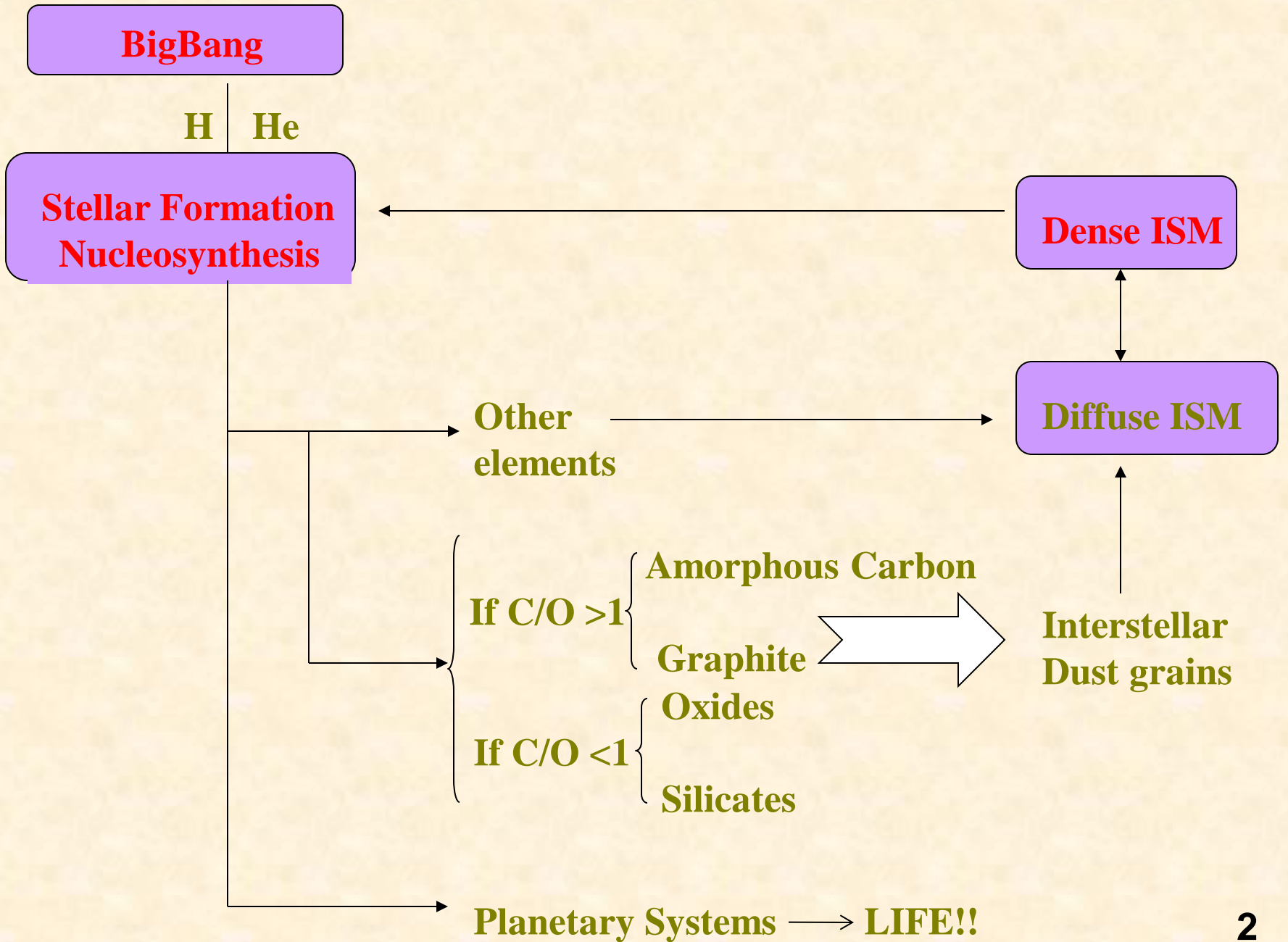


# ***Ion bombardment of materials relevant to Astrobiology***

**Giovanni Strazzulla**  
**INAF – Osservatorio Astrofisico di Catania**

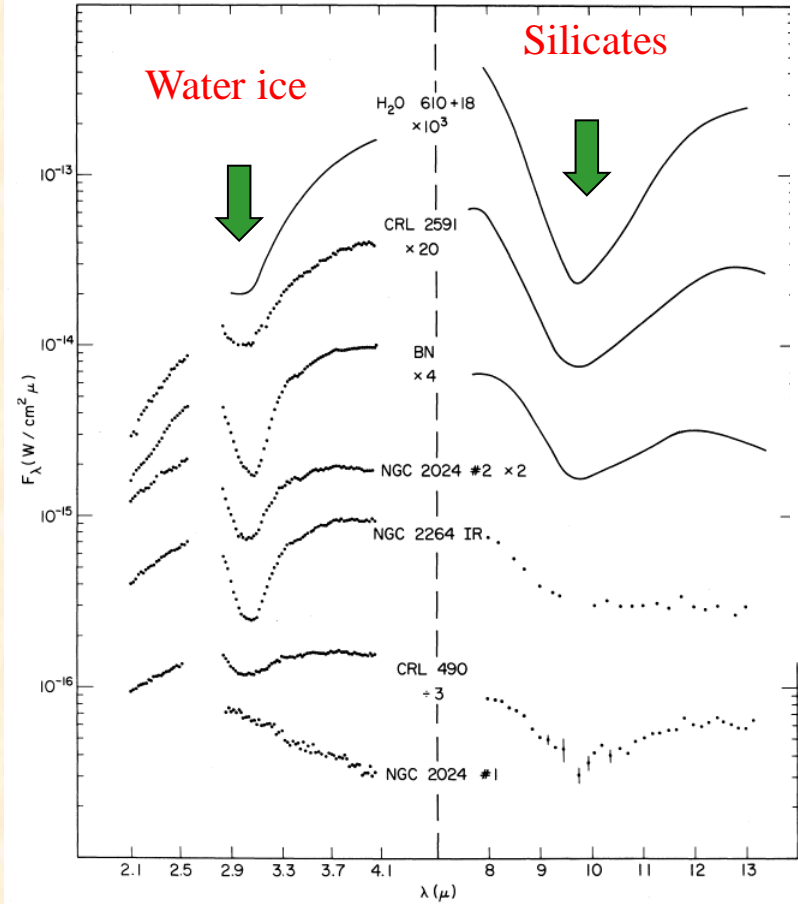
gianni@oact.inaf.it  
<http://web.ct.astro.it/weblab/>



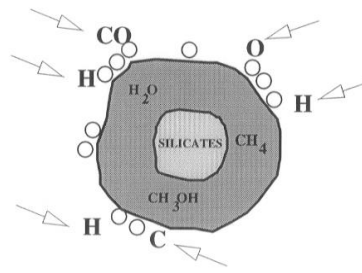
# Solid Materials in Space

	SILICATES	CARBONS	ICES
<u>WHAT:</u>	olivines piroxenes	PAHs graphite Amorphous carbons	H <sub>2</sub> O CO <sub>2</sub> CO NH <sub>3</sub> CH <sub>4</sub> OCS
<u>WHERE:</u>	Interstellar medium (ISM) Circumstellar regions Interplanetary medium Planets and satellites Minor objects (asteroids, comets, TNOs)		

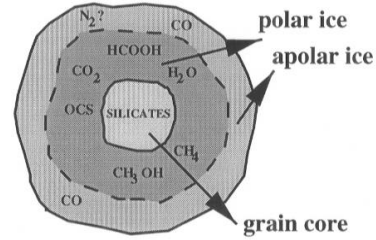
# Dense clouds



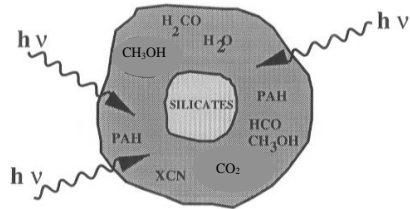
(A)



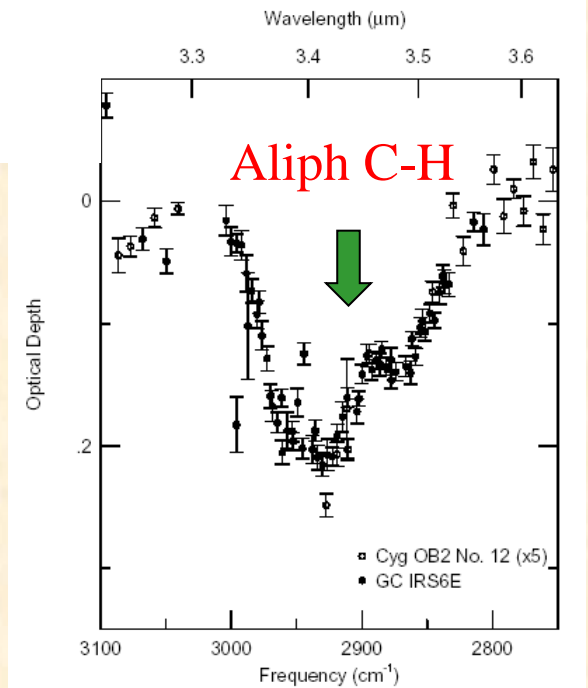
(B)



(C)



# Diffuse clouds



ICES



Table 1: Known Interstellar Molecules

2		3		4	5	6	7	8	9
H <sub>2</sub>	CH <sup>+</sup>	H <sub>2</sub> O	C <sub>3</sub>	NH <sub>3</sub>	SiH <sub>4</sub>	CH <sub>3</sub> OH	CH <sub>3</sub> CHO	CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>3</sub> CH <sub>2</sub> OH
OH	CN	H <sub>2</sub> S	HNC	H <sub>3</sub> O <sup>+</sup>	CH <sub>4</sub>	NH <sub>2</sub> CHO	CH <sub>3</sub> NH <sub>2</sub>	HCO <sub>2</sub> CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> O
SO	CO	SO <sub>2</sub>	HCN	H <sub>2</sub> CO	HCOOH	CH <sub>3</sub> CN	CH <sub>3</sub> CCH	CH <sub>3</sub> C <sub>2</sub> CN	CH <sub>3</sub> CH <sub>2</sub> CN
SO <sup>+</sup>	CS	NNH <sup>+</sup>	CH <sub>2</sub>	H <sub>2</sub> CS	HCCCN	CH <sub>3</sub> NC	CH <sub>2</sub> CHCN	C <sub>7</sub> H	H(CC) <sub>3</sub> CN
SiO	C <sub>2</sub>	HNO	H <sub>2</sub> D <sup>+</sup>	HNCO	CH <sub>2</sub> NH	CH <sub>3</sub> SH	H(CC) <sub>2</sub> CN	H <sub>2</sub> C <sub>6</sub>	H(CC) <sub>2</sub> CH <sub>3</sub>
SiS	SiC	CCS	HOC <sup>+</sup>	HNCS	NH <sub>2</sub> CN	C <sub>5</sub> H	C <sub>6</sub> H	CH <sub>2</sub> OHCHO	C <sub>8</sub> H
NO	CP	NH <sub>2</sub>	NaCN	CCCN	H <sub>2</sub> CCO	HC <sub>2</sub> CHO	c-CH <sub>2</sub> OCH <sub>2</sub>		C <sub>8</sub> H <sup>+</sup>
NS	CO <sup>+</sup>	H <sub>3</sub> <sup>+</sup>	MgNC	HCO <sub>2</sub> <sup>+</sup>	C <sub>4</sub> H	CH <sub>2</sub> =CH <sub>2</sub>	H <sub>2</sub> CC(OH)H		CH <sub>3</sub> CONH <sub>2</sub>
HCl	HF	NNO	AlNC	CCCH	c-C <sub>3</sub> H <sub>2</sub>	H <sub>2</sub> C <sub>4</sub>	C <sub>6</sub> H <sup>+</sup>		
NaCl	SH	HCO	SiCN	c-C <sub>3</sub> H	CH <sub>2</sub> CN	HC <sub>3</sub> NH <sup>+</sup>			
KCl	HD	HCO <sup>+</sup>	KCN	CCCO	C <sub>5</sub>	C <sub>5</sub> N			
AlCl	PO	OCS	MgCN	C <sub>3</sub> S	SiC <sub>4</sub>				
AlF	AlO	CCH	CCP	HCCH	H <sub>2</sub> C <sub>3</sub>	10	11	12	13
PN		HCS <sup>+</sup>	HCP	HCNH <sup>+</sup>	HCCNC	CH <sub>3</sub> COCH <sub>3</sub>	H(CC) <sub>4</sub> CN		H(CC) <sub>5</sub> CN
SiN		c-SiC <sub>2</sub>		HCCN	HNCCC	CH <sub>3</sub> C <sub>5</sub> N			
NH		CCO		H <sub>2</sub> CN	H <sub>2</sub> COH <sup>+</sup>	(CH <sub>2</sub> OH) <sub>2</sub>			
CH				c-SiC <sub>3</sub>	C <sub>4</sub> H <sup>+</sup>				

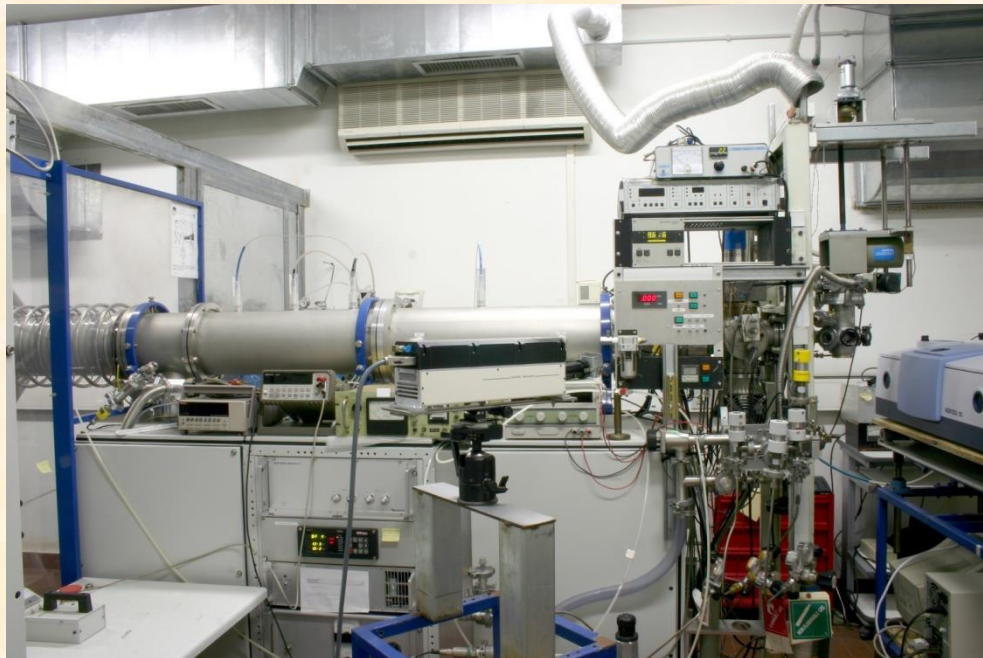
Species	Abundance
H <sub>2</sub> O	100
CO	0 – 40
CO <sub>2</sub>	10 – 25
CH <sub>3</sub> OH	3 – 60
SO <sub>2</sub>	0.3-0.8
OCS	0.04 – 0.1
CH <sub>4</sub>	0.3 – 4
H <sub>2</sub> CO	3 – 7
NH <sub>3</sub>	5 – 10
NH <sub>4</sub> <sup>+</sup>	1-10
OCN <sup>-</sup>	1 – 8

Gas 123

Molecules in Space

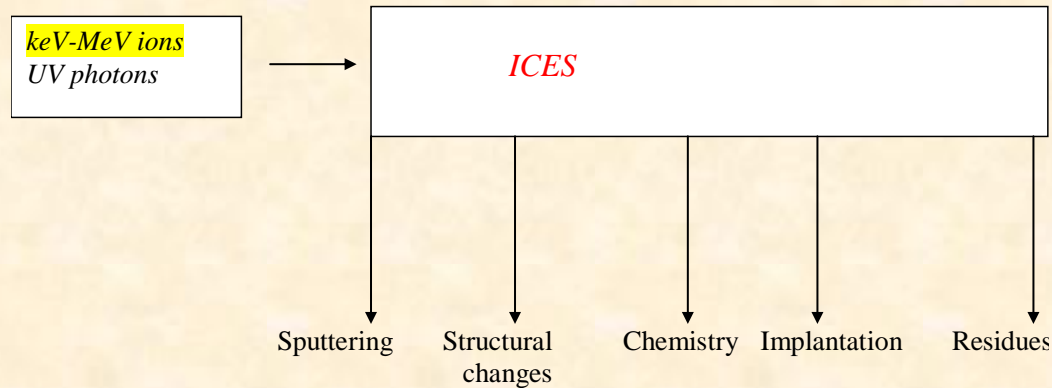


GANIL Laboratories  
(Caen, France)  
Ion Beams: Multi  
Charged; E from a few  
keV to hundreds MeV



LASp (Catania, Italy)  
Ion Beams: 30-400 keV  
singly or double charged

Experimental study of the effects induced by fast ions on solids of astrophysical interest have been performed in several laboratories in the world



Techniques of analysis :

IR Spectroscopy

Raman Spectroscopy

Mass Spectrometry

# Studied materials

ICES:  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ , ...

CARBONS: graphite, amorphous carbons,  
diamond, fullerene, ...

SILICATES: olivine, piroxene, ...

METEORITES: Murchison, Orgueil (carbonaceous)  
Epinal (ordinary condrite)

COSMIC DUST: Stratospheric IDPs, *Stardust*



✓ Synthesis of complex organics → How complex are the molecules synthesized by energetic processing and/or annealing of ices?

# Synthesis of Methyl formate

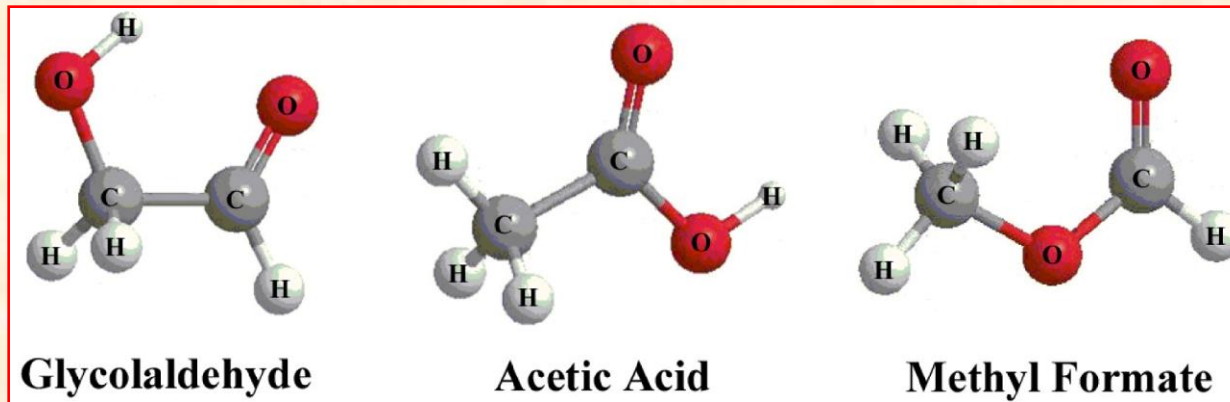
■  $\text{CH}_3\text{OH}:\text{HCOOCH}_3 = 10:1$

■  $\text{HCOOCH}_3$

■  $\text{CH}_3\text{OH}$

■  $\text{CO}:\text{CH}_3\text{OH} = 1.6:1$

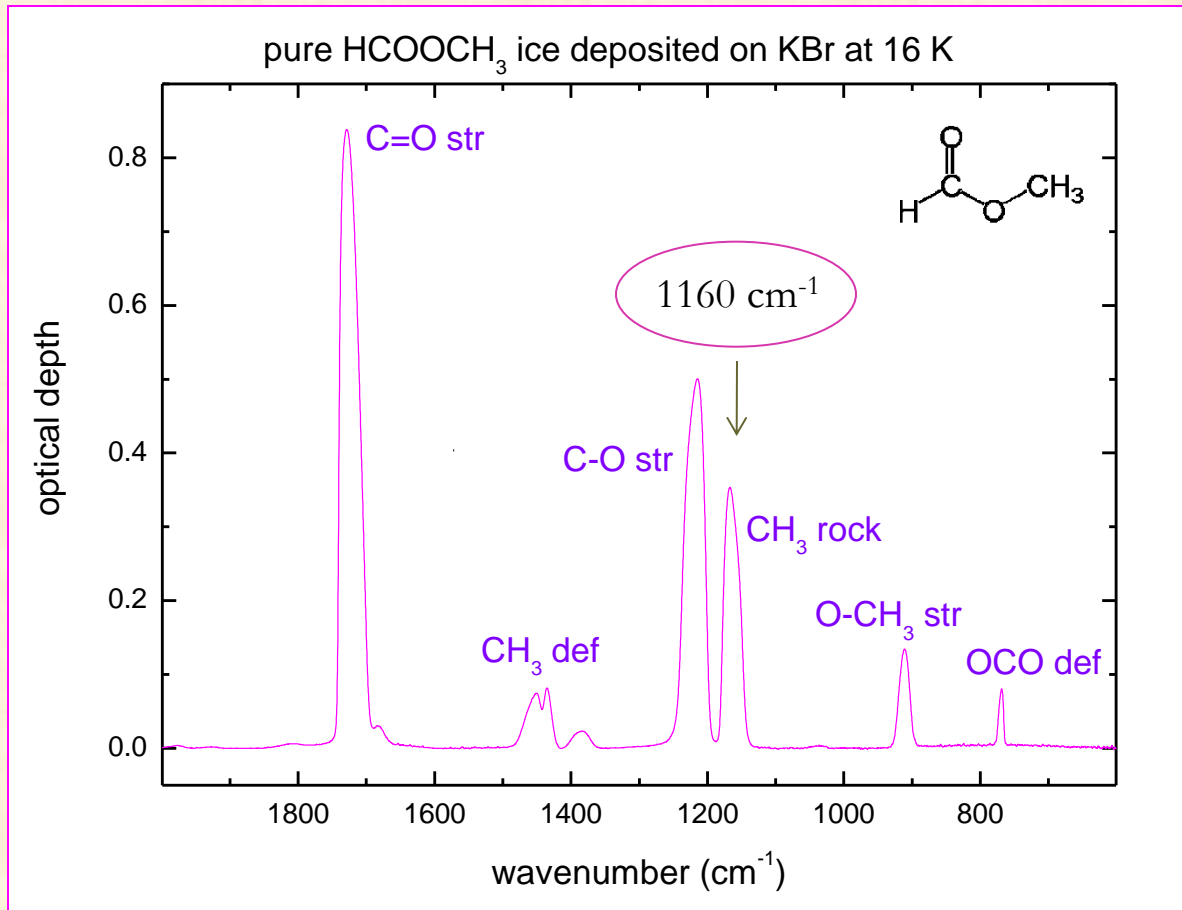
## $\text{C}_2\text{H}_4\text{O}_2$ isomers



**P. Modica, M.E. Palumbo** Formation of methyl formate after cosmic ion irradiation of icy grain mantles, *A&A* 519, A22, 2010

**P. Modica, M.E. Palumbo, G. Strazzulla**, Methyl formate in comets, *PLSpSci* 73, 425, 2012

# Methyl formate mid-IR spectrum



$$\int_{\nu_1}^{\nu_2} \tau_{\nu} d\nu = A \times N$$

$N$  column density (mol/cm<sup>2</sup>)  
 $A$  band strength (cm/mol)  
 $\tau_{\nu}$  optical depth  
 $\nu$  wavenumber (cm<sup>-1</sup>)

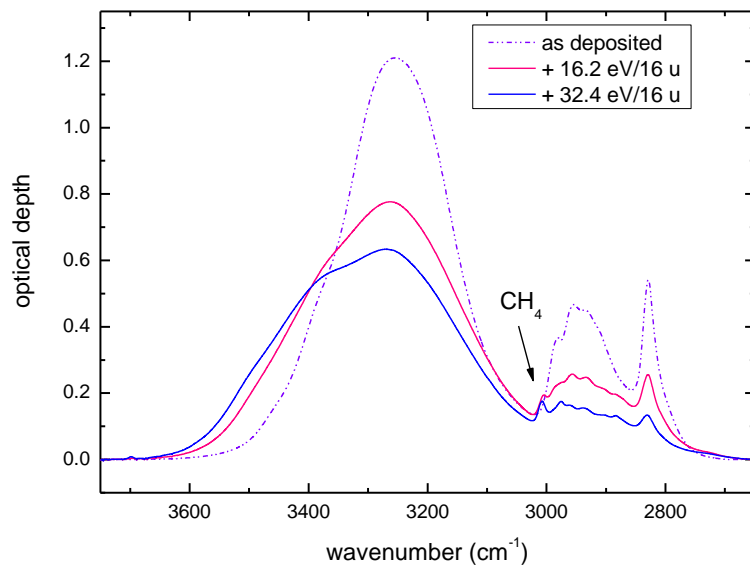
$$N = \frac{\rho s}{\mu}$$

$\rho$  density (g/cm<sup>3</sup>)  
 $s$  thickness (cm)  
 $\mu$  molecular weight (g)

Spectral range: 2000-600 cm<sup>-1</sup> (5-16  $\mu$ m)

# Chemistry on solid CH<sub>3</sub>OH

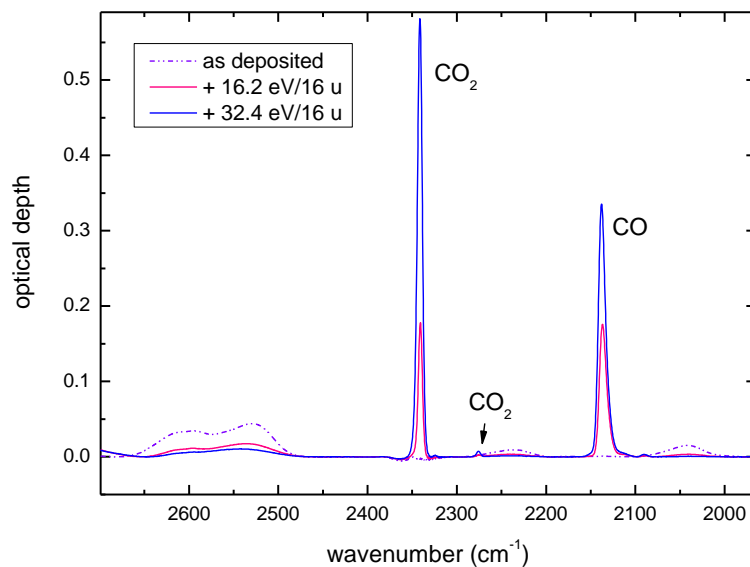
CH<sub>3</sub>OH + 200 keV H<sup>+</sup>



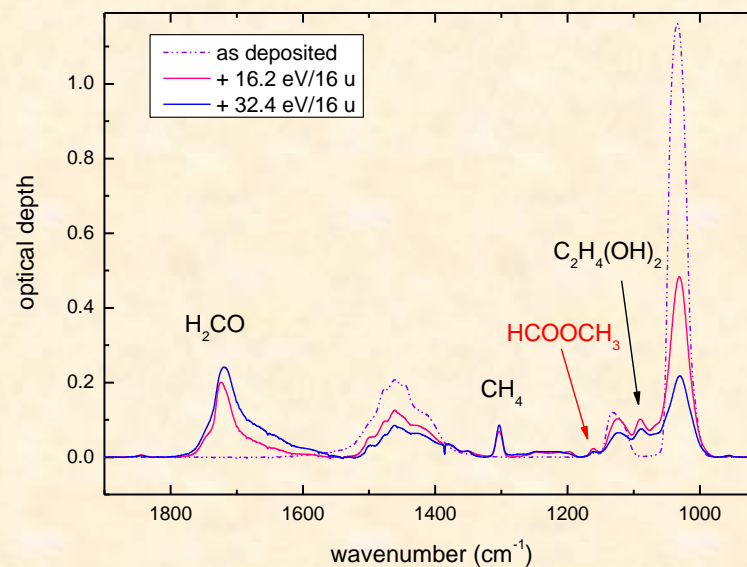
After ion irradiation at 16 K:

- CH<sub>3</sub>OH bands intensity decreases
- New bands appear

CH<sub>3</sub>OH + 200 keV H<sup>+</sup>



CH<sub>3</sub>OH + 200 keV H<sup>+</sup>

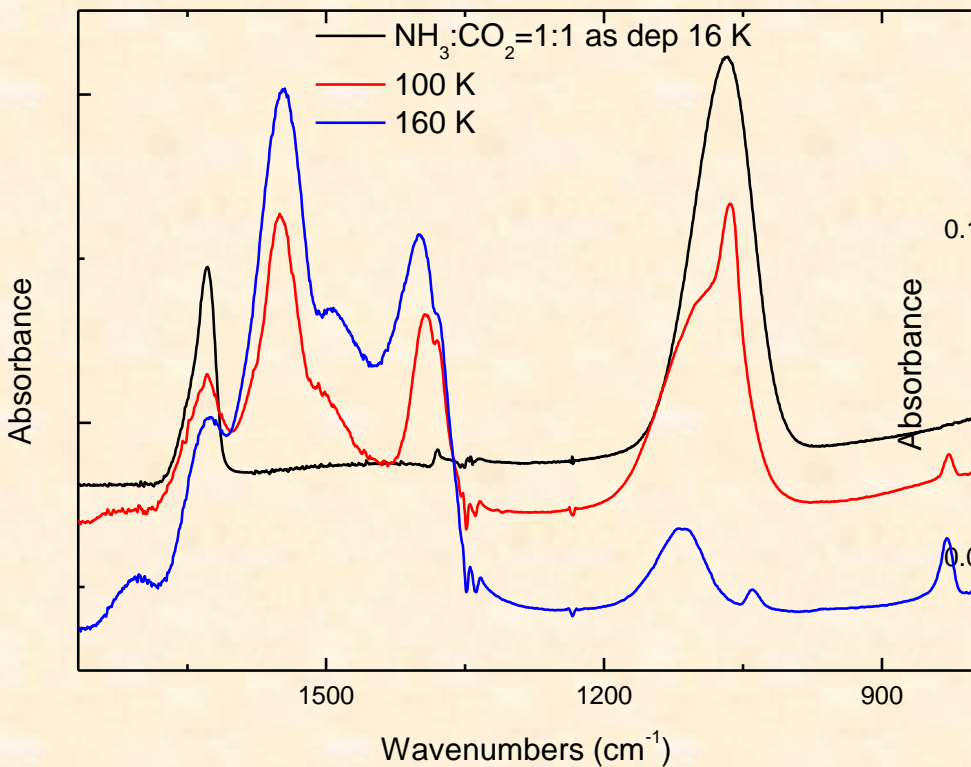


## Thermal and energetic processing of ammonia and carbon dioxide bearing solid mixtures

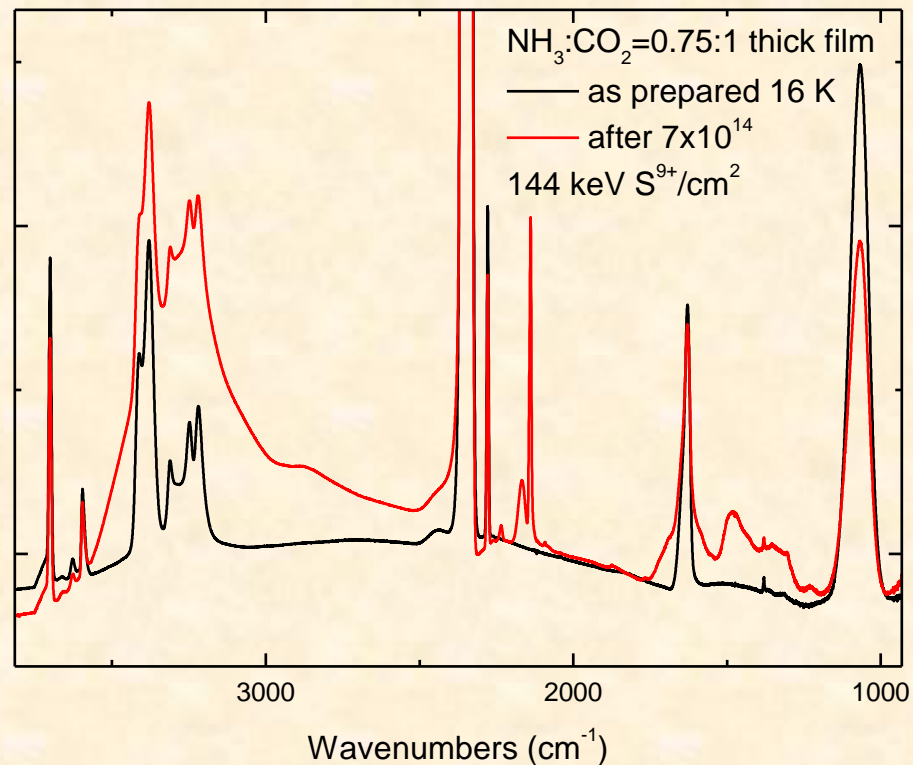
Cite this: *Phys. Chem. Chem. Phys.*,  
2014, 16, 3433

X. Y. Lv,<sup>ab</sup> P. Boduch,<sup>b</sup> J. J. Ding,<sup>b</sup> A. Domaracka,<sup>b</sup> T. Langlinay,<sup>b</sup> M. E. Palumbo,<sup>c</sup>  
H. Rothard<sup>d</sup> and G. Strazzulla<sup>\*c</sup>

### Thermal



### Ion Bombardment



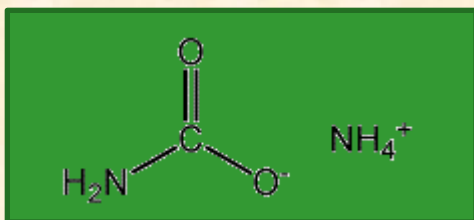
## Thermal and energetic processing of ammonia and carbon dioxide bearing solid mixtures

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2014, 16, 3433

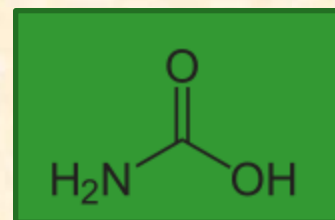
X. Y. Lv,<sup>ab</sup> P. Boduch,<sup>b</sup> J. J. Ding,<sup>b</sup> A. Domaracka,<sup>b</sup> T. Langlinay,<sup>b</sup> M. E. Palumbo,<sup>c</sup>  
H. Rothard<sup>b</sup> and G. Strazzulla<sup>\*c</sup>

# Thermal processing

## Ammonium carbamate

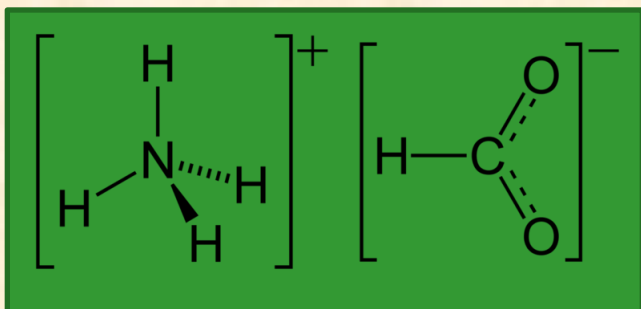


## Carbamic acid (dimer)



# Ion bombardment

## Ammonium formate



←

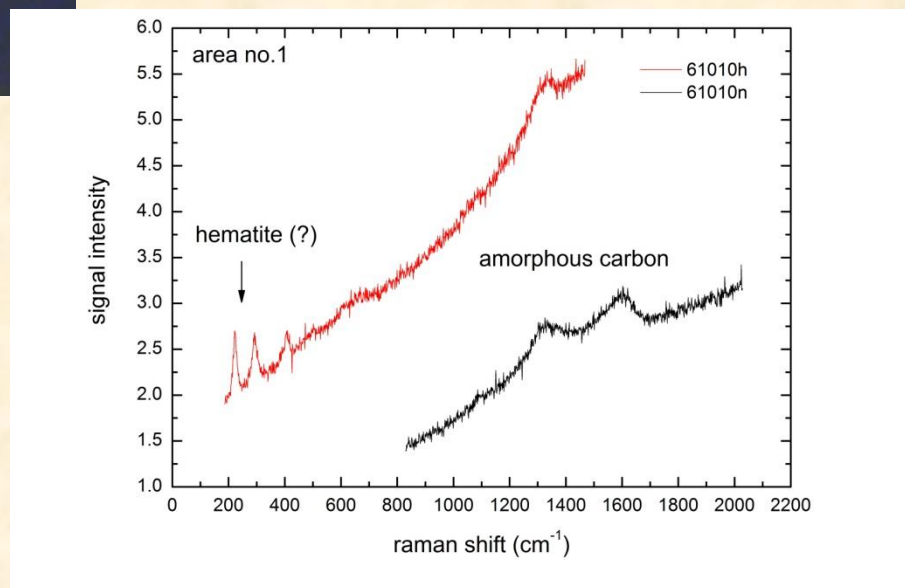
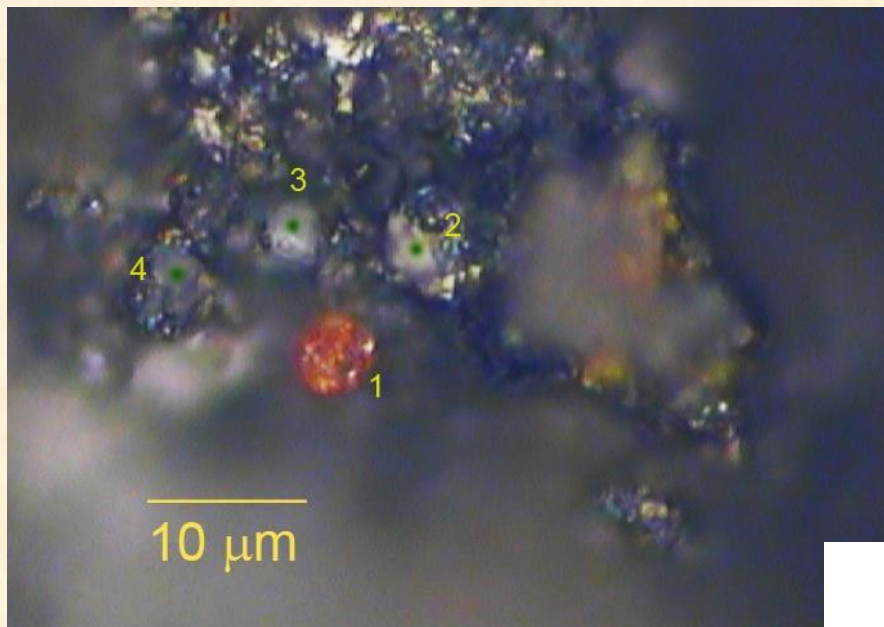
$\text{CO}, \text{OCN}^-$

Do comets/asteroids play a role in delivering biologically relevant material on Earth(s)?

- March 20, 2010 - Found 64 samples of the meteorite (total 3.92 kg)

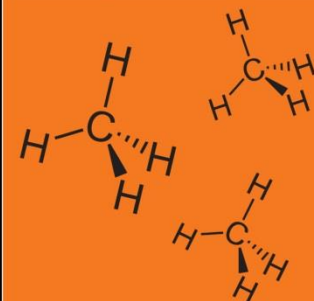
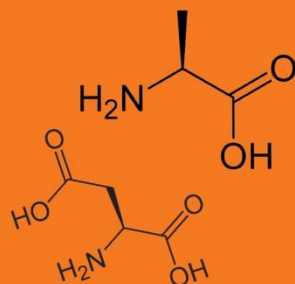
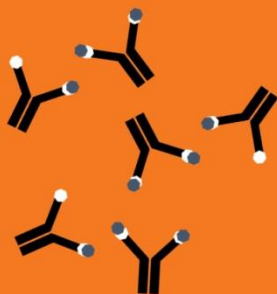




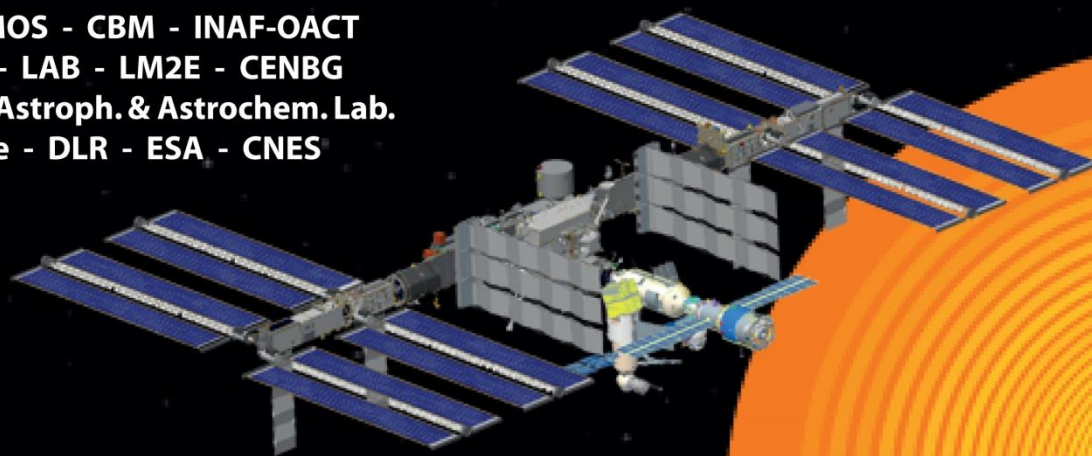


# PSS

## *Photochemistry on the Space Station*



LISA - LATMOS - CBM - INAF-OACT  
IBMM - LIC - LAB - LM2E - CENBG  
NASA Ames Astroph. & Astrochem. Lab.  
SETI Institute - DLR - ESA - CNES



# ION BOMBARDMENT OF COMETARY ICES ANALOGUES: PRODUCTION OF ORGANIC SAMPLES FOR THE EXPOSE-R2 MISSION ON THE INTERNATIONAL SPACE STATION

G. A. Baratta<sup>(1)</sup>, D. Chaput<sup>(2)</sup>, H. Cottin<sup>(3)</sup>, L. Fernandez Cascales<sup>(1)</sup>, M.E. Palumbo<sup>(1)</sup>, **G. Strazzulla<sup>(1)</sup>**

<sup>(1)</sup>INAF-Osservatorio Astrofisico di Catania, Italy

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<sup>(3)</sup>Laboratoire Interuniversitaire des Systemes Atmospheriques (LISA), UMR CNRS 7583, Université Paris Est Creteil et Université Paris Diderot, Institut Pierre Simon Laplace, France

Research supported by the Italian Space  
Agency (ASI)

# “Photochemistry on the Space Station (PSS)”

*Launch : July 23, 2014*

*Exposition will start in October, for 12-18 months*

## **30 samples:**

10 190 nm thick

10 130 nm thick

10 65 nm thick

For each thickness :

**4 will fly on board of the ISS**

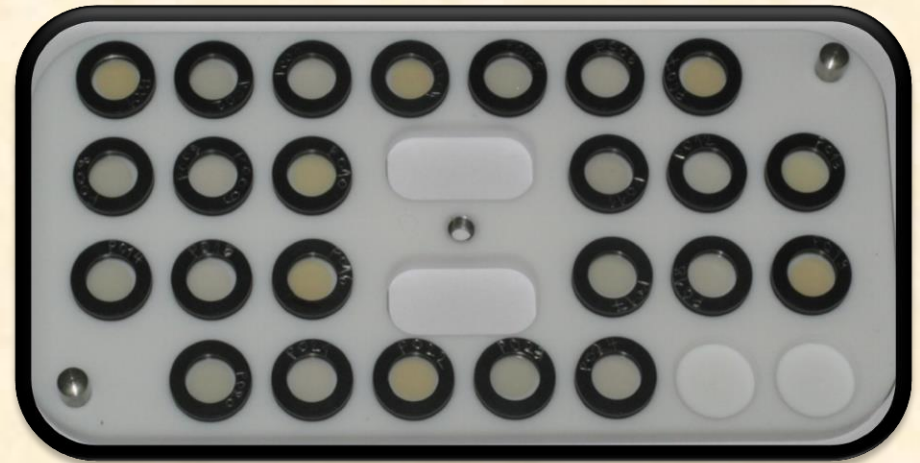
*2 exposed & 2 kept inside*

**6 sent to the ESA laboratories**

*2 in vacuum and same T variations as the ISS exposed ones*

*2 in vacuum and at room temperature*

*2 exposed to visible - near UV electromagnetic radiation*



**MgF<sub>2</sub> windows with organic samples**

**Additional samples will be exposed to vacuum UV (mostly Ly-alfa) photons in our laboratory**

# SAMPLE PREPARATION

## Deposition of frozen gases $N_2:CH_4:CO$

**experimental apparatus:** a stainless steel ultra high-vacuum chamber

**pressure:** lower than  $10^{-9}$  mbar

**cold finger:** 16-300 K

## Irradiation of frozen $N_2:CH_4:CO$ (1:1:1)

**irradiation:** 200 keV helium ion beams

**beam current density:**  $2 \times 10^{-1} \mu A cm^{-2}$

**energy received by each of the 30 samples:**

$110 \pm 5 eV/16u$



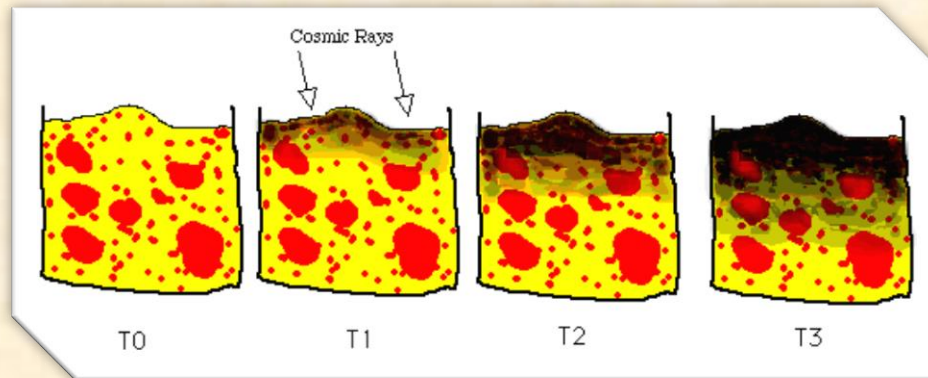
Picture of the cold finger with the  $MgF_2$  window used as substrate

**Warm up to room T and extraction of the residues**

# Irradiation effects on comets and TNOs

The surfaces of all the atmosphereless Solar System bodies are continuously irradiated by energetic ions from the Sun and the Galaxy.

Modification of the spectral signatures:  
band intensity, profile (shape, width, peak position), color etc.



# The Rosetta Mission



-Was approved in November 1993 by ESA

-‘The target is comet 67 P/Churyumov-Gerasimenko.

-During its 10 year journey towards the comet, the spacecraft has passed by two asteroids: 2867 Steins (in 2008) and 21 Lutetia (in 2010).

-The spacecraft entered deep-space hibernation mode in June 2011.

-On 20 January 2014 at 18:18 UTC, a signal was received by NASA's Goldstone and Canberra ground stations: hibernation exit sequence had been completed.

-----

-Arrived at comet August 2014

-Started global mapping August 2014

-Lander delivery November 2014

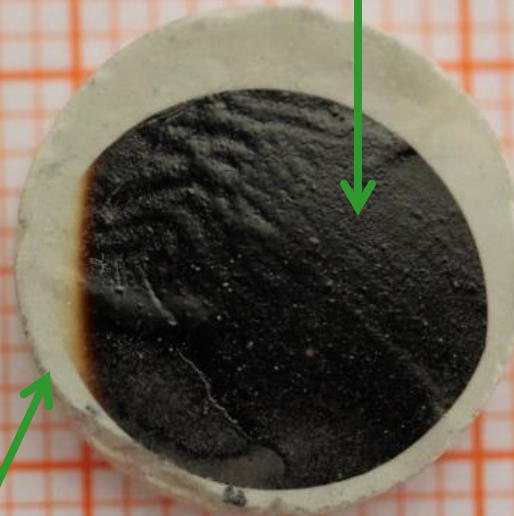
-Perihelion passage 13 August 2015

-End of mission 31 December 2015<sup>23</sup>

# Polystyrene film deposited on olivine

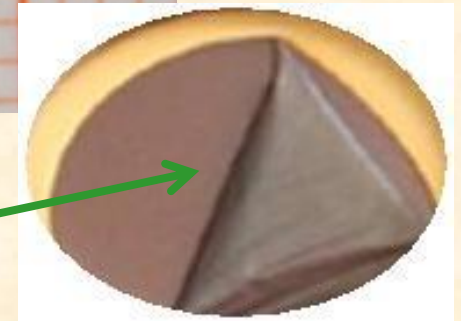
After 200 keV  $H^+$   
Irradiation

After 400 keV  $Ar^{++}$   
Irradiation



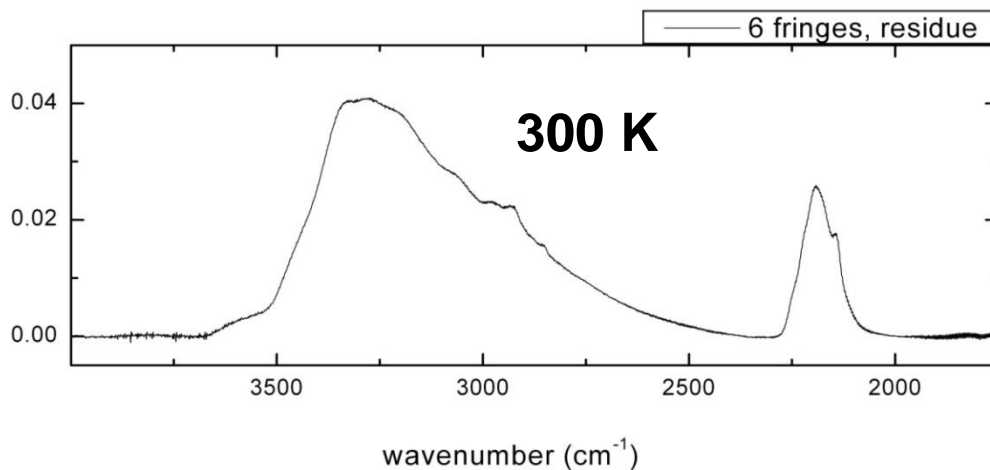
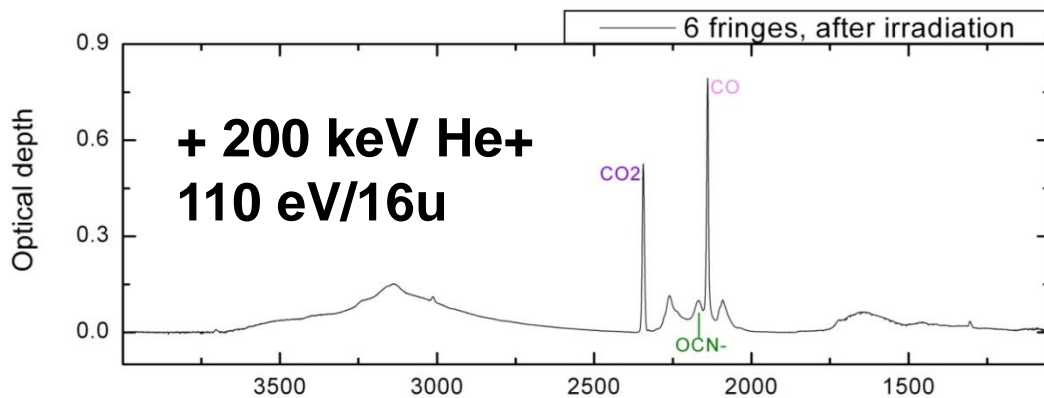
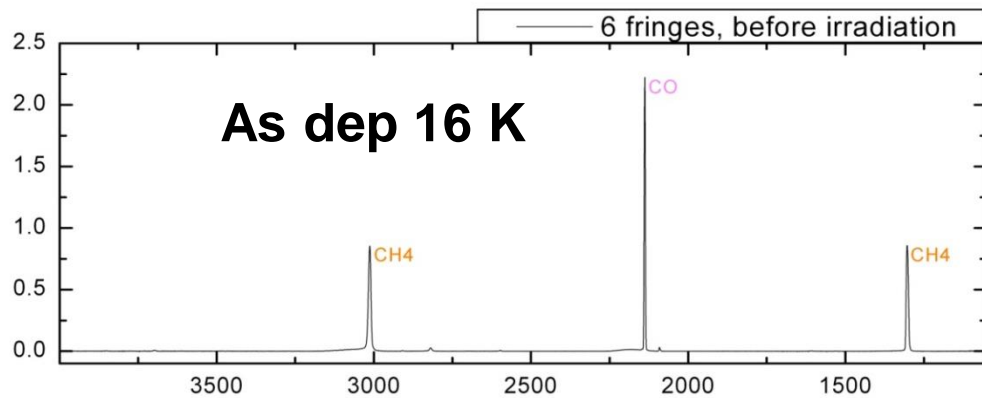
Unirradiated area

After 200 keV  $H^+$   
Irradiation of frozen methane





# $N_2:CH_4:CO$ (1:1:1)



CH<sub>4</sub>: 1302 cm<sup>-1</sup>

CO: 2140 cm<sup>-1</sup>

CH<sub>4</sub>: 3010 cm<sup>-1</sup>

CO<sub>2</sub>: 2340 cm<sup>-1</sup>

OCN<sup>-</sup>: 2167 cm<sup>-1</sup>

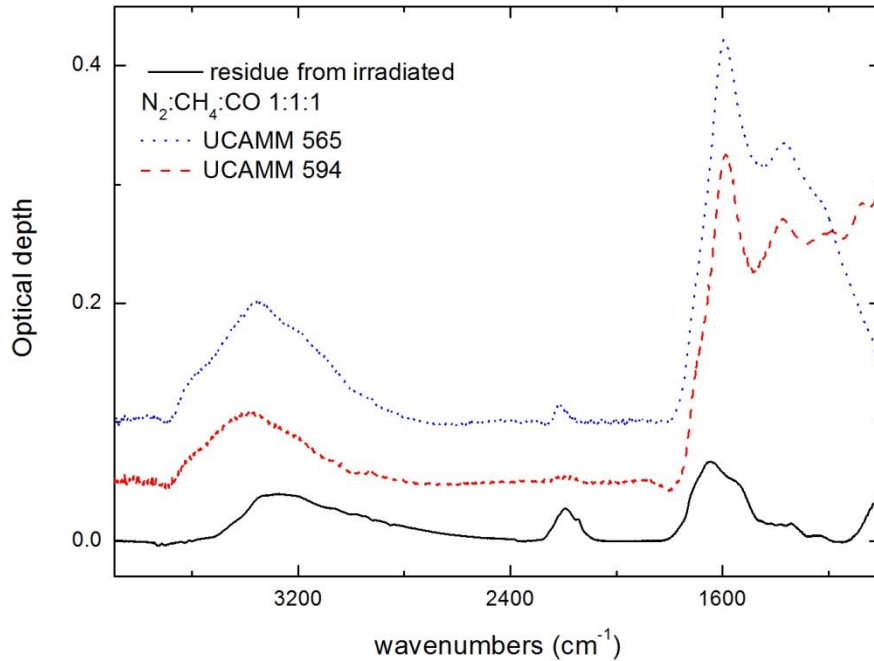
CO: 2140 cm<sup>-1</sup>

300 K  
from 3600 to 2400 cm<sup>-1</sup>:  
C-H, O-H & N-H groups

At about 2200 cm<sup>-1</sup> :  
CN double & triple bonds

**N<sub>2</sub>:CH<sub>4</sub>:CO**: representative of ices present on the surfaces of comets and TNOs

Comets release organic materials (thought to be similar to the present ones) when near to the Sun



The spectra of ultracarbonaceous antarctic meteorites are courtesy of E. Dartois and C. Engrand ([Dartois et al 2013, Icarus 224, 243](#))

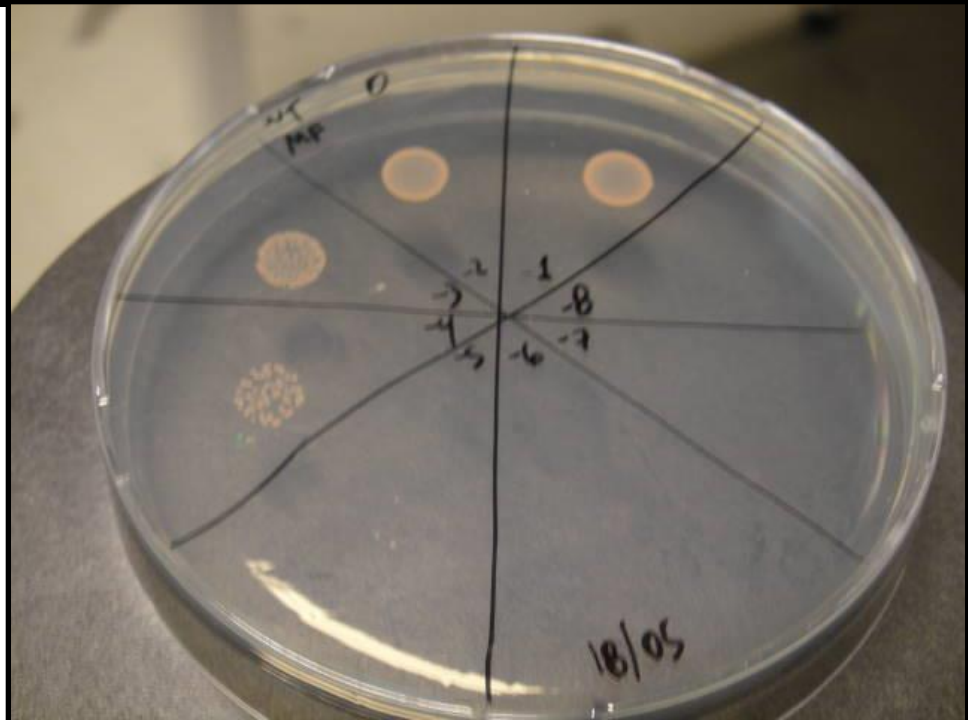
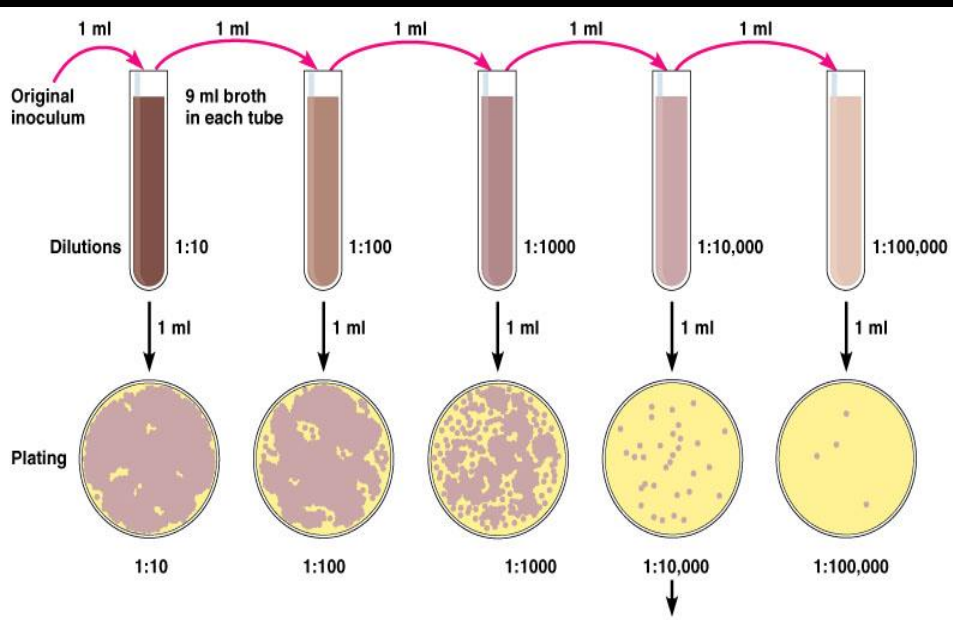
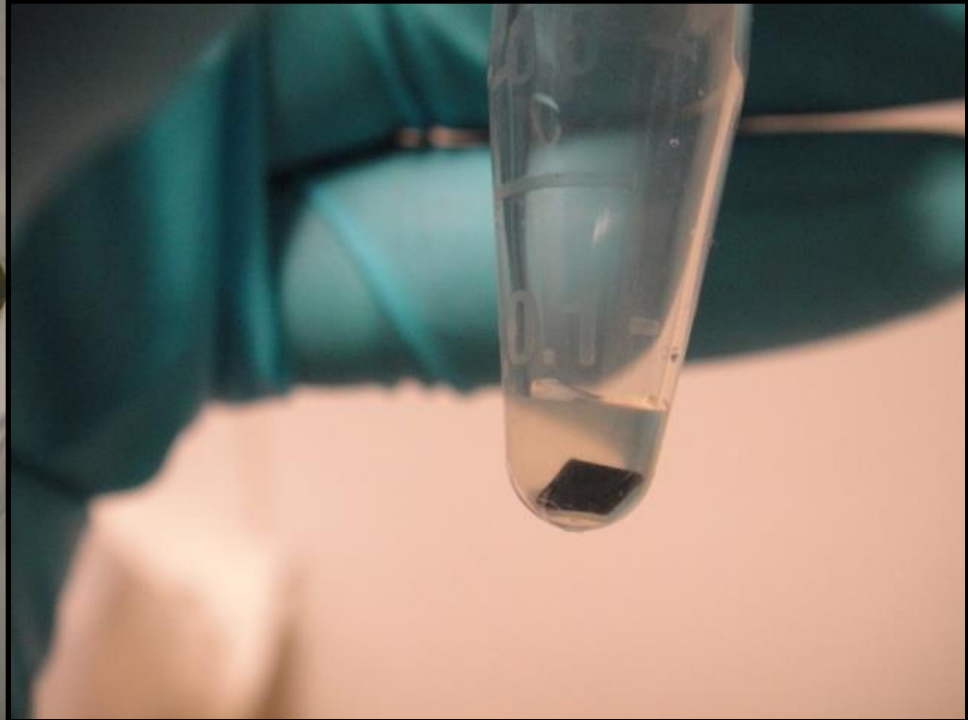
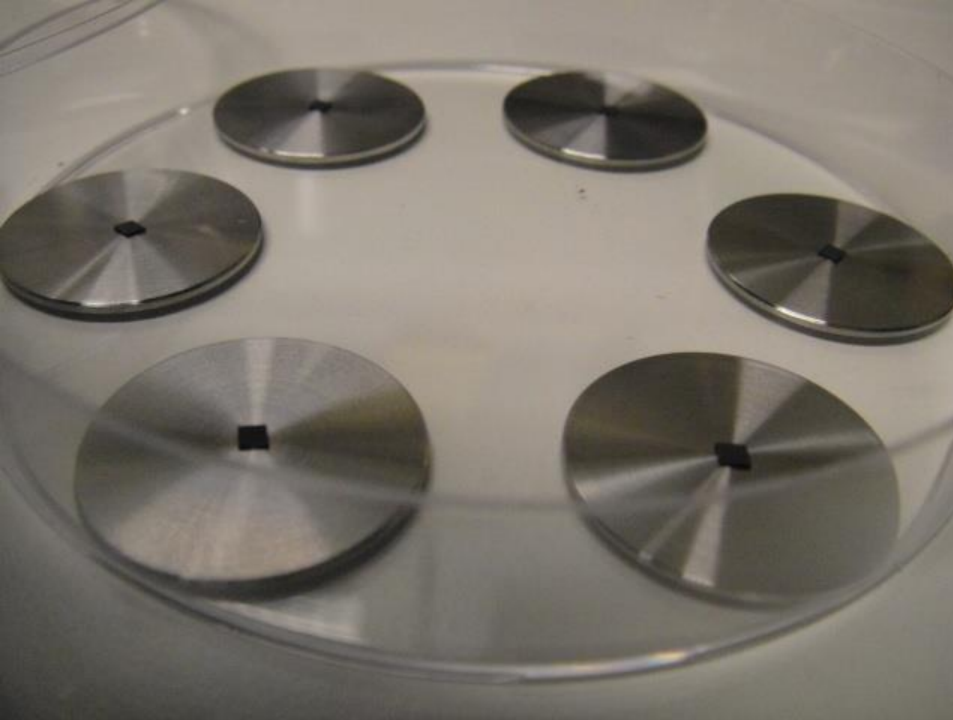
**How organic materials are modified by solar vacuum UV irradiation?**

ASTROBIOLOGY  
Volume 11, Number 9, 2011  
© Mary Ann Liebert, Inc.  
DOI: 10.1089/ast.2011.0649

## Survival of *Deinococcus radiodurans* Against Laboratory-Simulated Solar Wind Charged Particles

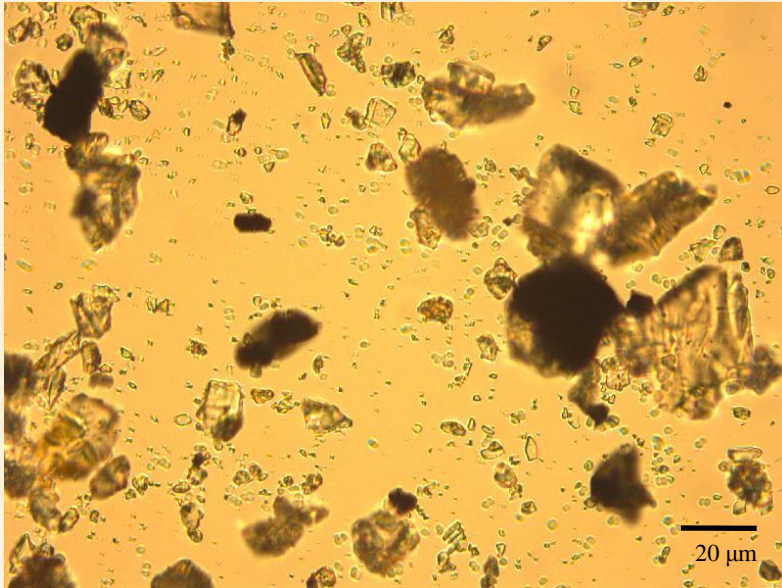
Ivan Gláucio Paulino-Lima,<sup>1,7</sup> Eduardo Janot-Pacheco,<sup>2,7</sup> Douglas Galante,<sup>2</sup> Charles Cockell,<sup>3</sup>  
Karen Olsson-Francis,<sup>3</sup> John Robert Brucato,<sup>4</sup> Giuseppe Antonio Baratta,<sup>5</sup> Giovanni Strazzulla,<sup>5</sup>  
Tony Merrigan,<sup>6</sup> Robert McCullough,<sup>6</sup> Nigel Mason,<sup>7</sup> and Claudia Lage<sup>1,7</sup>

✓ Effects on living organisms → Is panspermia possible?



Calculation: Number of colonies on plate  $\times$  reciprocal of dilution of sample = number of bacteria/ml  
 (For example, if 32 colonies are on a plate of  $1/10,000$  dilution, then the count is  $32 \times 10,000 = 320,000/\text{ml}$  in sample.)

Basalt



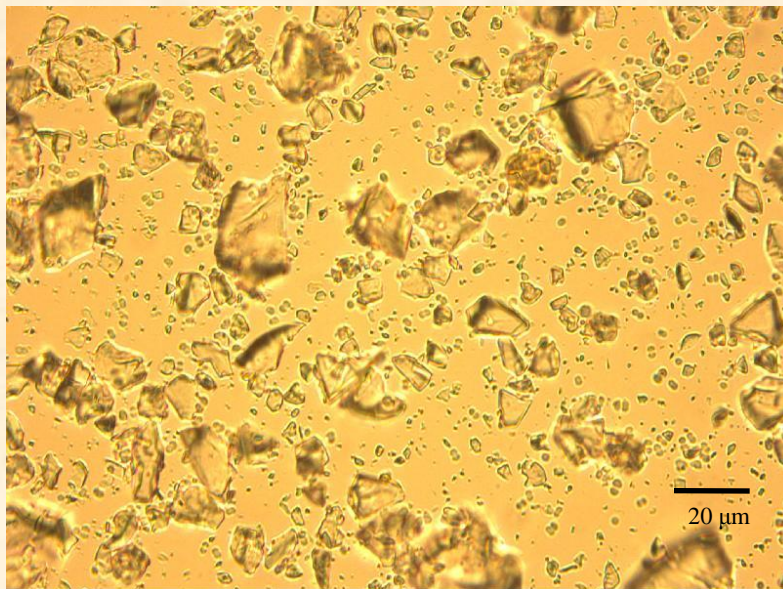
## Major elements

wt. %	BASALT	1:1 MIX	SANDSTONE
<b>SiO<sub>2</sub></b>	47.24	71.06	93.72
<b>TiO<sub>2</sub></b>	2.956	1.538	0.052
<b>Al<sub>2</sub>O<sub>3</sub></b>	16.51	10.21	3.88
<b>Fe<sub>2</sub>O<sub>3</sub></b>	11.19	5.77	0.21
<b>MnO</b>	0.167	0.085	0.004
<b>MgO</b>	5.82	2.79	0.03
<b>CaO</b>	10.03	5.16	0.03
<b>Na<sub>2</sub>O</b>	3.51	2.10	0.64
<b>K<sub>2</sub>O</b>	2.23	2.01	1.77
<b>P<sub>2</sub>O<sub>5</sub></b>	0.581	0.301	0.020
<b>LOI</b>	0.32	0.34	0.31

## Trace elements

X1936T	BASALT	1:1 MIX	SANDSTONE	Det.Lt.
<b>Rb</b>	56	46	35	<b>2</b>
<b>Sr</b>	849	478	117	<b>2</b>
<b>Y</b>	28.8	15.6	3.7	<b>2.0</b>
<b>Zr</b>	308	179	55	<b>2</b>
<b>Nb</b>	69.4	34.8	1.1	<b>1.5</b>
<b>Ba</b>	568	558	494	<b>12</b>
<b>Pb</b>	8	7	10	<b>5</b>
<b>Th</b>	11	7	0	<b>4</b>
<b>U</b>	3	2	0	<b>3</b>
<b>Sc</b>	22	11	1	<b>5</b>
<b>V</b>	288	139	6	<b>5</b>
<b>Cr</b>	77	39	4	<b>4</b>
<b>Co</b>	29	14	1	<b>2</b>
<b>Ni</b>	31	15	3	<b>3</b>
<b>Cu</b>	53	29	2	<b>3</b>
<b>Zn</b>	78	40	3	<b>3</b>
<b>Ga</b>	20	11	4	<b>3</b>
<b>Mo</b>	3	1	1	<b>2</b>
<b>As</b>	0	0	0	<b>5</b>
<b>S</b>	4	99	180	<b>50</b>
<b>TiO<sub>2</sub>%</b>	2.74	1.46	0.05	
<b>Fe<sub>2</sub>O<sub>3</sub>%</b>	10.16	4.79	0.63	

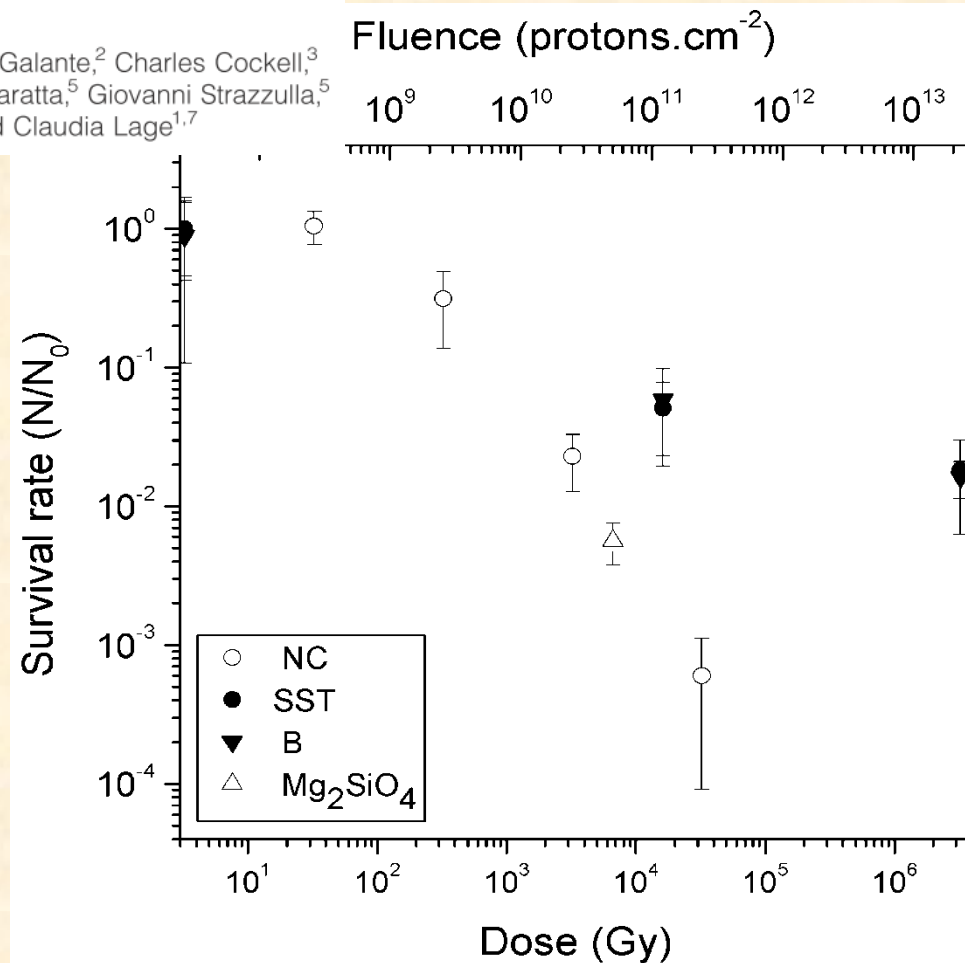
Sandstone



## Survival of *Deinococcus radiodurans* Against Laboratory-Simulated Solar Wind Charged Particles

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Survival curves of *D. radiodurans* after irradiation by a proton beam at 200 keV. NC = naked cells, SST = cells mixed with grains of sandstone, B = cells mixed with grains of basalt.  $\text{Mg}_2\text{SiO}_4$  represents cells deposited on forsterite substrate.



Target	Dose		Effect
	rad	eV/molecule	
Molecules	$10^{10}$ - $10^{12}$	5 ( $10^3$ )	Phys-Chem alteration
Polymers	$10^8$ - $10^{10}$	5 ( $10^1$ -10)	Phys-Chem alteration
DNA	$10^6$	5 $10^{-3}$	Inactivation
Enzymes	$10^5$ - $10^7$	5 ( $10^{-4}$ - $10^{-2}$ )	Inactivation
Virus	$10^5$	5 $10^{-4}$	Lethal
Bacteria	$10^4$ - $10^5$	5 ( $10^{-5}$ - $10^{-4}$ )	Lethal
Fungi	$10^3$ - $10^5$	5 ( $10^{-6}$ - $10^{-4}$ )	Lethal
Cells	$10^3$ - $10^4$	5 ( $10^{-6}$ - $10^{-5}$ )	Lethal
Mammalians	$10^2$ - $10^3$	5 ( $10^{-7}$ - $10^{-6}$ )	Lethal

Gray (Gy)	rad	Joule(J)/gr	eV/gr	eV/molec
1	100	$10^{-3}$	$6.25 \cdot 10^{15}$	$5 \cdot 10^{-7}$