Radiation effects in astrophysical ices and biomolecules

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

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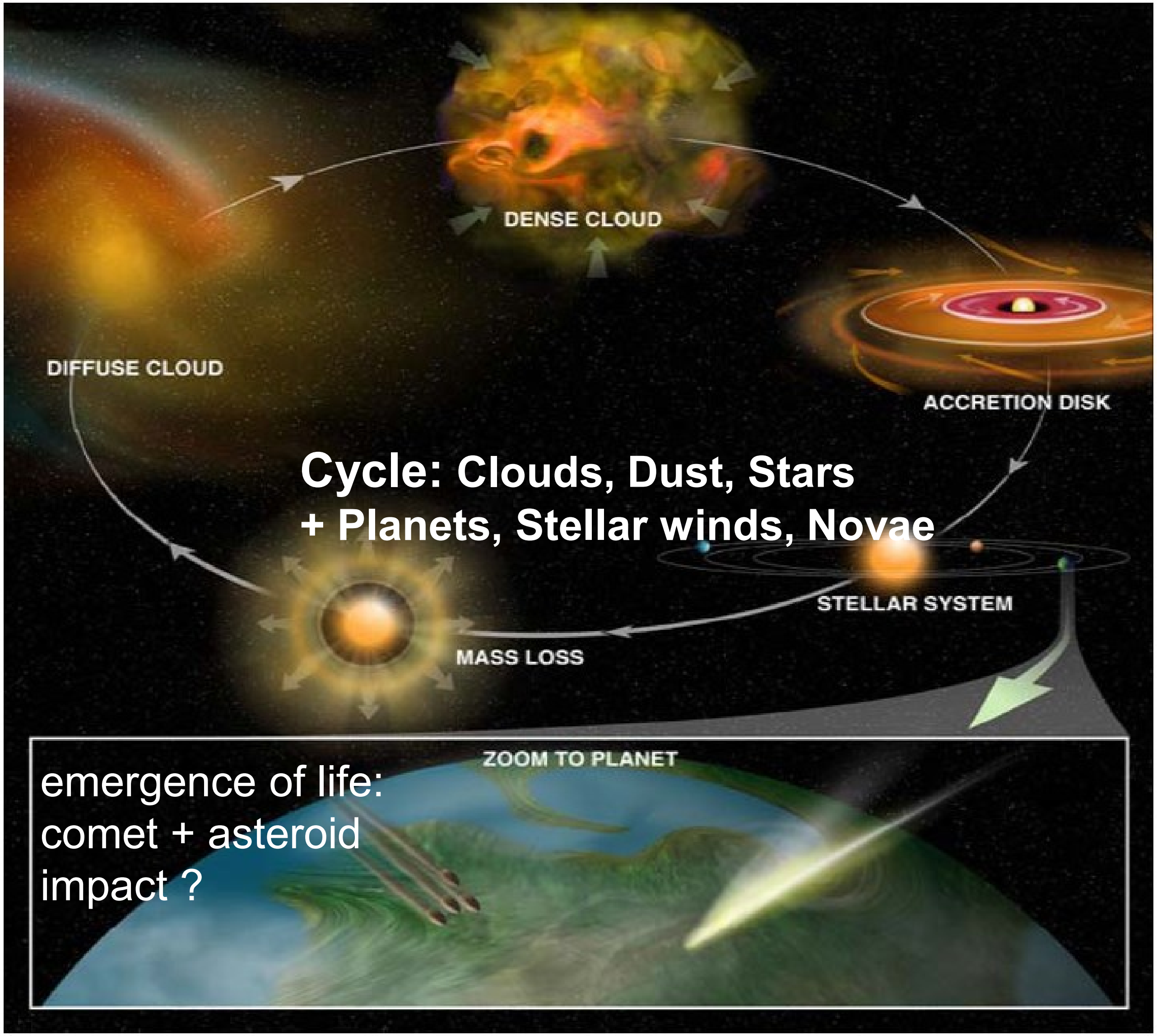
Astrochemistry and Astrobiology



Credit: Bill Saxton, NRAO/AUI/NSF

Astrophysics + Chemistry @ CIMAP-GANIL + GSI

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

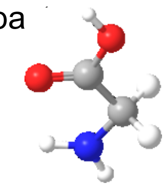
Why?

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?

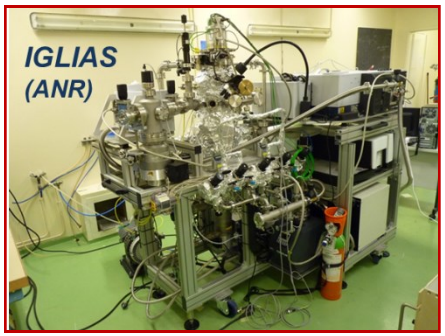
Structure: amorphous vs. cristalline, porous vs. compa

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?**



How?

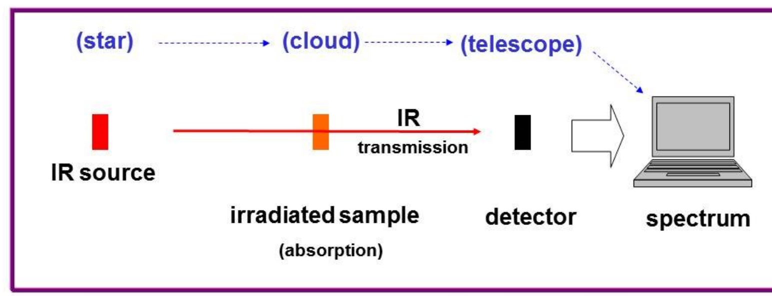
laboratory simulation of cosmic ray effects

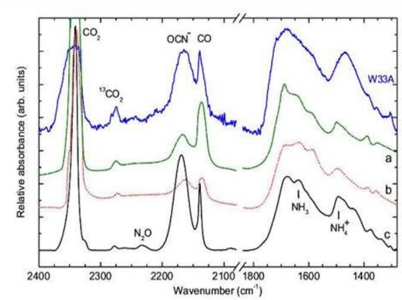
Heavy ions: wide dE/dx range (scaling laws)

Infrared Absorption Spectroscopy FTIR
(+ TOF-SIMS, QMS, UV-vis, Chromatography)

Comparison to space observations

Input to astrochemical models
(cross sections: scaling laws)



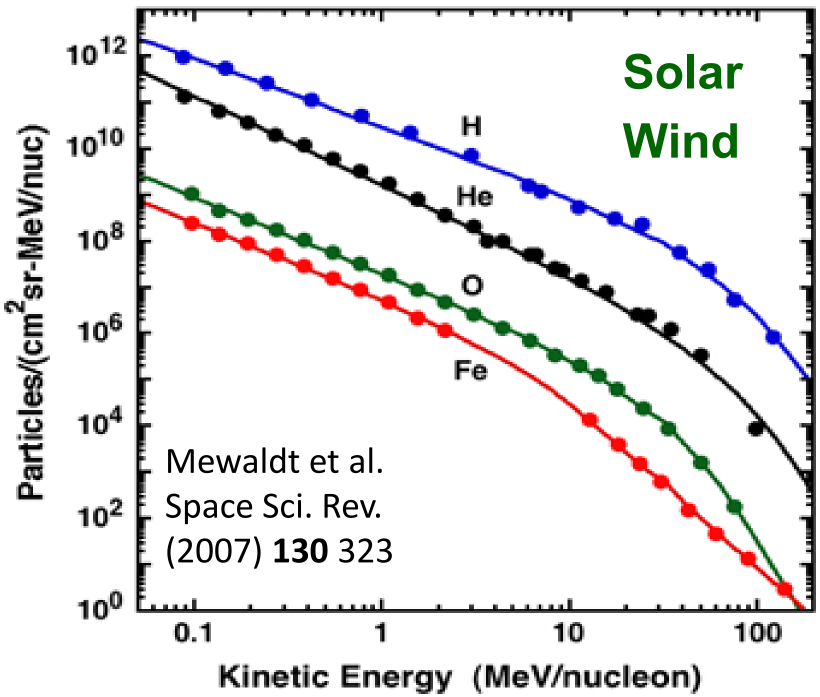


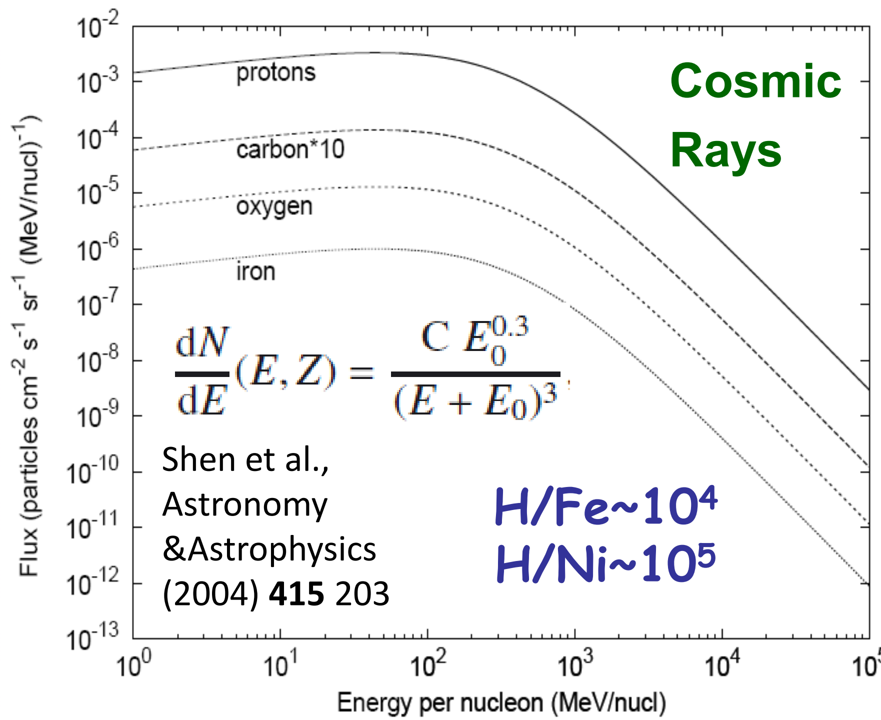
Space observation:
ISO Infrared Space Observatory, protostellar source W33a

Laboratory simulation:
UV photons
protons
heavy ions

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

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





Heavy Ions: why? - large electronic energy loss **S_e**

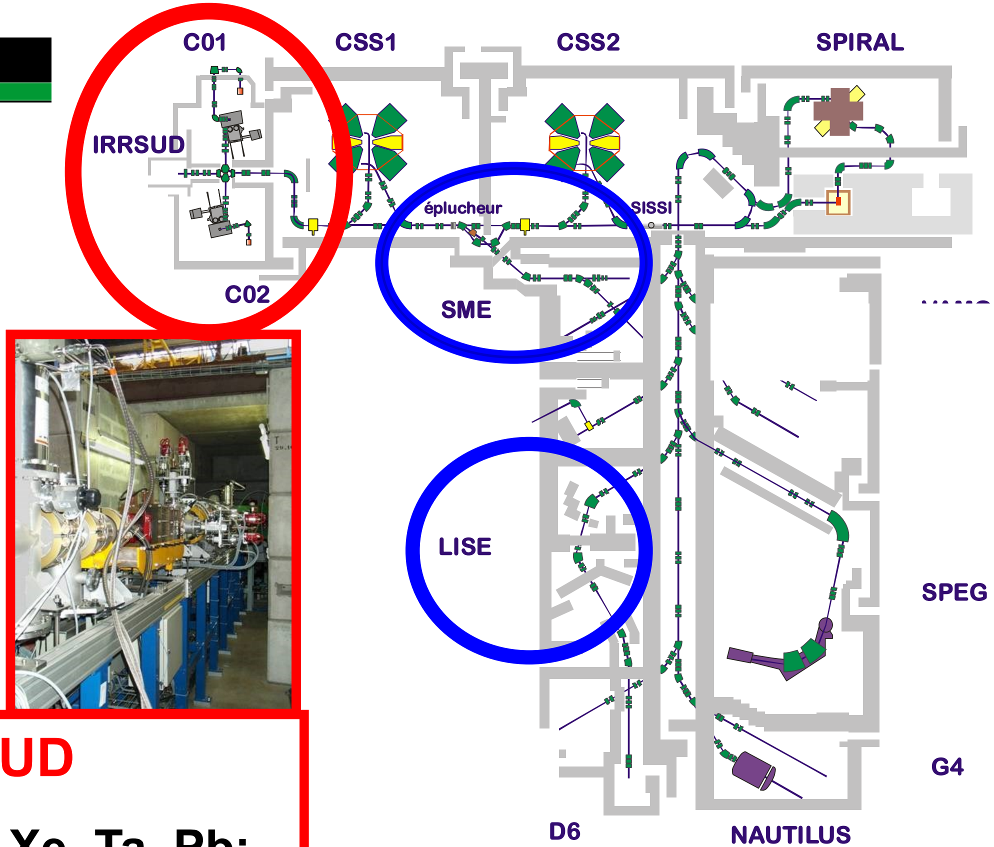
- Scaling laws: **$S_e^{\,n}$** with n ≈ ½,1,³/₂,**2**, ... 4)

- Unexplained findings (gas phase molecules in dense clouds...), few data

- Astrochemistry: origin of CO_2 and H_2SO_4 on Europe, emergence of life?

Astromaterials @GANIL

HE, SME, IRRSUD



+ARIBE low energy multiply charged ions

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

IRRSUD

O, Ni, Xe, Ta, Pb:

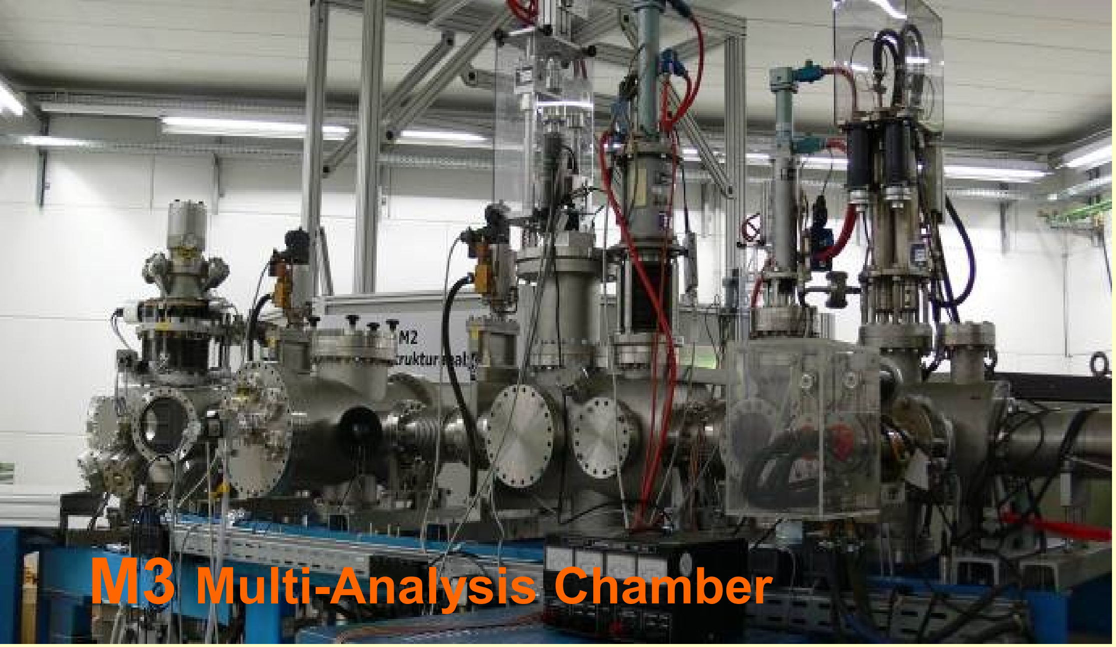
0.5 to 1 MeV/u

High Energy: LISE

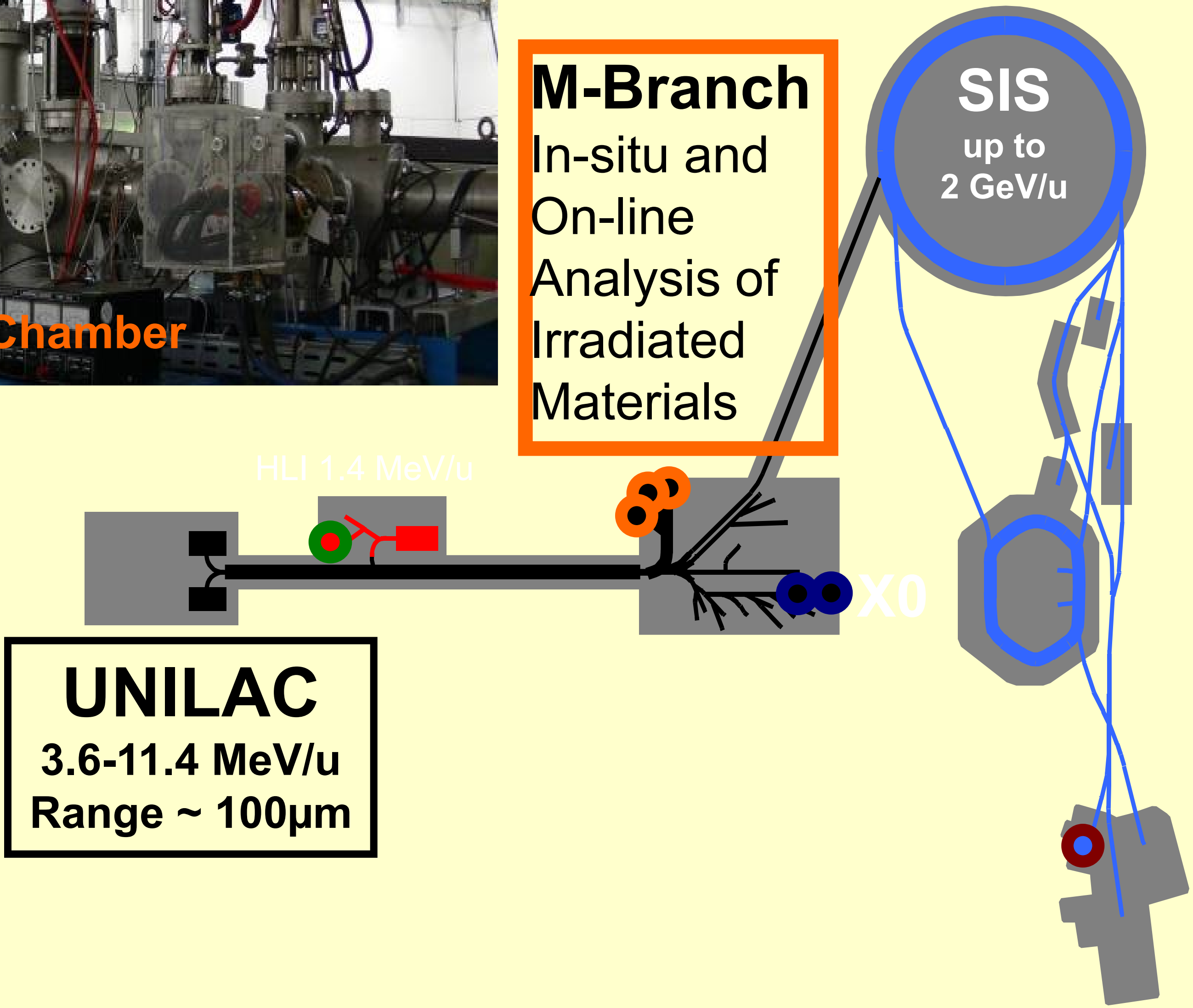
Fe: 70 MeV/u

Medium Energy: SME

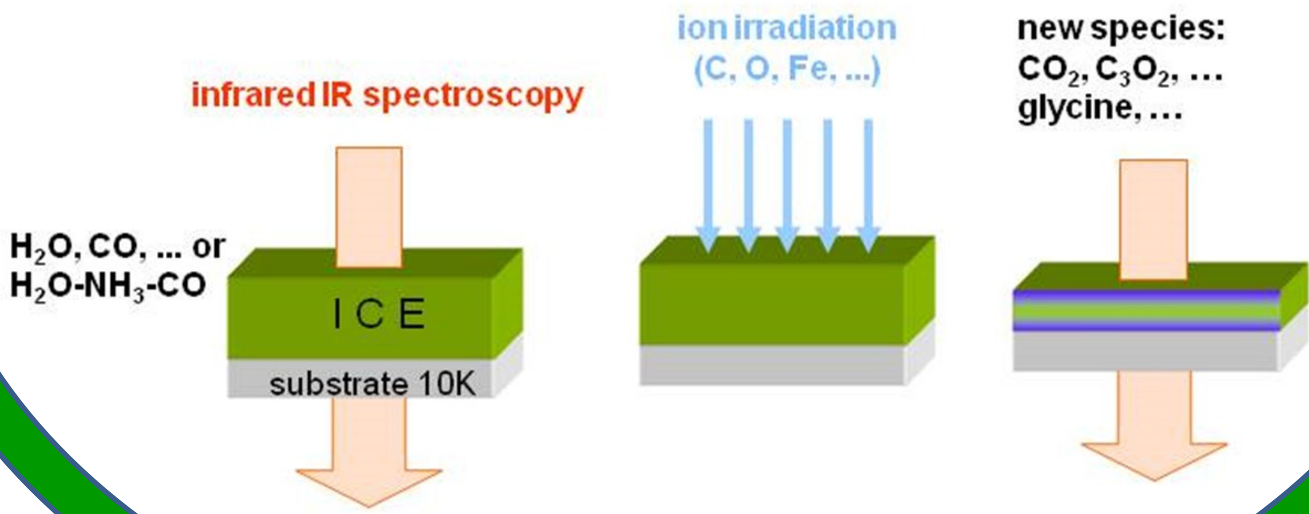
O, Fe, Ni, Kr: 5-13 MeV/u

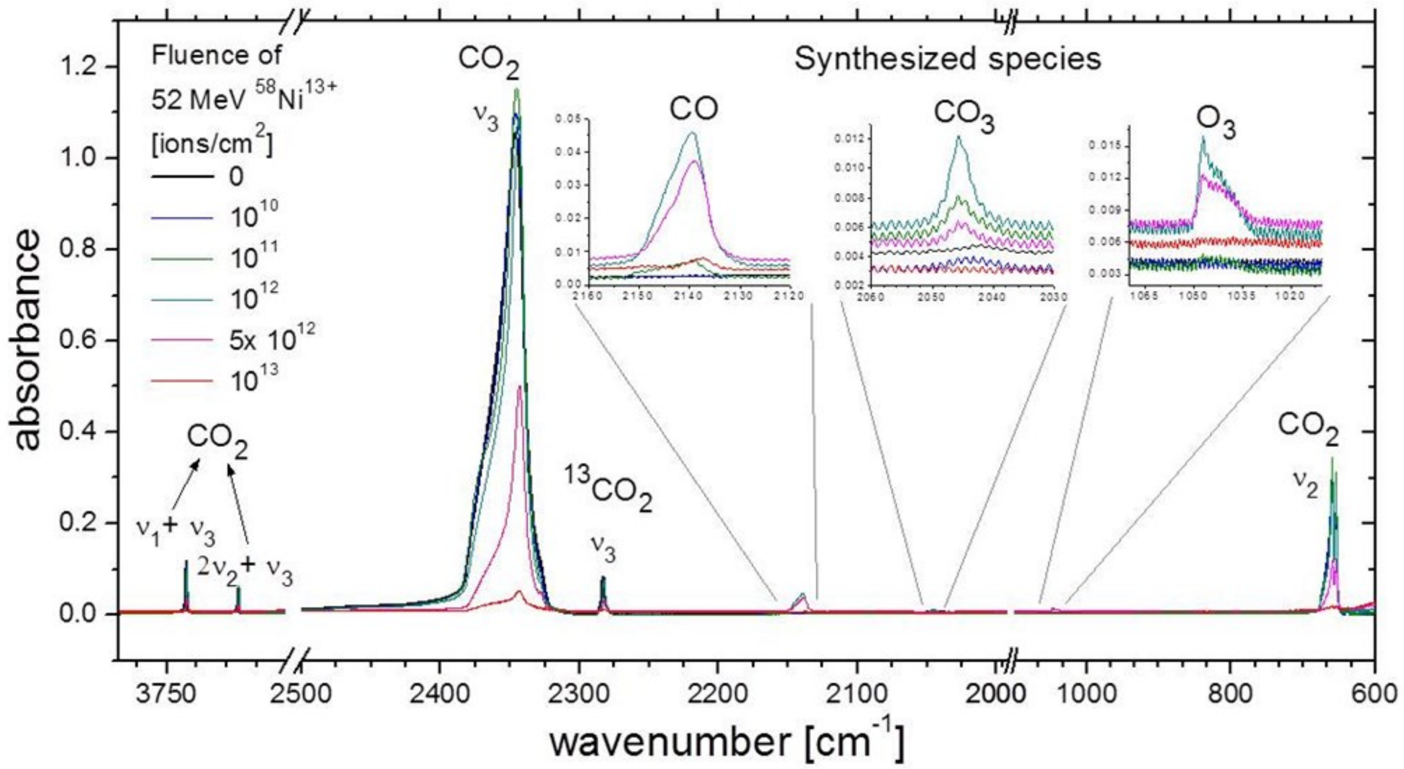


Materialforschung



Radiolysis of CO and CO_2 in dense molecular Clouds: UV versus Cosmic Rays.





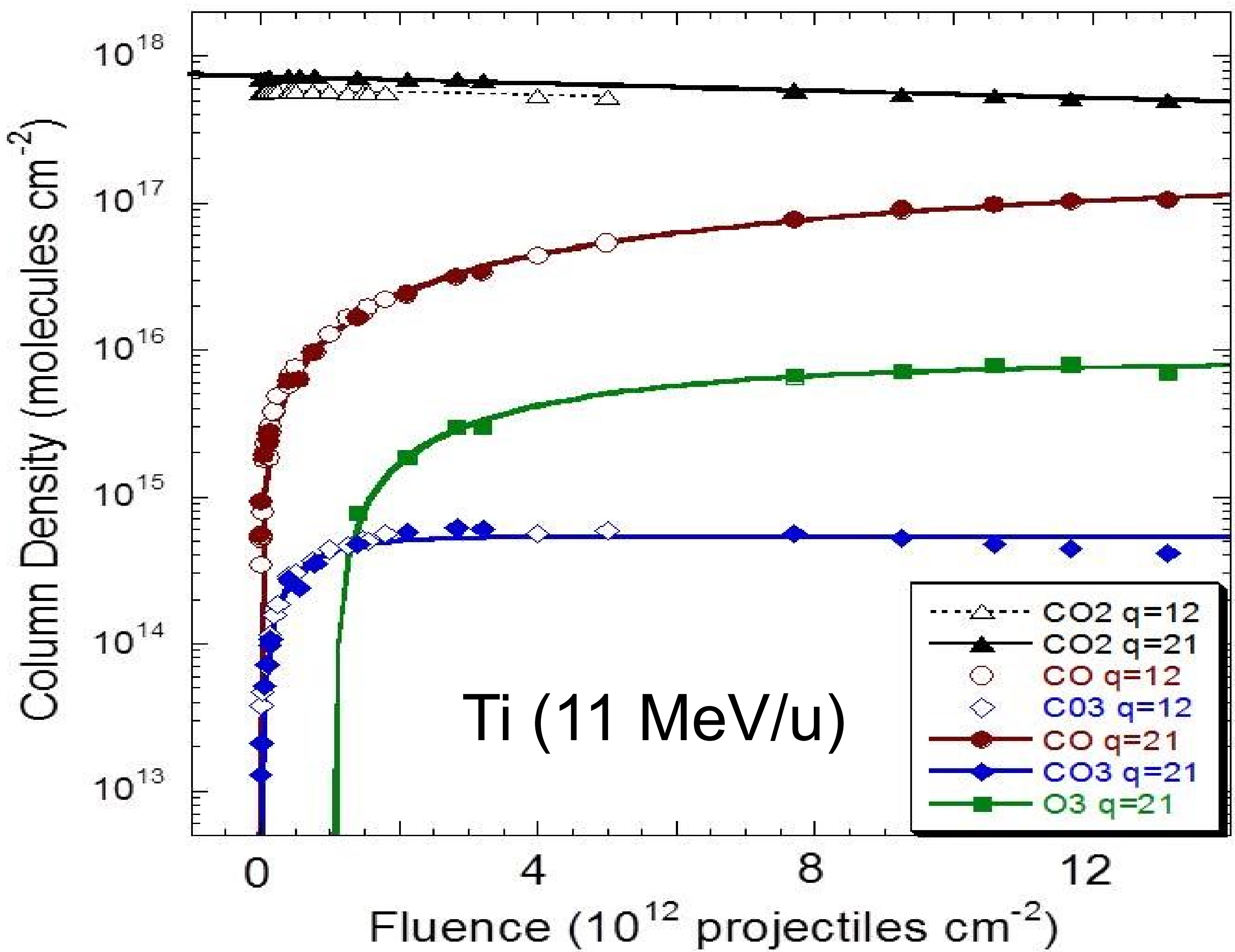
CO_2

@ GSI + GANIL

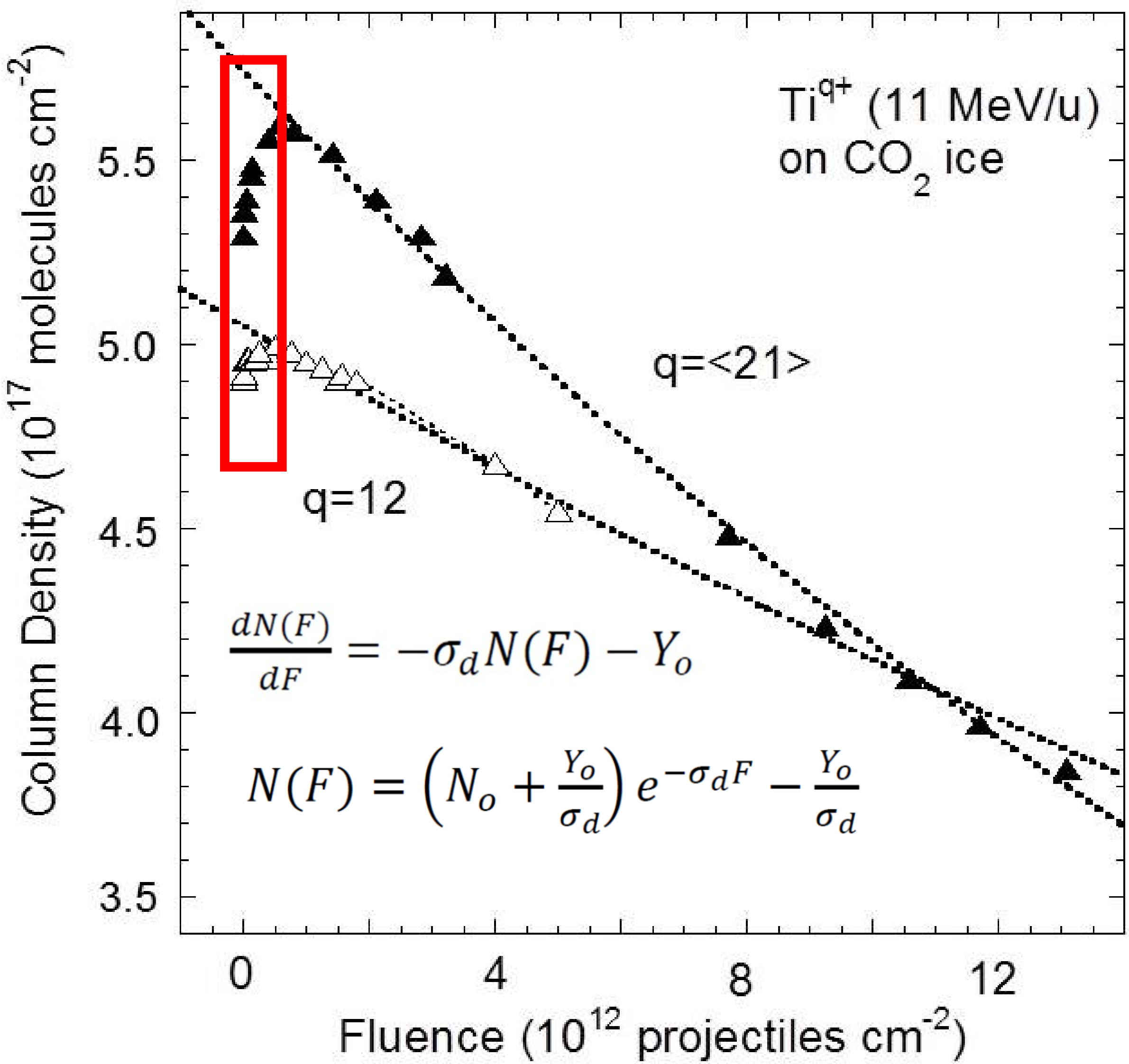
projectiles:
Ni
Ti
Xe

Materialforschung

Projectile fluence dependence



Projectile fluence dependence

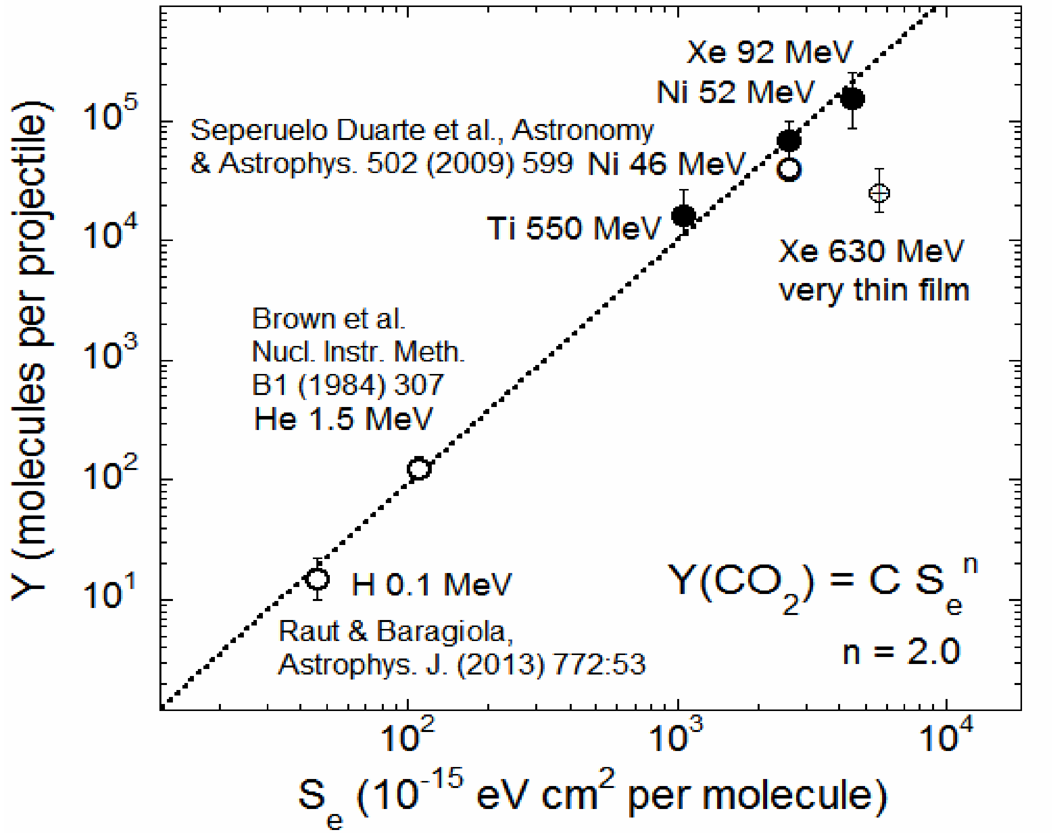


CO_2:
Compaction*
destruction
(fragmentation)
sputtering

Formation of
CO, O_3, CO_3

*C.F. Mejía, A.L.F. de Barros, E. Seperuelo Duarte, E.F. da Silveira, E. Dartois, A. Domaracka, H. Rothard, P. Boduch,
Compaction of porous ices rich in water by swift heavy ions
Icarus 250 (2015) 222

CO_2: Sputtering yield



C. Mejía, M. Bender, D. Severin, C.Trautmann, Ph. Boduch, V. Bordalo, A. Domaracka, X.Y. Lv, R. Martinez, H. Rothard
Nucl. Instrum. Meth. B365 (2015) 477

Y scales with S_e^2 !

(universal ... CO, H_2O)

$S_e \sim Z_P^2$

$Y \sim Z_P^4$

very strong dependence!

Interstellar Medium: Dense Molecular Clouds

Density of 10^3-10^6 particles cm^{-3}, mainly H_2, T~10 K. Star formation.

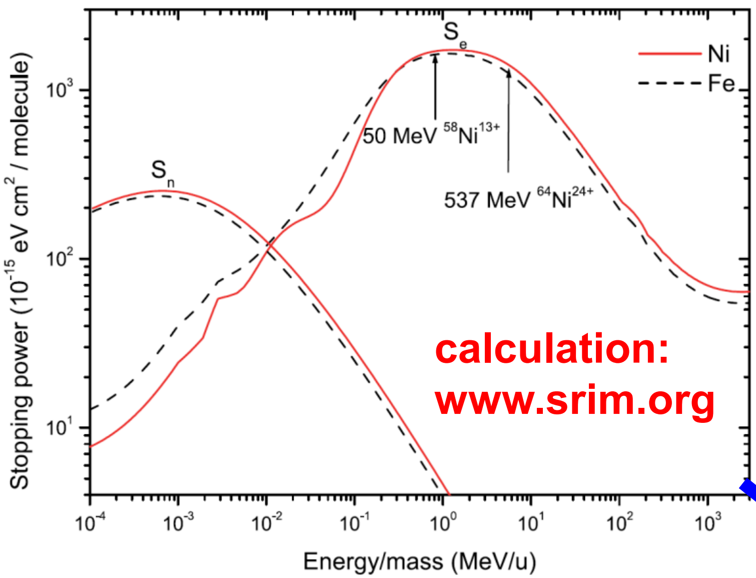
Molecules in gas phase and dust grains covered by ice mantles.

Possibly complex organic chemistry in ice mantles due to:
- Surface reactions
- UV and ion processing.

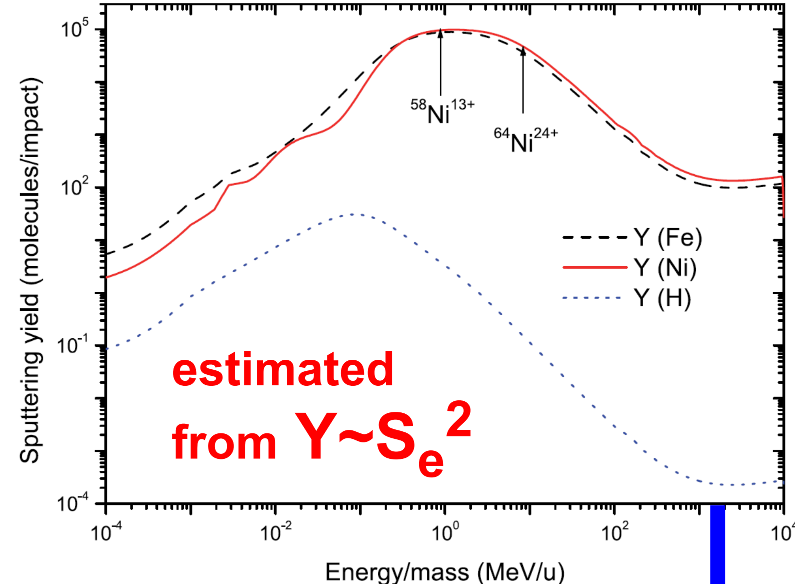
Horsehead Nebula

Size: up to some tens of Parsecs
Lifetime: 10^6-10^9 years

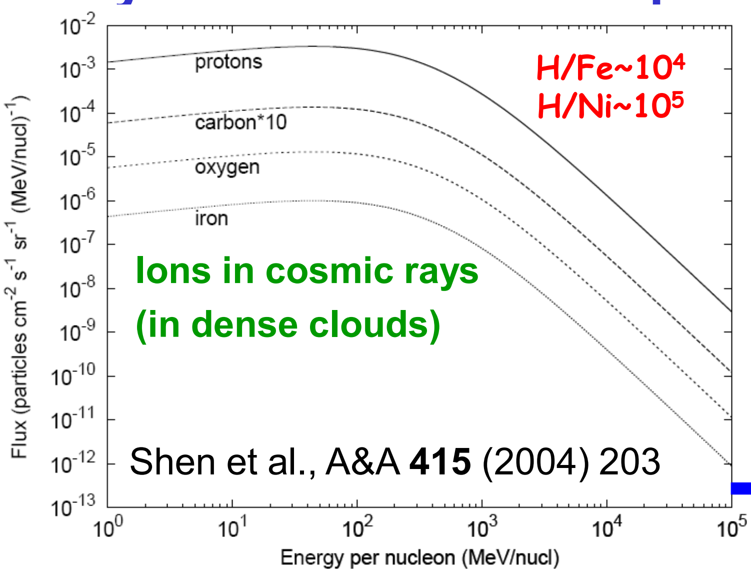
Electronic Energy Loss in CO

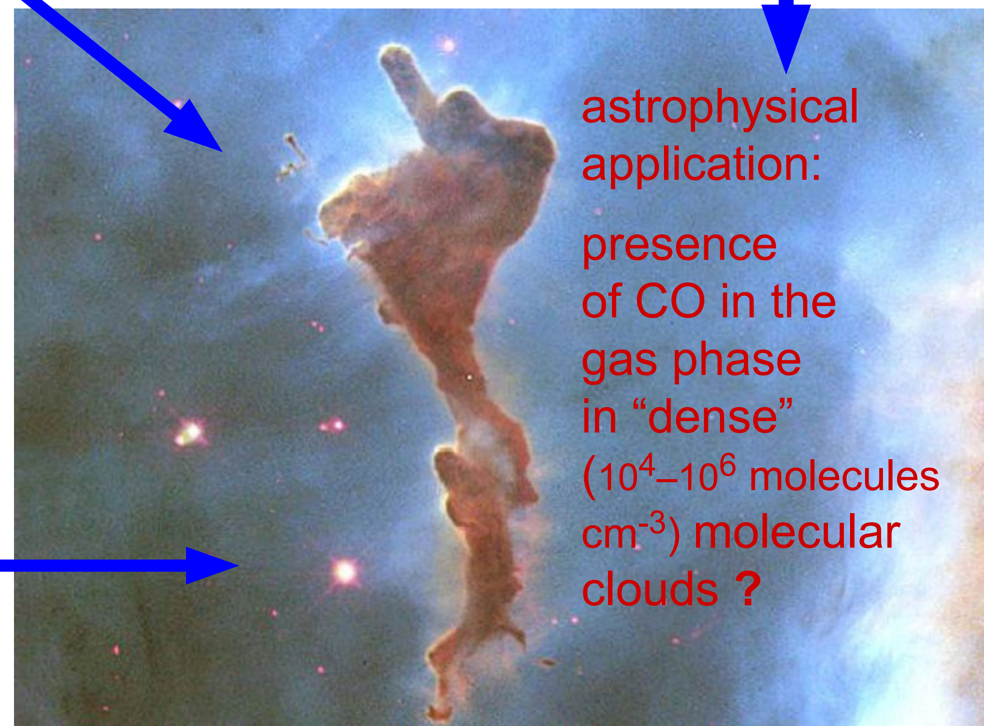


CO Sputtering Yield

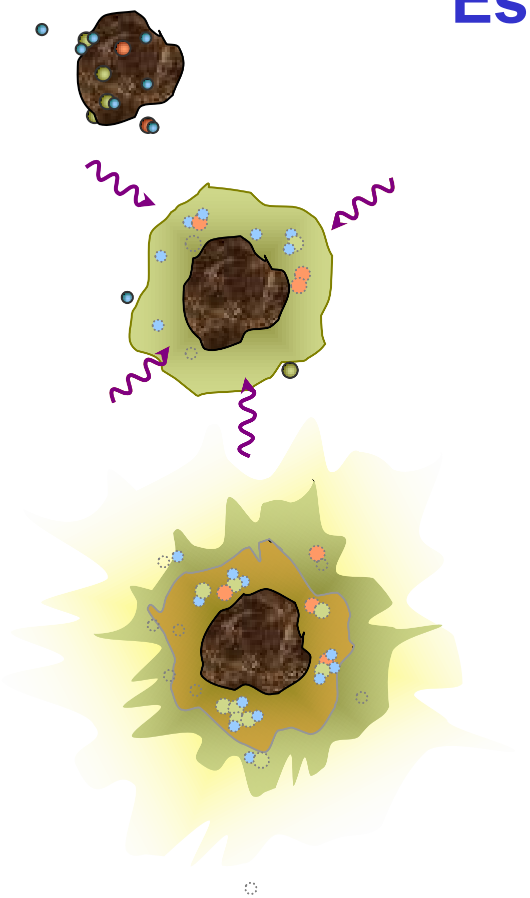


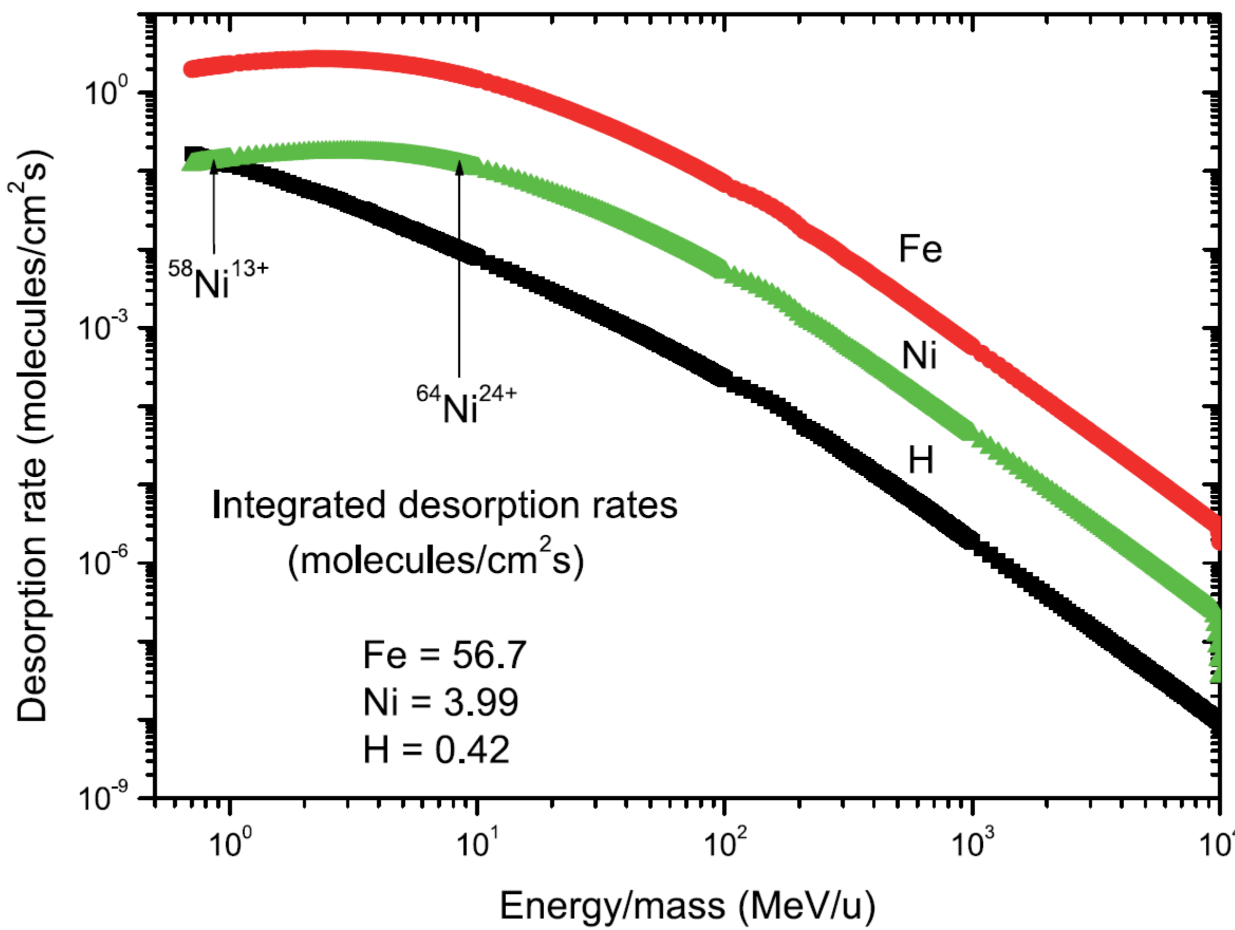
Heavy ion Abundance in space





Estimated ion induced CO Desorption Yield



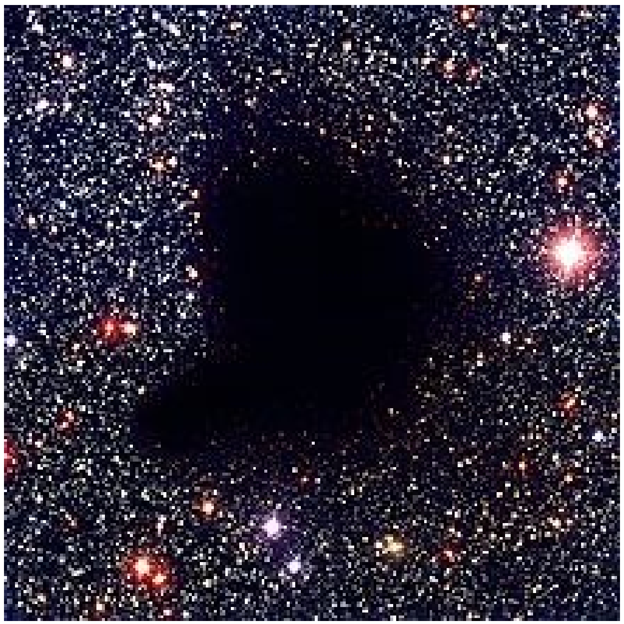


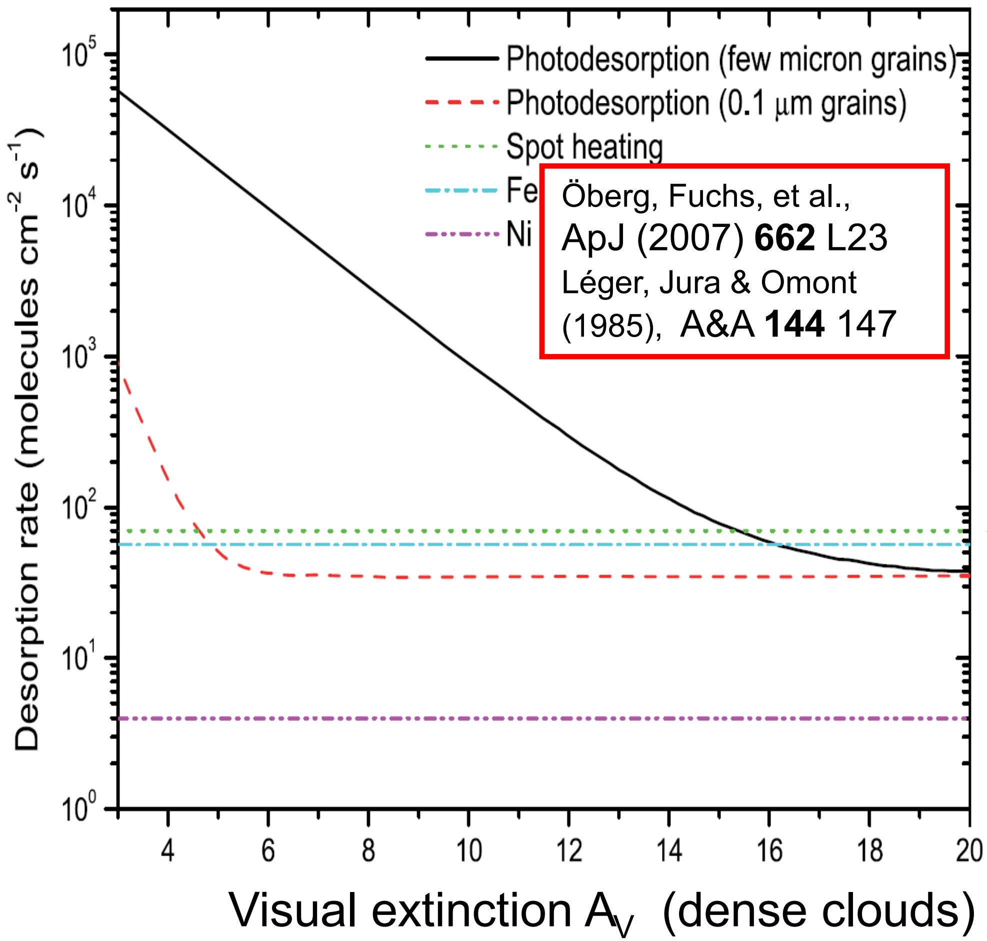
E. Seperuelo Duarte et al.
Laboratory simulation of heavy ion cosmic ray interaction with condensed CO
Astronomy & Astrophysics 512 (2010) A71

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 (Topical Review)

Desorption rate of CO as a function of visual extinction

penetration depth dependence in dense molecular clouds



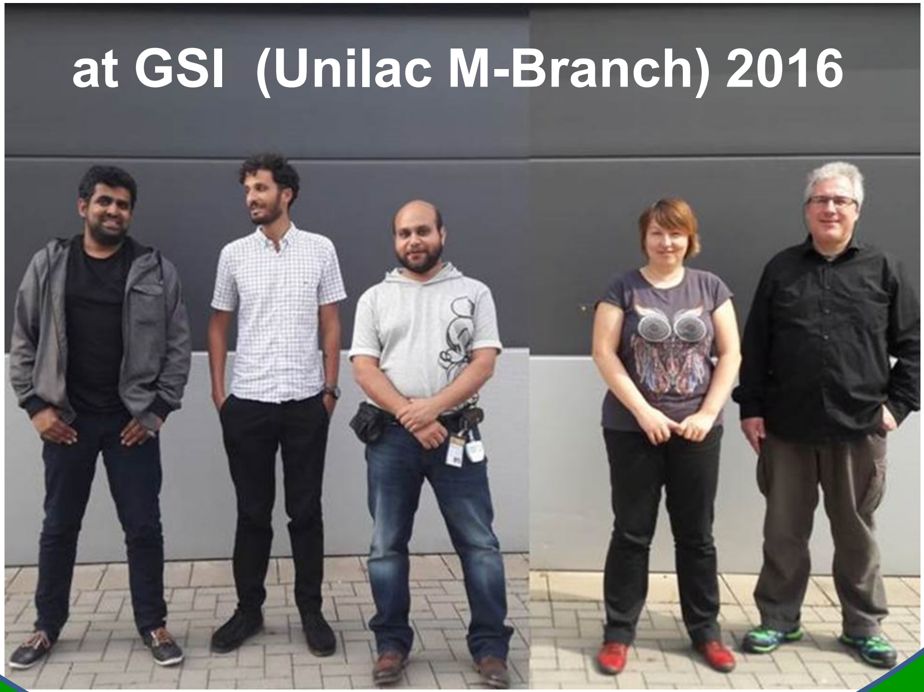


Heavy Ions

UV photons

E. Seperuelo Duarte, A. Domaracka, P. Boduch, H. Rothard, E. Dartois, E.F. da Silveira
Astronomy & Astrophysics 512 (2010) A71

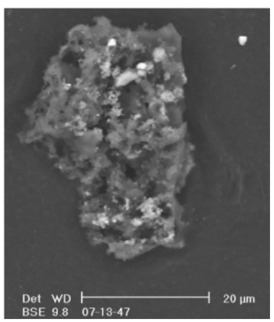
Formation and radioresistance of COMs



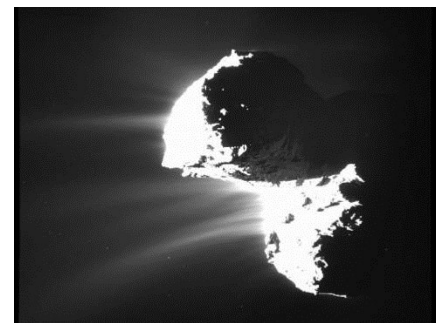
CiMap

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)

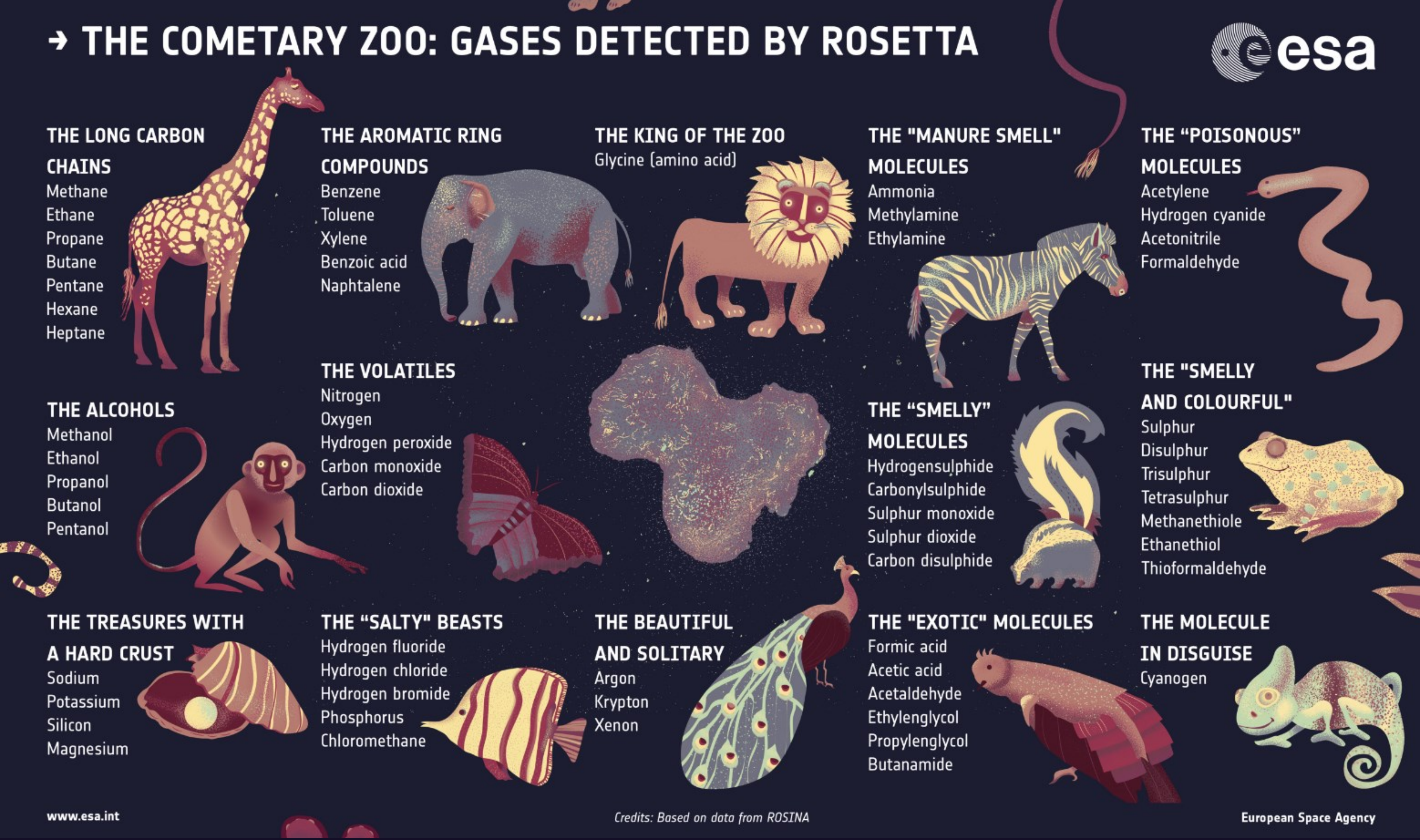


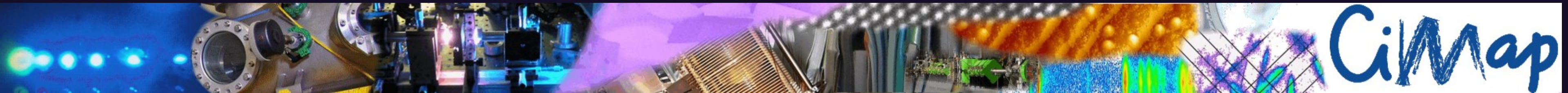
Formation in ice?



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 VOLATILES
Nitrogen
Oxygen
Hydrogen peroxide
Carbon monoxide
Carbon dioxide
THE ALCOHOLS
Methanol
Ethanol
Propanol
Butanol
Pentanol
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

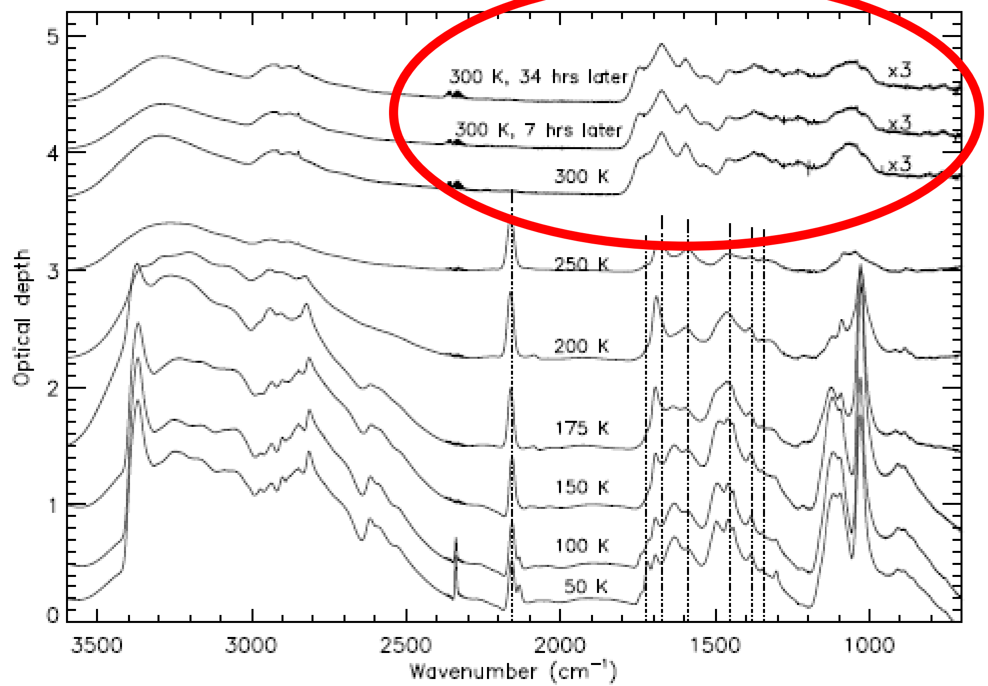

CiMap

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.

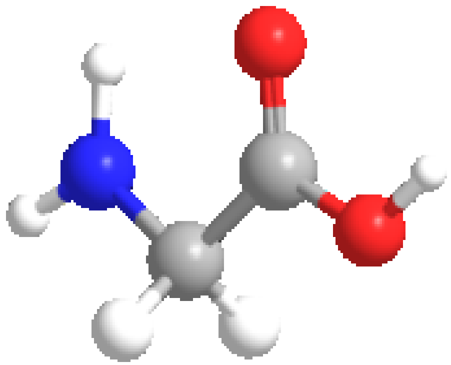
at 300K: stable organic Residues!

SPIRIT

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	$N_2O^\dagger$

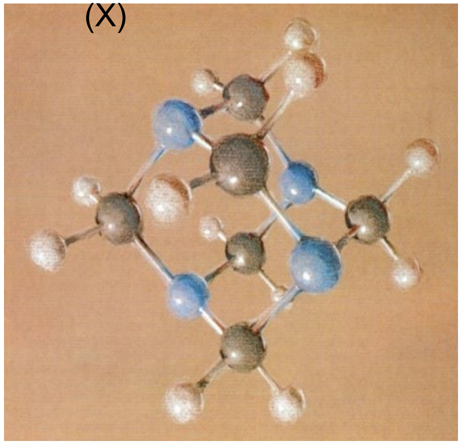
H_2O - CO - NH_3 ice

⇒ glycine (amino acid)



$C_2H_5NO_2$

(X)



hexamethylene-tetramine HMT

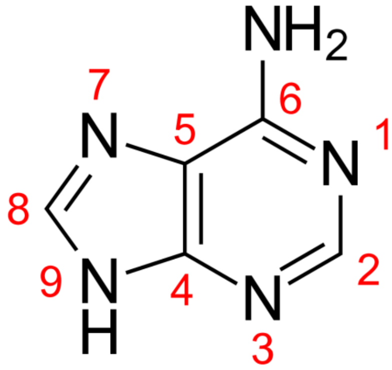
S. Pilling, E. Seperuelo Duarte, E. F. da Silveira, E. Balanzat, H. Rothard, A. Domaracka, P. Boduch
Radiolysis of ammonia-containing ices by energetic, heavy and highly charged ions inside dense astrophysical environments,
Astronomy & Astrophysics 509 (2010) A87

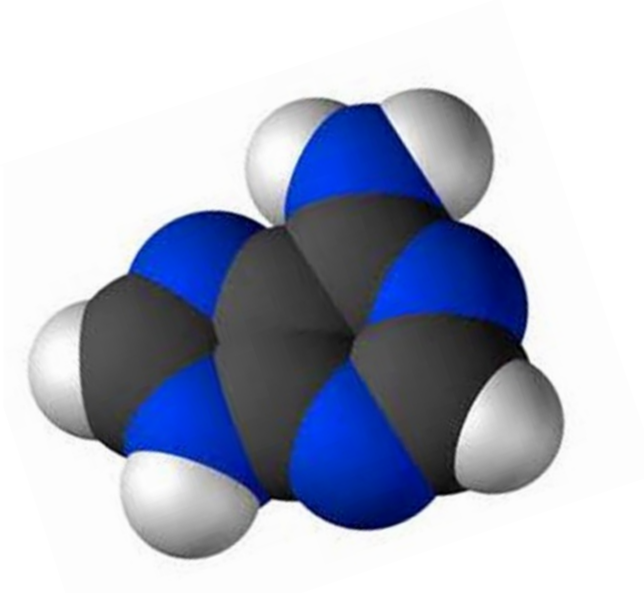
(X) http://osulibrary.oregonstate.edu/specialcollections/coll/pauling/bond/index.html

Radiation resistance of complex organic molecules

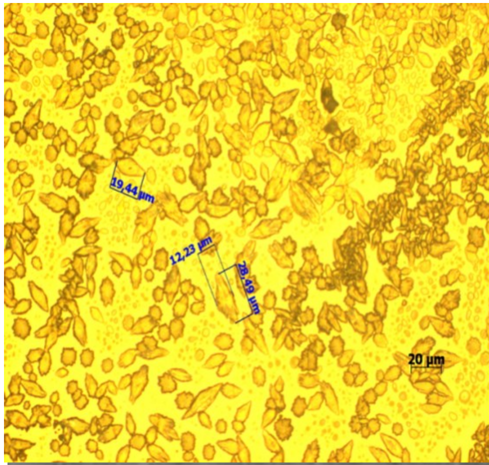
irradiation with swift heavy ions at GANIL and GSI
Laboratory simulation of cosmic ray effects

First results: **adenine**





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



sample on ZnSe

CiMap

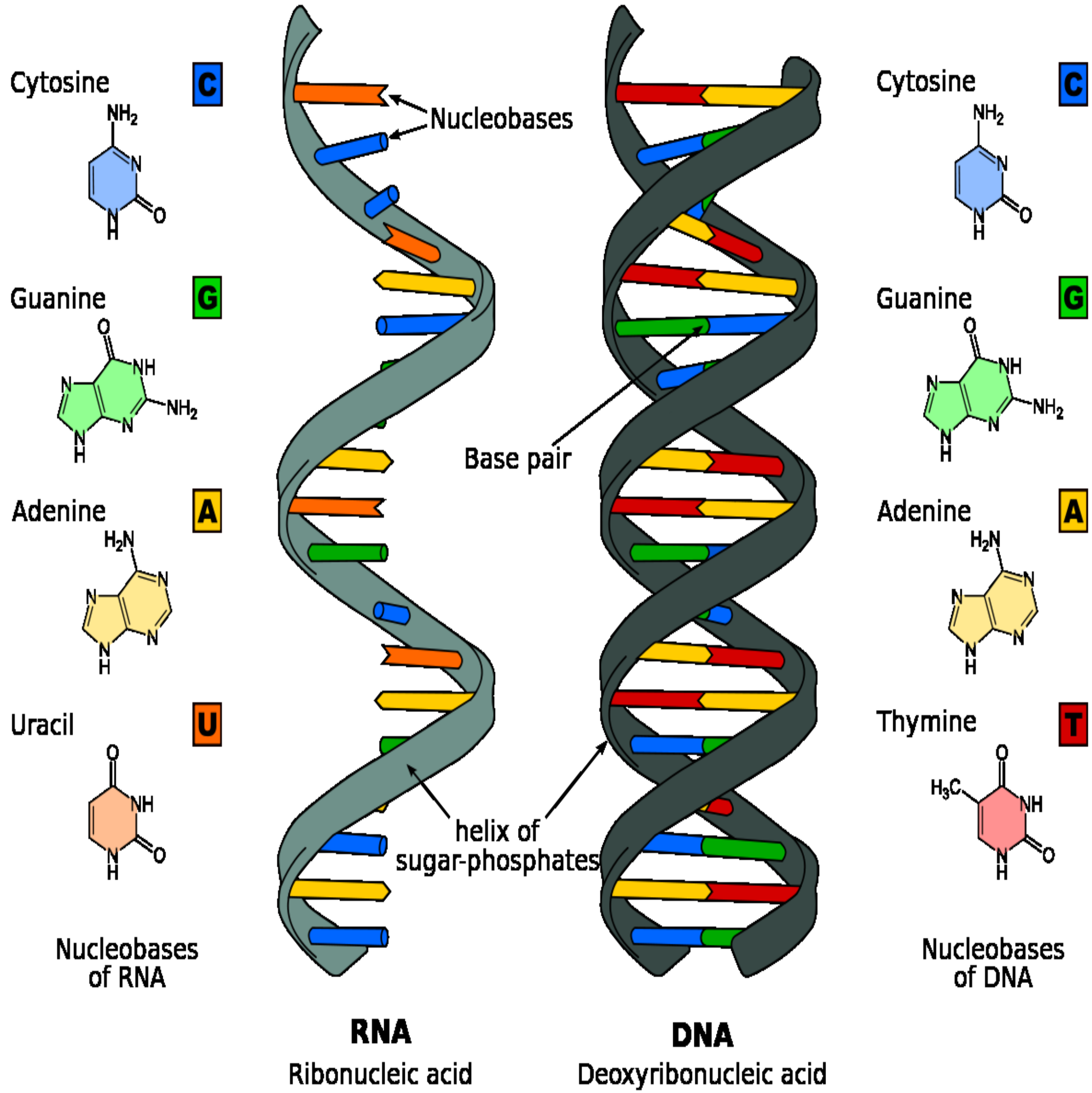
Adenine

$C_5H_5N_5$

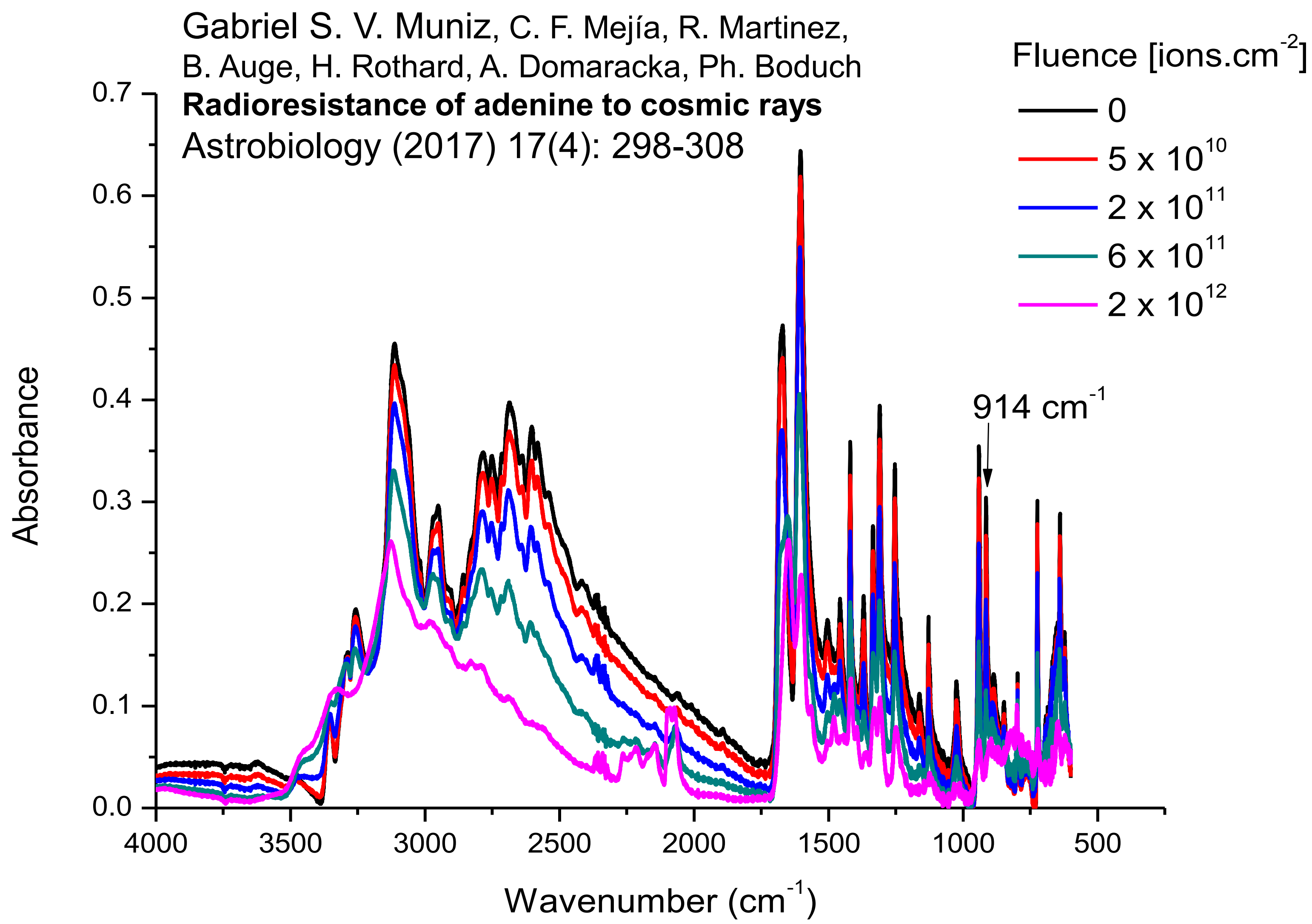
purine nucleobase

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

evolutionarily
preserved in all
living beings,
including viruses.

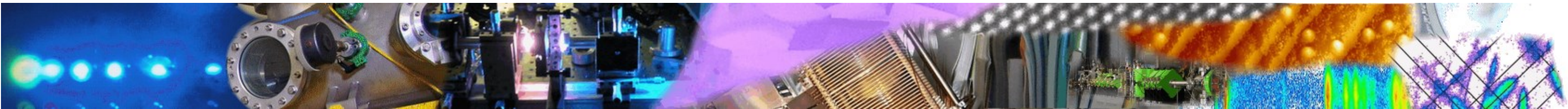


IR spectra: Evolution with projectile fluence

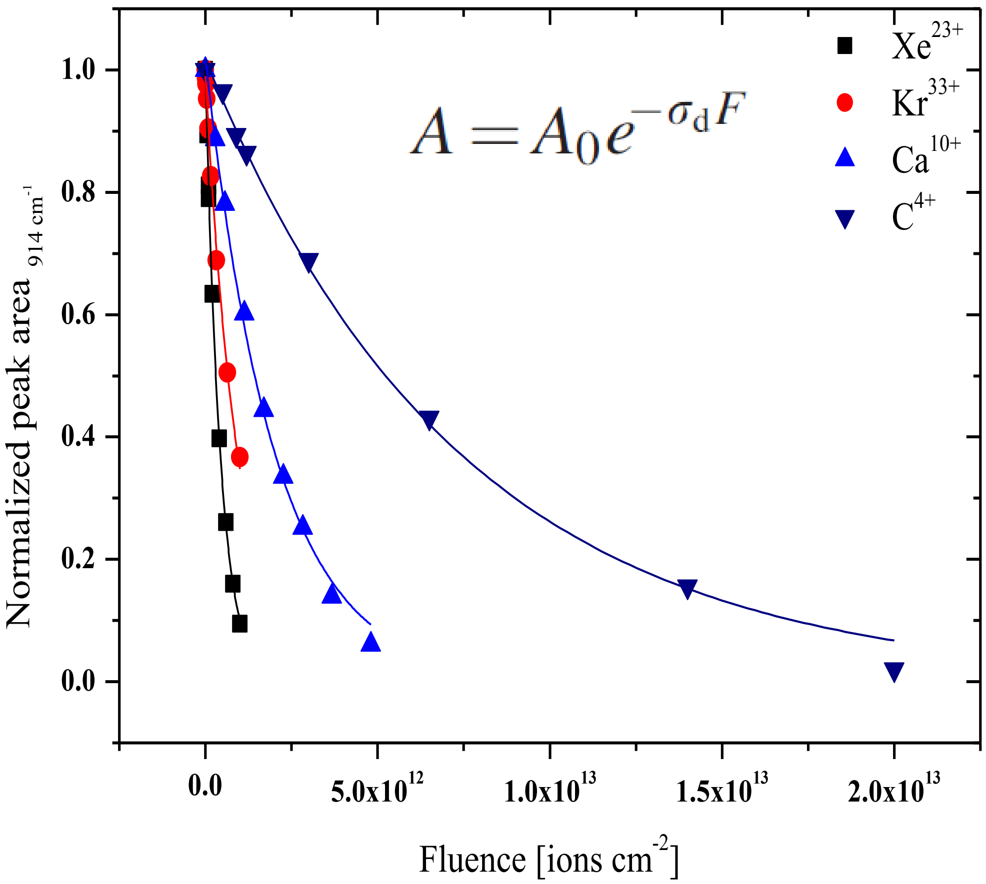


Adenine irradiation experiments at Ganil (IRRSUD, SME) and GSI (Unilac M-Branch)

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

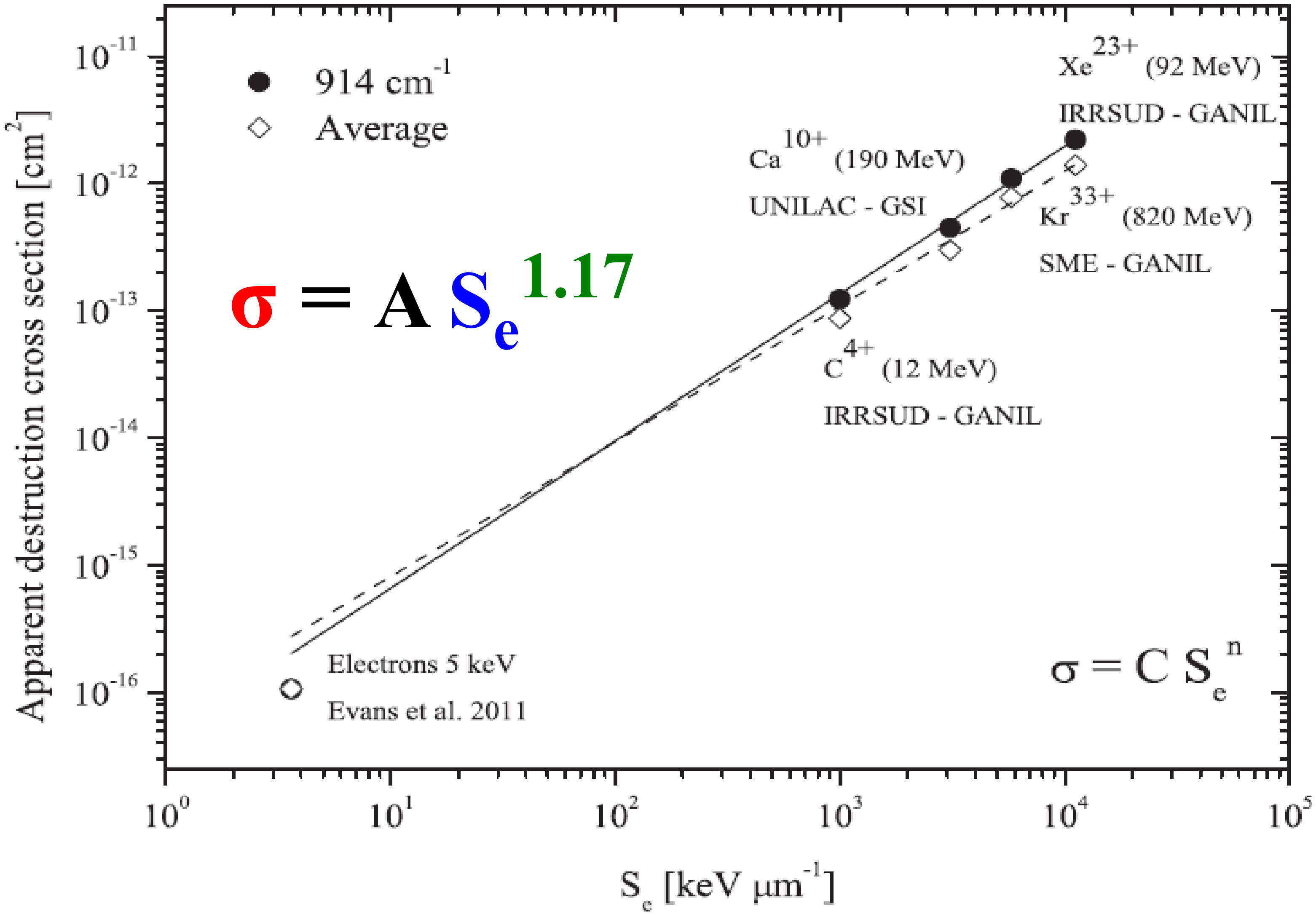


Evolution with projectile fluence: peak intensity (914 cm^{-1})

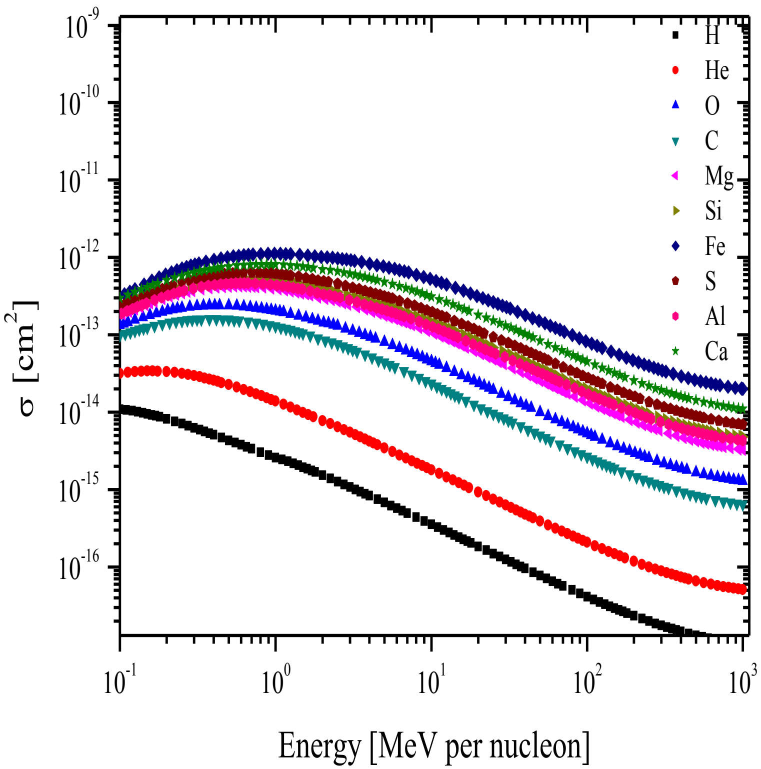


Projectile	Destruction cross section (x10^{-13} cm^2)
Xe^{23+}	22.1 ± 0.1
Kr^{33+}	11.4 ± 0.3
Ca^{10+}	4.5 ± 0.2
C^{4+}	1.24 ± 0.06

Cross section as a function of the stopping power:

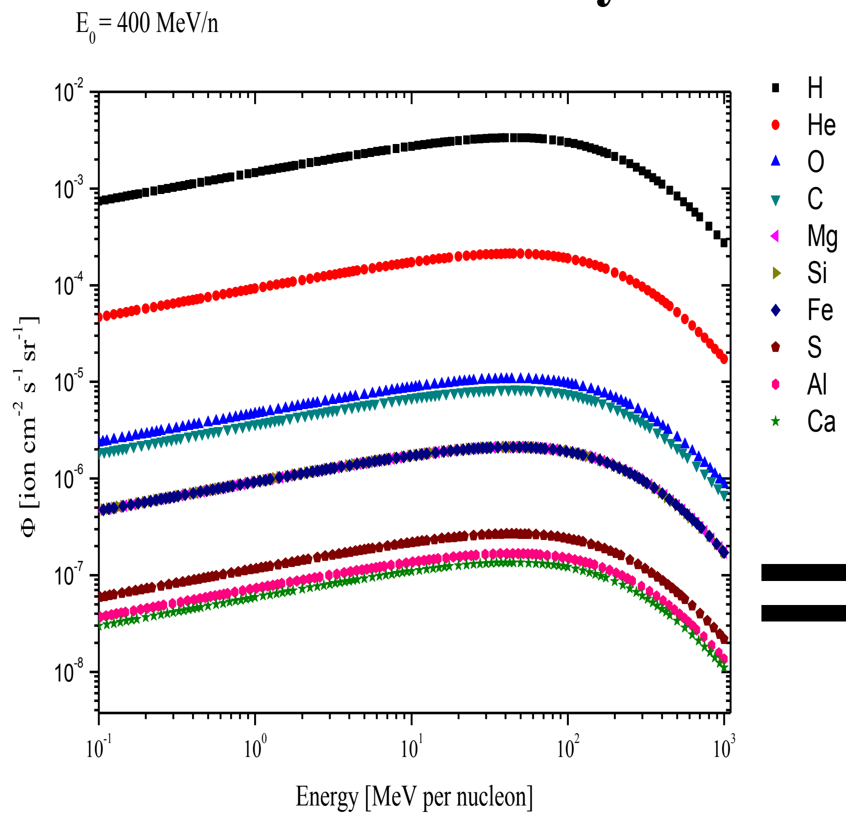


Destruction cross section



X

Cosmic Ray Flux

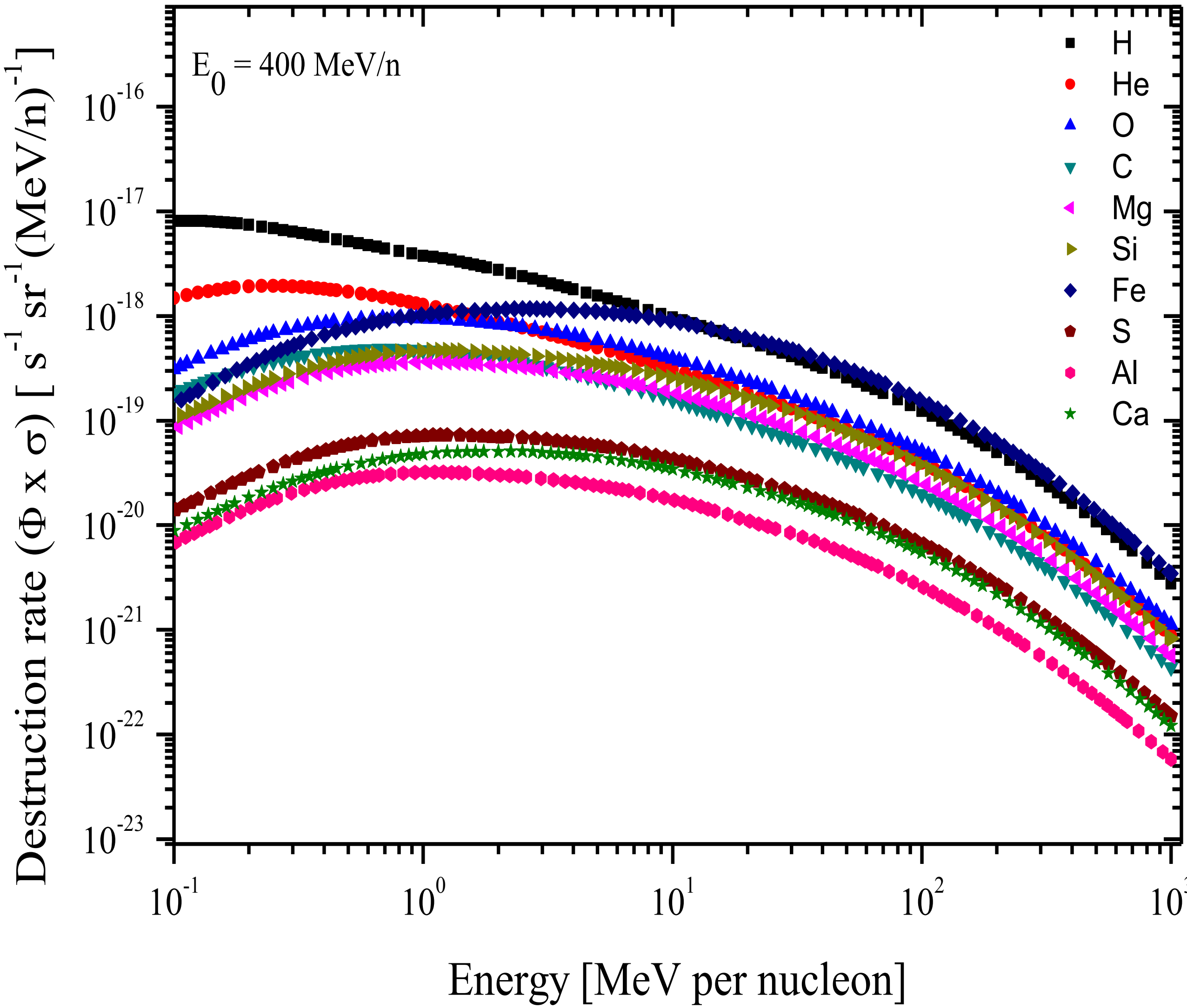


=

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

Webber WR, Yushak SM. 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: 10^6-10^9 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

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Radioresistance of adenine to cosmic rays
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