

# Swift heavy ions, ices and astrophysics

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Ices?

Ions? In space, in the lab (GANIL) and in matter.

Laboratory simulations :  
Several examples

Water : compaction and amorphisation

Role of CR : CO ice

Jovian moon, magnetosphere  
and sulfur implantation : exogenic production?

Gaz mixture, UCAMMs, complex molecules...

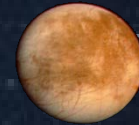
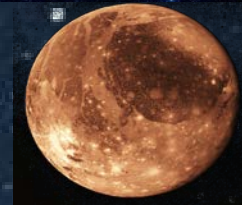
**Perspectives : IGLIAS**

# Astrophysical Ices ...

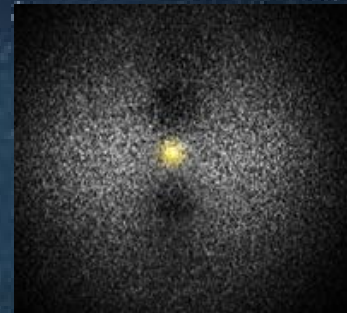
→ Comets



→ Giant Planet's Moons  
(Europa, Ganymede, ...)



→ Dust Grains

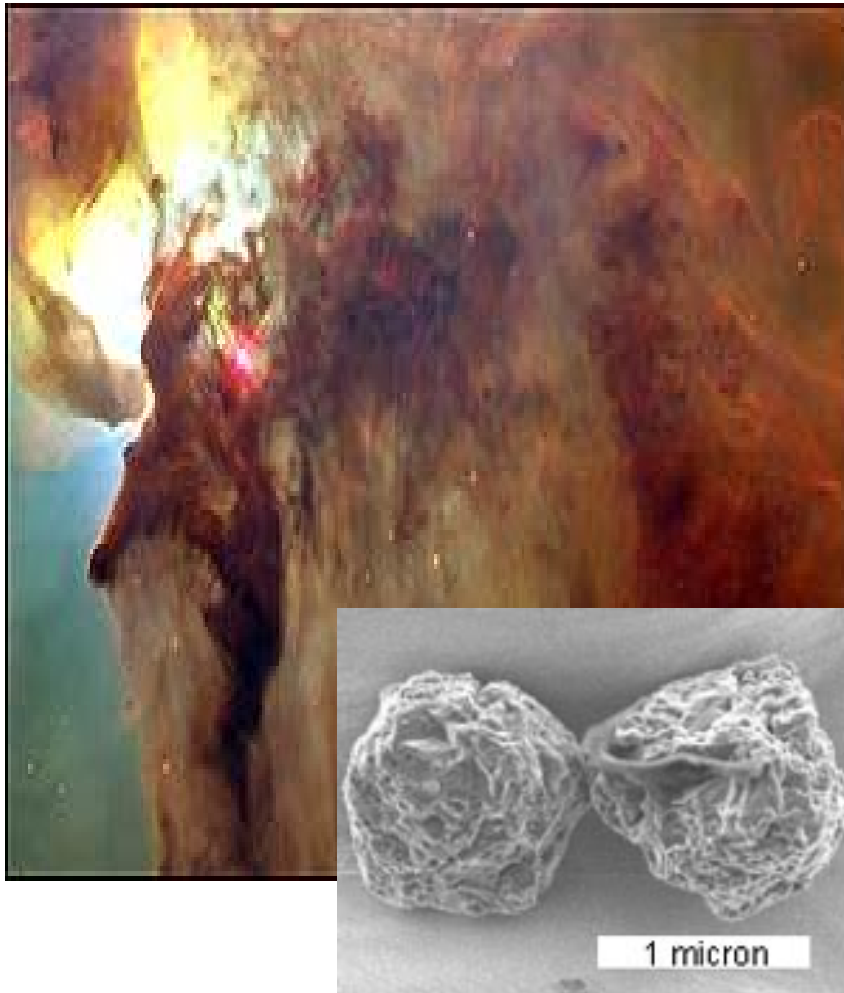


Rings

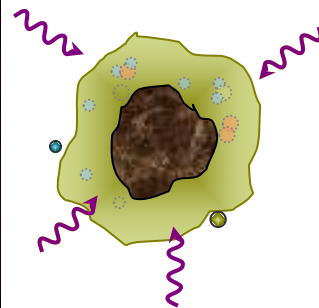
Dense Interstellar Clouds

(birthplaces of suns and planets)

# Interstellar dust grains (dense molecular clouds)

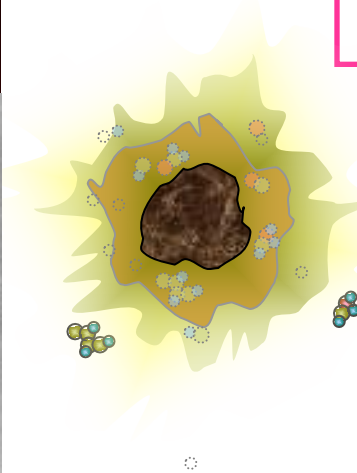


... covered with thin layers of ices ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{NH}_3$ , ...)



are exposed to

- cosmic rays; (protons, helium, heavy ions)
- stellar wind ( $\text{H}$ ,  $\text{He}$ ,  $\text{C}$ ,  $\text{O}$ ,  $\text{S}$  ...)
- UV photons
- electrons



irradiation leads to ...

**Radiolysis**

fragmentation/destruction

formation of molecules (radiation chemistry)

Desorption / Sputtering

Compactation / Amorphization

# What are Cosmic Rays ?

- Primary Cosmic Rays are very energetic ( $10^3$  to  $10^{22}$  eV) charged particles that traverse outer space



1 kJ

- Basically, they are:
  - **light ions**: protons + deuterons (87%) and  $\alpha$  particles (11%)
  - **heavy 4n ions** :  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{20}\text{Ne}$ ,  $^{24}\text{Mg}$ ,  $^{28}\text{Si}$ ,  $^{32}\text{S}$ ,  $^{40}\text{Ar}$ ,  $^{40}\text{Ca}$  and  $^{56}\text{Fe}$  (Ni)
  - **electrons** (~1%)

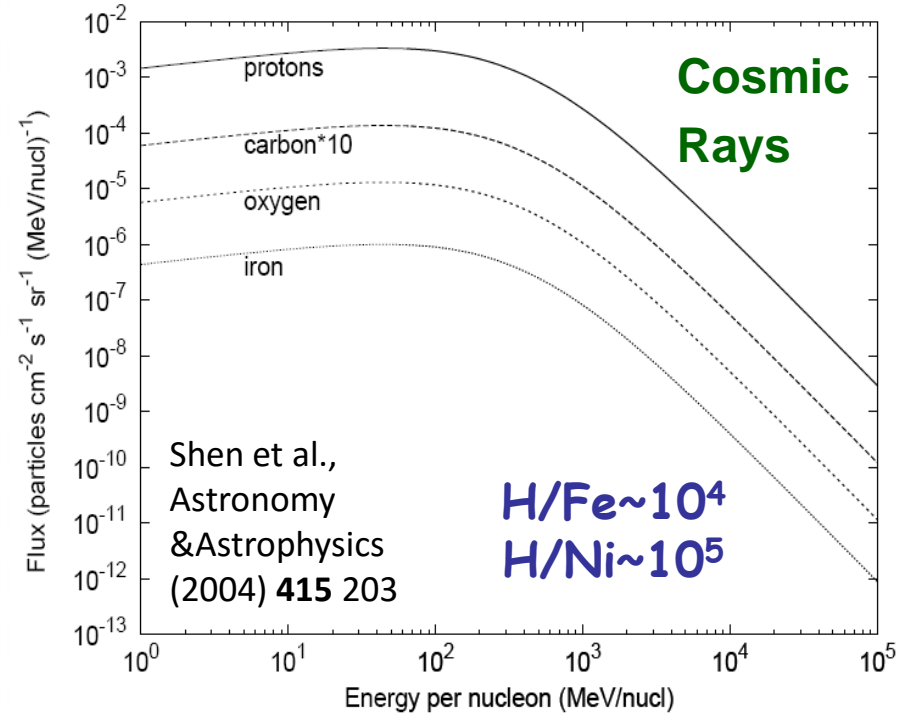
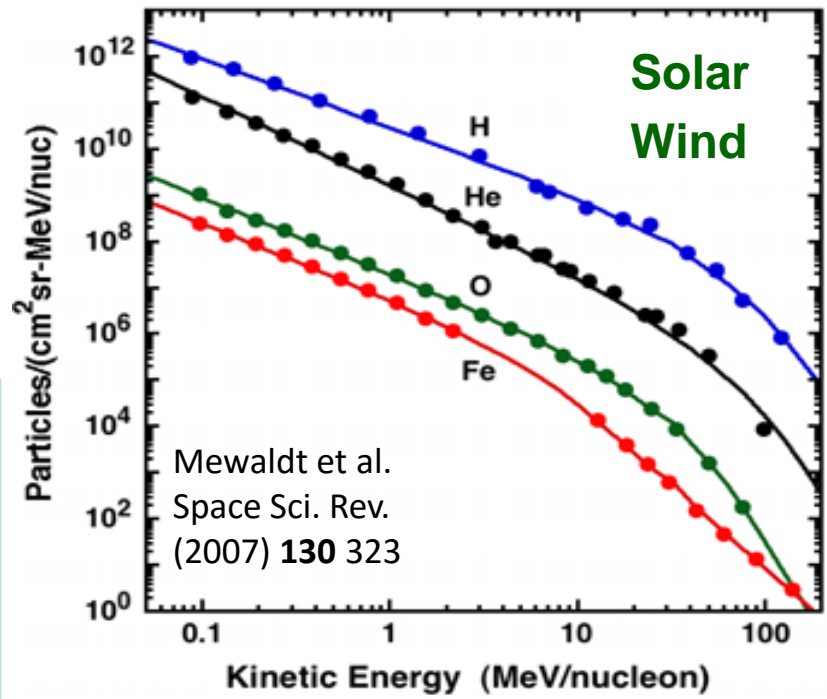
[unstable ions or neutrals are excluded: neutrons, neutrinos, X-rays,  $\gamma$  rays]

- After collision with interstellar matter and atmosphere,

Secondary Cosmic Rays are formed. They are constituted by:

- **Li, Be, B, neutrons** (formed by spallation)
- **pions, kaons, mesons, positrons and  $\gamma$  rays**

# Concerning heavy ions in space:

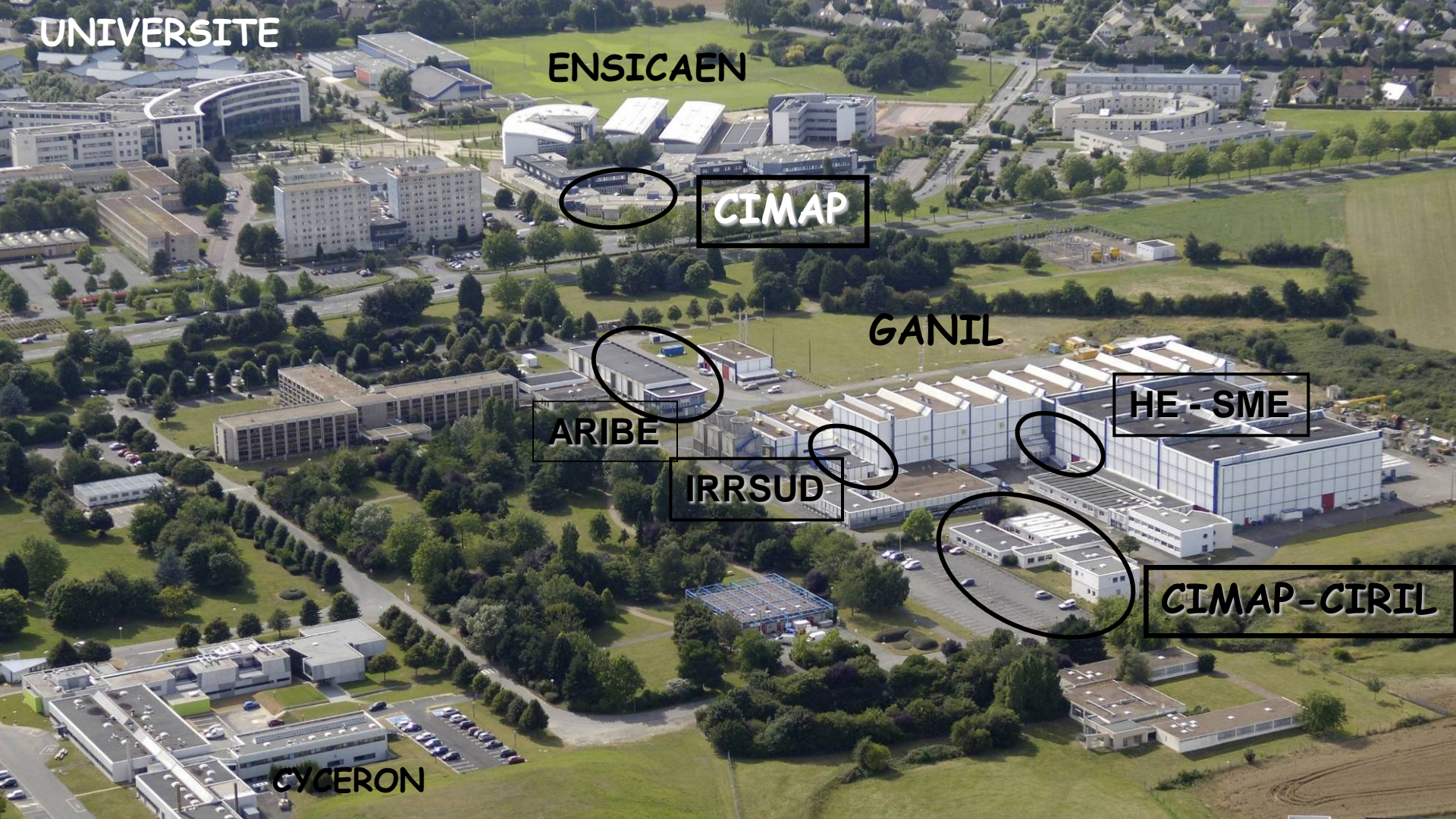


- Heavy multiply charged ions:**
- Large electronic energy loss  $S_e$
  - Scaling laws:  $S_e^n$  with  $n \approx 1/2, 1, 3/2, 2, \dots, 4$
  - Unexplained findings (gas phase CO in dense clouds...), few data
  - Astrochemistry: origin of CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> on Europa, implantation.
  - Shorter time for experiments...



Caen: a big accelerator of particles, GANIL



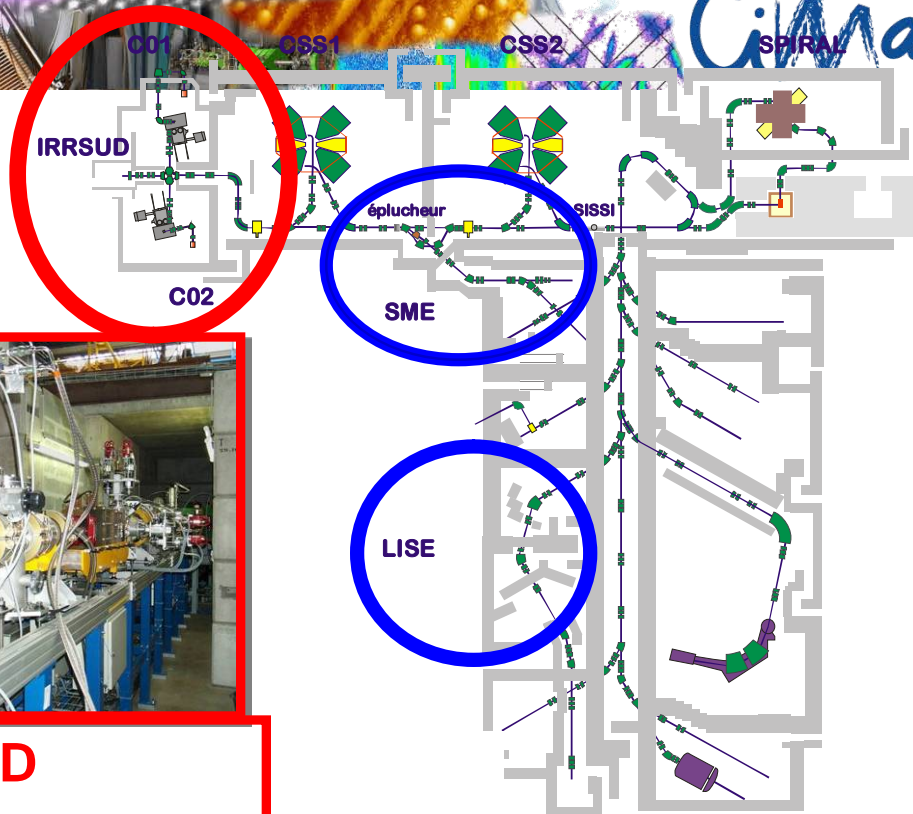


*Du carbone à l'uranium, de l'eV au GeV*  
*From Carbon to Uranium, from eV to GeV*



# GANIL

HE, SME, IRRSUD



**+ARIBE** low energy  
multiply charged ions  
He, C, O, S, Ar, Xe:  
q keV



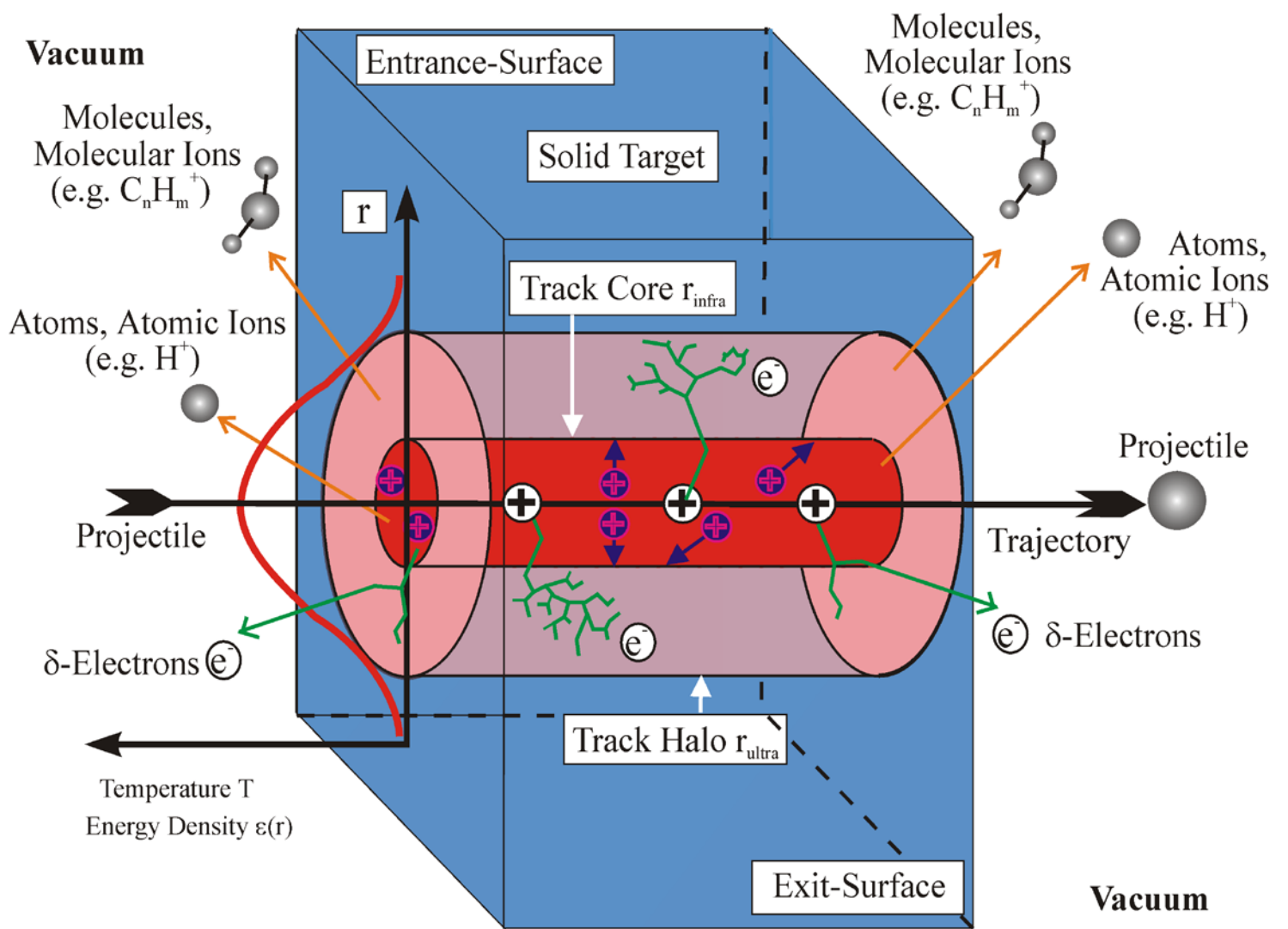
**IRRSUD**  
O, Ni, Xe, Ta, Pb:  
0.5 to 1 A MeV

High Energy: **LISE**  
Fe, Ni: 70 A MeV  
Medium Energy: **SME**  
O, Fe, Ni, Kr: 5-13 A MeV

**3 GeV for iron ion!**



# ions in condensed matter: nuclear tracks



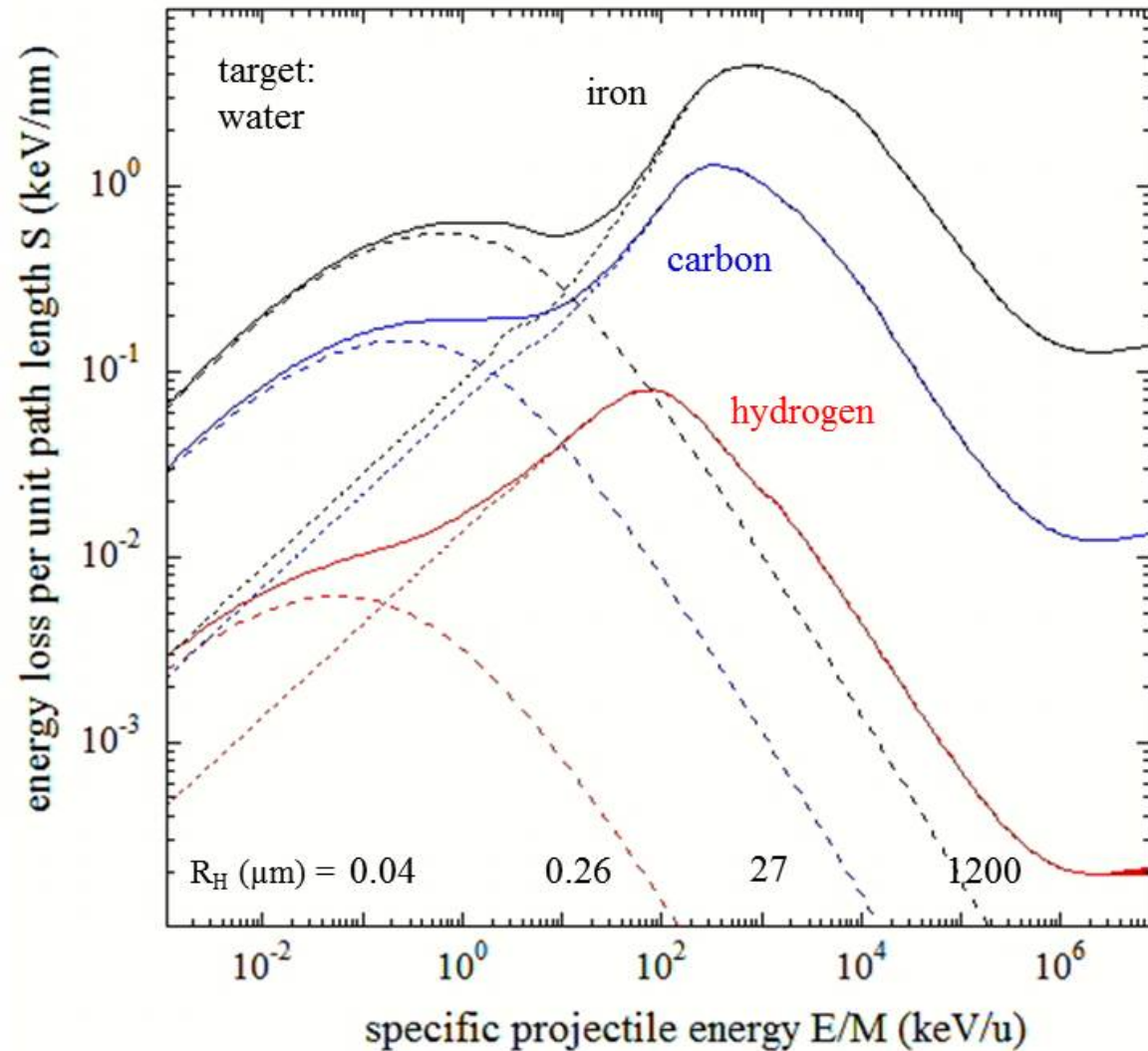
- Fast process  
 $10^{-15}s$
- 1-30 MeV/ $\mu m$   
(1-30 KeV/nm)
- $V_e$ : 0 to  $2V_p$
- Radicals
- 20000 K for  
Picoseconde
- $Y_{sput}$  :  
 $10^4-10^5$

nom

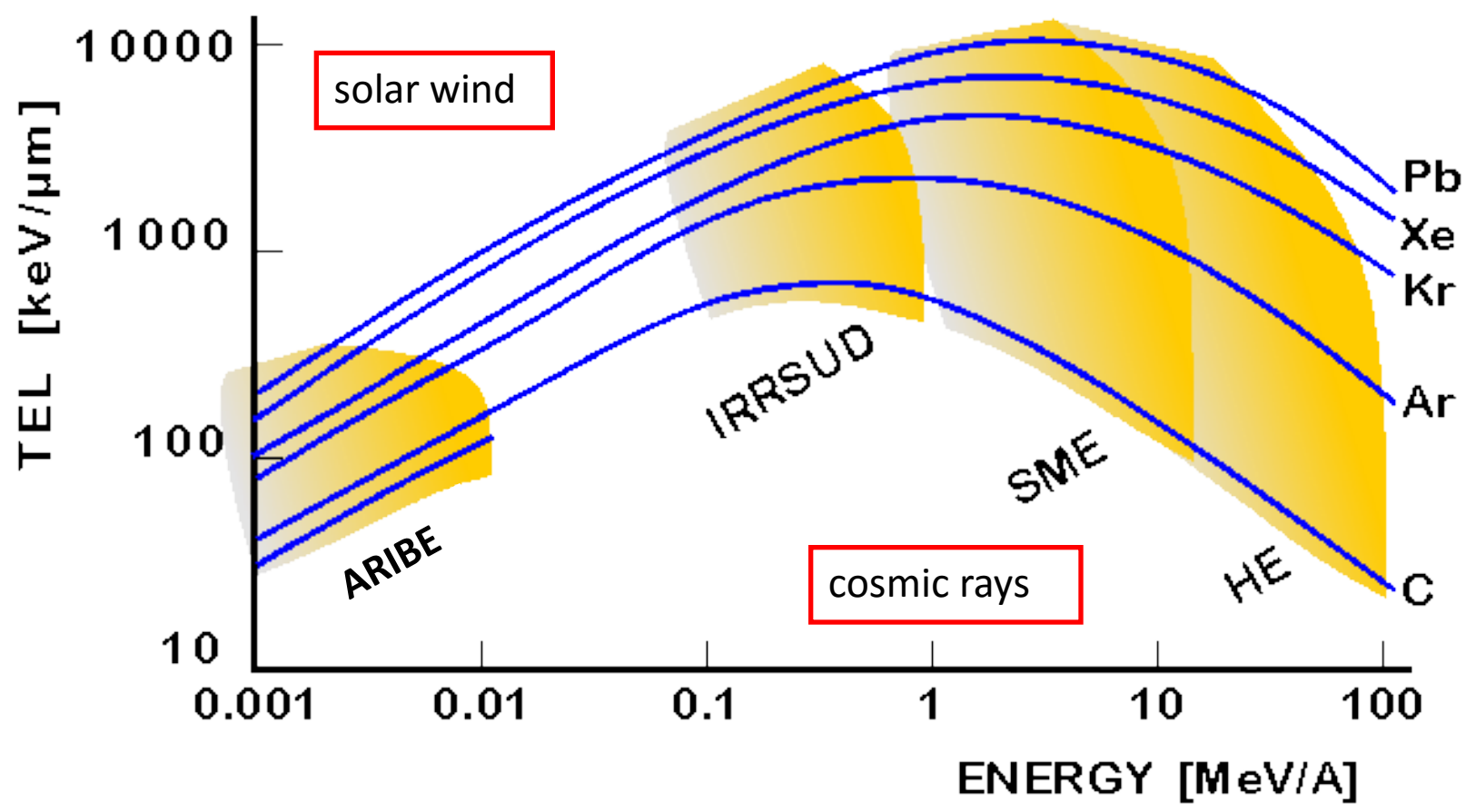
For the incoming projectile:  
 The stopping power  $dE/dx$  :  
 Energy loss per length unit

Projectile	Se (keV/nm)
$^{58}\text{Ni}^{13+}$	3.0
$^{58}\text{Ni}^{11+}$	2.9
$^{64}\text{Ni}^{24+}$	2.0
$^{20}\text{Ne}^{6+}$	0.92
$^{16}\text{O}^{2+}$	0.79
$^{16}\text{O}^{5+}$	0.67

$\text{H}^+(100\text{keV}) S_e=0,08 \text{ KeV/nm}$



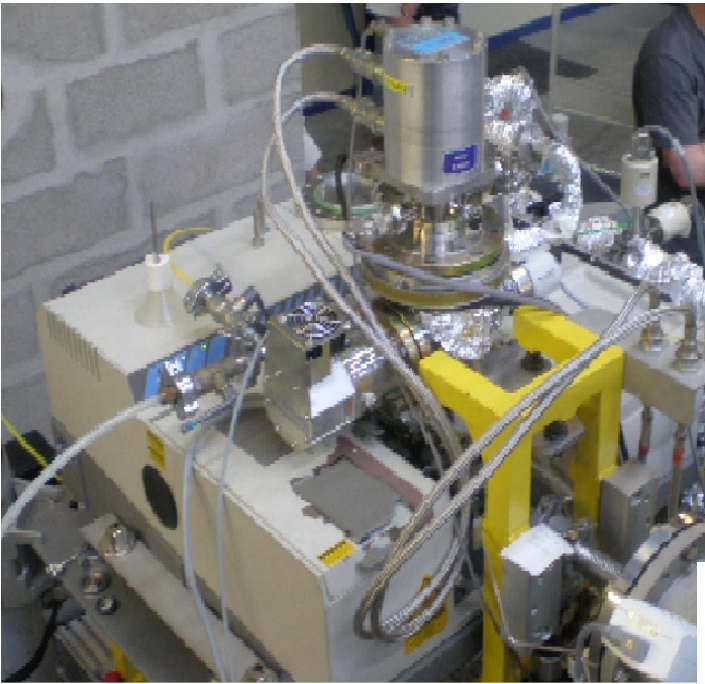
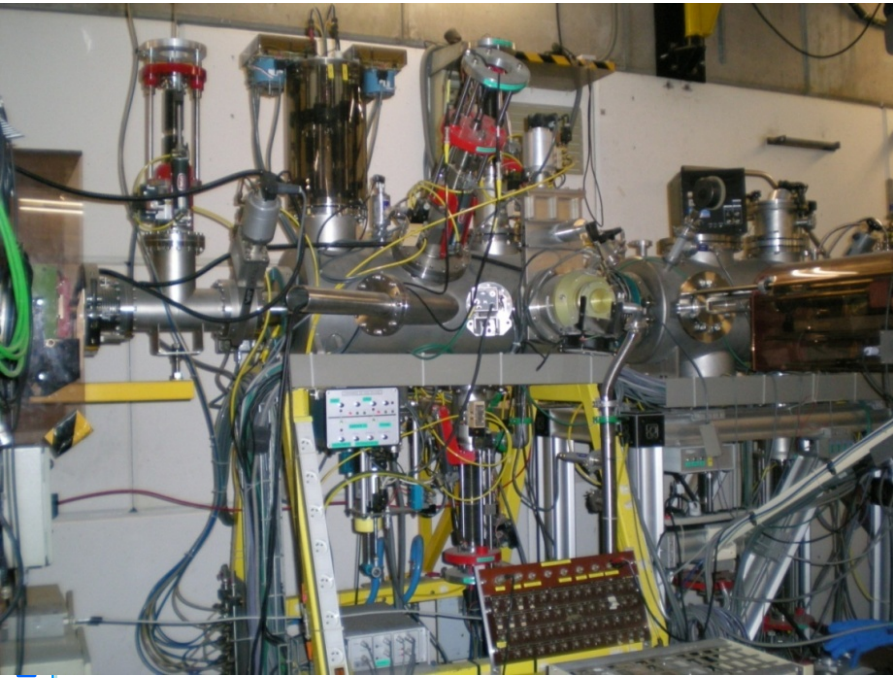
nom



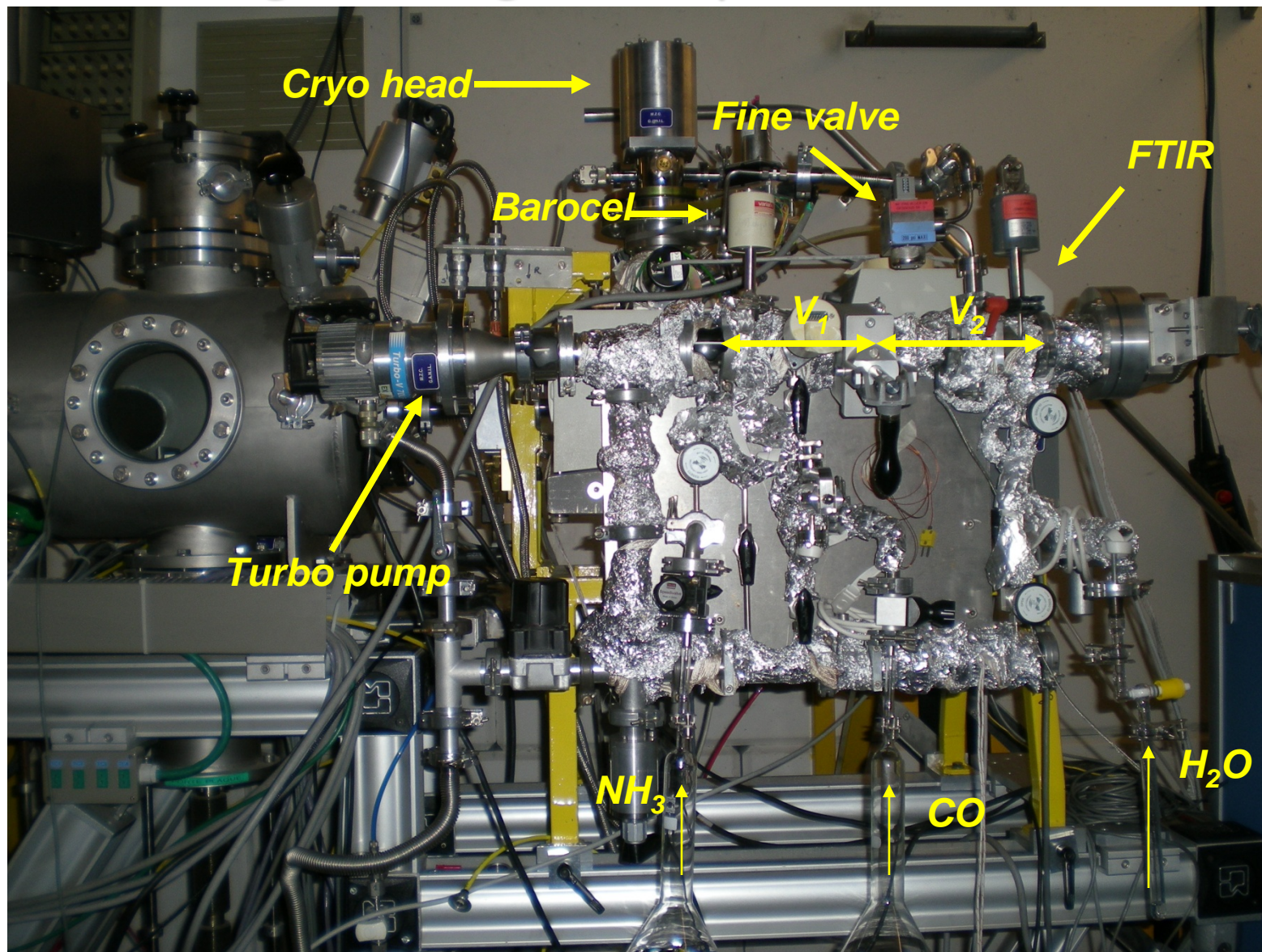
$S_e$ : 3 orders of magnitude



**experimental set-up CASIMIR:  
FTIR of condensed gases at 14 K**



# the "gas mixing and deposition machine" CiMap





# Experimental details

## Pressure in irradiation chamber

$\sim 2 \times 10^{-8}$  mbar (14 K)

## Substrate

CsI, ZnSe windows

## Temperature

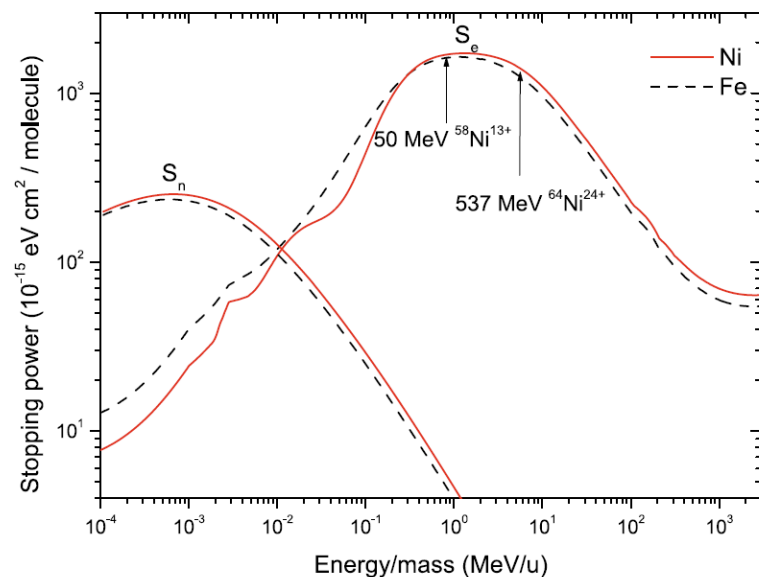
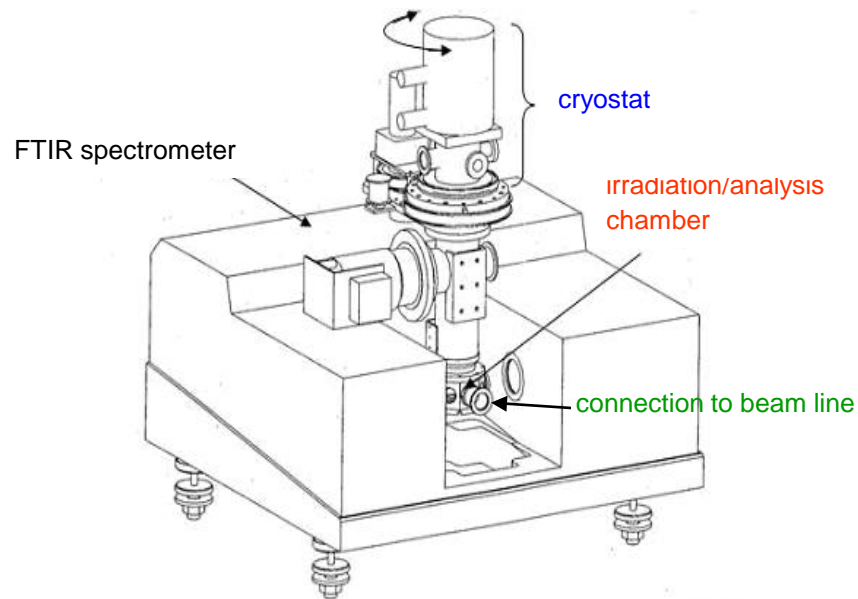
$13 \text{ K} < T < 300 \text{ K}$

## Samples (ices)

- in situ gas deposition
- thickness  $\sim 0.1 - 2 \mu\text{m}$  ( $10^{17} - 10^{18}$  molecules/cm<sup>2</sup>)
- ion penetration depth  $>$  ice thickness (HE exp.)
- ion implantation (Low E exp.)

## Ion beam (Grand Accélérateur National d'Ions Lourds, Caen, France)

- 50 MeV  $^{58}\text{Ni}^{13+}$ , 537 MeV  $^{64}\text{Ni}^{24+}$
- flux  $\sim 10^9$  ion/cm<sup>2</sup> s
- fluence upto  $2 \times 10^{13}$  ion/cm<sup>2</sup> (typically 4 hours)

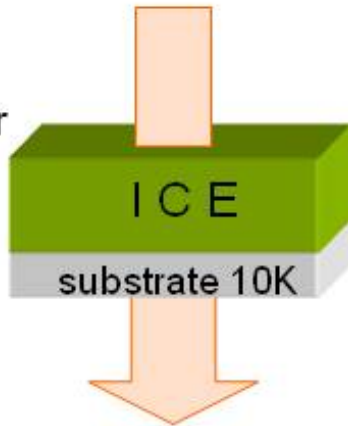




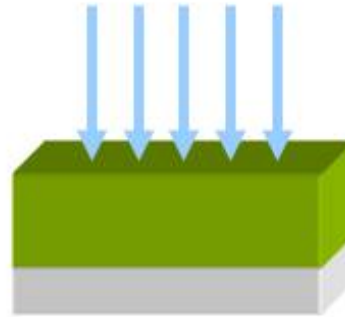


**infrared IR spectroscopy**

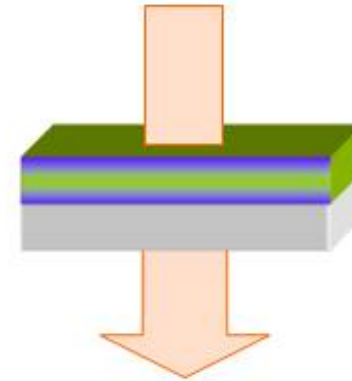
H<sub>2</sub>O, CO, ... or  
H<sub>2</sub>O-NH<sub>3</sub>-CO



**ion irradiation  
(C, O, Fe, ...)**



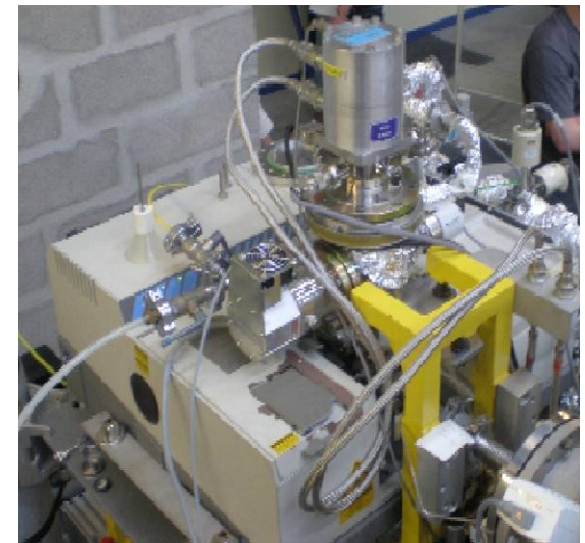
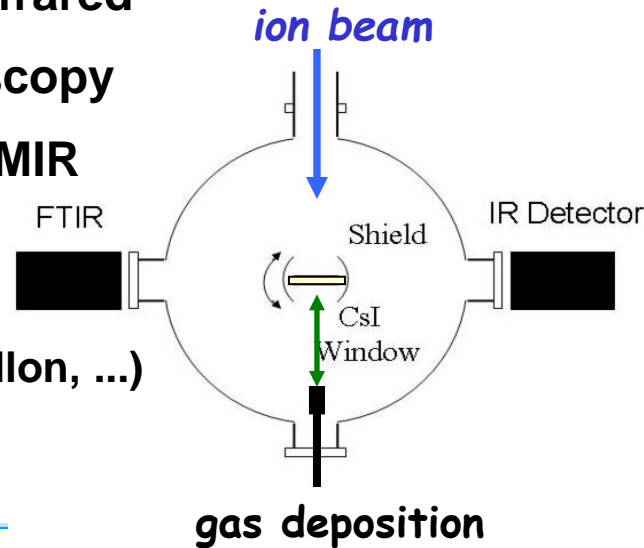
**new species:  
CO<sub>2</sub>, C<sub>3</sub>O<sub>2</sub>, ...  
glycine, ...**



**Fourier Transform Infrared  
Absorption Spectroscopy**

**FTIR @CIMAP: CASIMIR**

**(E. Balanzat, J.M. Ramillon, ...)**

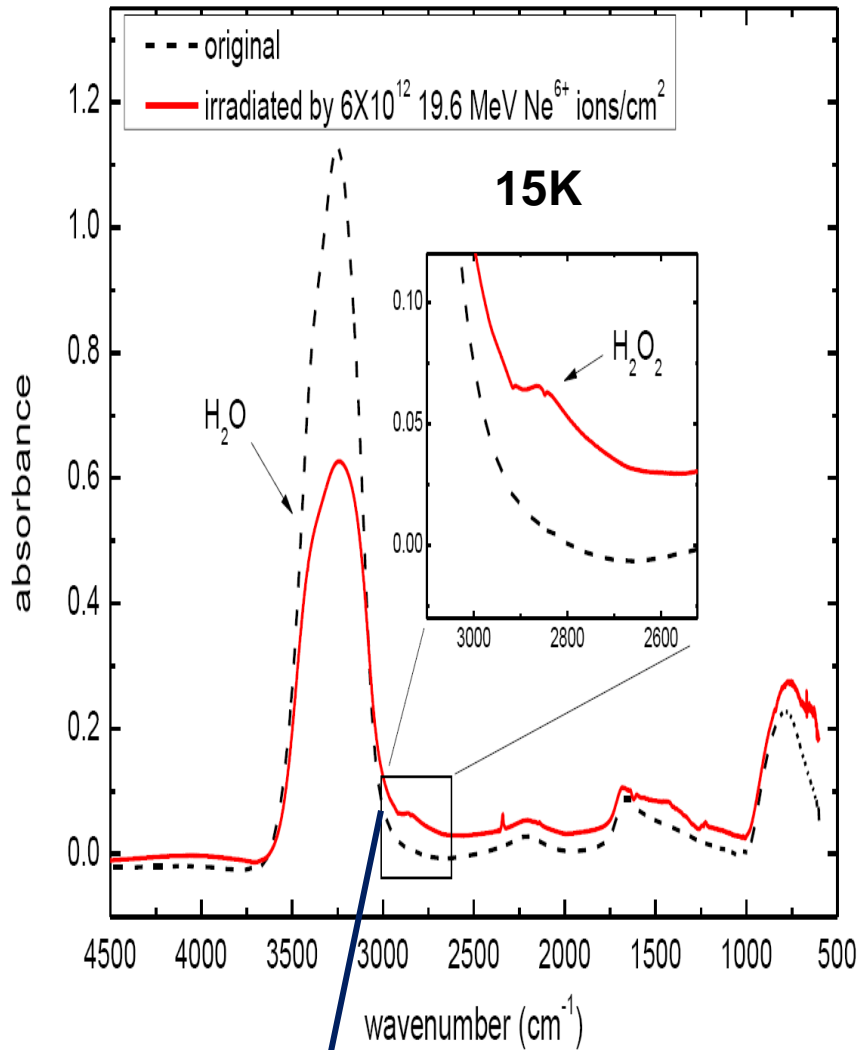




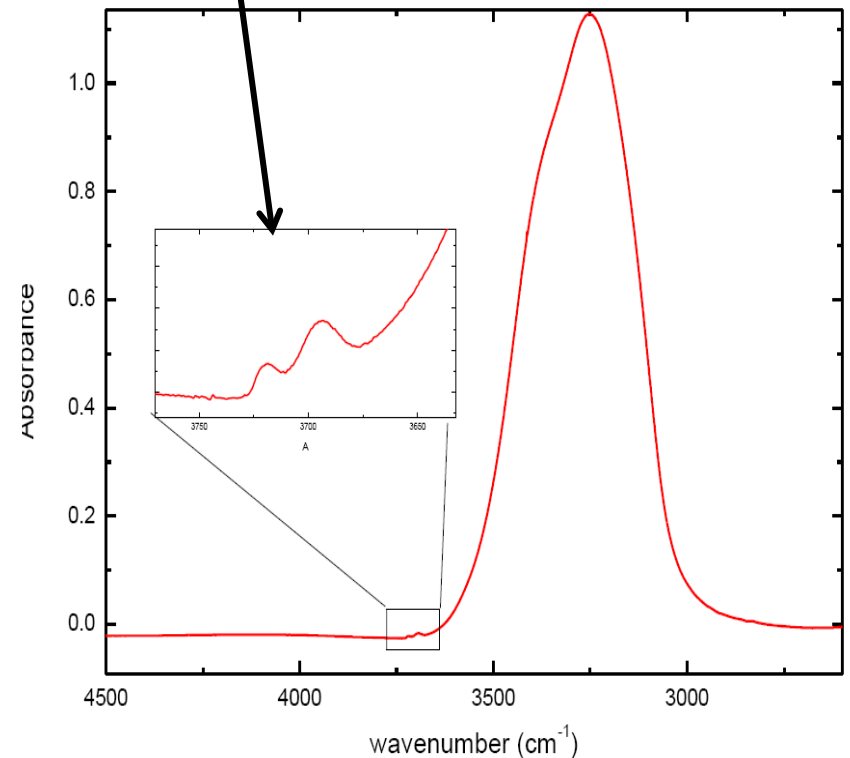
# Water ice: Compaction and Amorphization



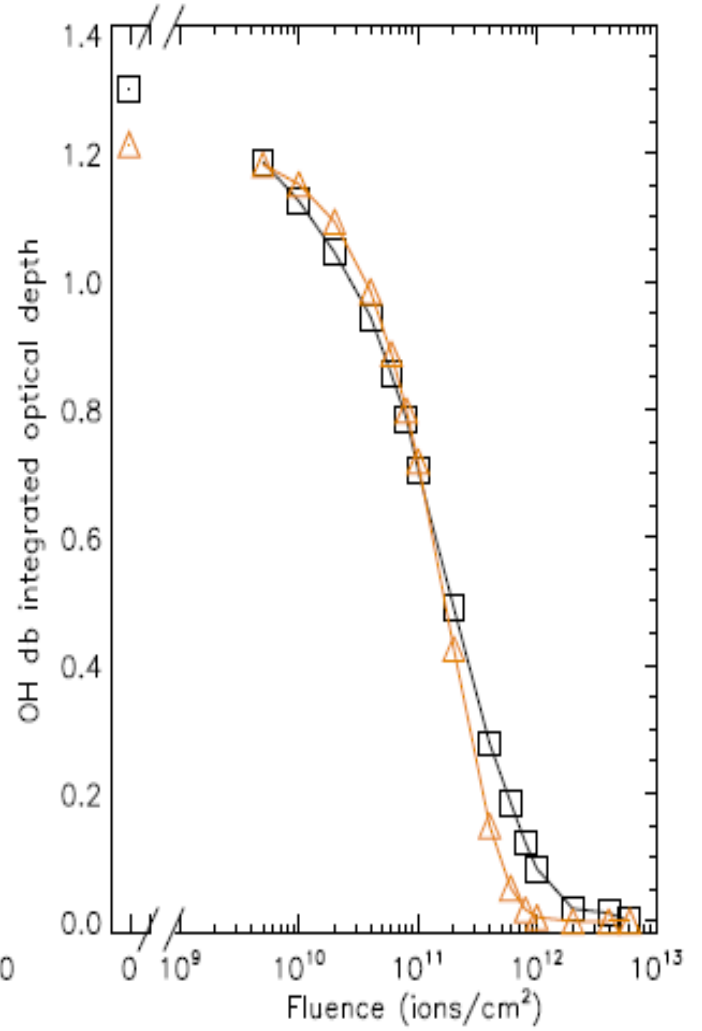
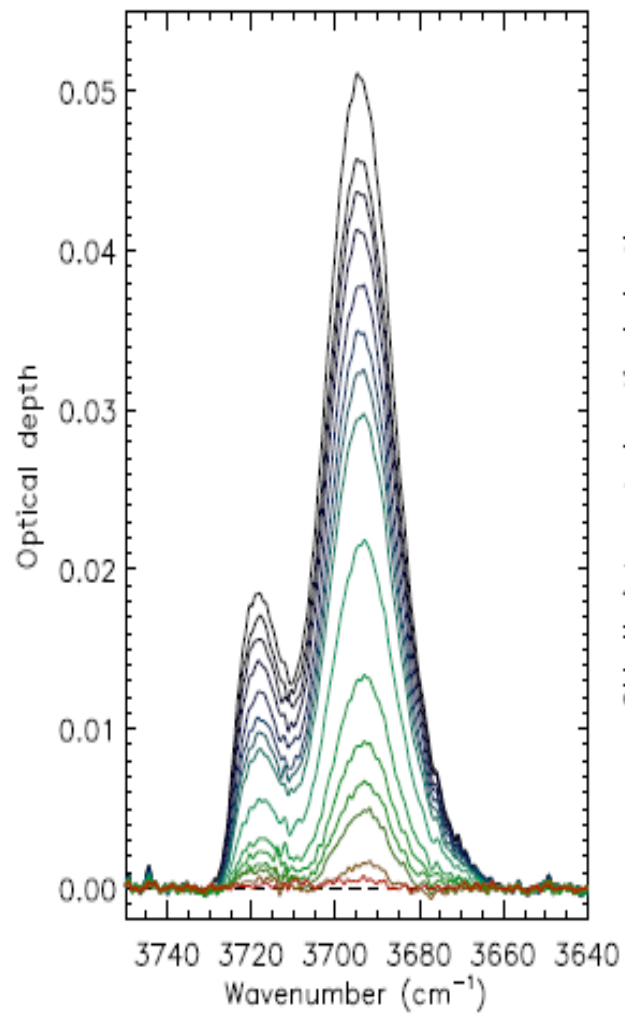
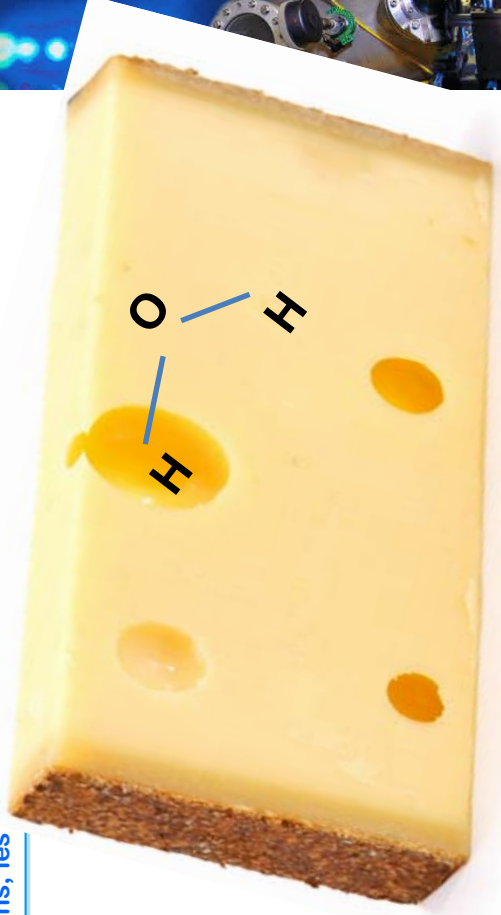
The most abundant molecule  
in interstellar ices:  
**Water H<sub>2</sub>O**



**Porosity:  
OH dangling bonds**

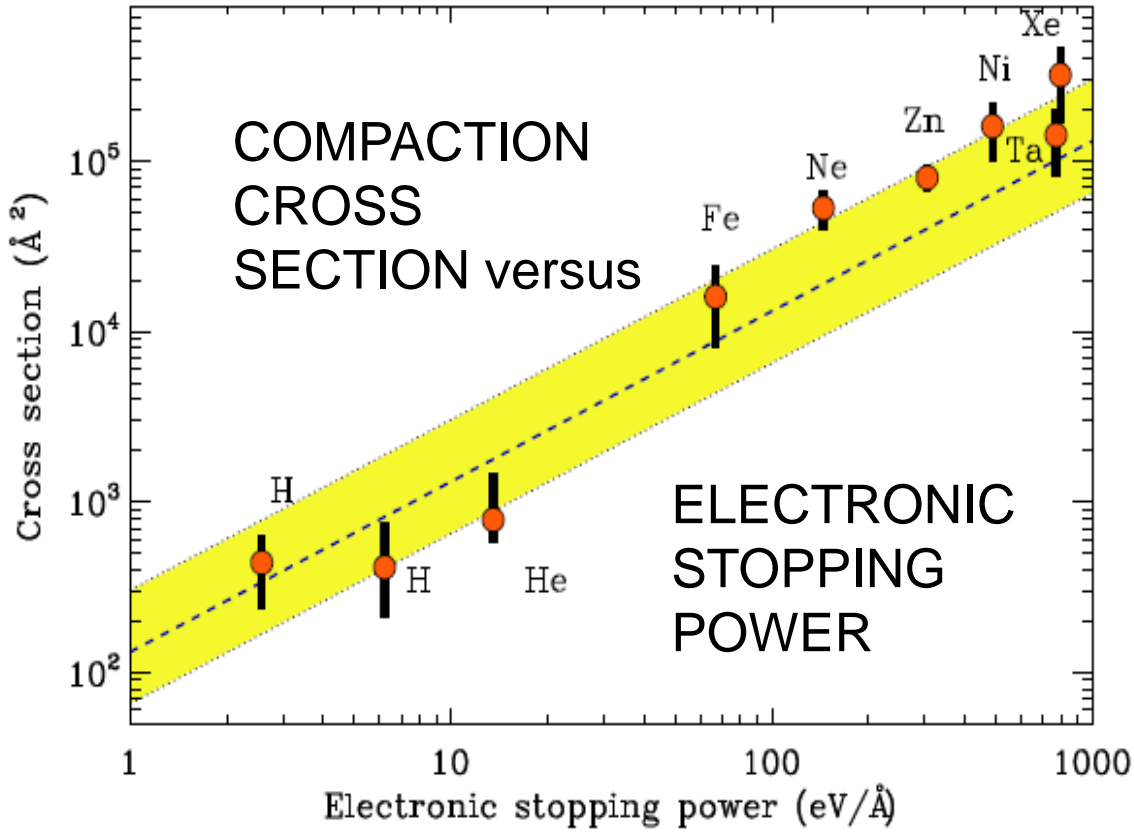


**Irradiation of H<sub>2</sub>O ice:  
formation of H<sub>2</sub>O<sub>2</sub>**



**compaction "dose": 1 eV/molecule**





$$\sigma_c = A S_e^n \text{ with } n=1,0\pm 0,2$$

$t_{comp} = 1 \times 10^5$   
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 557 (2013) A97

# Crystal versus amorphous ice: a competition

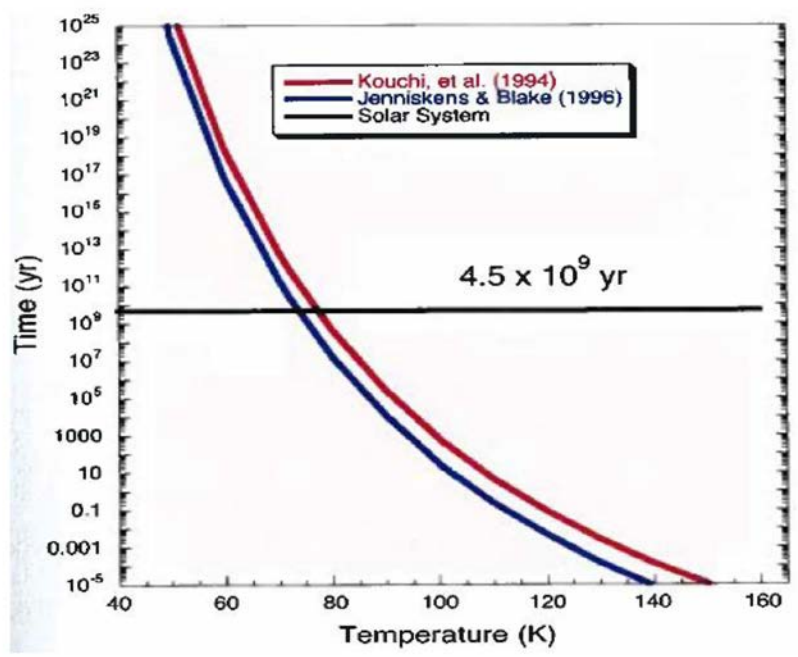
## Thermal induced transition:

- At 100K amorphous ice converted in crystal in about  $10^3$  years.

Irradiation : it induces amorphization.

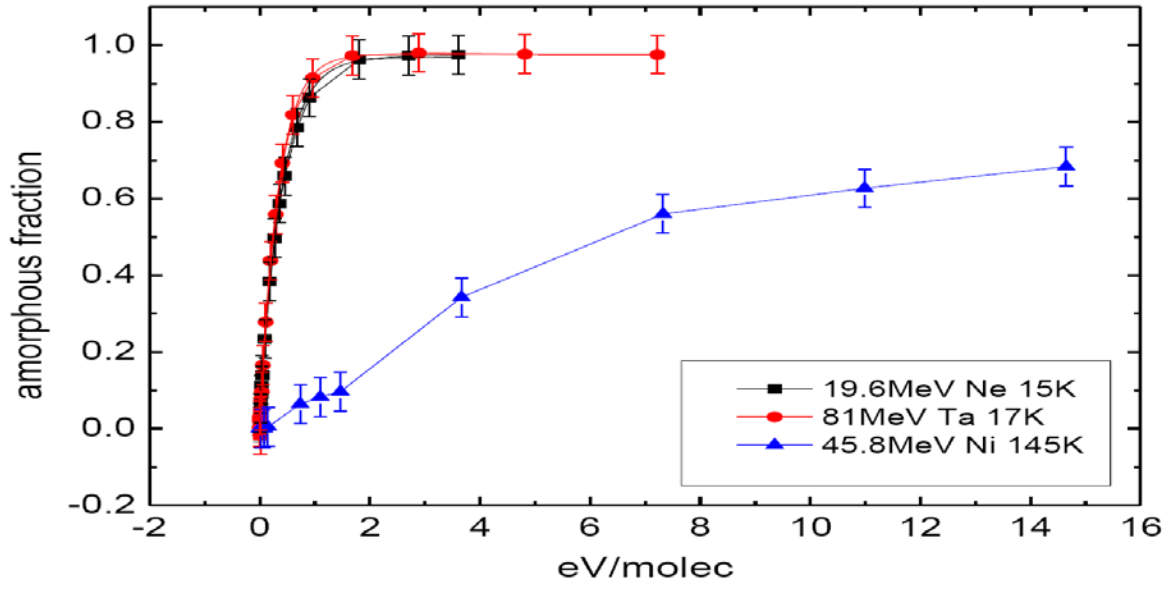
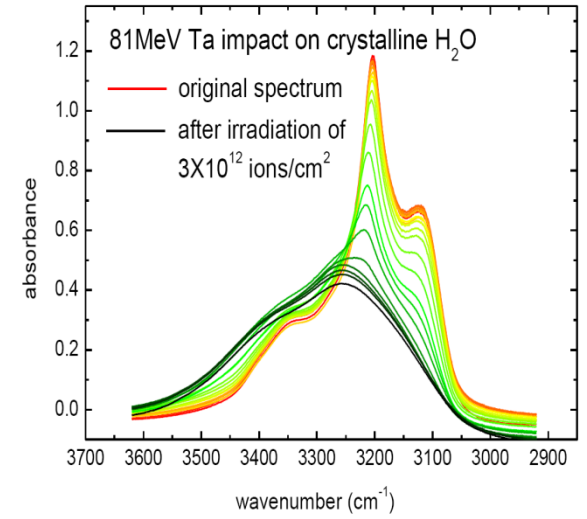
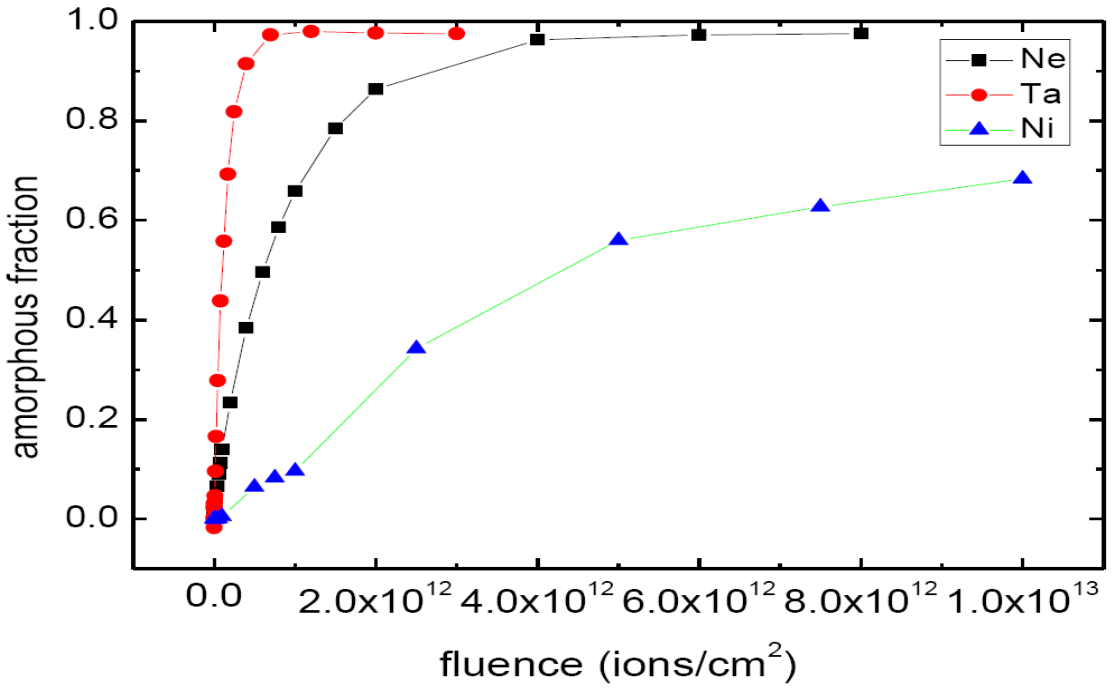
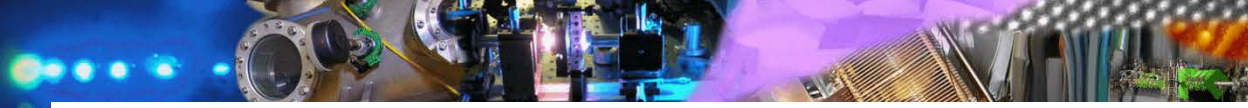
Table3-2: Ions used for irradiation, their electronic stopping power  $S_e$ , their nuclear stopping power  $S_n$ , and the irradiation temperature.

	Energy (MeV)	Irradiation temperature	$S_e$ (eV/Å)	$S_n$ (eV/Å)
Ne	19.6	15K	143	0.2
Ta	81	17K	757	12.7
Ni	46	145K	460	1.4



*Mastrapa et al, 2013*

$$f = A_c \times f_c + A_a \times f_a$$



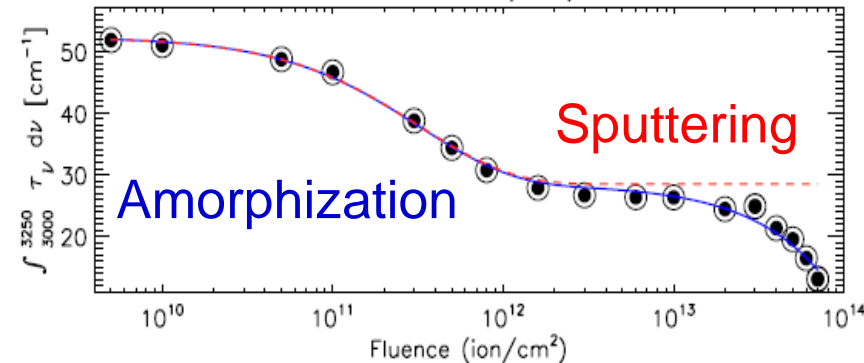
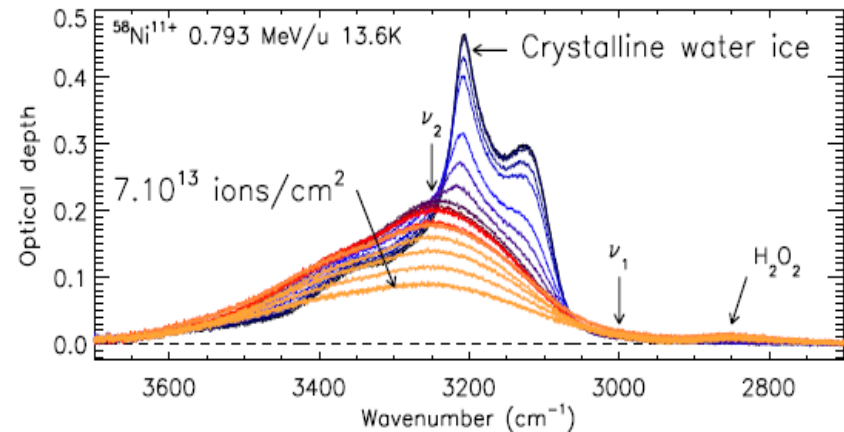
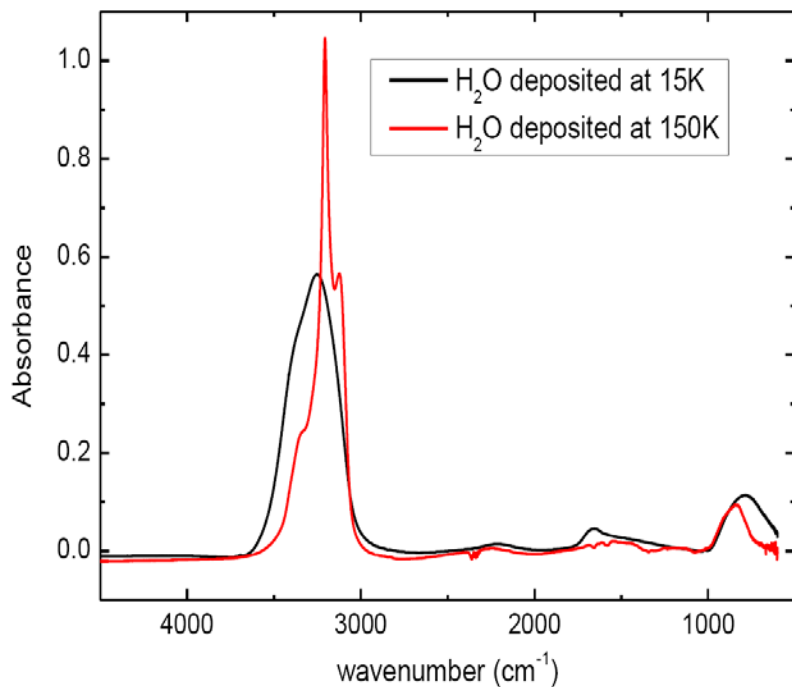
Local dose: the key parameter!

95% at 1,4 eV @ 15K

Around 3eV for 100%

At 145 K, much longer due to the thermal crystallization

*Thesis JJ Ding*



Total Amorphisation 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





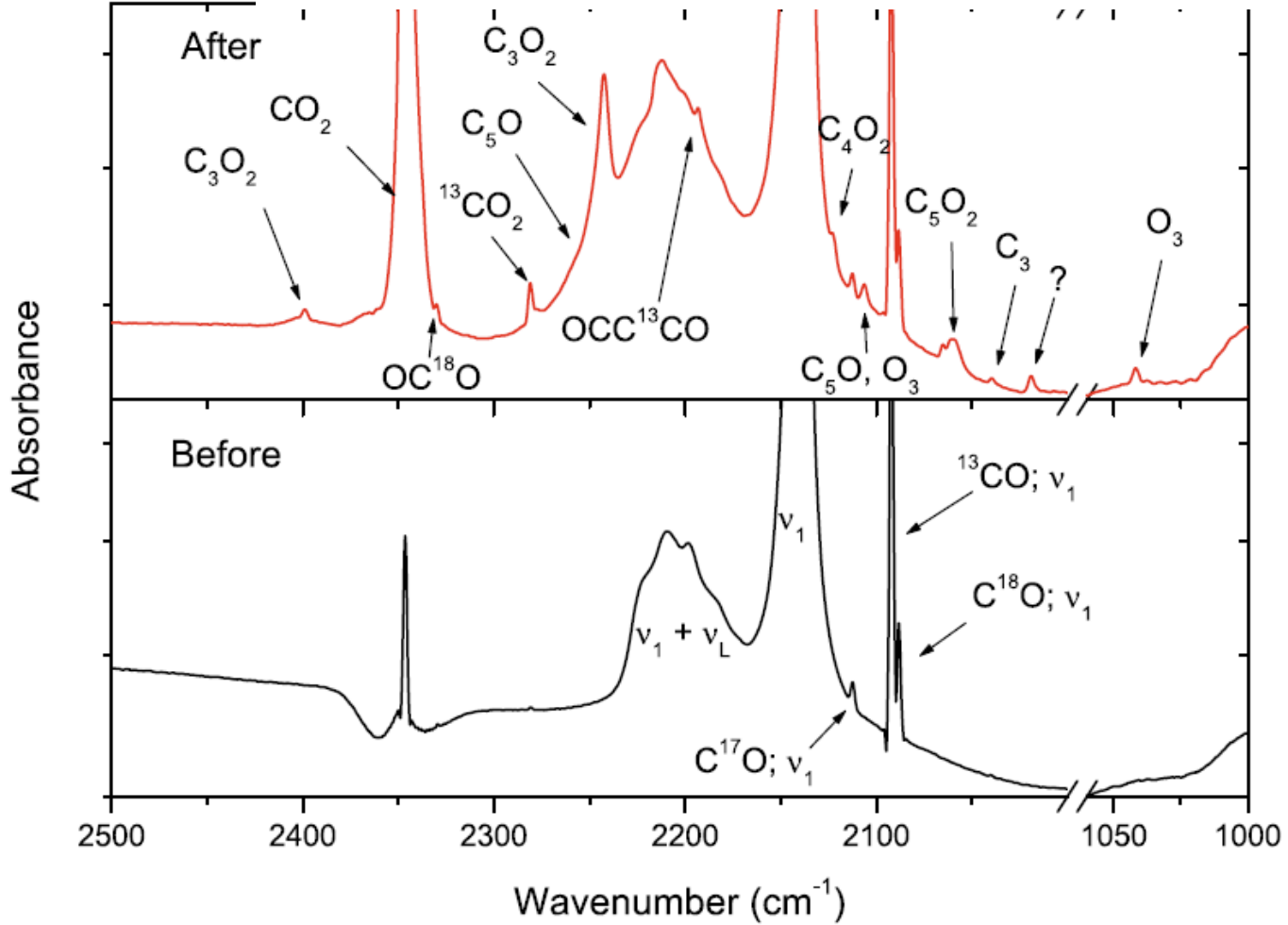
**Carbon Oxide CO,  
dense molecular clouds,  
and cosmic rays.**

*The starting point: the Eduardo's thesis, cotutella with Enio.*



# Second example: CO ice

(the second most abundant molecule in space ices after H<sub>2</sub>O)



CO  
destruction

Production of  
CO<sub>2</sub>, O<sub>3</sub>, C<sub>x</sub>  
and C<sub>x</sub>O<sub>y</sub>

Main  
« observable  
» daughter:  
CO<sub>2</sub>

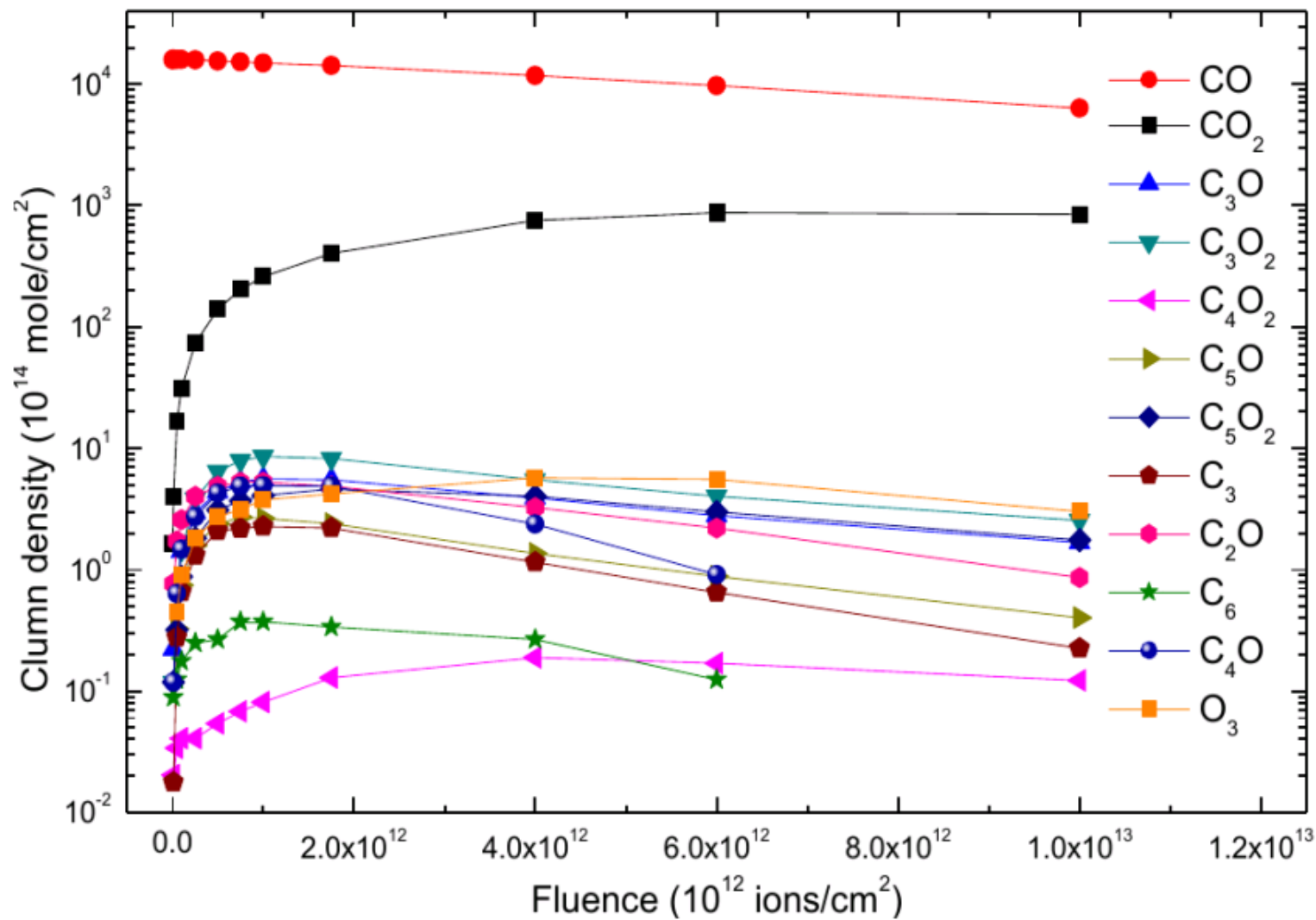
Infrared spectrum of CO ice before and after 50 MeV <sup>58</sup>Ni<sup>11+</sup> irradiation with a fluence of 1.0 × 10<sup>12</sup> cm<sup>-2</sup>.

ion	$E_0$	$S_e$	$S_n$	$P_d$	$\ell_0$	$N_0$
$^{16}\text{O}^{7+}$	220	94	0.04	812	0.41	7.16
$^{16}\text{O}^{5+}$	16	385	0.4	25	0.39	6.78
$^{16}\text{O}^{2+}$	6	452	1.0	11	0.53	9.22
$^{64}\text{Ni}^{24+}$	537	1136	0.7	226	0.39	6.88
$^{70}\text{Zn}^{26+}$	606	1255	0.7	228	0.74	12.86
$^{56}\text{Fe}^{24+}$	270	1318	1.0	112	0.24	4.15
$^{58}\text{Ni}^{11+}$	46	1690	5.5	29	0.85	14.8
$^{58}\text{Ni}^{13+}$	52	1706	4.9	31	0.54	9.45
$^{58}\text{Ni}^{13+}$	52	1706	4.9	31	0.66	11.5
$^{86}\text{Kr}^{31+}$	774	1731	1.1	233	0.05	0.83

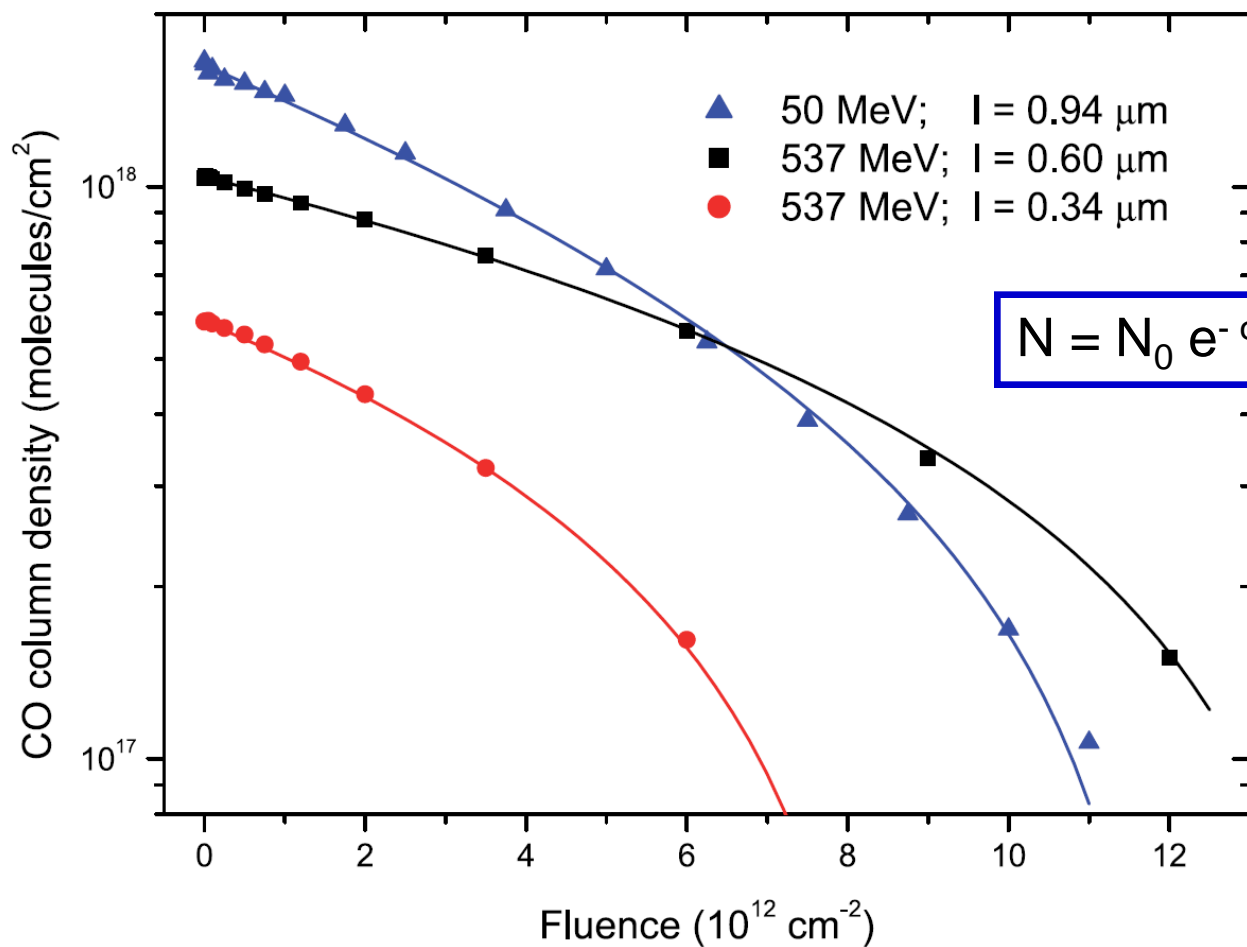
**Sputtering yield , destruction and formation cross sections...**

**... as a function of  $S_e$ ,  
the electronic stopping power**

# CO ice: formation of **new molecular species**



# CO ice: disappearance of CO Molecules during Nickel Ion Irradiation:



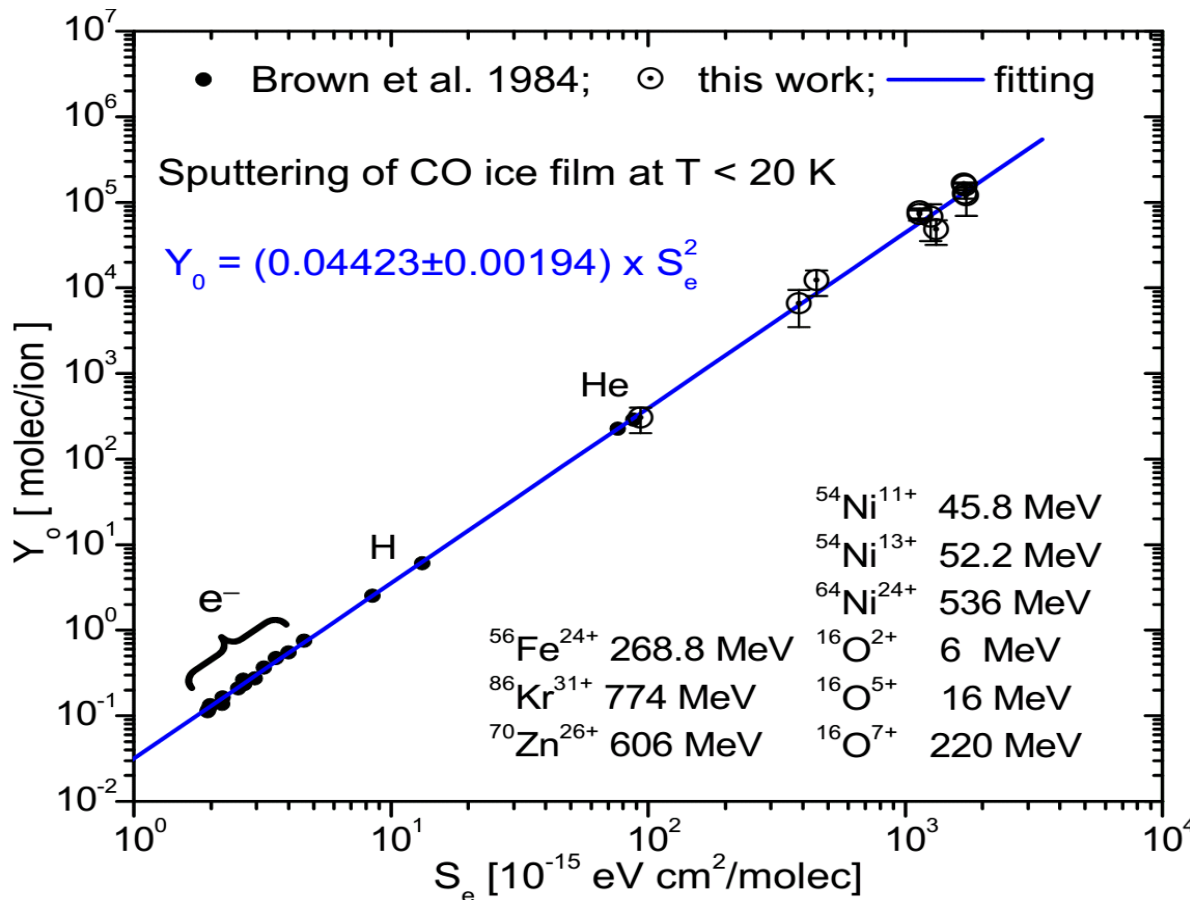
$$N = N_0 e^{-\sigma_d F} - (Y / \sigma_d) (1 - e^{-\sigma_d F})$$

**deduced quantities:**

- Destruction Cross Section  $\sigma_d$
- Sputtering Yield  $Y$**



# CO ice: Ion induced Sputtering Yield



$$Y \sim S_e^2$$

$$S_e \sim Z_p^2$$

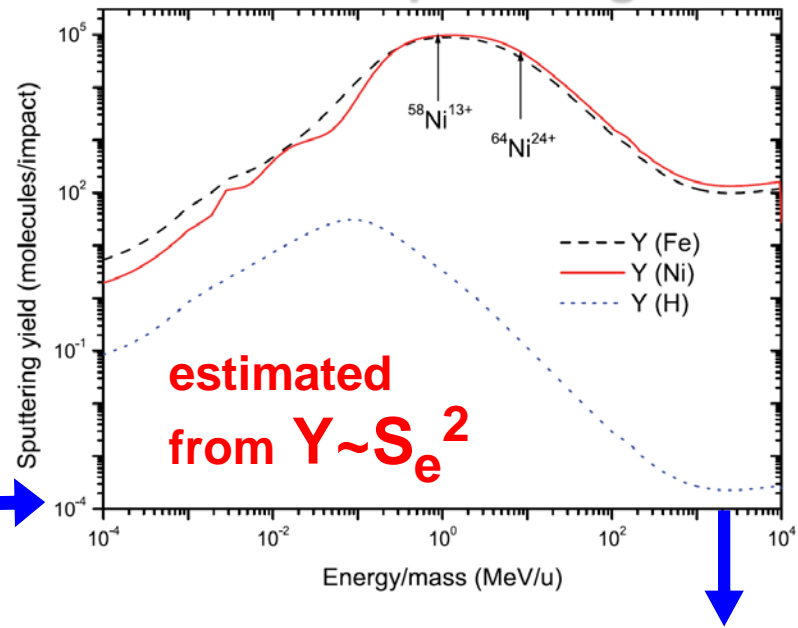
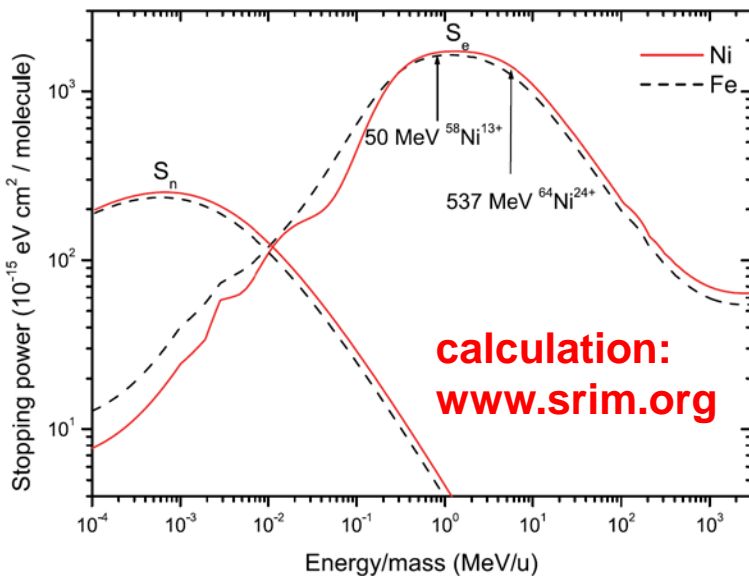
$$Y \sim S_e^2$$

$$Y \sim Z_p^4$$

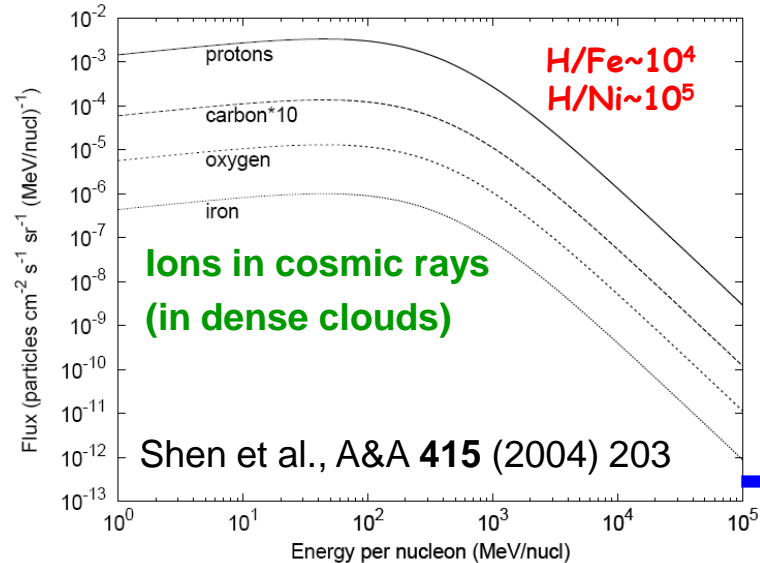
very strong dependence!

W.L. Brown, W.M. Augustyniak, K.J. Marcantonio, E.H. Simmons, J.W. Boring, R.E. Johnson, C.T. Reimann, Nucl. Instrum. Meth. B1 (1984) 307

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

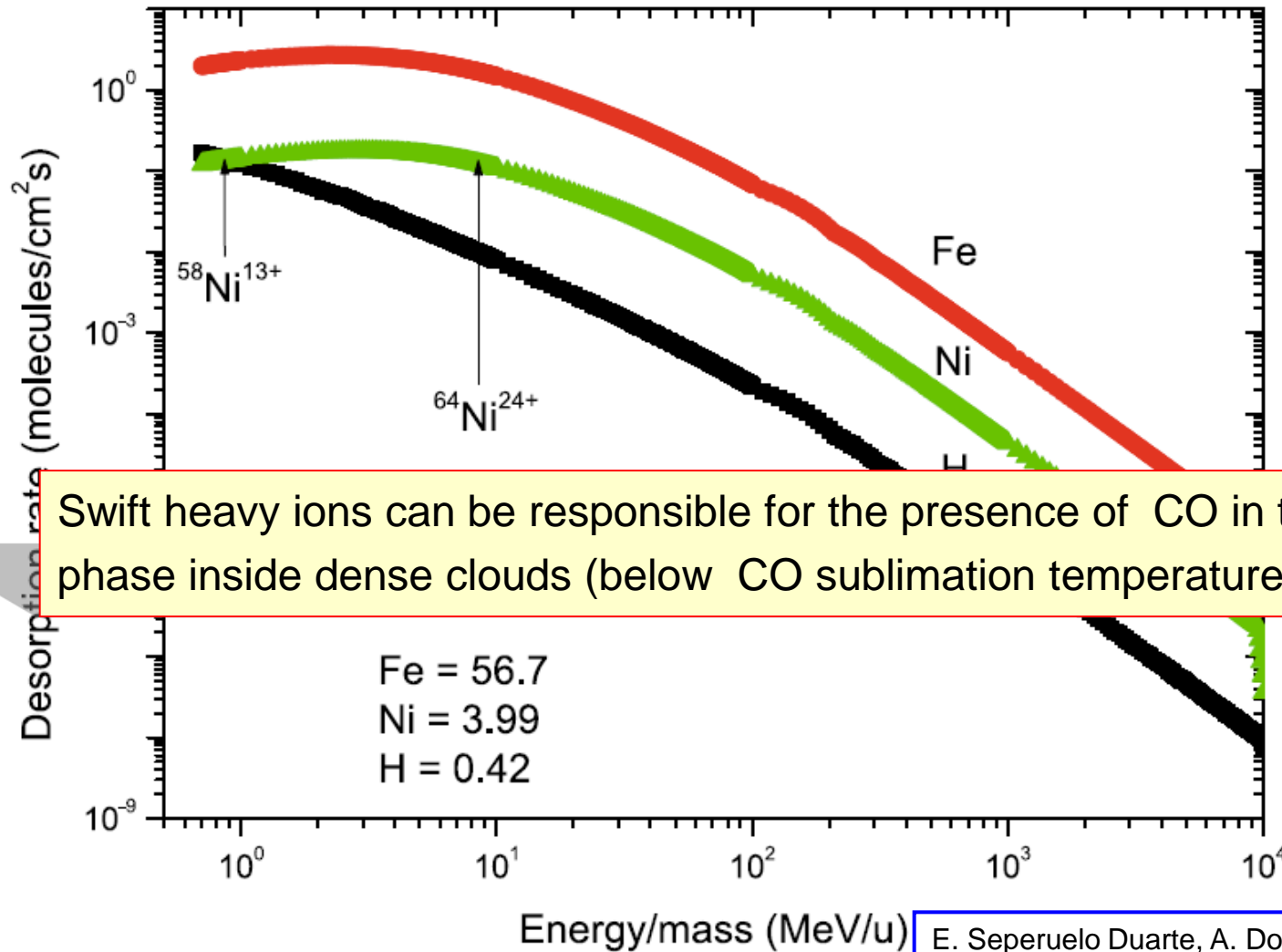


## Heavy Ion Abundance in Space



astrophysical application:  
presence of CO in the gas phase in "dense" ( $10^4 - 10^6$  molecules cm<sup>-3</sup>) molecular clouds ?

# Astrophysical implication



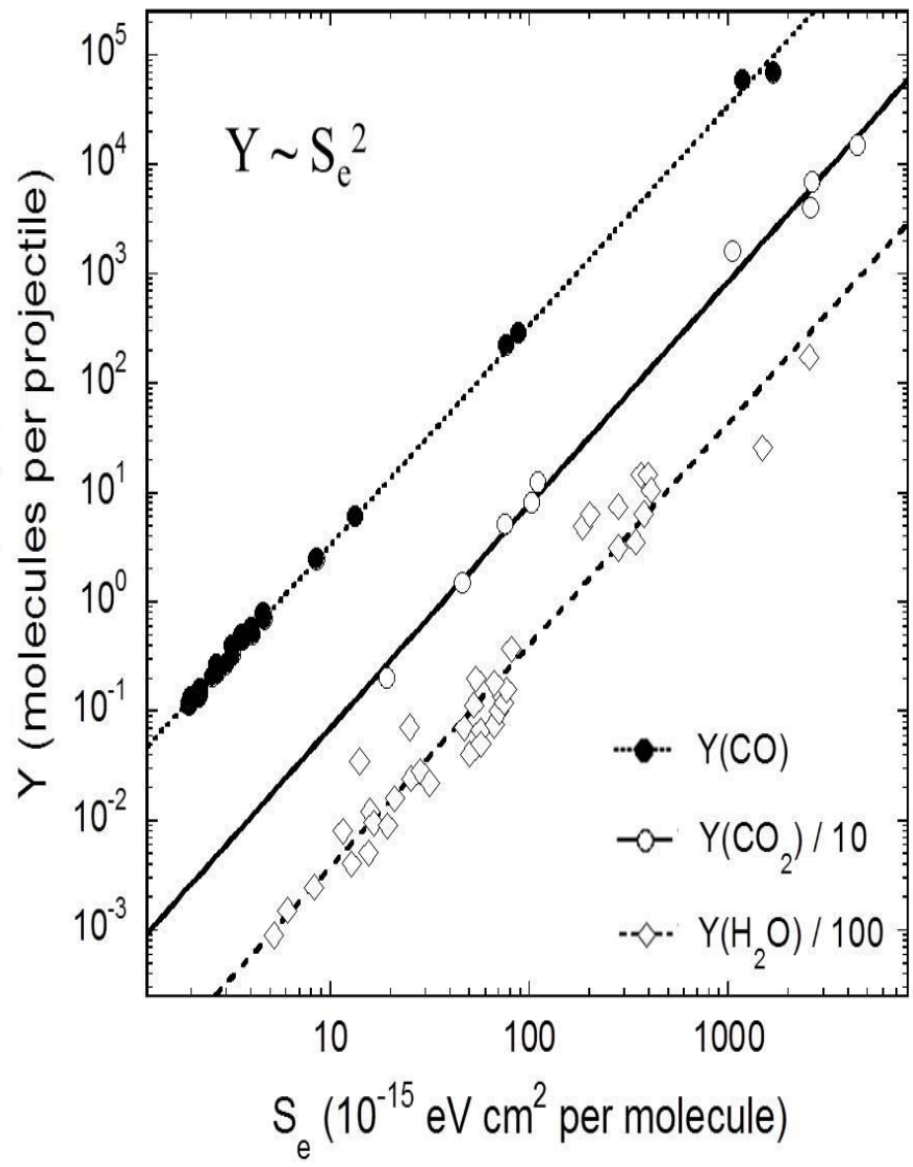
Swift heavy ions can be responsible for the presence of CO in the gas phase inside dense clouds (below CO sublimation temperature, 10 K).

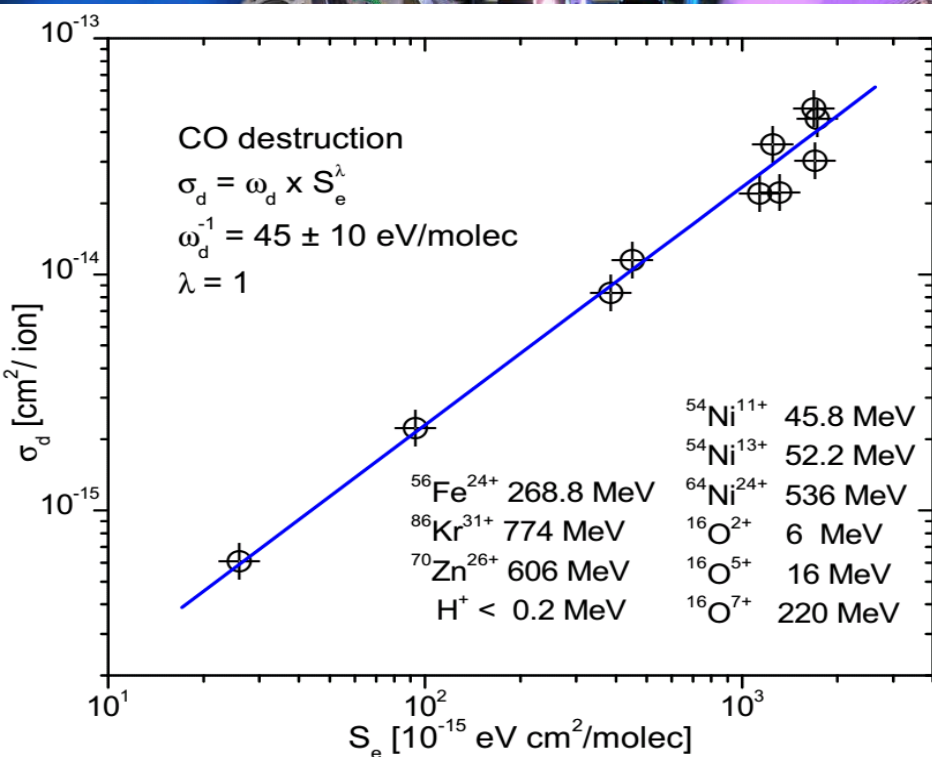
E. Seperuelo Duarte, A. Domaracka, P. Boduch,  
H. Rothard, E. Dartois, E.F. da Silveira  
**Laboratory simulation of heavy ion cosmic ray  
interaction with condensed CO**  
Astronomy & Astrophysics 542 (2010) A71



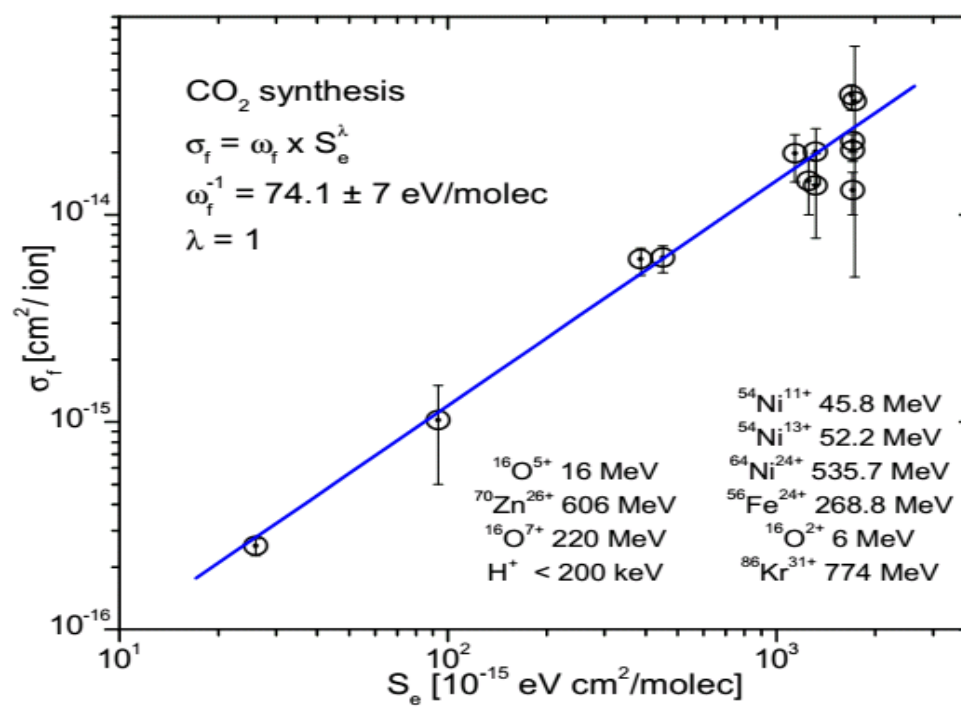


The same results for:  
CO, CO<sub>2</sub> and H<sub>2</sub>O





$$\sigma_d(\text{CO}) \propto S_e$$



$$\sigma_f(\text{CO}_2) \propto S_e$$

# Destruction and formation

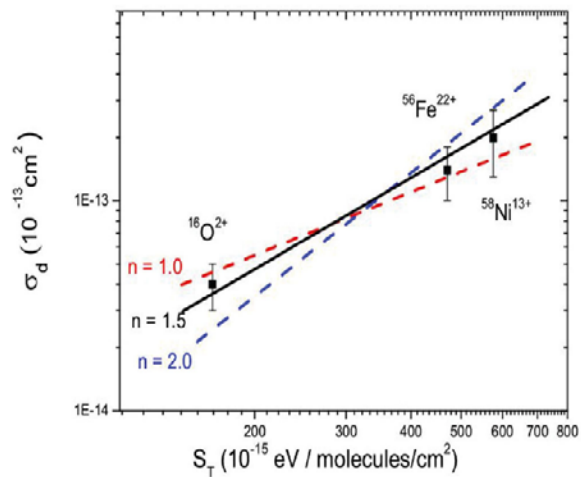
Formation proportional to destruction

# CO ice-different projectiles: **destruction**/formation cross sections

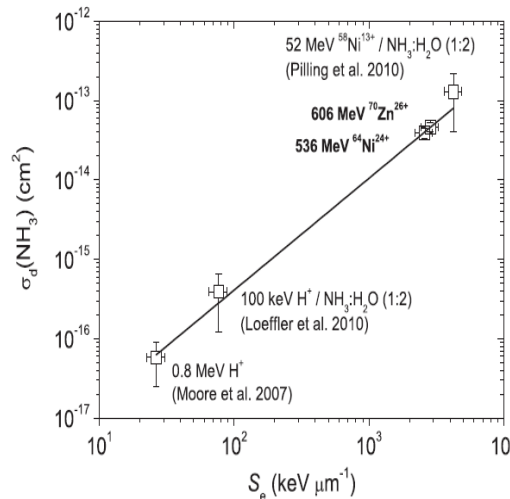
## Comparison with "other projectiles"

Molecules	Projectile	$\sigma$ ( $10^{-15}$ cm <sup>2</sup> )	Reference	
<b>destruction</b>	CO	50 MeV Ni <sup>13+</sup>	100	This work
	537 MeV Ni <sup>24+</sup>	30	This work	
	200 keV H <sup>+</sup>	0.28	Loeffler et al. (2005)	
	10.2 eV photons	0.0003	Loeffler et al. (2005)	
	>6 eV photons	<0.000001	Cottin et al. (2003)	
	>6 eV photons	<0.00008	Gerakines et al. (1996)	
<b>formation</b>	CO <sub>2</sub>	50 MeV Ni <sup>13+</sup>	20	This work
	537 MeV Ni <sup>24+</sup>	18	This work	
	200 keV H <sup>+</sup>	6	Loeffler et al. (2005)	
	10.2 eV photons	0.017	Loeffler et al. (2005)	
	>6 eV photons	0.000013	Gerakines et al. (1996)	

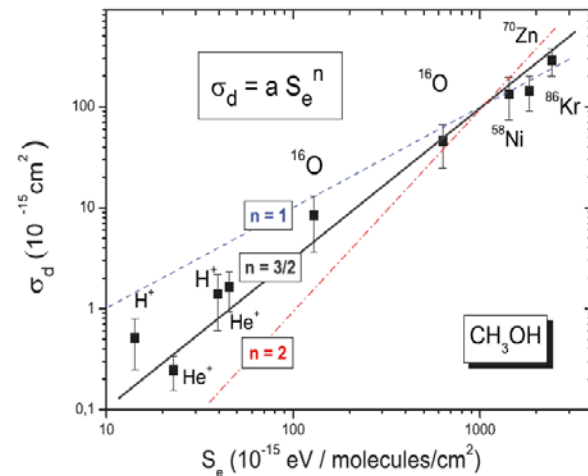
Astron.Astrophys. **512** (2010) A71



**Figure 6.** The dependence of the HCOOH destruction cross-section on the total stopping power. Data are for 6 MeV (O), 52 MeV (Ni; in preparation) and 267 MeV (Fe; the results of the current work). The lines correspond to the function  $\sigma_d \sim S_e^n$ , for  $n = 3/2$  (solid line).



**Figure 16.** Destruction cross-section ( $\sigma_d$ ) and stopping power ( $S_e$ ) relationship. The power law  $\sigma_d(\text{NH}_3) \propto S_e^{1.4 \pm 0.1}$  is derived from  $\sigma_d(\text{NH}_3)$  obtained in this work and those compiled from the literature. See details in the text.



**Figure 8.** The dependence of CH<sub>3</sub>OH destruction cross-section on the electronic stopping power. Data for 16- and 220-MeV O, Zn and Kr are results of the current work; Gerakines et al.(2001), Brunetto et al. (2005) and Baratta et al.(2002). The lines correspond to the function  $\sigma_d \sim S_e^n$ , for  $n = 1, 3/2$  (solid line) and 2.

Diana P. P. Andrade et al(MNRAS 2013)

$n=1,5$  for formic acid

Vinicius Bordalo et al (Astro. Journal (2013)

$n=1,4$  for ammonia

Ana L, F, de Barros et al (MNRAS 2011)

$n=1.5$  for methanol

**Conclusion: for the destruction, always between 1 and 1,5 for simple molecules**



**Galilean moons,  
Jupiter's magnetosphere,  
sulfur cycles.**





Jupiter, NASA's spacecraft *GALILEO*, and the Galilean Moons Io, Europa, Ganymede, Callisto

**Io:** SO<sub>2</sub> ice dominant

**Europa, Callisto, Ganymede:** H<sub>2</sub>O ice dominant

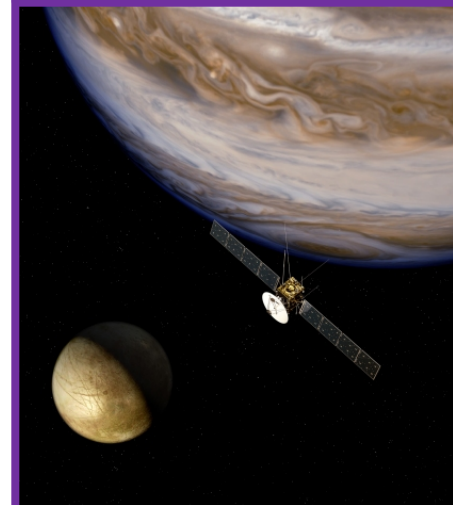
**Europa:** significant quantities of magnesium, sodium sulfate Na<sub>2</sub>SO<sub>4</sub>, carbonate hydrates

Other absorption features and prime candidates:

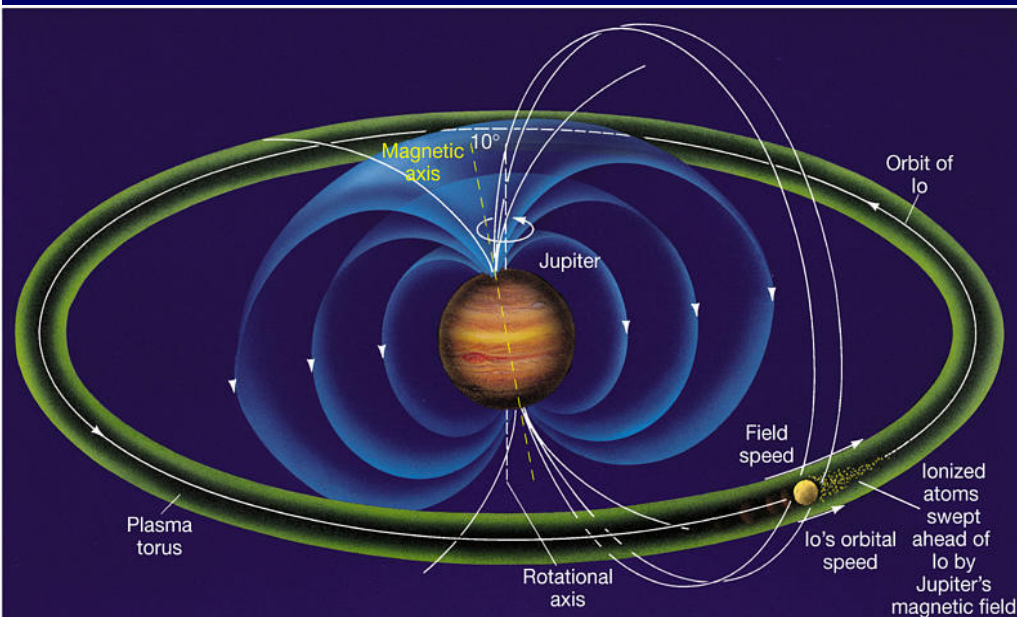
3.4 μm	(~2940 cm <sup>-1</sup> )	C-H
3.5 "	(~2857 cm <sup>-1</sup> )	H <sub>2</sub> O <sub>2</sub>
3.88 "	(~2580 cm <sup>-1</sup> )	S-H, H <sub>2</sub> CO <sub>3</sub>
4.05 "	(~2470 cm <sup>-1</sup> )	SO <sub>2</sub>
4.25 "	(~2350 cm <sup>-1</sup> )	CO <sub>2</sub>
4.57 "	(~2190 cm <sup>-1</sup> )	CN

**Open question:**  
are these species **native** from the satellites or **synthesized** by **exogenic processes** e.g. ion implantation ?

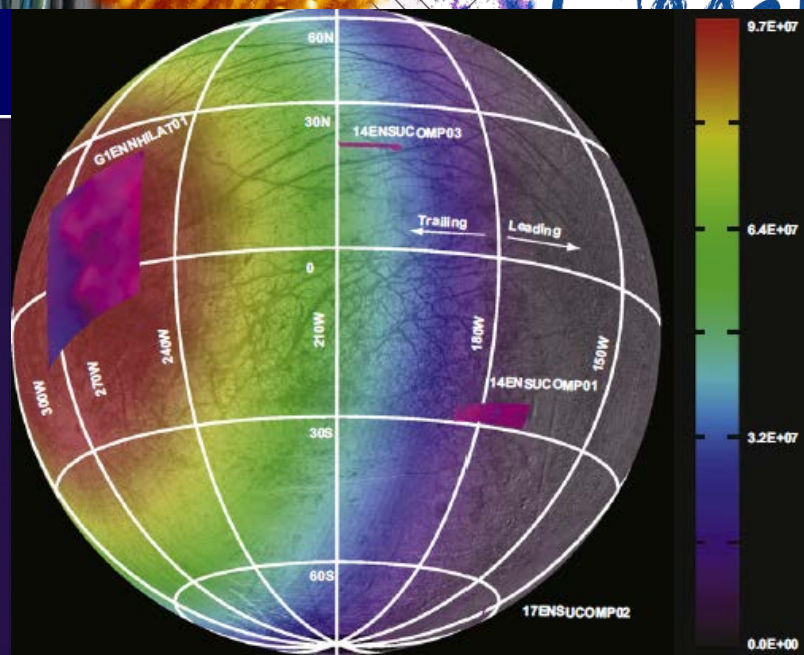
**JUICE 2022 - 2033**  
**ESA Cosmic Vision**



# The Jovian Magnetosphere



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## EUROPA: Sulfur Ion Flux

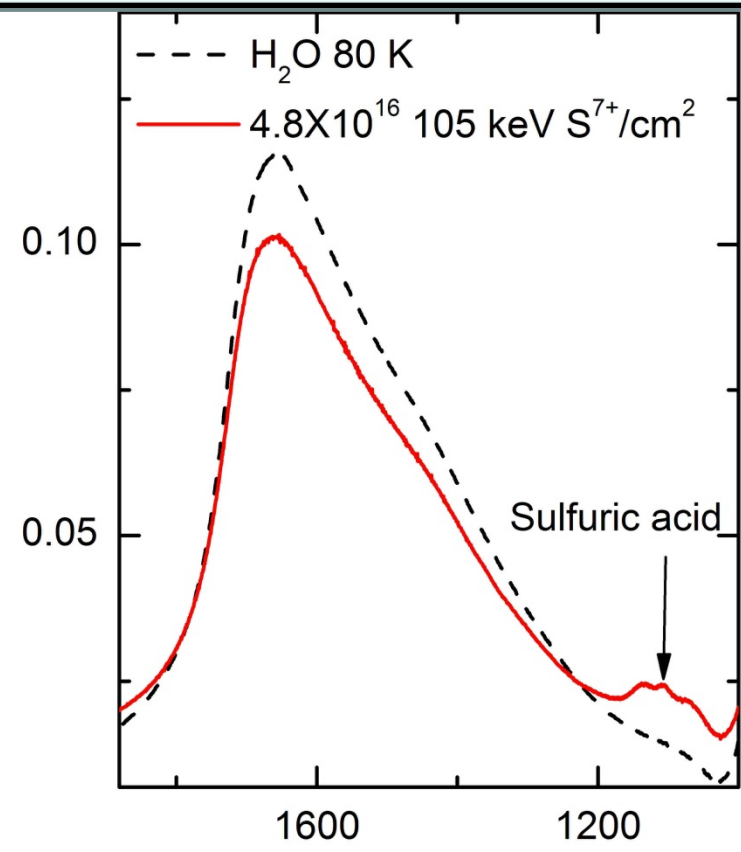
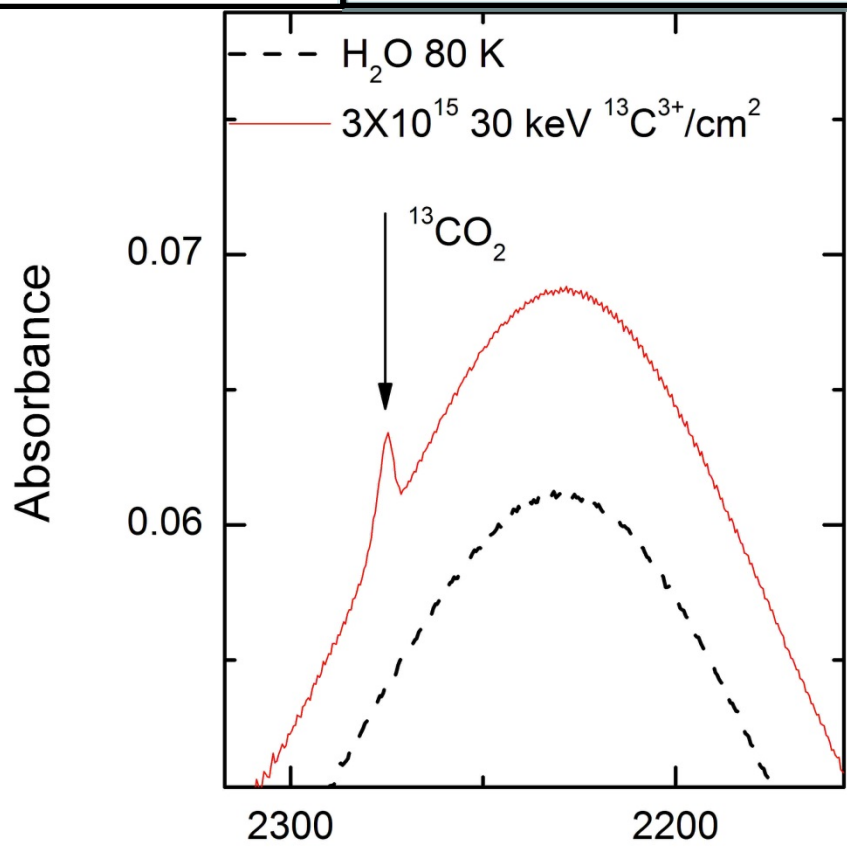
J.B. Dalton III, T. Cassidy, C. Paranicas,  
J.H. Shirley, L.M. Prockter, L.W. Kamp  
Planetary and Space Science 77 (2013) 45

Flux of sulfur ions: up to  $9,7 \cdot 10^7 \text{ s}^{-1} \text{ cm}^{-2}$   
It depends on the « region »



Implantation experiments

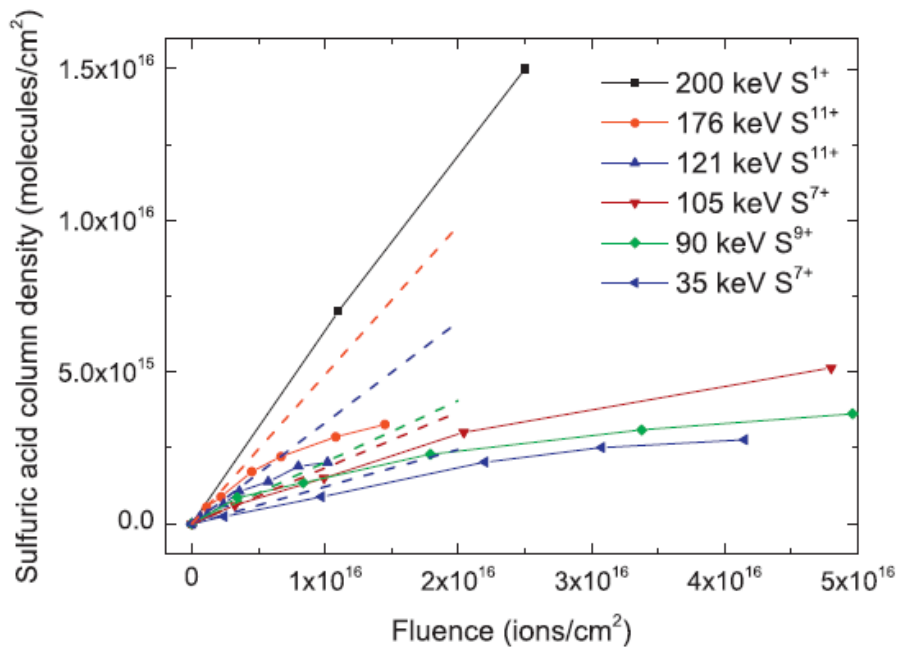
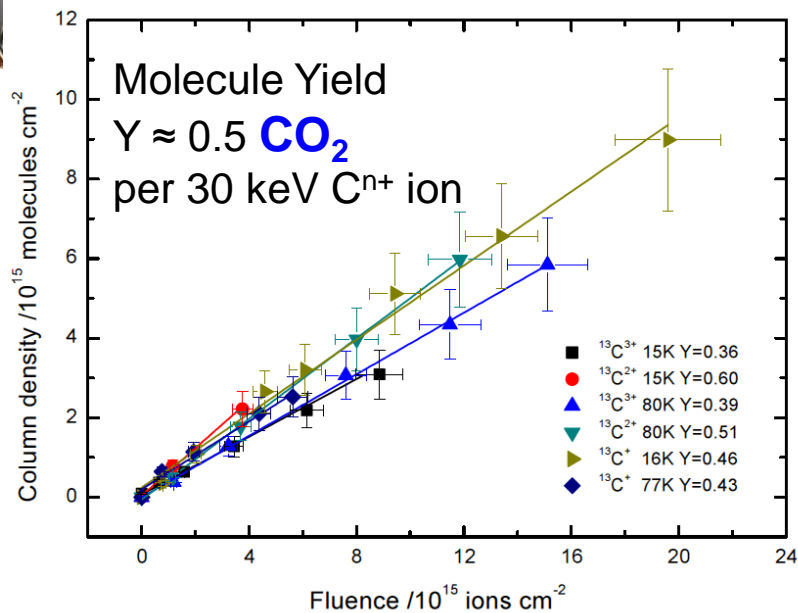
What can we do in the laboratory?  
we can measure formation yields of carbon dioxide and sulfuric acid



IR spectra of water ice before and after implantation of carbon and sulfur ions



X.Y. Lv, A L F. de Barros, P. Boduch, V. Bordalo, E.F. da Silveira, A. Domaracka, D. Fulvio, C. A.Hunniford, T. Langlinay, N.J. Mason, A.R. W. McCullough, M.E. Palumbo, A.S. Pilling, H. Rothard, G. Strazzulla  
**Implantation of multiply charged Carbon Ions in Water Ice**  
*Astronomy & Astrophysics* 546 (2012) A81



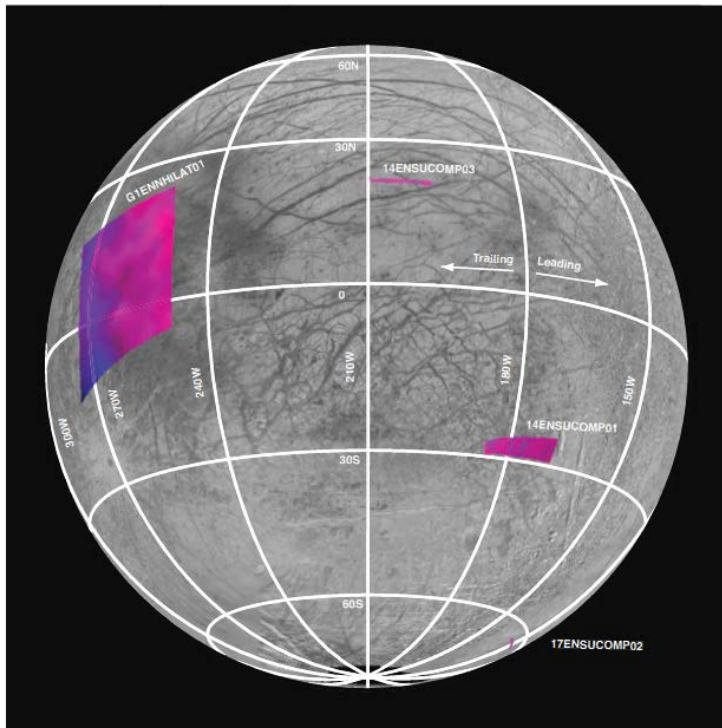
**Molecule Yield**  
 $Y(\text{H}_2\text{SO}_4) \approx 0.12$  (35 keV)  
 $\approx 0.64$  (200 keV)  
 per  $\text{S}^{n+}$  ion

J. J. Ding, P. Boduch, A. Domaracka, S. Guillous, T. Langlinay, X.Y. Lv, M.E. Palumbo, H. Rothard, G. Strazzulla  
**Implantation of Multiply Charged Sulfur Ions in Water Ice**  
*Icarus* 226 (2013) 860–864



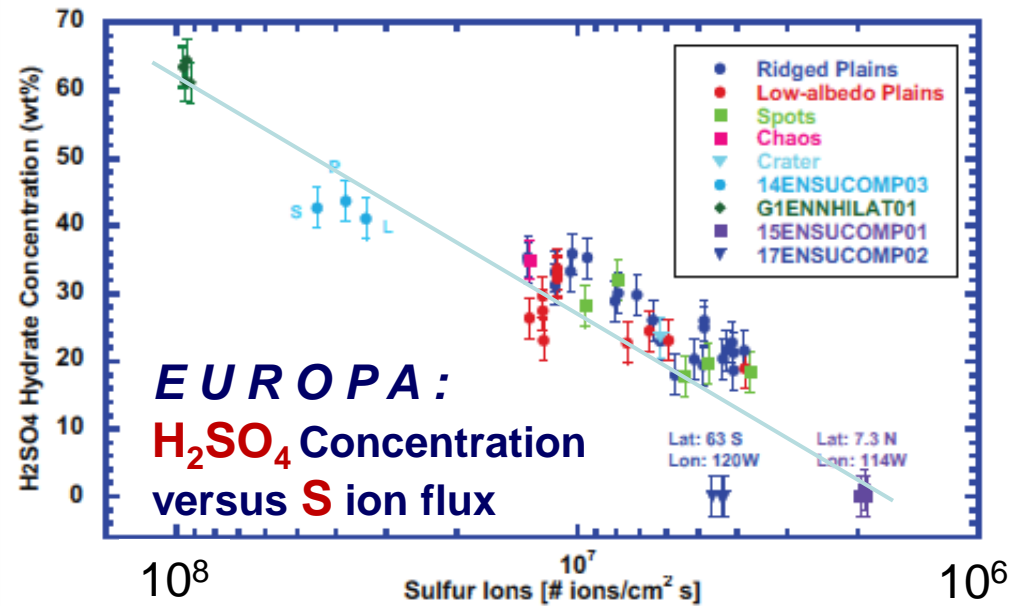
*Table 4-3: Fluxes of sulfur ions estimated for some regions of the surface of Europa and times necessary to produce  $3 \times 10^{19}/\text{cm}^2$  of hydrated sulfuric acid. The highest flux has been measured for NIMS observations of a region (GIENNHILQT01) of the trailing hemisphere, the lowest for a region in the leading hemisphere (15ENSUCOMP01).*

Flux of S-ions ( $\text{cm}^{-2} \text{s}^{-1}$ )	Time (years) Using $Y=0.12$	Time (years) Using $Y=0.64$
$2 \times 10^6$	$4 \times 10^6$	$7 \times 10^5$
$1 \times 10^8$	$9 \times 10^4$	$1.4 \times 10^4$



*J.B. Dalton III et al.,  
Planetary and Space Science 77 (2013) 45:*

Correlation of H<sub>2</sub>SO<sub>4</sub> hydrate concentration  
with sulfur ion flux



*Ding et al., Icarus 336 (2013) 860:*

**Concentration compatible with measured  
Molecule Yield from Implantation!**

but ... C implantation in water ice does  
**not** explain observed **CO<sub>2</sub> concentration**.

and ... no evidence (yet) for  
production of SO<sub>2</sub> or H<sub>2</sub>S in **water ice ...**

# Sulfur implantation in CO and CO<sub>2</sub> ices

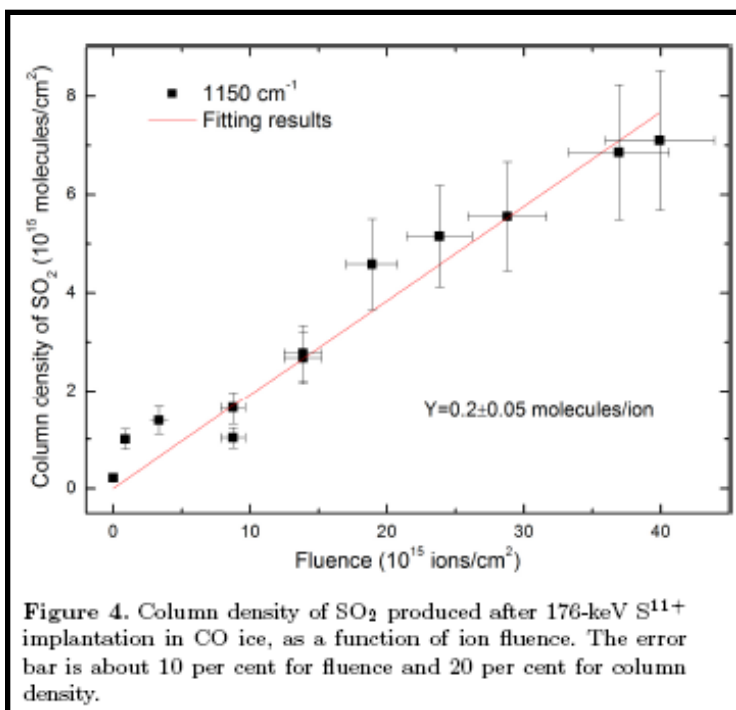
X. Y. Lv<sup>1,2\*</sup>, P. Boduch<sup>2</sup>, J. J. Ding<sup>2</sup>, A. Domaracka<sup>2</sup>, T. Langlinay<sup>2</sup>, M. E. Palumbo<sup>3</sup>,  
H. Rothard<sup>2</sup> and G. Strazzulla<sup>3†</sup>

<sup>1</sup>School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

<sup>2</sup>Centre de Recherche sur les Ions, les Matériaux et la Photonique (CEA/CNRS/ENSICAEN/UCBN), CIMAP-CIRIL-GANIL, Boulevard Henri Becquerel, BP 5133, F-14070 Caen Cedex 05, France

<sup>3</sup>INAF-Osservatorio Astrofisico di Catania, Catania, Italy

Monthly Notices of the Royal Astronomical Society (2013)



S implantation in CO and CO<sub>2</sub>:

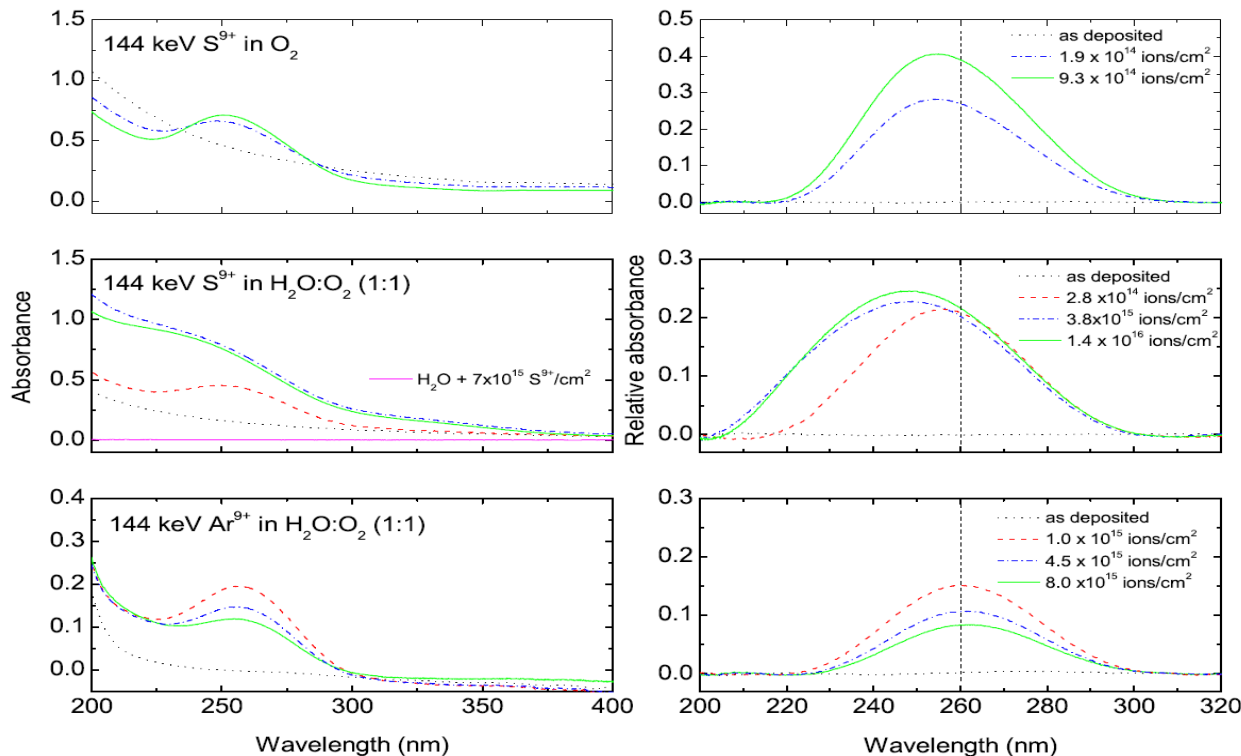
$Y(\text{SO}_2) = 0.20 \pm 0.05$  molec./ion at 176 keV in CO

$Y(\text{SO}_2) = 0.38 \pm 0.02$  molec./ion at 90 keV in CO<sub>2</sub>

and ... CS<sub>2</sub> produced in CO<sub>2</sub> and OCS in CO

**Europa:** time to produce observed amount of SO<sub>2</sub> depends strongly on CO<sub>2</sub> concentration: 200 years ... up to 20000 years

**Star forming regions:** strong flux of stellar wind from young stars (T-Tauri phase) interacts with CO<sub>2</sub> rich dust, later incorporated in comets



Targets representative of parents molecules for  $SO_2$  and  $O_3$

No  $SO_2$  formed (280 nm)

$O_3$  efficiency formed at 260 nm with S and Ar

New band at 255 nm not existing with Ar

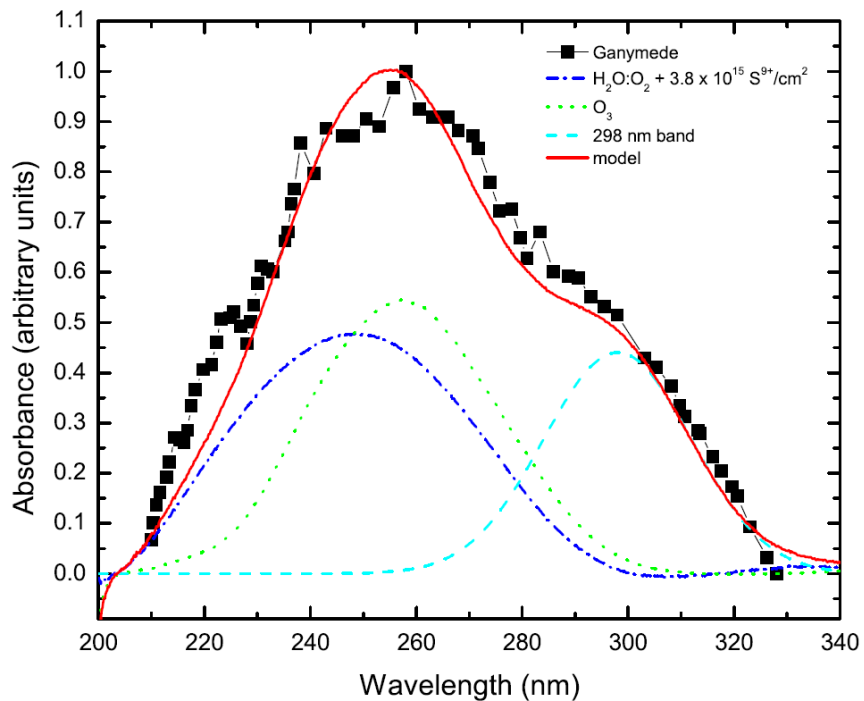
Complementary experiments in the UV domain:

$Ar^{q+}$  and  $S^{q+}$  on  $O_2$ ,  $H_2O+O_2$  (1:1)

No effect of implantation for  $Ar^{q+}$

Appearance at 255nm for  $H_2O-O_2$  then shifted at 247nm for higher S fluence

Formation of  $SO_3^-$  and  $HSO_3^-$



Ozone at 260 nm  
HSO3 at 247 nm

And 298 nm????

Figure 7: The absorption band observed on Ganymede (Noll et al., 1996) is fitted by using three components as indicated in the figure (see details in the text).



# Mixtures and complex organic molecules

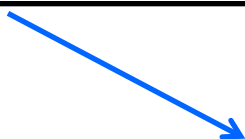
# High energy ion versus UV irradiation of methanol:ammonia ice

## Formation of common organic products

G. M. Muñoz Caro, E. Dartois,  
P. Boduch, H. Rothard, et al.  
(A&A, 2013)

**NH<sub>3</sub>:CH<sub>3</sub>OH ice**

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

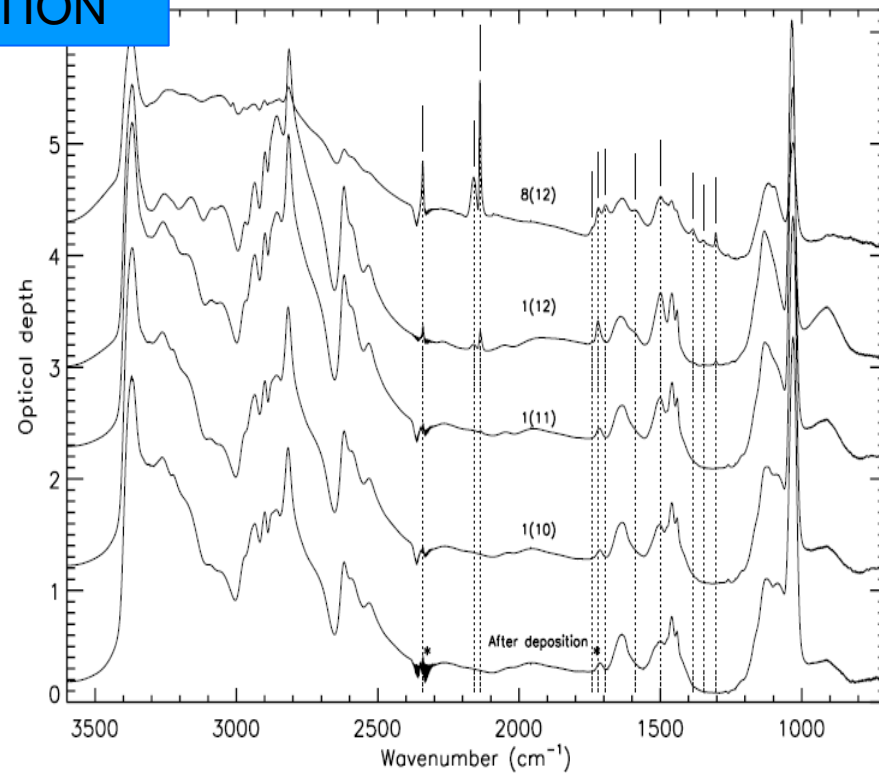
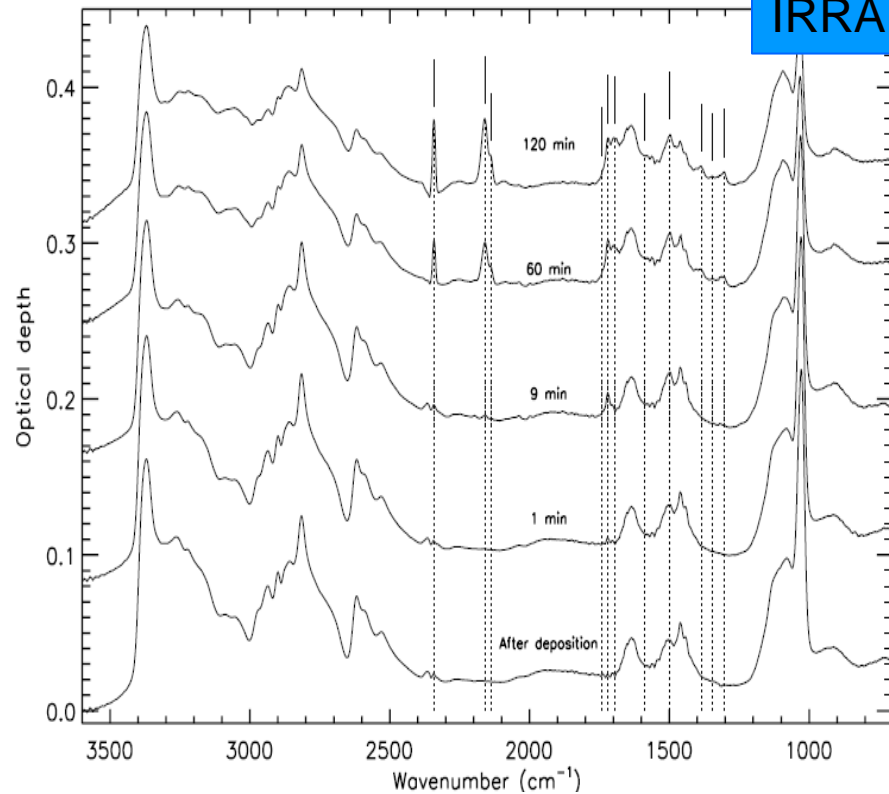


2,5 10<sup>14</sup> photons/cm<sup>2</sup>/s (10eV) **versus** Zn<sup>26+</sup> at 620 MeV (flux  
10<sup>9</sup> ions/cm<sup>2</sup>/s)

Local dose up to 30 eV/molecule



# IRRADIATION



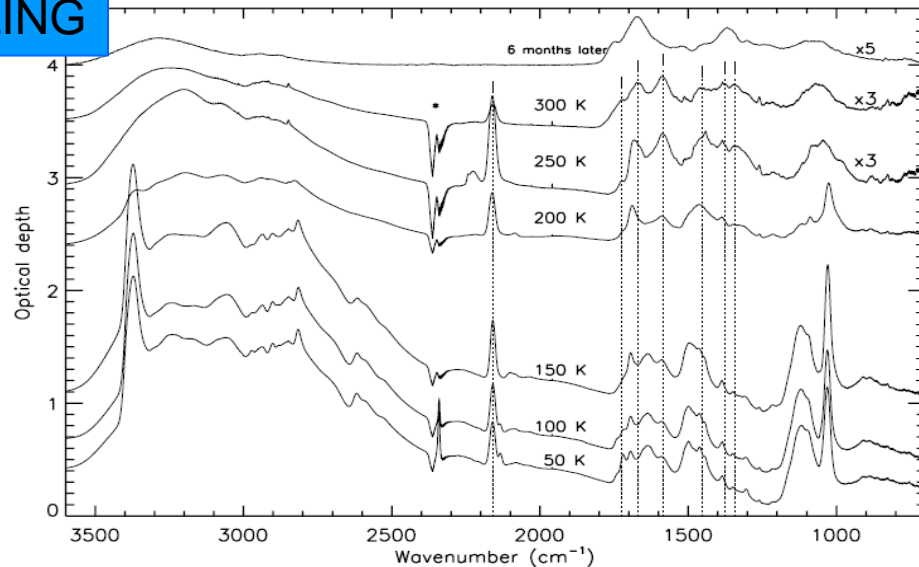
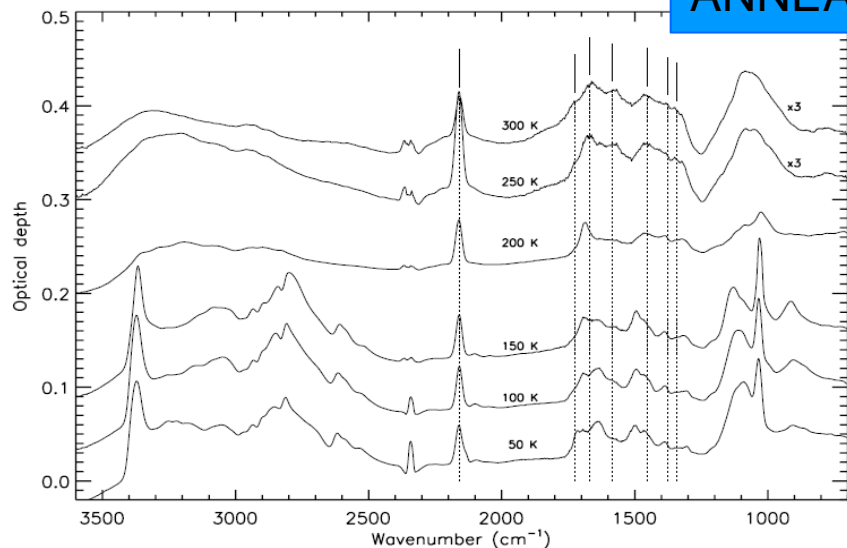
**Table 1.** New bands attributed to irradiation products

position <sup>a</sup> (cm <sup>-1</sup> )	Assignment	vibration mode	UV after dep.	Zn (620 MeV)
2340	CO <sub>2</sub>	CO str.	×	×
2160	OCN <sup>-</sup>	CN str.	×	×
2138	CO	CO str.	×	×
1740	C=O ester/aldehyde	CO str.	×	×
1720	H <sub>2</sub> CO	CO str.	×	×
1694	HCONH <sub>2</sub> ?	CO str.	×	×
1587	COO <sup>-</sup> in carb. ac. salts <sup>b,c</sup>	COO <sup>-</sup> asym. str.	×	×
1498	H <sub>2</sub> CO	CH <sub>2</sub> scis.	×	×
1385	CH <sub>3</sub> groups	CH <sub>3</sub> sym. def.	×	×
1347	COO <sup>-</sup> in carb. ac. salts <sup>b,c</sup>	COO <sup>-</sup> sym. str.	×	×
1303	CH <sub>4</sub>	def.	×	×

<sup>a</sup> Position varies slightly due to interaction of species within the matrix, <sup>b</sup> Muñoz Caro & Schutte (2003) ; <sup>c</sup> Nuevo et al. 2006.

Same  
« products » for  
both  
experiments!

# ANNEALING



PH |

**Table 2.** Assigned feature carriers of the IR residue spectrum formed by UV irradiation of  $\text{NH}_3:\text{CH}_3\text{OH} = 1:1$  ice.

Position $\text{cm}^{-1}$	Assignment	Vibration mode	UV after dep.	Zn (620 MeV)
3600-2300	R-COOH, alcohols, $\text{NH}_4^+$	OH str., NH str.	X	X
2930?confirm	$-\text{CH}_2\text{OH}^b$	$2\nu_{19}$ antisym. $-\text{CH}_2$ str.	X	X
2875?confirm	$-\text{CH}_2\text{OH}^b, \text{NH}_4^+^a$	$\nu_{18}$ sym. $\text{CH}_2$ str., $2\nu_4$ of $\text{NH}_4^+^a$	X	X
2160	$\text{OCN}^-$	CN str.	X	X
1723	Aldehydes	C=O str.	X	X
1670	Amides	C=O str.	X	X
1586	$\text{COO}^-$ in carboxylic acid salts $^{c,d}$	$\text{COO}^-$ antisym. str.	X	X
1454	$\text{NH}_4^+^a$	$\nu_4^a$	X	X
1378	$\text{CH}_3$ groups	CH scissoring $^a$	X	X
1342	$\text{COO}^-$ in carboxylic acid salts $^{c,d}$	$\text{COO}^-$ sym. str.	X	X
1050	CH <sub>2</sub> -OH in primary alcohols	C-O str.	X	X

<sup>a</sup> Wagner & Hornig (1950)

<sup>b</sup> Muñoz Caro & Dartois (2009)

<sup>c</sup> Muñoz Caro & Schutte (2003)

<sup>d</sup> Nuevo et al. 2006

Same residues  
for both  
experiments!

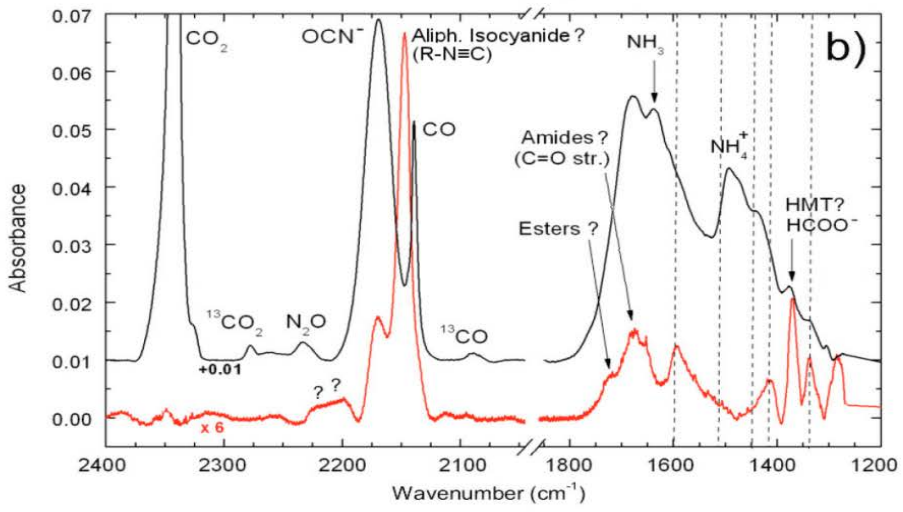
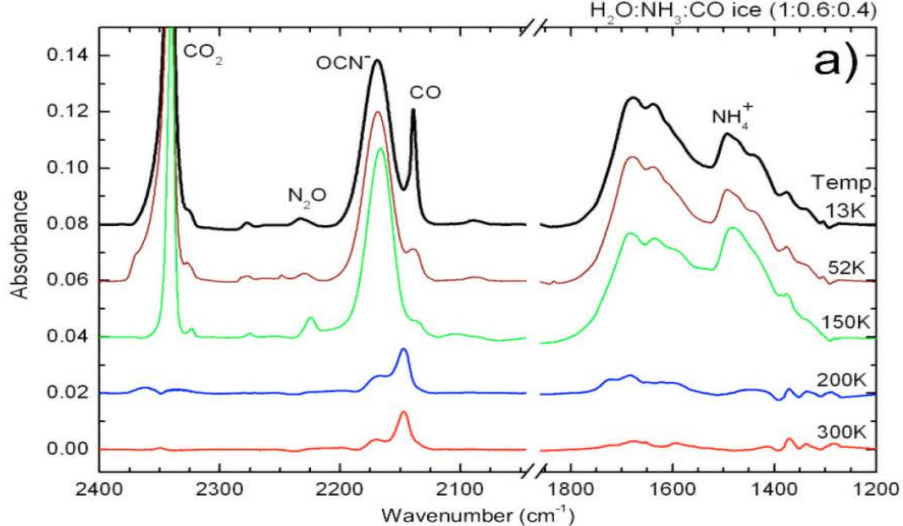
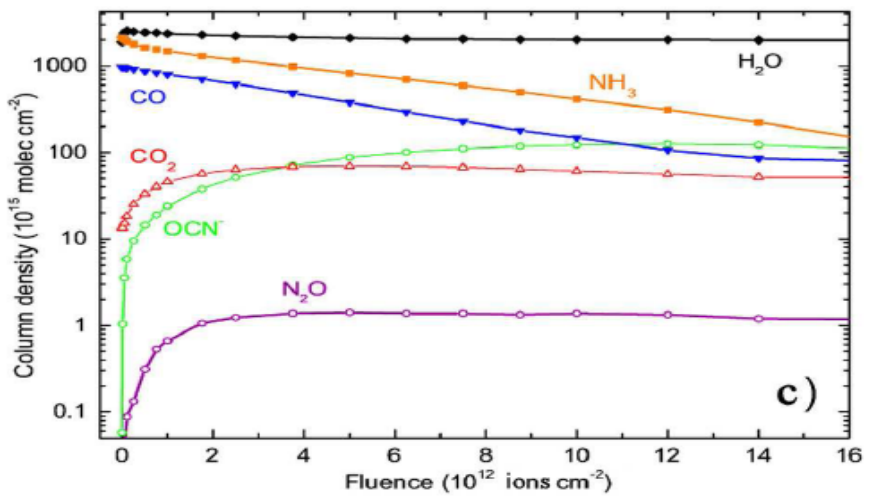
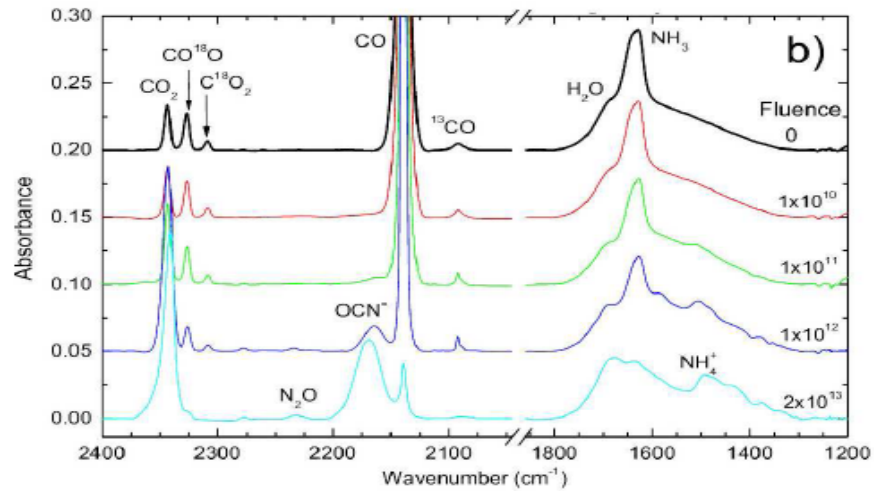
# Conclusion :

- Same local dose (eV/molecule)
- Formation : the same species
- Residues very similar
- Rich in organic molecules.
  
- Sputtering of HCl very strong vs UV
- G values are different, higher for HCl.
- Projected range: Higher for ions
  - Thicker sample
  - Better for other analysis...



# H<sub>2</sub>O – CO - NH<sub>3</sub> ice

## 46 Mev <sup>58</sup>Ni<sup>13+</sup>



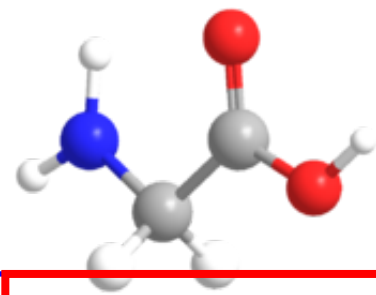
**Fig. 6. a)** Infrared spectra of H<sub>2</sub>O:NH<sub>3</sub>:CO ice (1:0.6:0.4) from 2400 to 1200 cm<sup>-1</sup> during heating to room temperature. The sample temperature of each spectrum is given. Each spectrum has an offset of 0.02 for clearer visualization. **b)** Comparison between the irradiated ice at 13 K (top spectrum) and the 300 K residue (bottom spectrum). Vertical dashed lines indicate the frequencies of some vibration modes of zwitterionic glycine (NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>).

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

Frequency (cm <sup>-1</sup> )	Wavelength (μm)	Temp. (K)	Molecule
2233	4.48	13	N <sub>2</sub> O
2218–2200	4.51–4.54	300	nitriles <sup>†</sup>
2168	4.61	13, 300	OCN <sup>-</sup>
2147	4.66	300	aliph. isocyanide <sup>†</sup>
~2112	4.73	300	NCO <sup>†</sup> <sub>2</sub>
1725	5.80	300	ester <sup>†</sup>
1683	5.94	300	amides <sup>†</sup>
1652	6.05	300	asym-N <sub>2</sub> O <sub>3</sub> <sup>†</sup>
1637	6.11	13	?
1593	6.28	300	NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> COO <sup>-†</sup>
1558	6.42	300	?
1533	6.52	300	?
1506	6.64	300	NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> COO <sup>-†</sup>
~1490	6.71	13	NH <sub>4</sub> <sup>+</sup>
1474	6.78	13	NO <sub>3</sub> <sup>†</sup>
1440	6.94	13	NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> COO <sup>-†</sup>
1415	7.07	300	NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> COO <sup>-†</sup>
~1370	7.30	13, 300	HMT <sup>†</sup> HCOO <sup>-</sup>
~1338	7.47	13, 300	NH <sub>3</sub> <sup>+</sup> CH <sub>2</sub> COO <sup>-†</sup> NH <sub>2</sub> CH <sub>2</sub> COO <sup>-†</sup> HCOO <sup>-</sup>
1305	7.66	13	N <sub>2</sub> O <sub>3</sub> <sup>†</sup> ; N <sub>2</sub> O <sub>4</sub> <sup>†</sup>
1283	7.80	300	N <sub>2</sub> O <sup>†</sup>

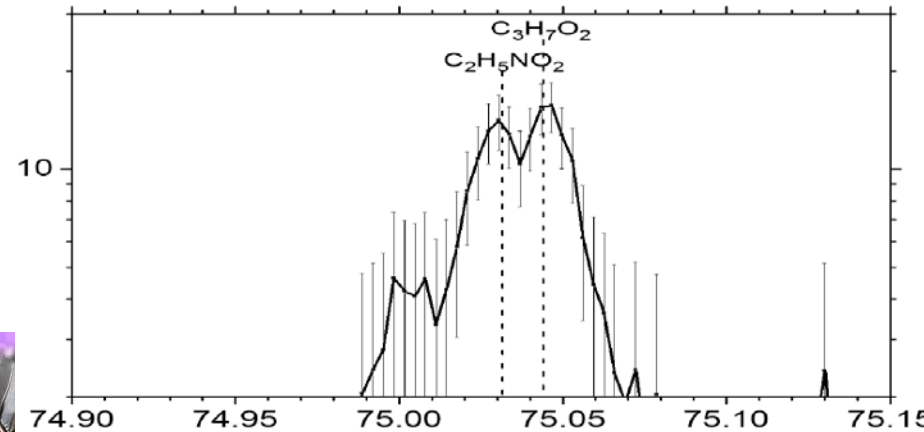
## H<sub>2</sub>O - CO - NH<sub>3</sub> ice

⇒ glycine (amino acid)



Analysis of the **Residues** by **Chromatography**?  
**The amount of residue?**

Prebiotic chemicals  
 amino acid in the coma of  
 comet 67P/Churyumov-Gerasimenko



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

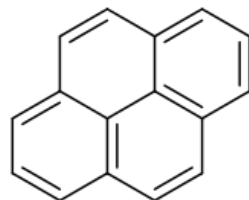
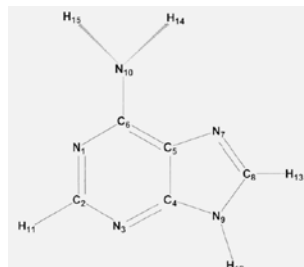
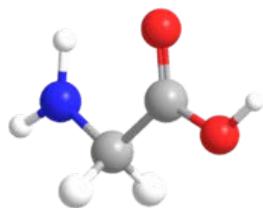
S. Pilling, E. Seperuelo Duarte, E. F. da Silveira, E. Balanzat, H. Rothard, A. Domaracka, P. Boduch  
**Radiolysis of ammonia-containing ices by energetic, heavy and highly charged ions inside dense astrophysical environments**,  
 Astronomy & Astrophysics 509 (2010) A87

*Kathrin Altwegg et al, Space sciences, 2016.*

# Radiation resistance of organic molecules

⇒ Irradiation of ices containing complexe molecules

e.g. glycine, adenine, PAH (Polycyclic aromatic hydrocarbons)



**other materials:**  
carbonaceous, silicates  
**chemistry at interfaces?**

Swift heavy ion irradiation on frozen  $N_2-CH_4$  ices  
relevant to surfaces of Oort Cloud objects :  
toward understanding formation of  
UltraCarbonaceous Antarctic MicroMeteorites

UCAMMs

*AUGÉ Basile's thesis*

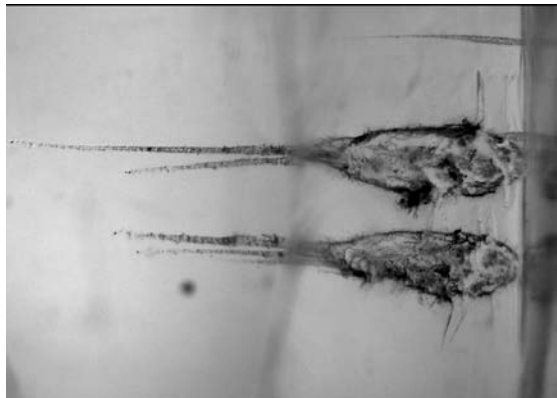
auge@ganil.fr



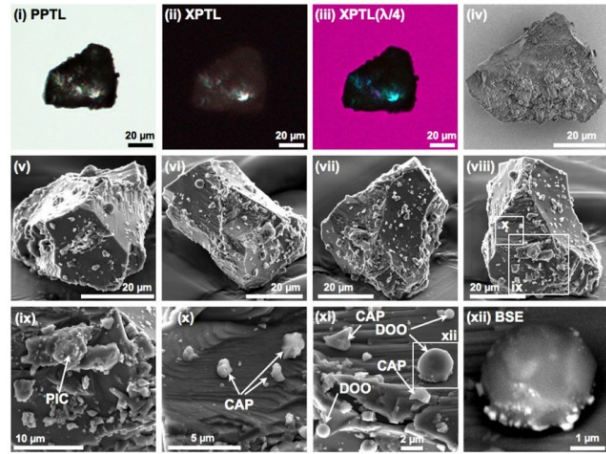


# Extraterrestrial Matter on Earth

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



Impacts from comet 81P/Wild particles (*Stardust*)



Fragments from Itokawa (*Hayabusa 1*)



Orgueil Meteorite (Muséum de Montauban)

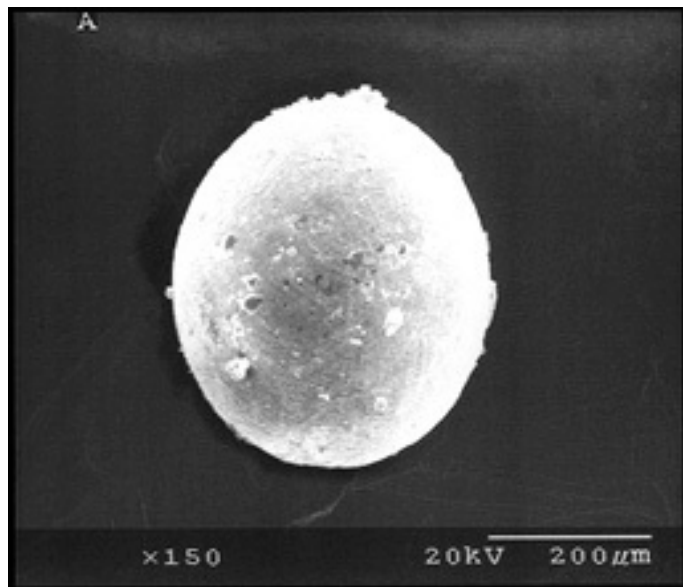
- Stardust : 7 years in space
- Hayabusa 1 : 7 years in space (5 years late)
- About 40 t of meteorites falling on Earth every year
- Dozens of meteorites collected every year

↳ Not enough raw matter

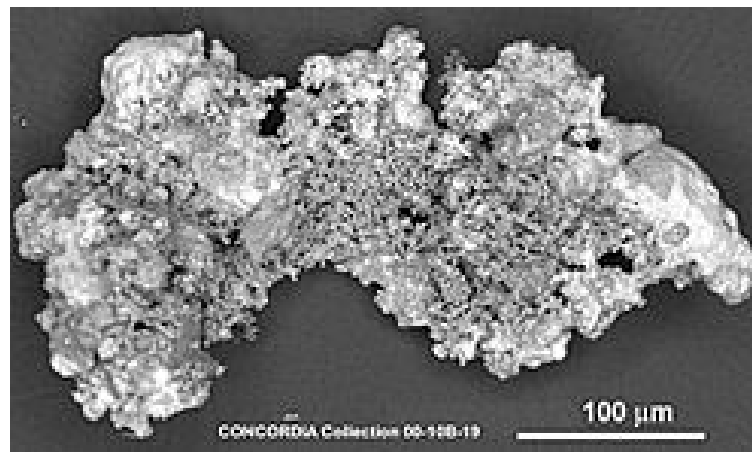
Love et al. 1993



# Extraterrestrial Matter on Earth : Micrometeorites



Micrometeorite (Washington State University)

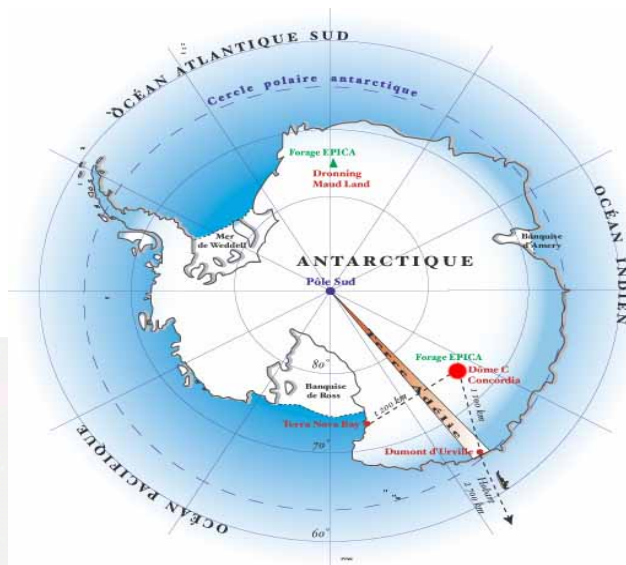


Micrometeorite (CONCORDIA Collection)

- About 40 000 t of mm falling on Earth every year
- About 35 000 impacts by second

Love et al. 1993

# Antarctic micrometeorites



- 1100 km inland, 3200 m elevation
- Katabatic wind
- 3.5 km of ice
- $-80^{\circ}\text{C} < T < -30^{\circ}\text{C}$

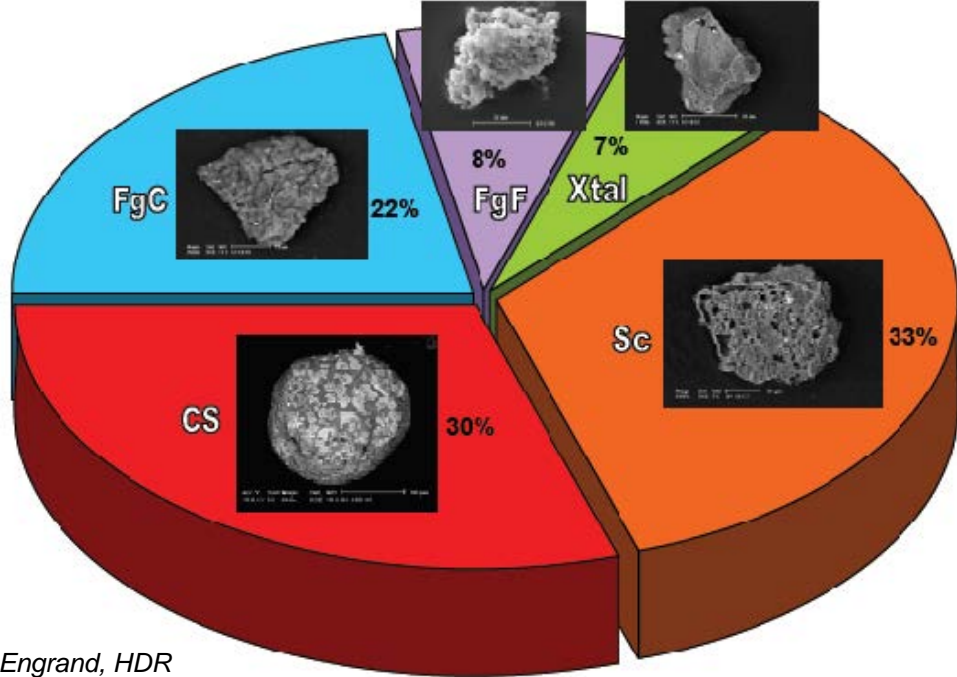


- Low human contamination
- Excellent dust conservation
- Ratio ET/T optimal

**HIGH DISCOVERY POTENTIAL**



# Different types of micrometeorites:



- FgC, fined-grained compact
- Xtal, crystalline
- Sc, scorie
- CS, cosmic spherule
- FgF, fined-grained fluffy

C. Engrand, HDR

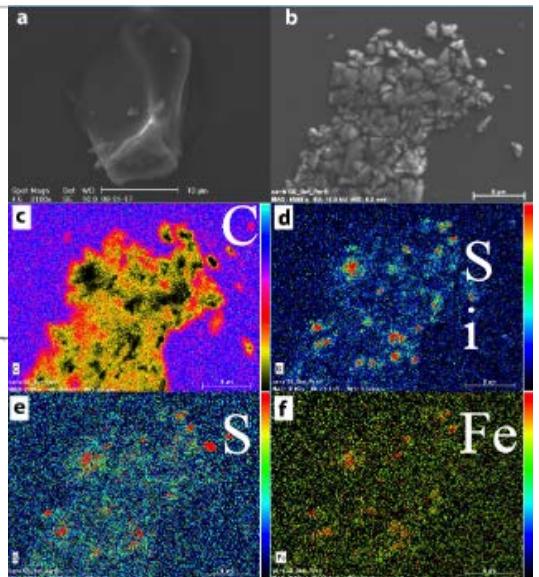
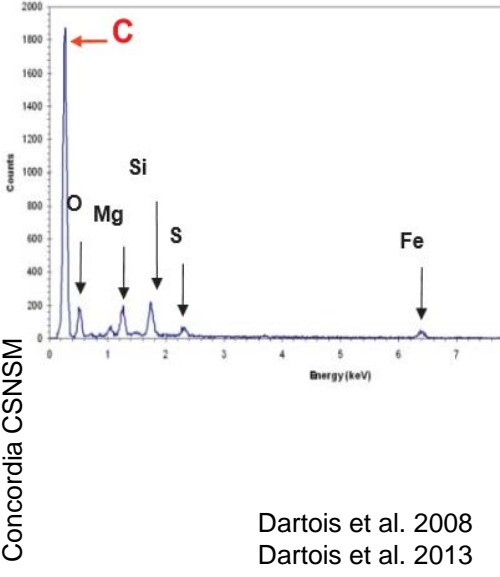
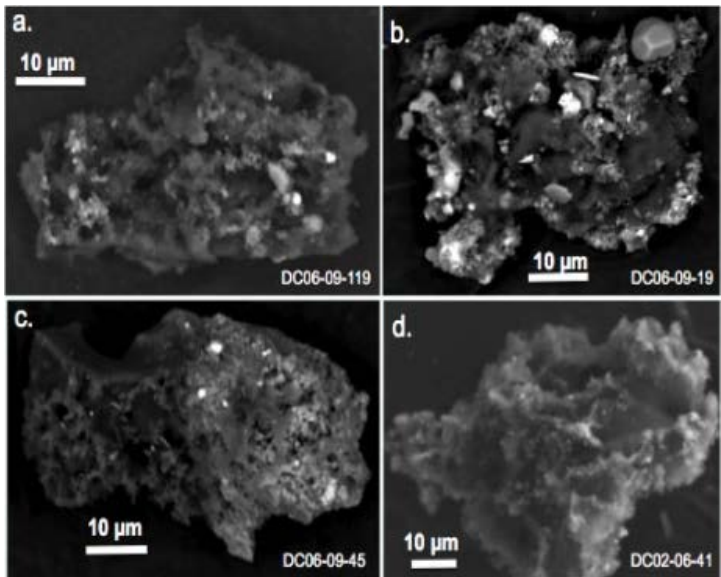
2000 micrometeorites in the CONCORDIA collection



**Ultracarbonaceous micrometeorites** (2% of the FgF)



# UCAMMs (UltraCarbonaceous Antarctic MicroMeteorites)

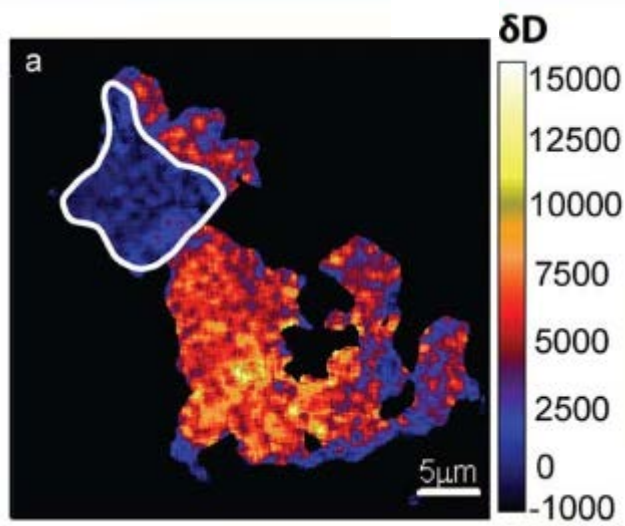


- Up to 65 w% and 50 vol% of carbonaceous matter (C chondrite : 4w%)

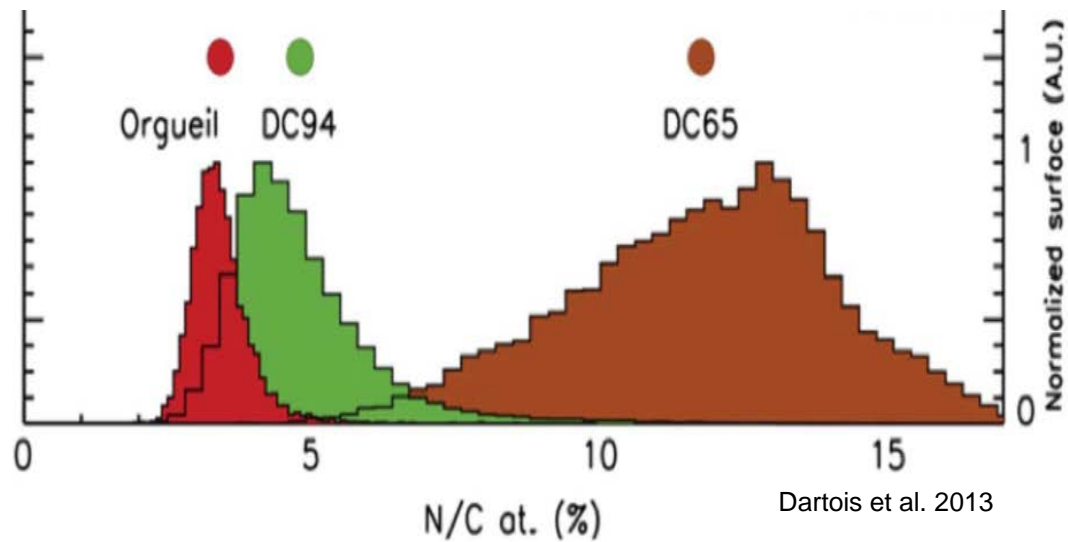


# UCAMMs (UltraCarbonaceous Antarctic MicroMeteorites)

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Duprat et al. 2010



Dartois et al. 2013

- $D/H \sim 10-30 * D/H$



Formation in the cold regions of the protoplanetary disk

Bockélé et al. 1998

And no Oxygen...

- N-rich matter



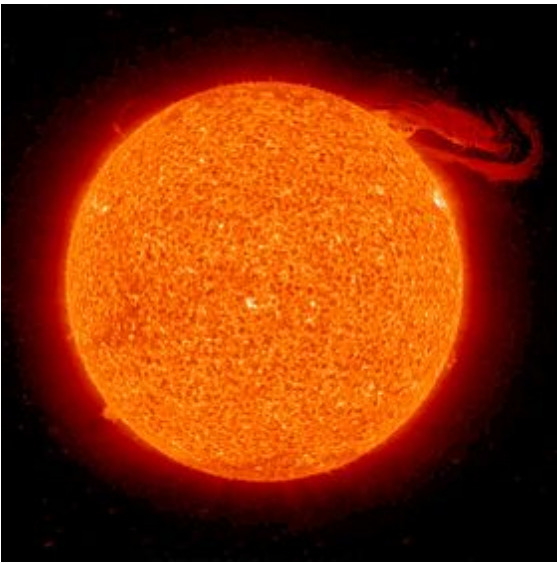
Efficient energy source

Gerakines et al. 2001



# Energy sources in the Solar System

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

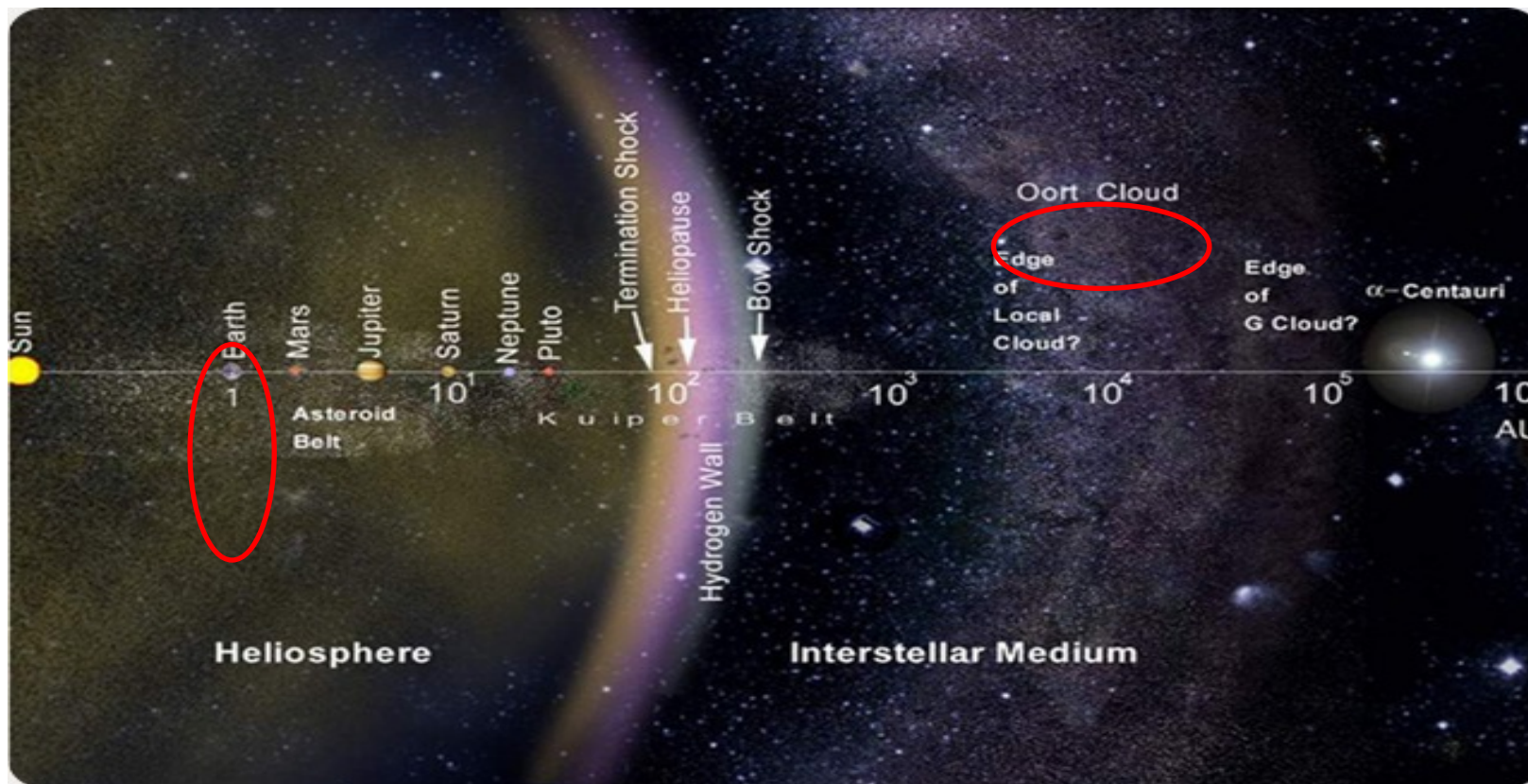


Solar wind



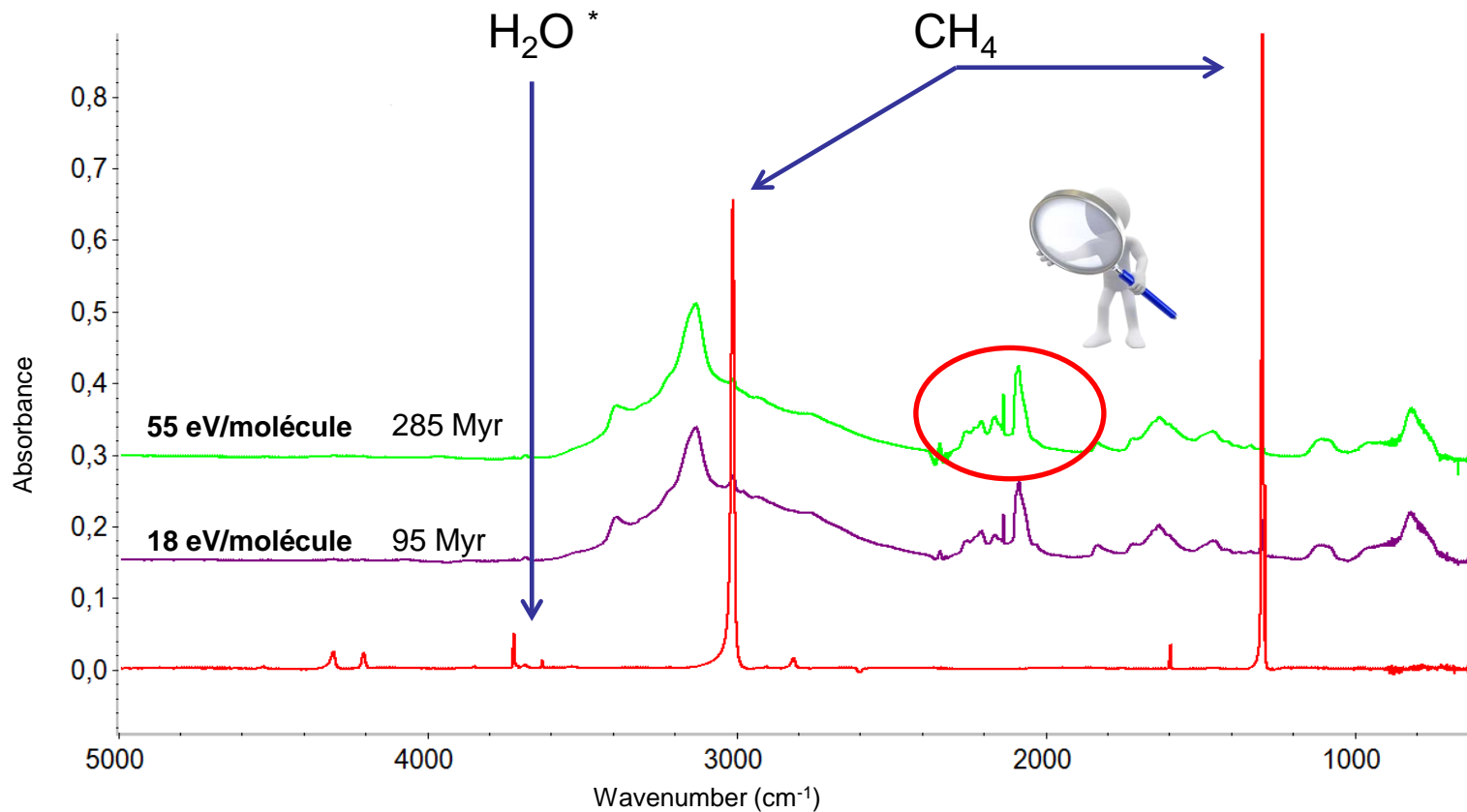
Galactic Cosmic Rays

# UCAMMs (UltraCarbonaceous Antarctic MicroMeteorites)



- Production of N<sub>2</sub>-CH<sub>4</sub> ices relevant to Oort Cloud objects surfaces
- Irradiation on IRRSUD and SME beam lines to simulate GCR irradiation
- *In-situ* FTIR spectroscopy to monitored ices chemical evolution
- Annealing to obtain solid residues at room temperature
- *Ex-situ* analysis of the residues

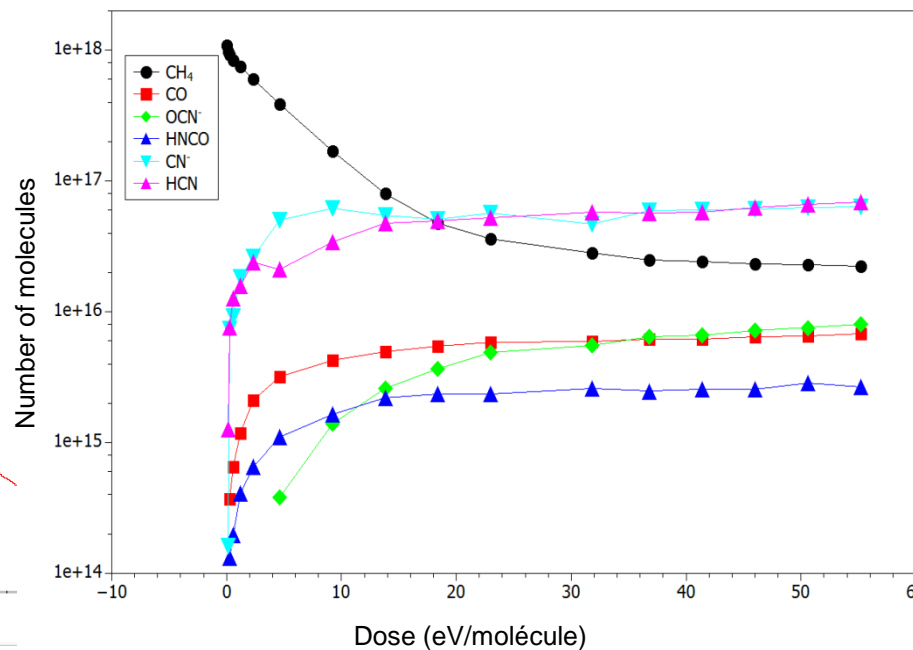
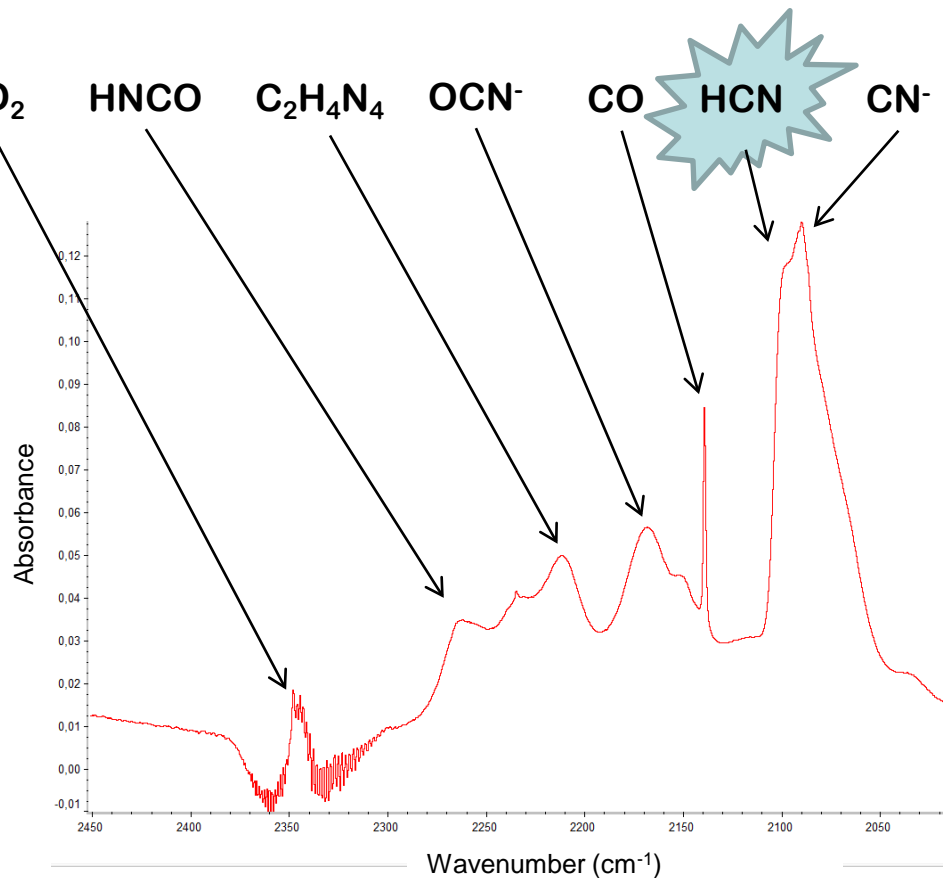
# N<sub>2</sub>-CH<sub>4</sub> (90:10) ices, IRRSUD (Ni<sup>11+</sup>, 44 MeV)



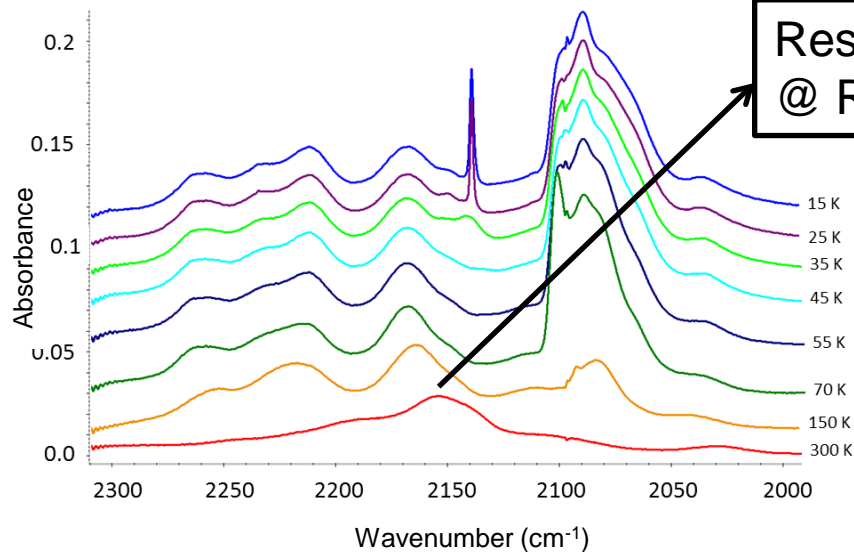
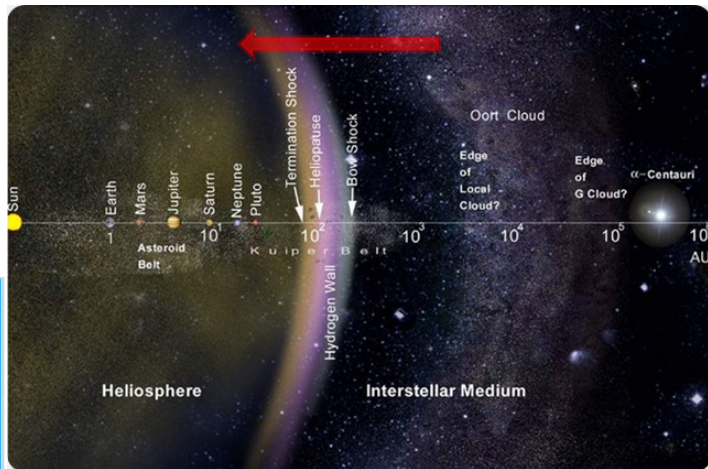
Basile Augé et al, A&A  
accepted 2016



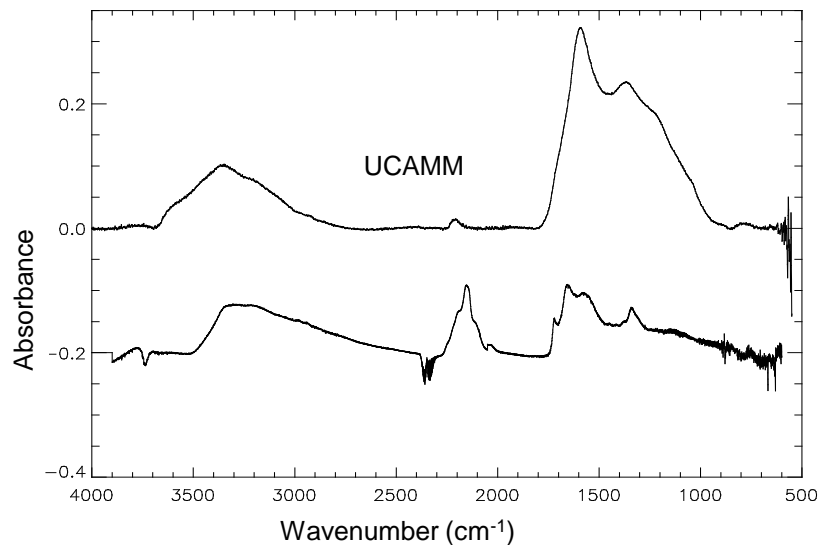
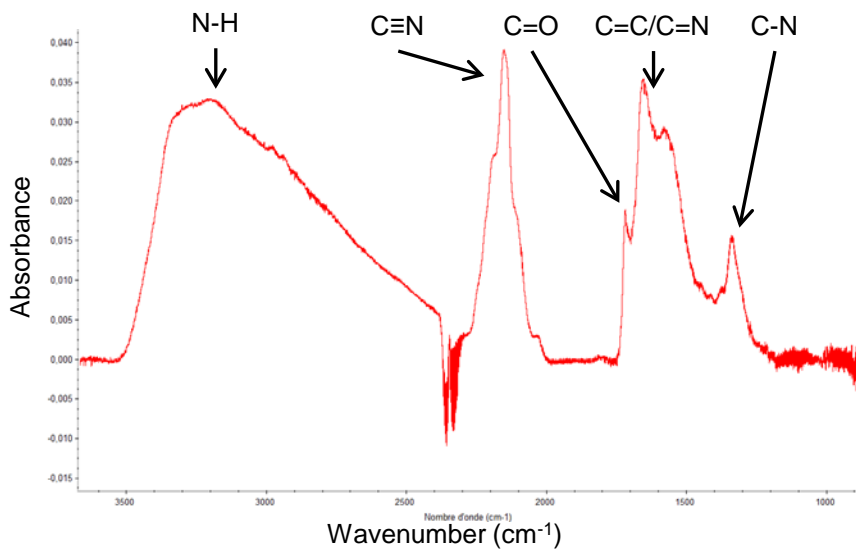
# N<sub>2</sub>-CH<sub>4</sub> (90:10) ices, IRRSUD (Ni<sup>11+</sup>, 44 MeV)



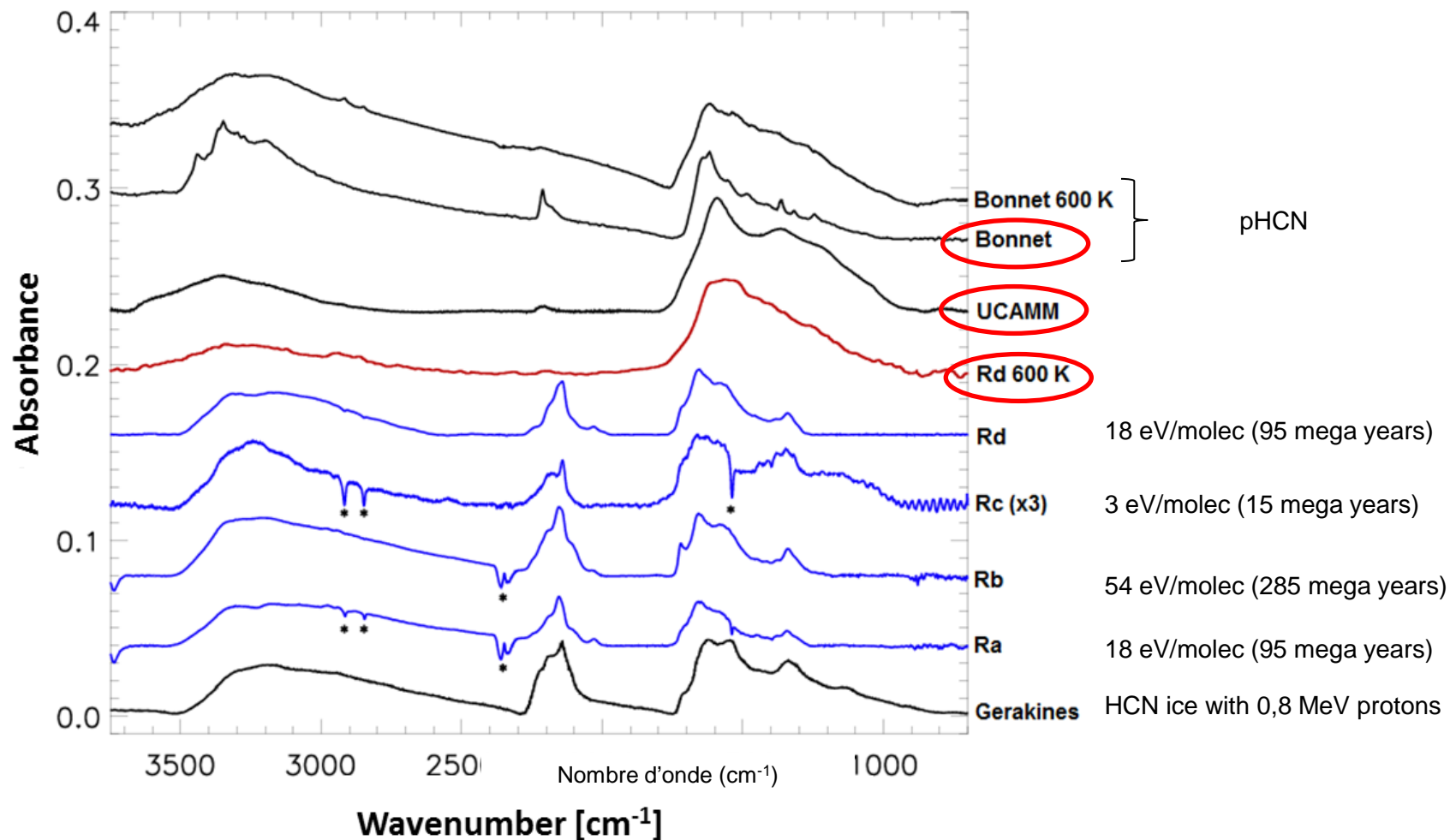
# Residue and UCAMM: comparaison after annealing



Residue @ RT



# Residues analysis : different proportions, different doses, different T

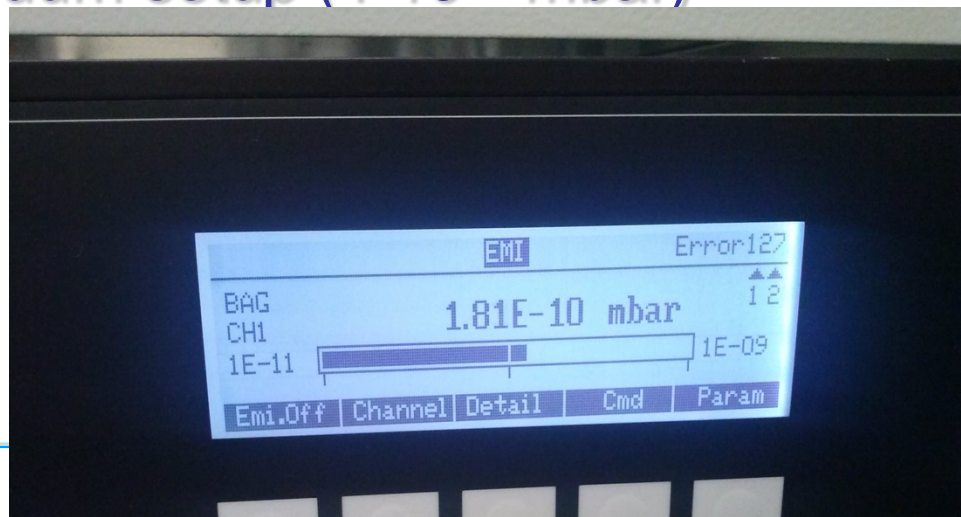


- HCN : the good « material »
- What next ?

➔ Longer irradiation (1 Gy) (nitrile band?)

- With no redeposition of water : (No R-C=O band)

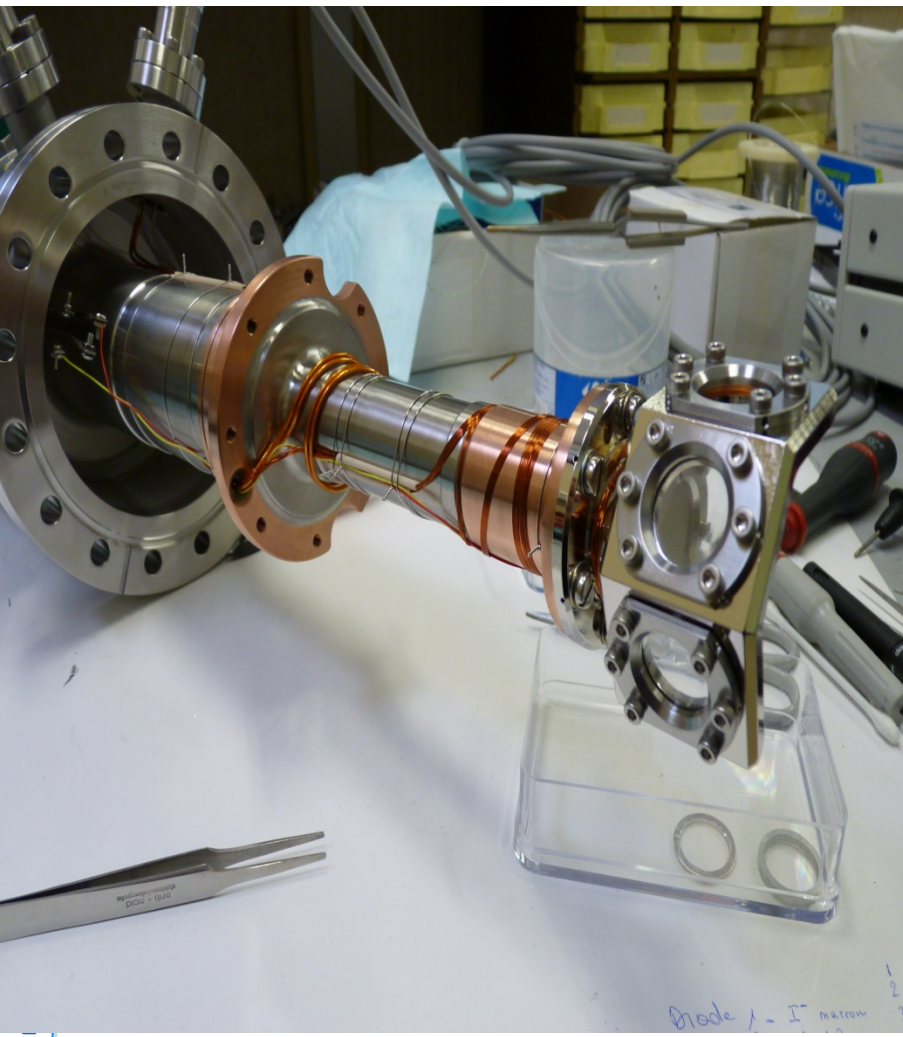
- IGLIAS : new ultra high vacuum setup (1  $10^{-10}$  mbar)

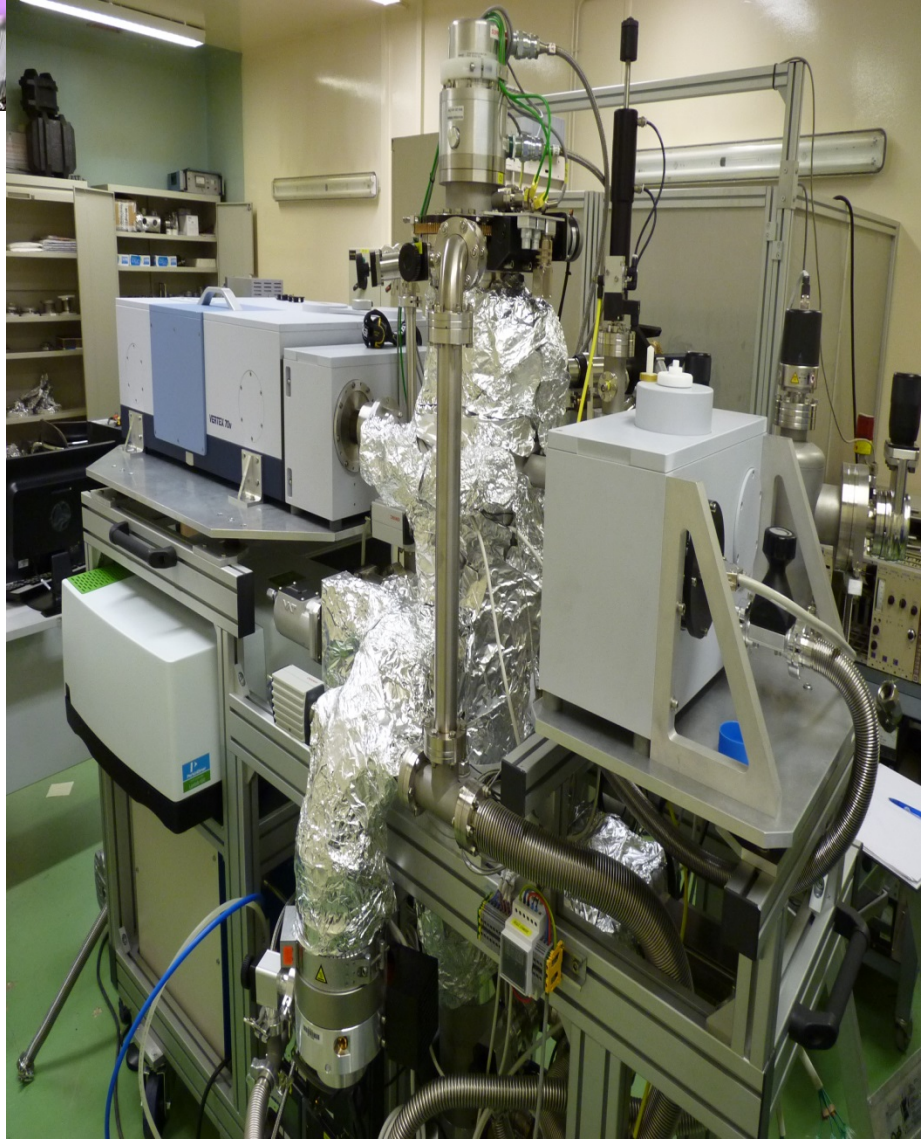
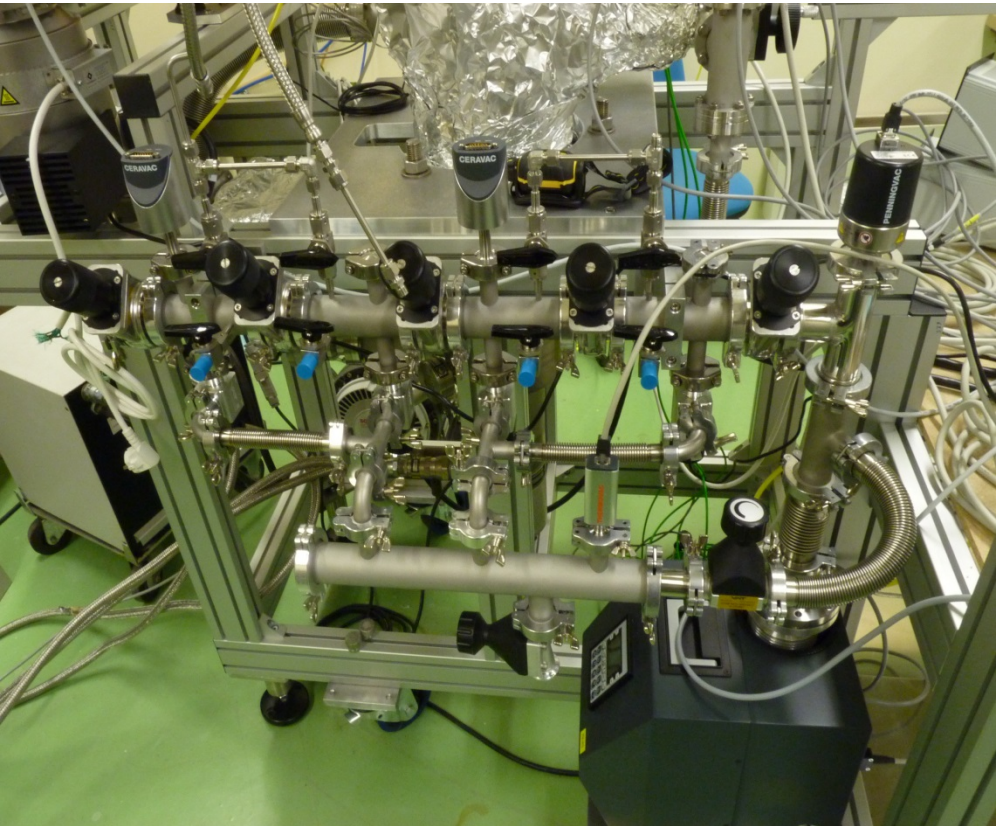




- New system :
- $1 \cdot 10^{-10}$  mbar (1 ML of water per hour)
- Online device with two spectrometers:
  - - IR Bruker V70 (under primary vacuum,  $(500-6000 \text{ cm}^{-1})$ )
  - - UV visible Perkin (200-800 nm, transmission, optical fiber).
  - - for samples: 3 windows, 20 mm diameter (bigger residues).
  - Up to 4 gas for the deposition, co deposition available.
  - QMS, electron gun.
  
- Open to the scientific community!

# Some pictures:





Centre de Recherche sur les Io

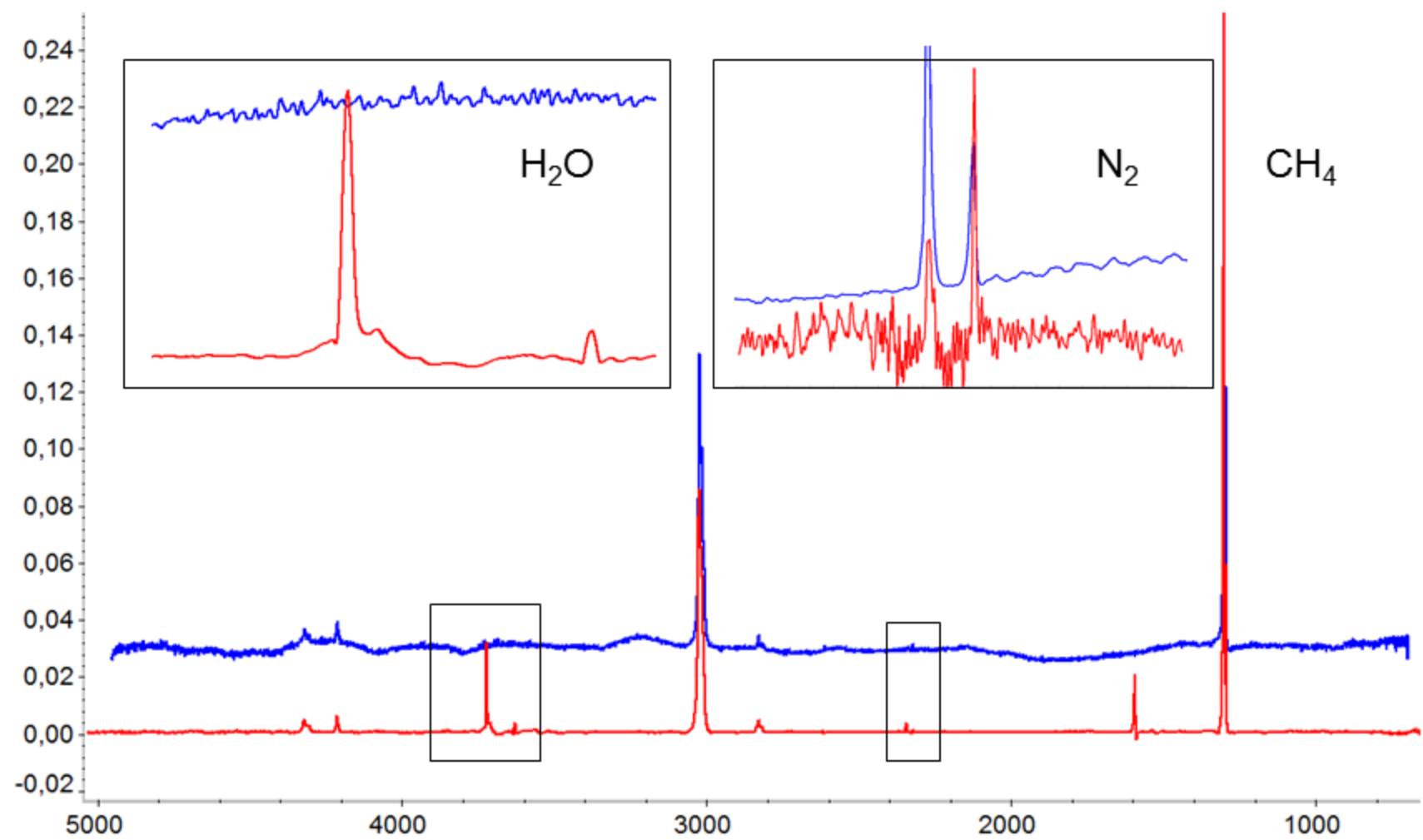
nom

date

réunion

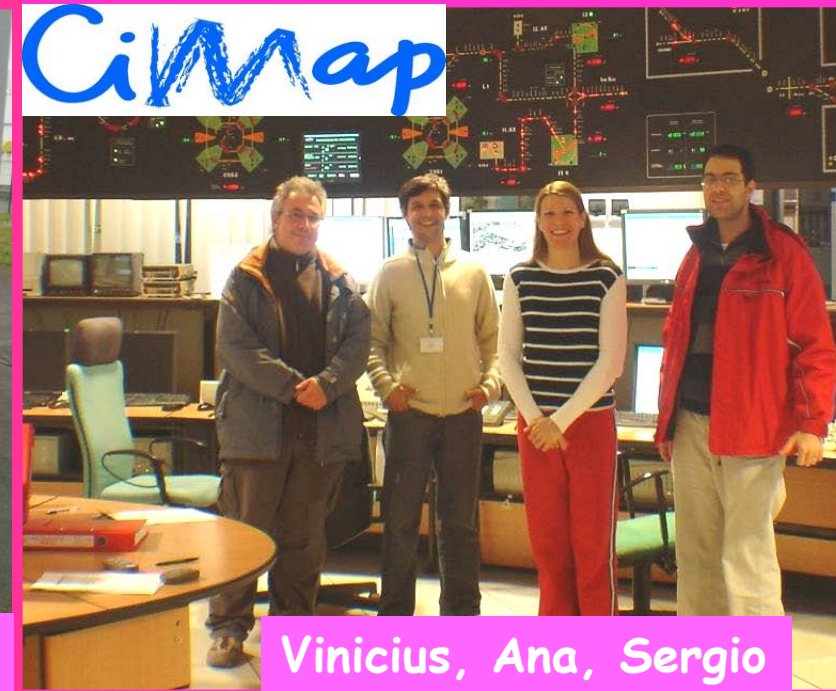


# N<sub>2</sub>-CH<sub>4</sub> (98:2), CASIMIR and IGLIAS



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





Jingjie, Xueyang, Gianni, Thomas,  
Hermann, Philippe, Stéphane

Vinicius, Ana, Sergio



# Thank you

Hussein+Enio

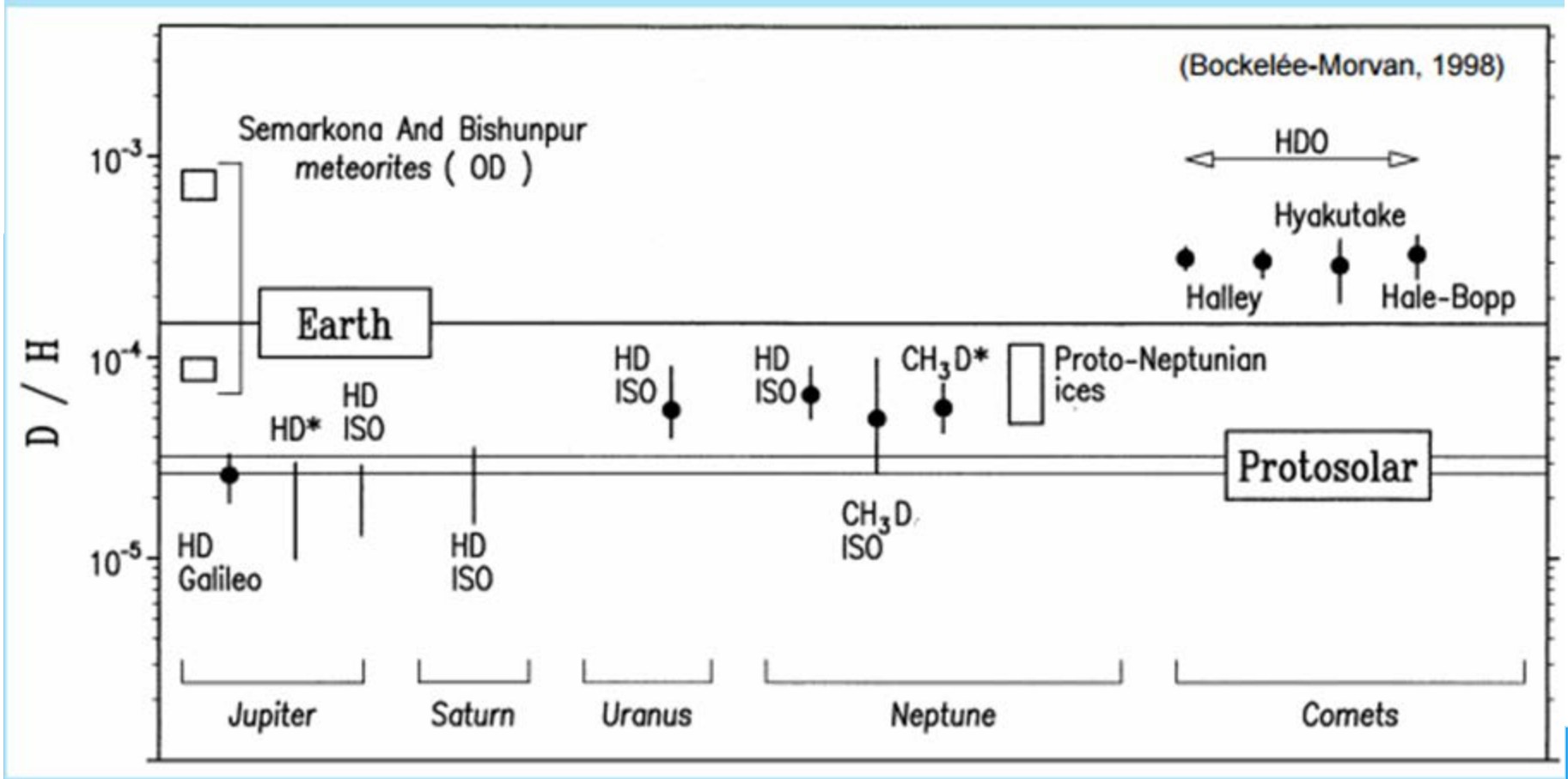
Eduardo



Emmanuel

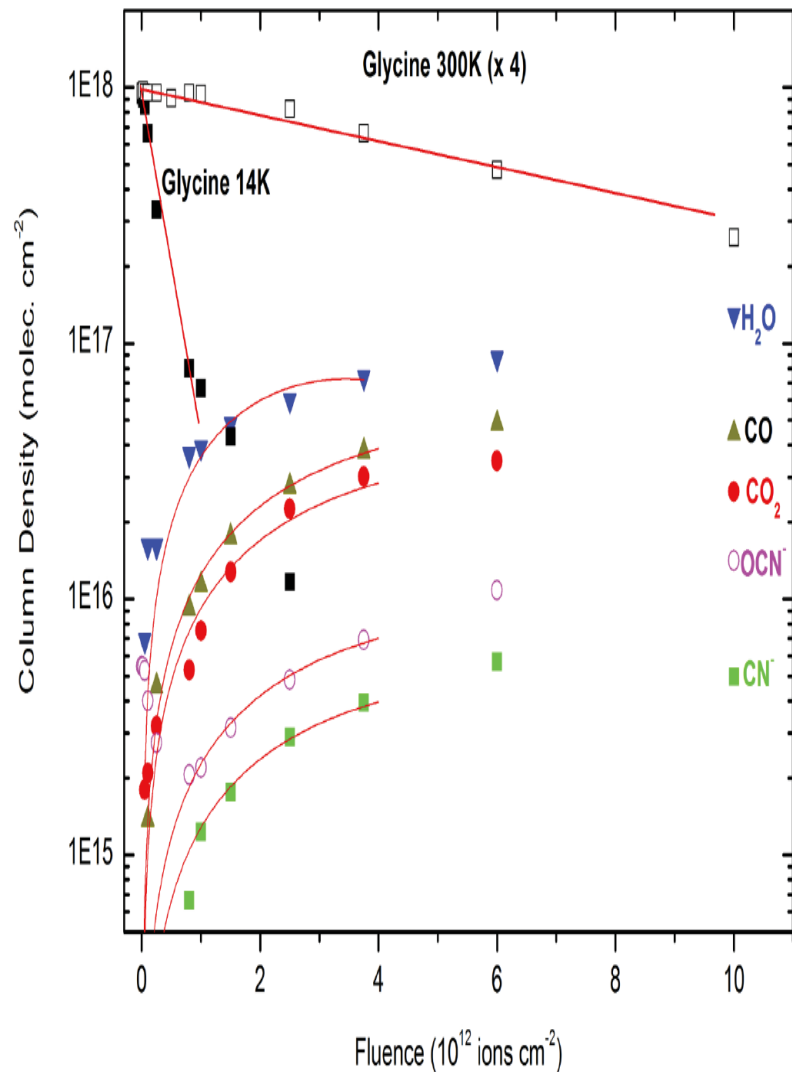
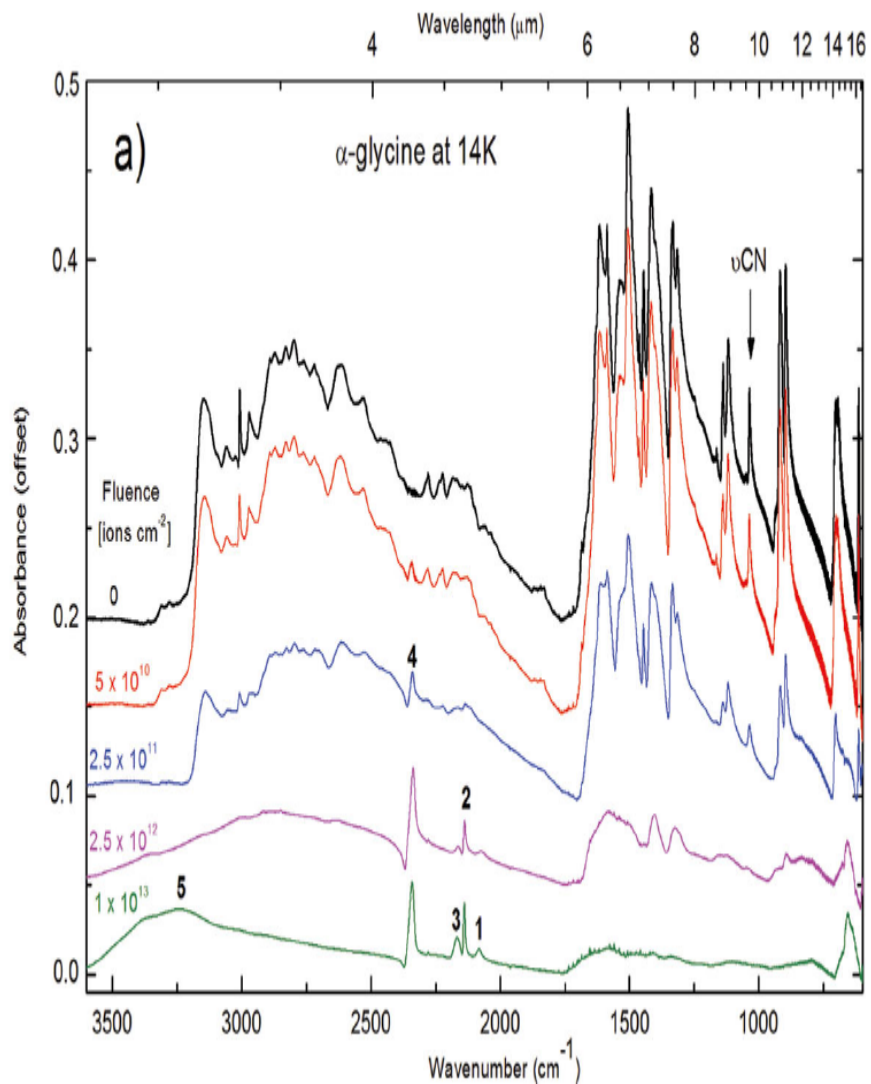


Alicja



# Glycine at 14K and 300 K $^{58}\text{Ni}^{11+}$ @ 46MeV

Curmap



Destruction cross section:

$$\sigma = 2,4 \cdot 10^{-12} \text{ cm}^2 @ 14\text{K}$$

$$\sigma = 3,4 \cdot 10^{-13} \text{ cm}^2 @ 300\text{K}$$

$$\sigma = A S_e^n$$

Temperature (K)	$n$
14	1.3
300	0.5

Temperature effect

