6 years

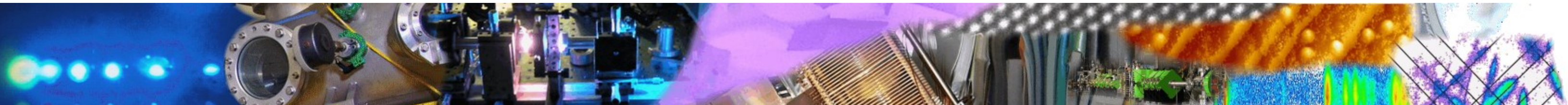
Dense Molecular **C**loud
lifetime: max. 10^7 years
High survival probability!

UV photons		
Region	**Half-life (Myears)**	**UV flux ($cm^{-2}\ s^{-1}$)**
ISM	**0.45**	**1.0 x 10^8**
Dense Clouds (DC)	**4.5 x 10^4**	**1.0 x 10^3**

Cosmic Rays	
Region	**Half-life (Myears)**
ISM	**10**
Dense Clouds (DC)	**≈10**

Comparison to UV radiation:
Cosmic ray destruction dominates inside the DC

Gabriel S. V. Muniz, C. F. Mejía, R. Martinez, **B. Auge**, H. Rothard, A. Domaracka, Ph. Boduch
Radioresistance of adenine to cosmic rays
Astrobiology (2017) 17(4): 298-308



Perspectives :

NUMEROUS!

ANR
IGLIAS
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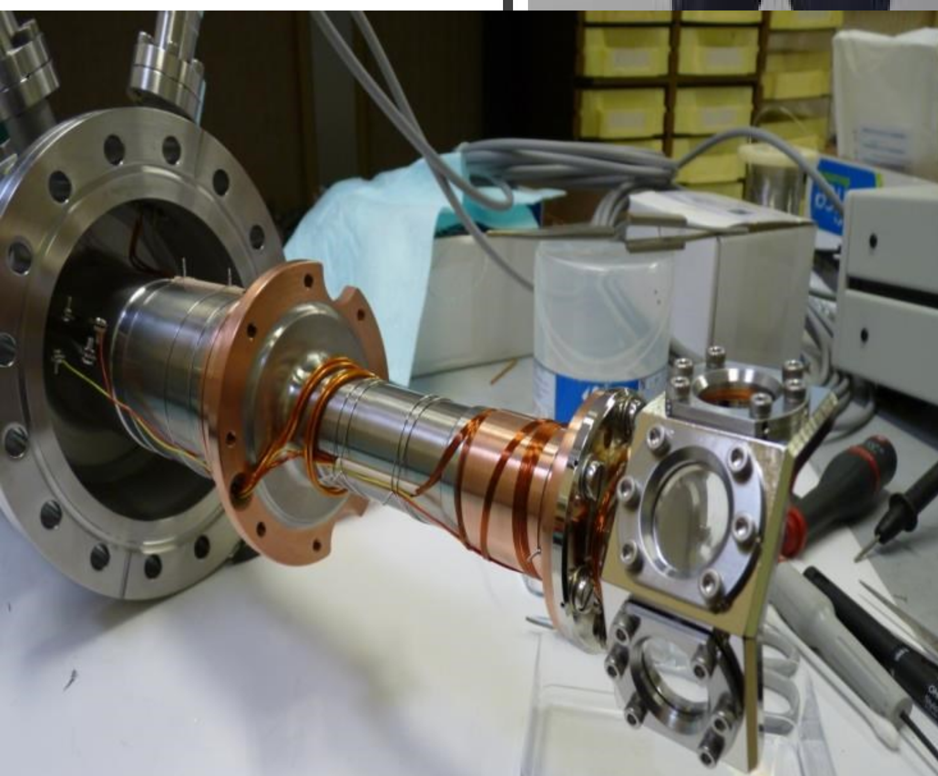
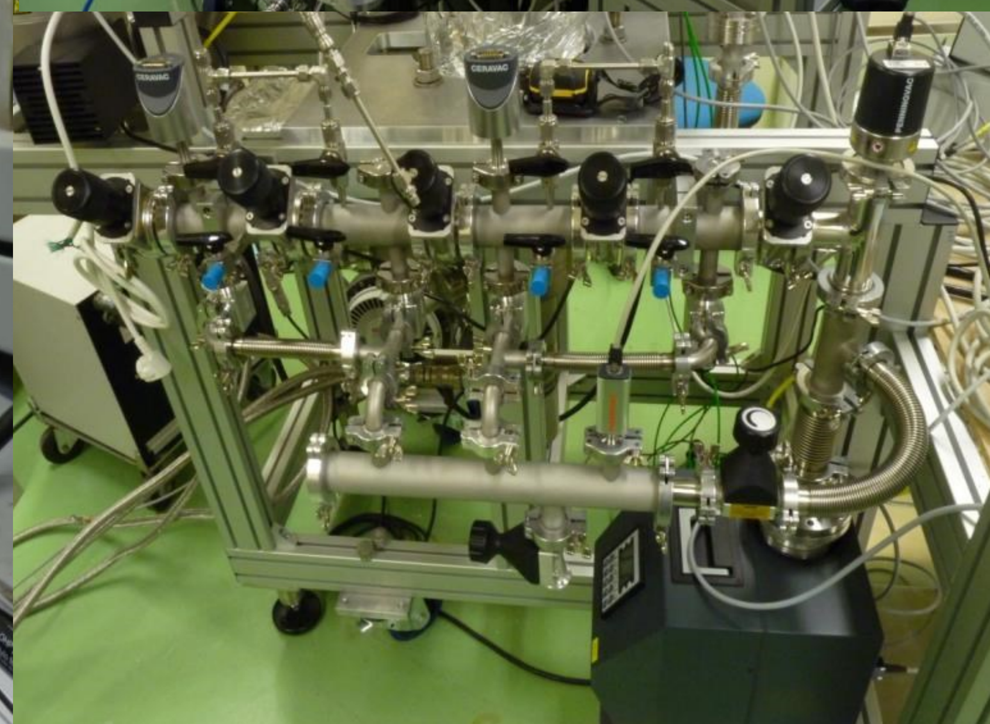
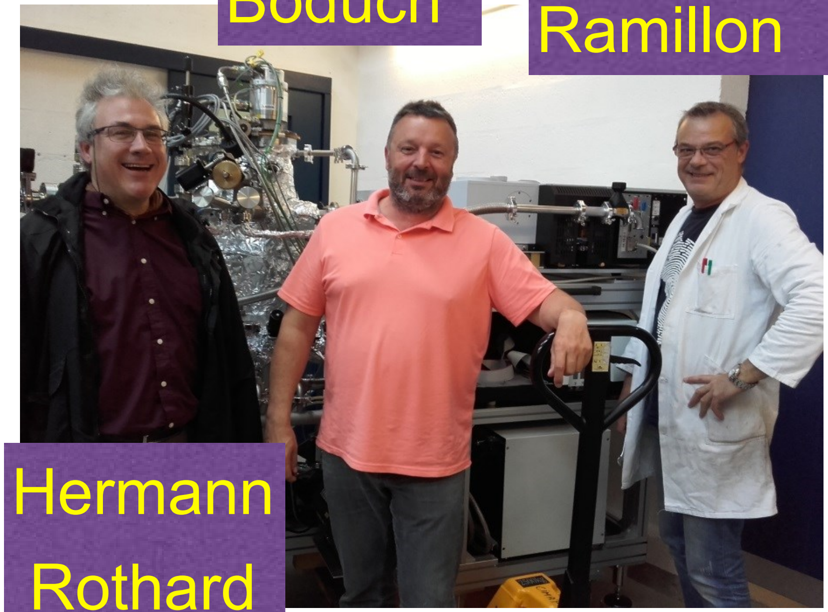
B. Augé, thesis defended Oct. 12, 2017





The Team 2017



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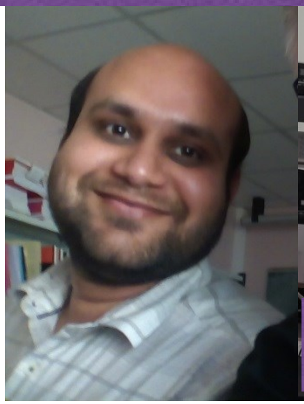

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Call for abstracts:
November 2017

Abstract submission:
February 2018