ASTROBIOLOGIA

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4 STAFF

3 Post-docs

2 Undergraduate

2 STAND-BY

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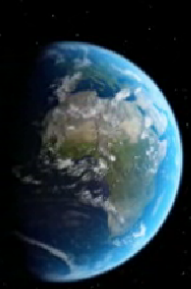
MARCOPOLO-R

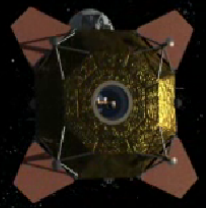
NEAR-EARTH OBJECT SAMPLE RETURN MISSION

16 Countries
564 Scientists
121 Italians
11 WGs

Team Coordinator:
Prof. A. Barucci
LESIA Paris

IT Science Study Team:
J.R. Brucato INAF – Oss. Firenze
E. Dotto INAF – Oss. Roma

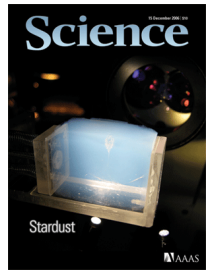


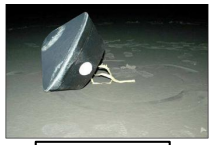


Programmatic
International Framework

Apollo & Luna

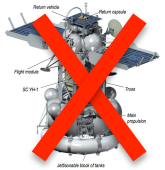
Genesis





Stardust

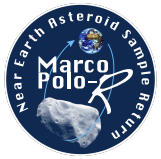
Hayabusa



Phobos-Grunt

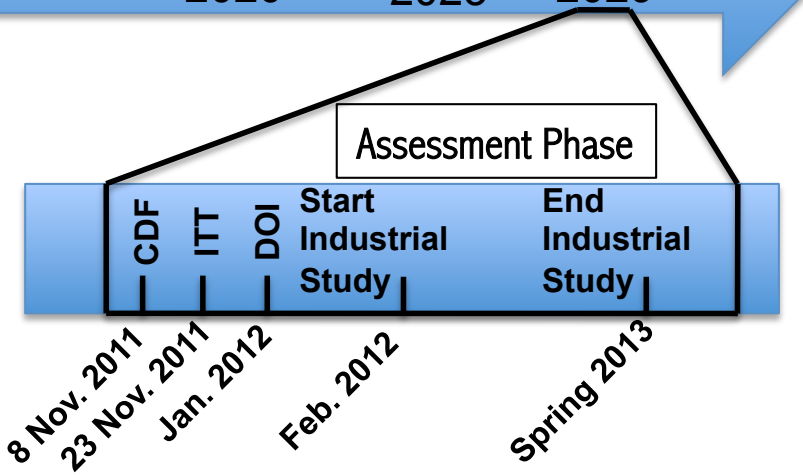
Hayabusa 2

Osiris-Rex



MarcoPolo-R

	Apollo & Luna	Genesis	Stardust	Hayabusa	Phobos-Grunt	Hayabusa 2	Osiris-Rex	MarcoPolo-R
Launch		2001	1999	2003	2011	2014	2016	2022
Return	1969	2004	2006	2010	2014	2020	2023	2029



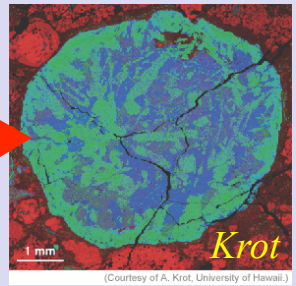
Why a Sample Return?

Complexity

- Same sample analysed by many instruments
- Complex sample selection and preparation

Initial selection

Process characterisation



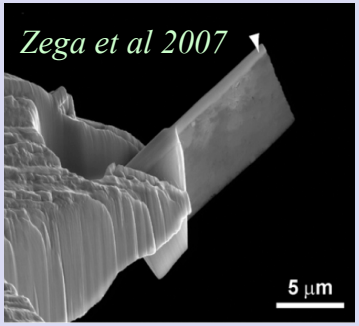
Split

Example: isotope dating of chondritic components

Isotope dating

- Dissolution
- Purification
- Analysis
- Calibration

Context (mm–µm) – check secondary effects



The Binary: 1996 FG3

- It provides for an **exciting science**

  One of the lowest albedo of any known asteroid (0.035) and a spectral signature suggesting a carbon- and volatile-rich surface.

- It is a class of object **never before visited** by a spacecraft

  Binary and Primitive C-class carbonaceous asteroid, a class that has never been studied up

- Its size, shape, and rotation state are **known**

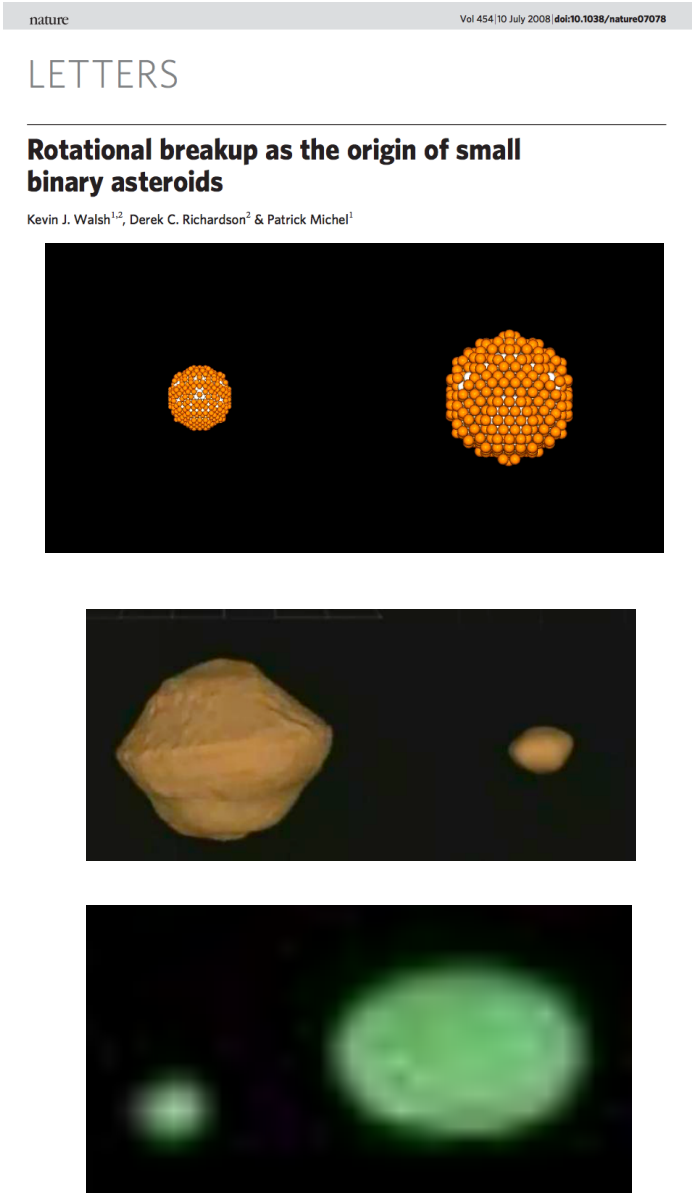
  A unique opportunity to study the dynamical evolution driven by the YORP/Yarkovsky thermal effects

- There is **fresh material on the** pole

  Collecting samples from the pole of the primary can therefore provide a means of obtaining material that was originally inside the body without having to drill into it.

- Formation mechanism

  Measurements of the mutual orbit and rotation state of both components will be used to probe higher-level harmonics of the gravitational potential, and therefore internal structure.



The Primitive: 2001 SG286

- It provides for an **exciting science**

  Primitive material originated from comets and which is abundant in Tojans population.

- It is a class of object **restricted**

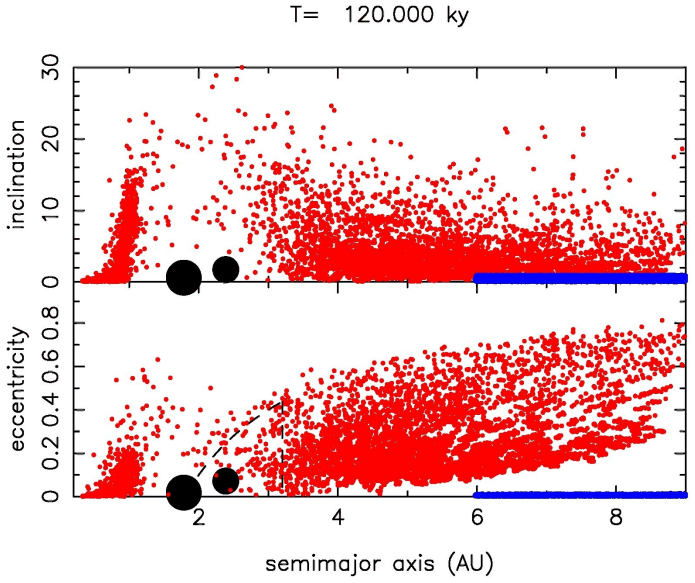
  Sample returned from a D-type required a strict containment by Planetary Protection Policy. Recently relaxed as un-restricted.

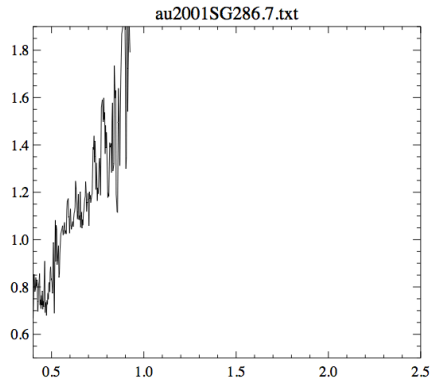
- There is **cometary-like material**

  We might expect composition of organics, carbon, anhydrous silicates and water.

- Missing link with meteorite

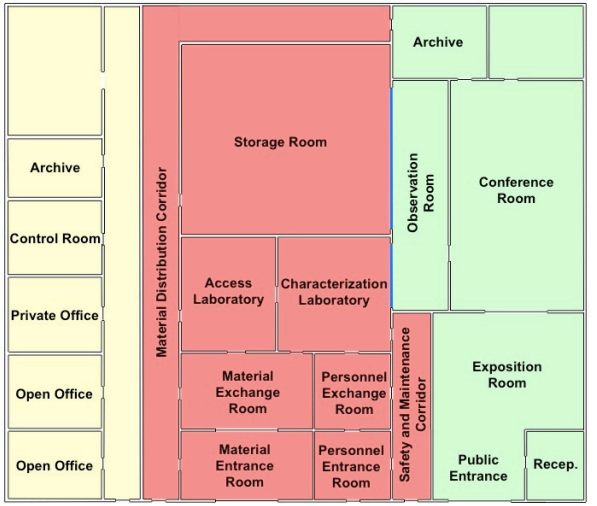
  There is not strong evidence of collected meteorites with D-type objects as parent source.





SCF

Sample Curation Facility



PI: J.R. Brucato (INAF-OAA, Italy)

IT Institutes: INAF-OAA, Univ. Florence, Univ. Siena, Univ. Pisa, Univ. Parthenope NA.

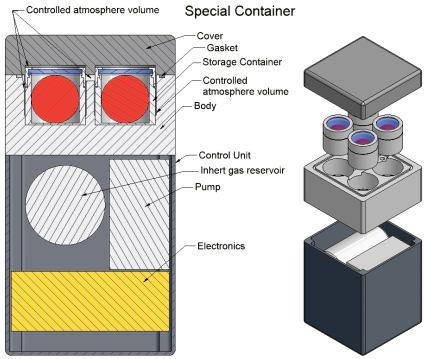
IT Contribution: Preliminary Design, Procedures and Protocols, Sample handling, Laboratory Examinations, Data Base,

Heritage: National Antarctic Museum, Museum of Planetary Science.

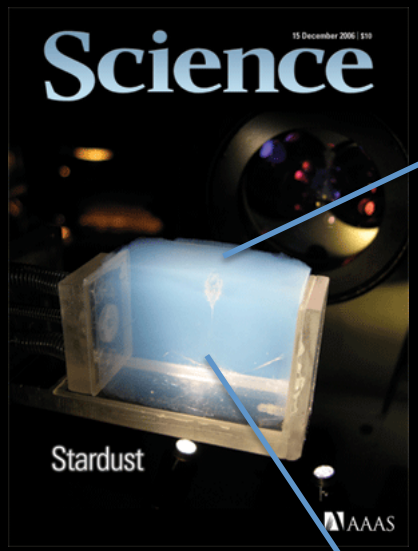
IT Industries: Kayser-Italia

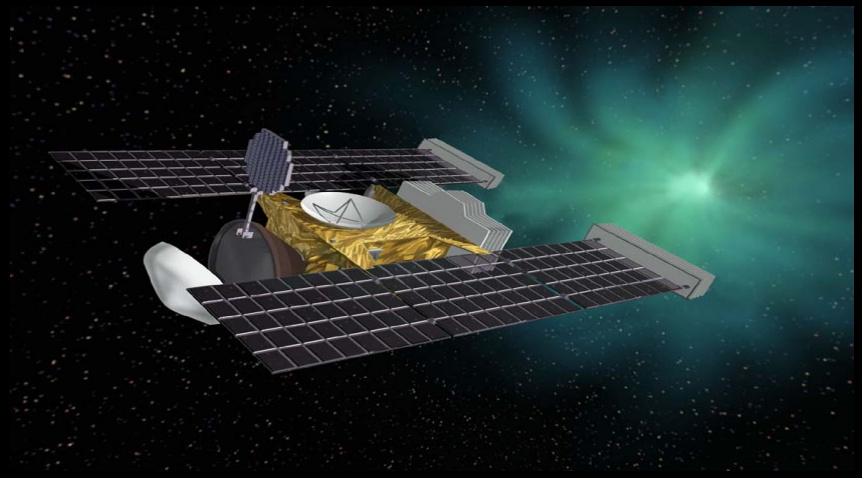
The key activities of the facility are:

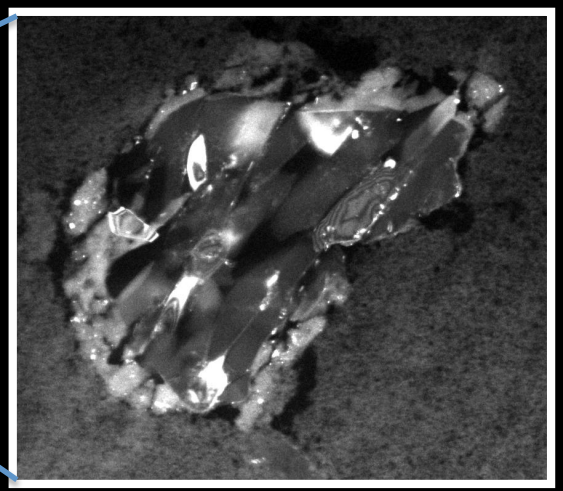
- secure and appropriate long term storage,
- preliminary characterization of the sample,
- preparation and distribution of sub-samples,
- accurate documentation of the samples



Analisi in laboratorio dei campioni di polvere cometaria riportati a terra dalla sonda Stardust della NASA



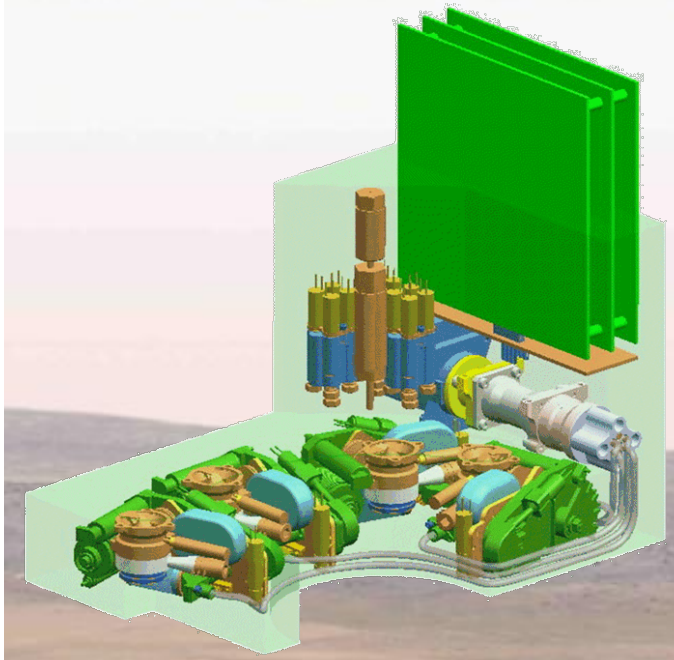




In collaborazione con:
A. Rotundi – Univ. Parthenope Napoli
J. Borg – Ist. Astrofisica Spaziale Orsay, Francia


esa
E X O M A R S

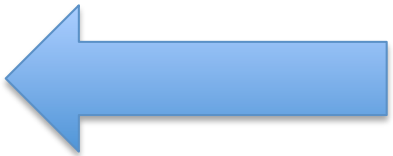
ESA's ExoMars rover
(CGI version 2010)



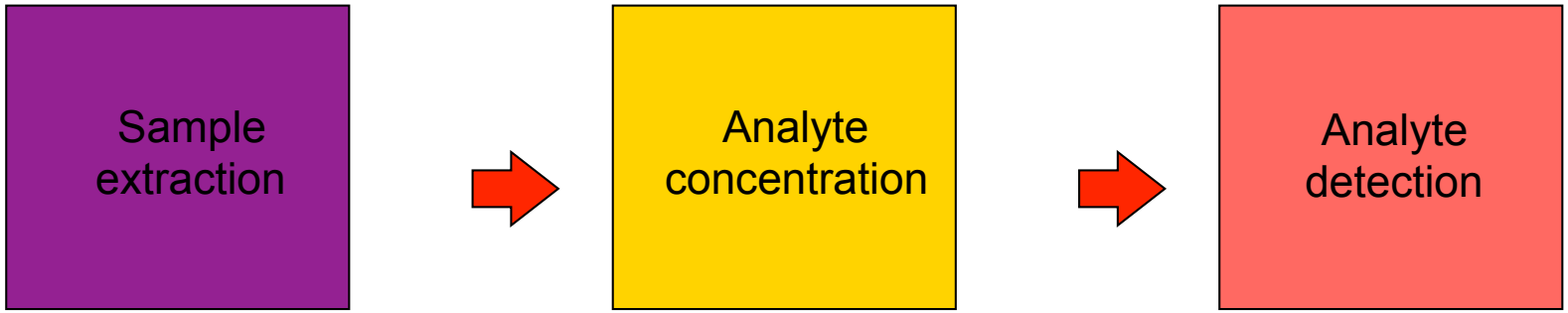
Life Marker Chip
Flight Model design
(early 2010)

LMC definition

- The Life Marker Chip (LMC) is an instrument that will be part of the Pasteur Payload of ESA's ExoMars Mission scheduled for 2018.
- It will examine soil/regolith samples for signs of extinct and extant life
- LMC will be situated in the ALD (Analytical Laboratory Drawer) of the rover
- Consortium team is composed of the following partners:
  - University of Leicester
  - Magna Parva
  - Dutch Space
  - Kayser Italia



Life Marker Chip extraction issues



Comprehensive & representative extraction of organic contents

Removal of solvent to concentrate target molecules

Compatibility of solvent with chip components and antibodies

- LMC will test Martian soil samples for specific life molecules
- Require a solvent system to extract all target abio- and bio-markers
- Extraction efficiencies important for representativity and sensitivity
- Concentration methods must be established
- Solvents must be compatible with LMC components

Main Goals of the Thesis and Expected Results:

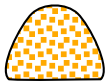
✓ Evaluation of extraction efficiency of biomarkers from Martian soil analogues and systematic study of the possible effects of the mineral grain sizes on the extraction efficiency.

✓ Development of extraction protocols that will be used by the *LMC* instrument.

Determination of **adsorption** kinetics/thermodynamics and **desorption** thermodynamics of biomarkers onto Mars soil analogues

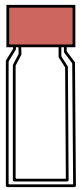
Studies of the **effects of UV radiation** on the biomarkers adsorbed onto Mars soil analogues, determination of degradation kinetics under space-like conditions and possible catalytic effects of the mineral

Extraction Procedure



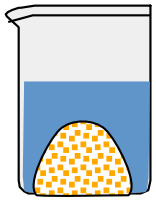
JSC-1
(preextracted)

+

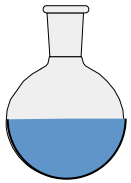


Spike with procedural standards
- Hexadecane (nonpolar)
- Squalene (non polar)
- Anthracene (non polar)
- Stigmasterol (non polar)
- Benzo[a]pyrene (nonpolar)
- Phytane (nonpolar)
- Phytanic acid (polar)
- Atrazine (polar)
- 1-Pyrene, butyric acid (polar)

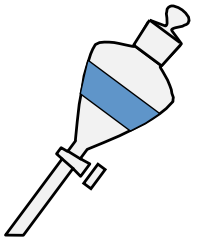
0.1 mg each standard per g rock (ca. 100 ppm)



Extraction

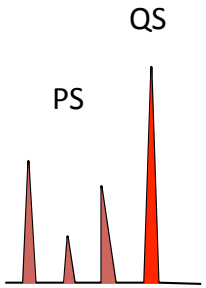


Extract #1

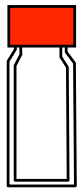


Prepare for analysis
- Liquid/liquid extraction
- Derivatisation
- Solvent modification

Extract never reaches complete dryness



GCMS (nonpolars) and LCMS (polars)
- Compare areas of procedural and quantitation standards to obtain extraction efficiencies



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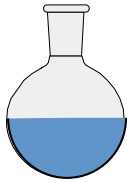
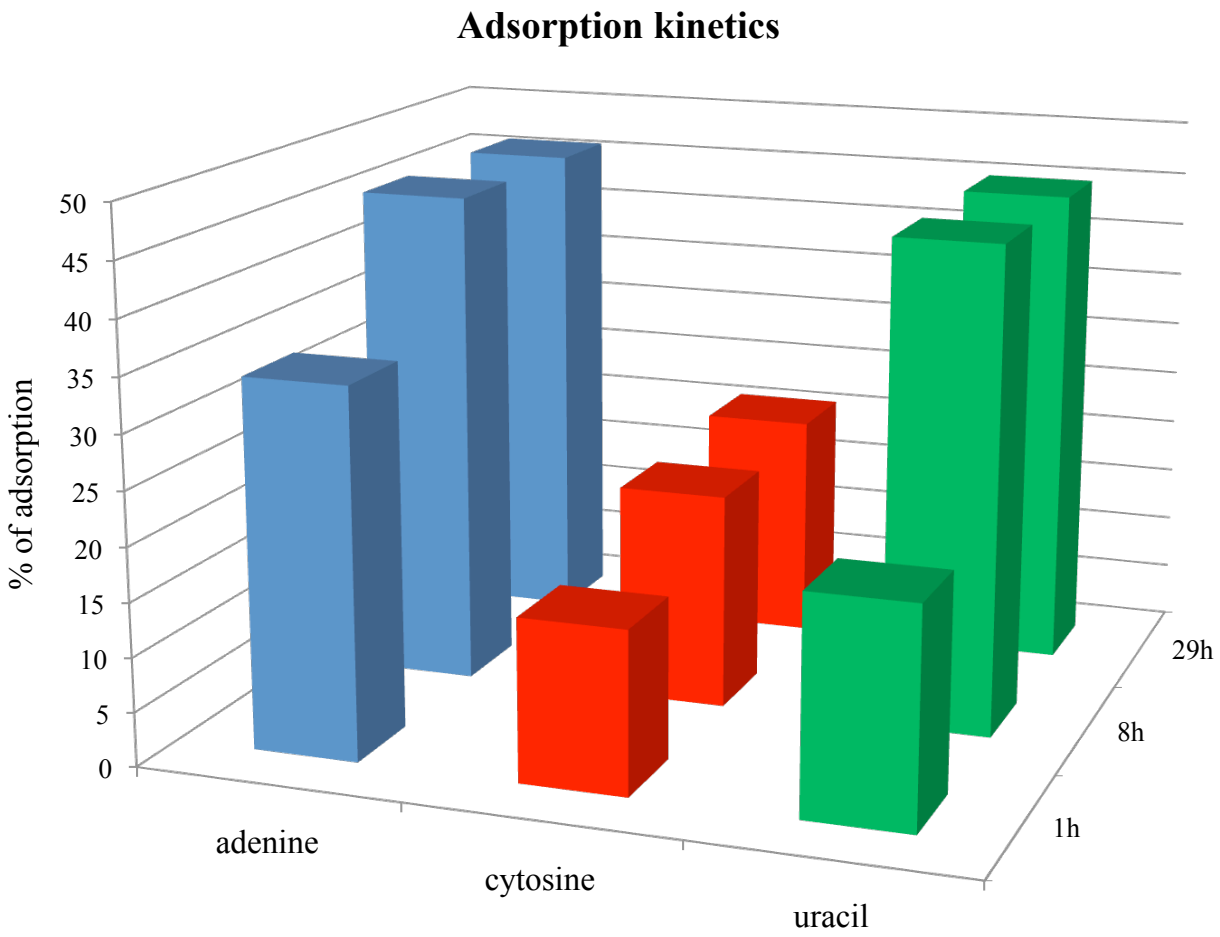


Extract #2

Add quantitation standards
- Terphenyl (non-polar)
- 0.01 mg

Results [1]:

ADSORPTION of Adenine, Cytosine, Uracile onto MgO



Experimental conditions

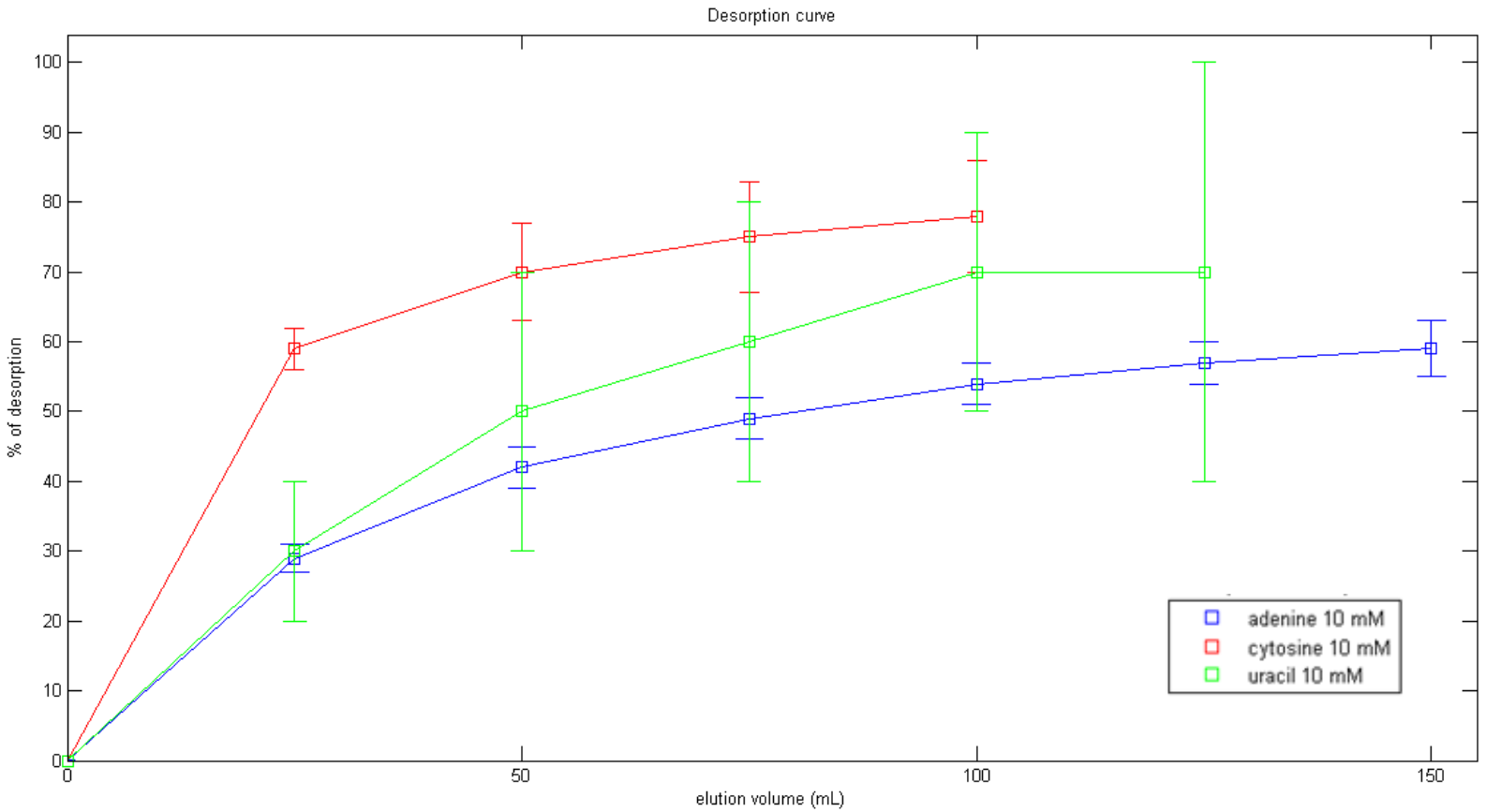
- Adenine, cytosine and uracil 10 mM solutions in 0.1 M NaCl
- Untreated MgO at 30 mg/mL concentration

Saturation of the nucleobases onto MgO is reached after 8h adsorption

The adsorption order onto MgO is: cytosine < uracil ≤ adenine

Results [2]:

DESORPTION of Adenine, Cytosine, Uracil from MgO

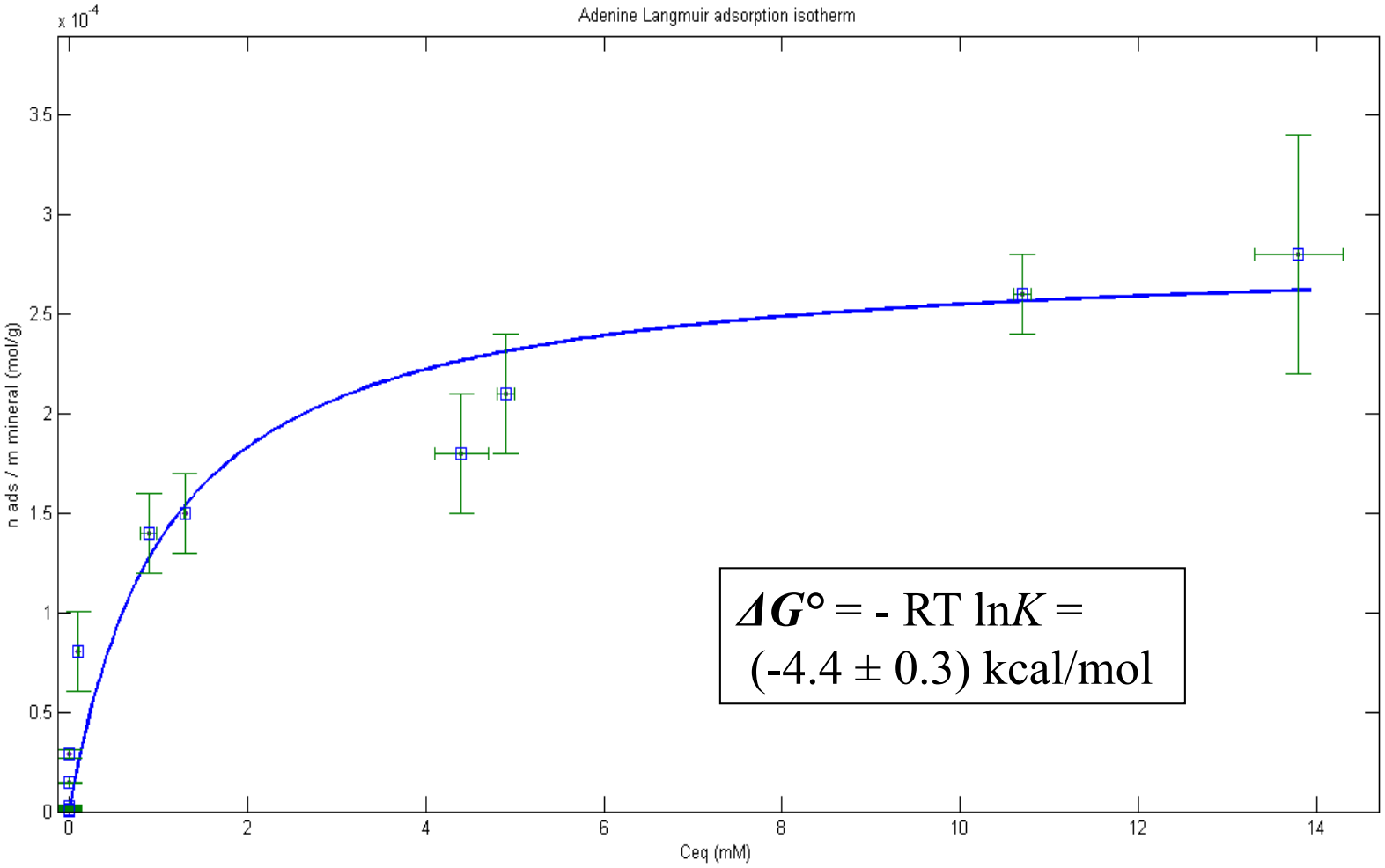


- Adenine, cytosine and uracil 10 mM solutions in 0.1 M NaCl
- Untrated MgO with concentration of 30 mg/mL
- Washing cycles with a 0.1 M NaCl aqueous solution

The desorption order from MgO is: adenine < uracil < cytosine

Results [3]: ADSORPTION ISOTHERM of adenine onto MgO

$$n_{ads}/m_{mineral} = KbC_{eq} /(1+ KC_{eq})$$



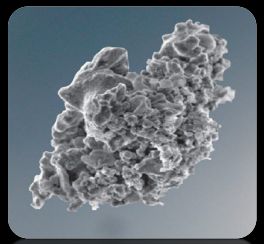
$\Delta G° = -$ RT ln$K$ = (-4.4 ± 0.3) kcal/mol

Experimental conditions

- 20 - 0.01 mM Adenine solutions in distilled sterilized water
- Untreated MgO at 30 mg/mL concentration

The adsorption process is thermodynamically favored

Studi sulle proprietà catalitiche delle polveri cosmiche nella sintesi di biomolecole



Fase Gassosa

Reazioni di ricombinazione di atomi a 10 - 100 K

In collaborazione con:
Univ. Syracuse, NY

Fase Liquida

Reazioni Termiche
Irraggiamento UV

In collaborazione con:
Univ. Viterbo
INFN-LNF Frascati

Fase Solida

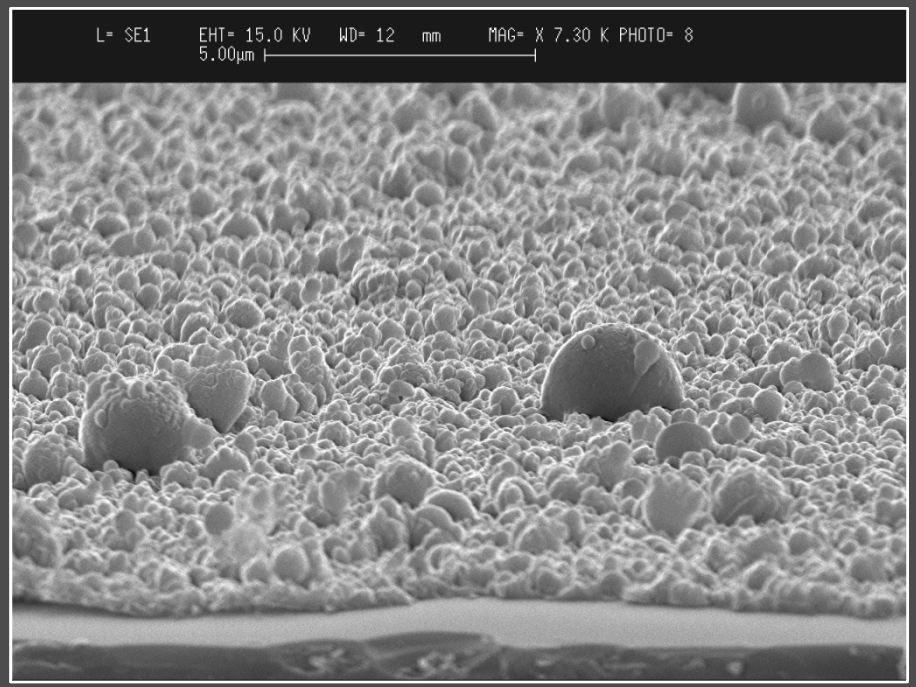
Irraggiamento con ioni di ghiacci a 20 K

In collaborazione con:
INAF Catania

Silicate production in laboratory

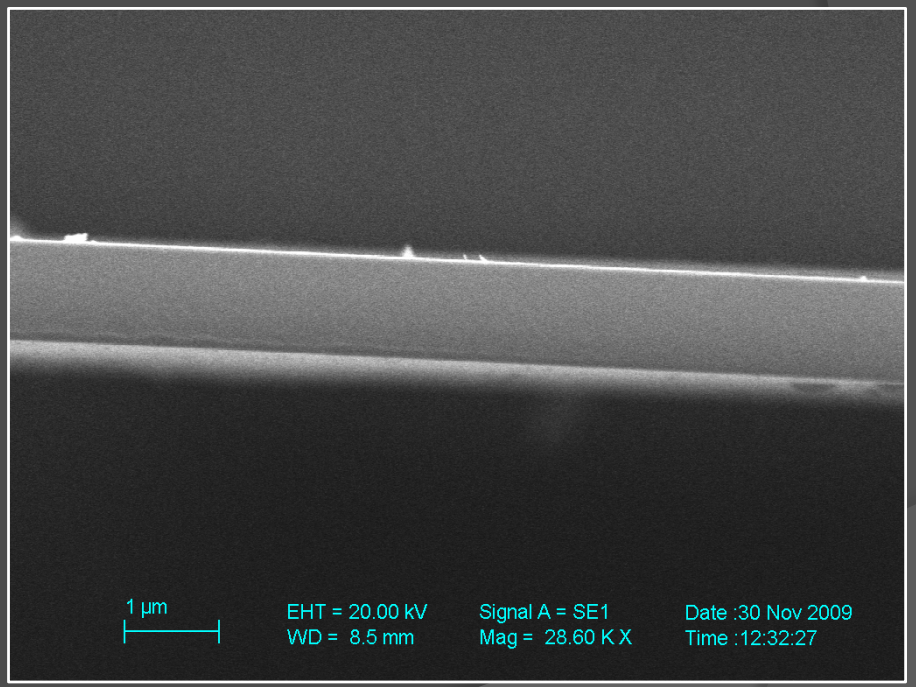
Amorphous olivine & pyroxene

Laser ablation



P= 10 mbar O_2

Electron Beam

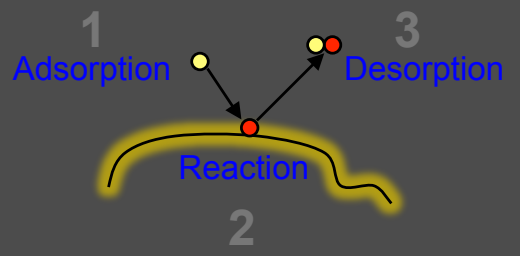


P= 10^{-5} mbar

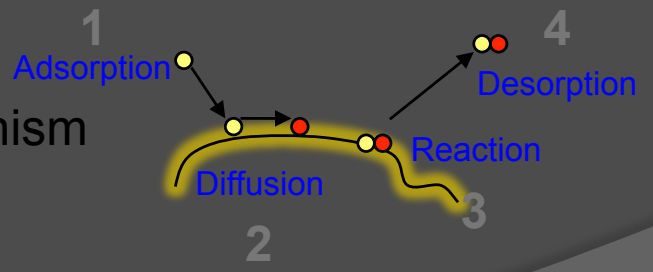
Surface catalysis

Surface catalysis allow molecules formation that are not possible in the gas phase. It open pathways for the chemical evolution in space.

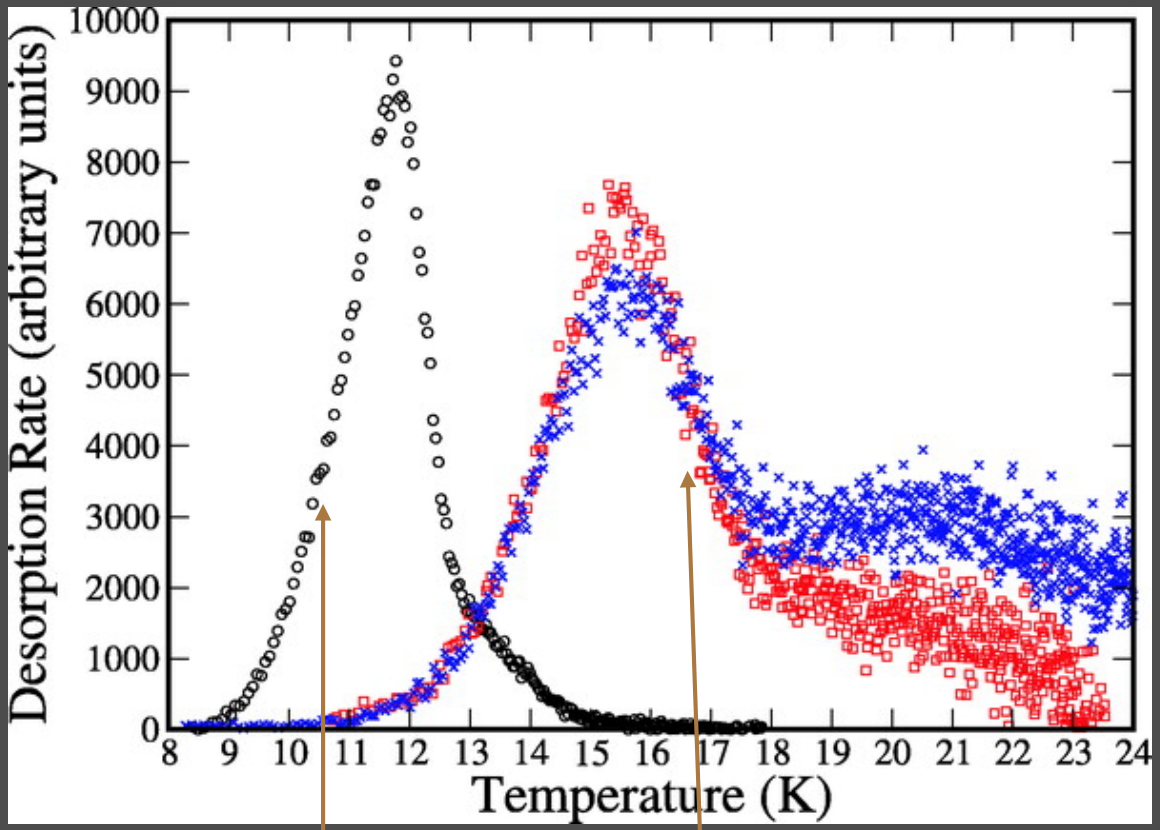
Eley-Rideal mechanism



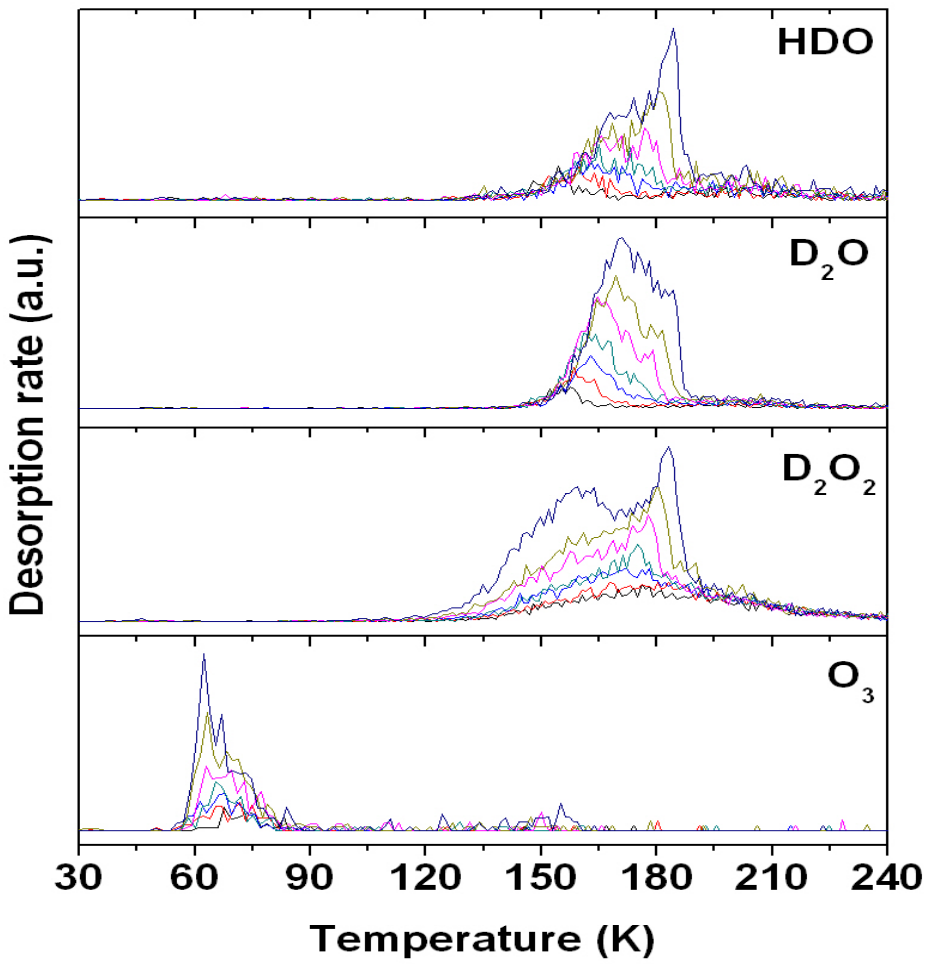
Langmuir-Hinshelwood mechanism



H & D beams irradiation of amorphous olivine silicate (Fe, Mg)SiO_4

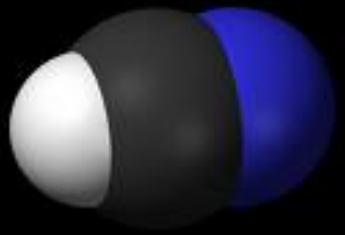


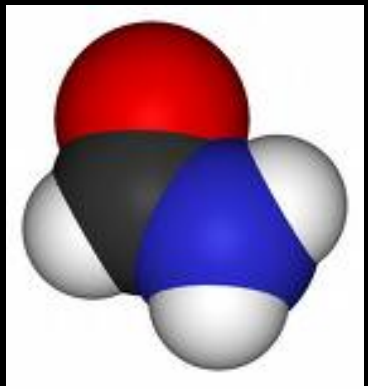
Desorpion rate of HD molecules vs. surface temperature during TDP on polycrystalline and amorphous silicates



Desorption peaks for various species after D and O co-exposure. From bottom to top: 10 min, 15 min, 22.5 min, 30 min, 45 min, 60 min and 90 min.

HCN



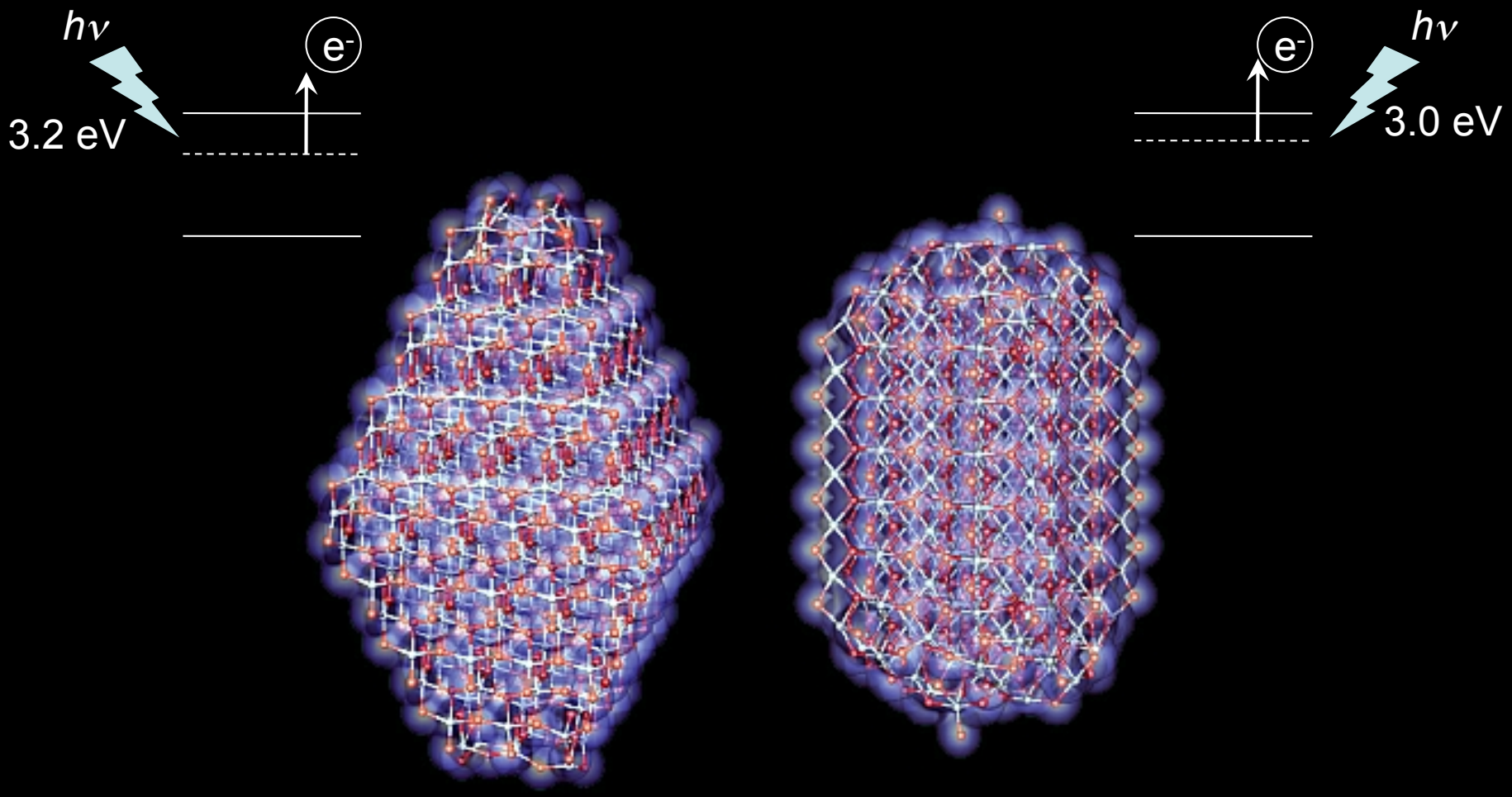


$HCONH_2$

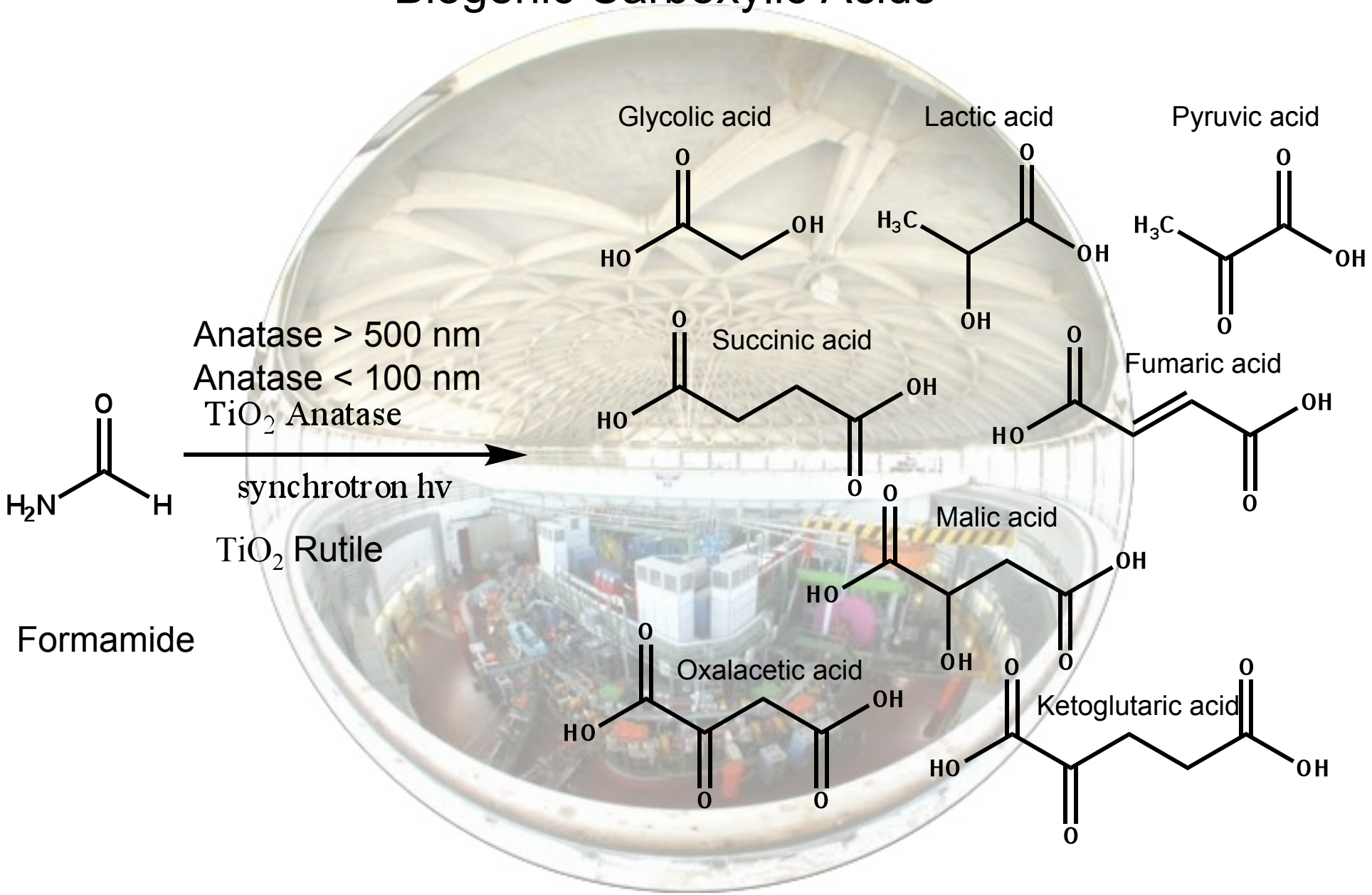
Interstellar organic molecules (79)

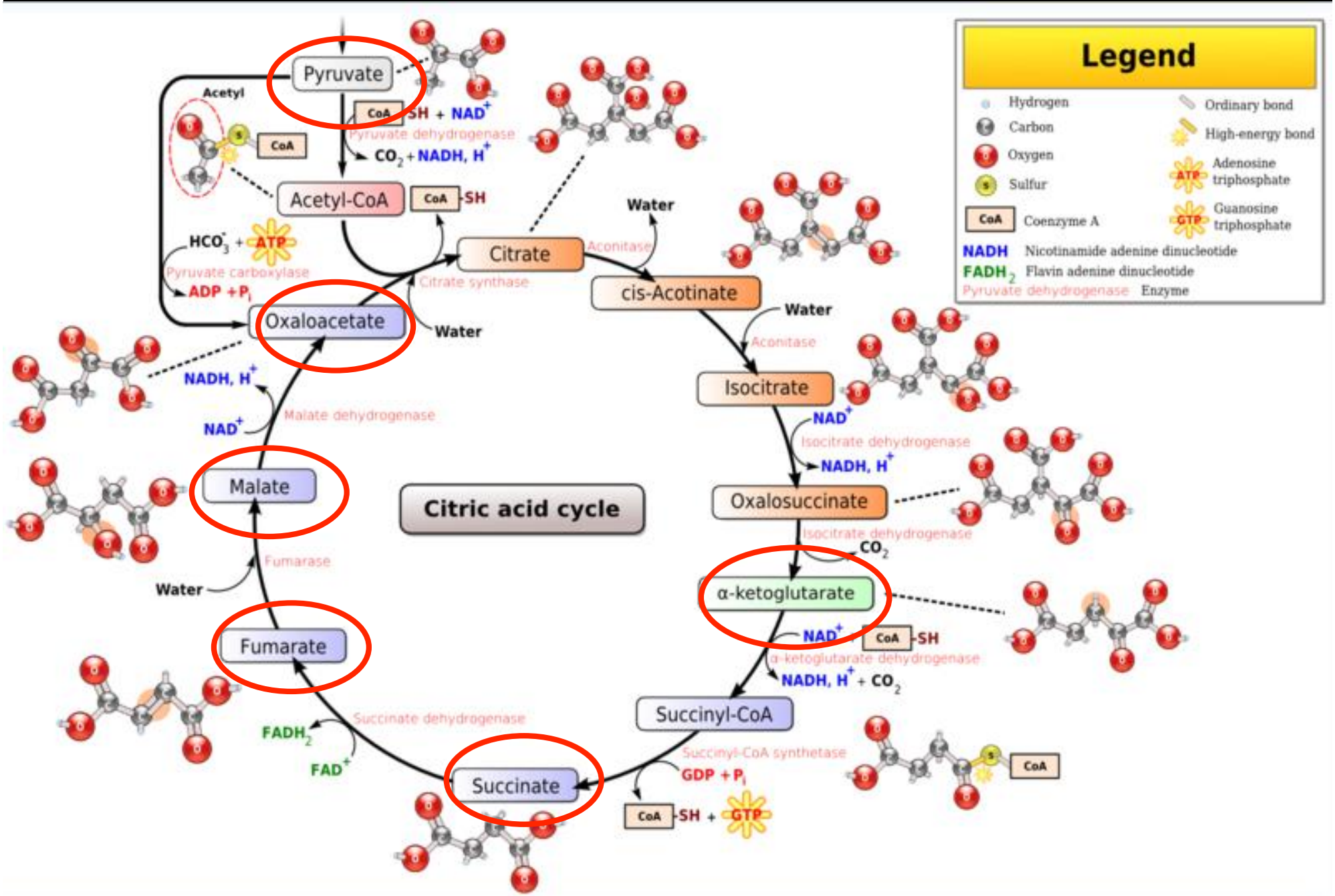
CH^+	HCN	H_2CO	HC_3N	CH_3OH	HC_5N	$HCOOCH_3$	HC_7N
CH	HNC	H_2CS	C_4H	CH_3CN	CH_3CCH	CH_3C_3N	CH_3OCH_3
CN	HCO	HNCO	CH_2NH	CH_3NC	CH_3NH_2	CH_3COOH	CH_3CH_2OH
CO	OCS	HNCS	CH_2CO	CH_3SH	CH_3CHO	H_2C_6	CH_3CH_2CN
CS	HCO^+	c-C_3H	NH_2CN	NH_2CHO	CH_2CHCN	CH_2OHCHO	CH_3C_4H
C_2	HOC^+	l-C_3H	HOCHO	HC_2CHO	C_6H		CH_3C_5N
CO^+	HCS^+	C_3N	c-C_3H_2	C_5H	c-C_2H_4O		CH_3COCH_3
	C_2H	C_3O	CH_2CN	H_2CCCC	CH_2CHOH		HC_9N
	C_2O	C_3S	H_2CCC	HC_3NH^+			$HC_{11}N$
	C_2S	H_2CN	HCCNC				$OHCH_2CH_2OH$
	CH_2	CH_3	HNCCC				
	CO_2	C_2H_2	CH_4				
	C_3	$HOCO^+$	H_2COH^+				
		$HCNH^+$					

Titanium dioxide Photochemistry



Biogenic Carboxylic Acids

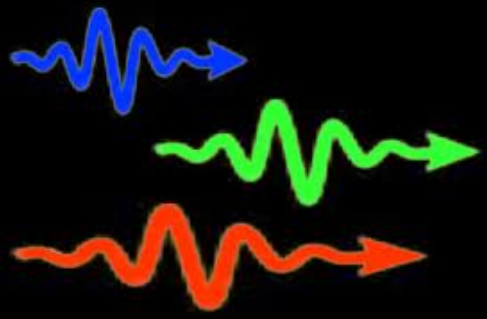


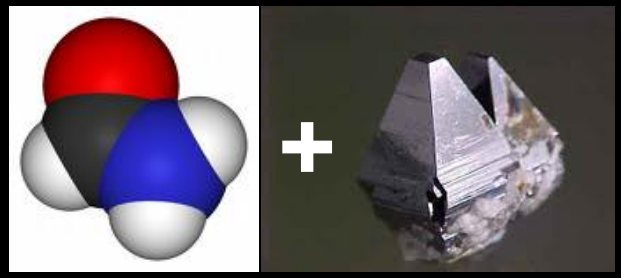

Legend
Hydrogen
Carbon
Oxygen
Sulfur
CoA Coenzyme A
NADH Nicotinamide adenine dinucleotide
FADH2 Flavin adenine dinucleotide
Pyruvate dehydrogenase Enzyme
Ordinary bond
High-energy bond
ATP Adenosine triphosphate
GTP Guanosine triphosphate
Citric acid cycle
Pyruvate
Acetyl
CoA
SH + NAD+
Pyruvate dehydrogenase
CO2 + NADH, H+
Acetyl-CoA
CoA
SH
HCO3- + ATP
Pyruvate carboxylase
ADP + Pi
Oxaloacetate
Citrate synthase
Water
Citrate
Aconitase
Water
cis-Acotinate
Aconitase
Water
Isocitrate
NAD+
Isocitrate dehydrogenase
NADH, H+
Oxalosuccinate
Isocitrate dehydrogenase
CO2
α-ketoglutarate
NAD+
CoA
SH
α-ketoglutarate dehydrogenase
NADH, H+ + CO2
Succinyl-CoA
Succinyl-CoA synthetase
GDP + Pi
CoA
SH + GTP
Succinate
Succinate dehydrogenase
FADH2
FAD+
Fumarate
Fumarase
Water
Malate
Malate dehydrogenase
NADH, H+
NAD+

?

GENETIC SYSTEM

METABOLIC SYSTEM

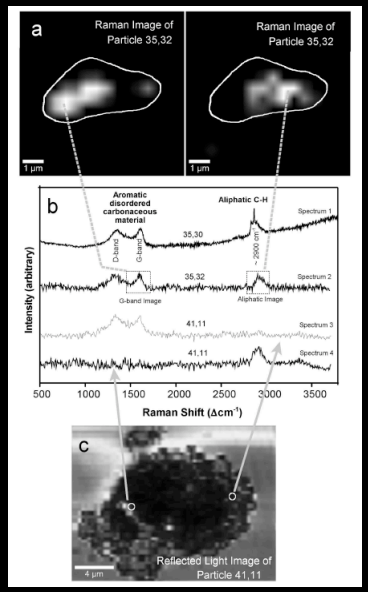




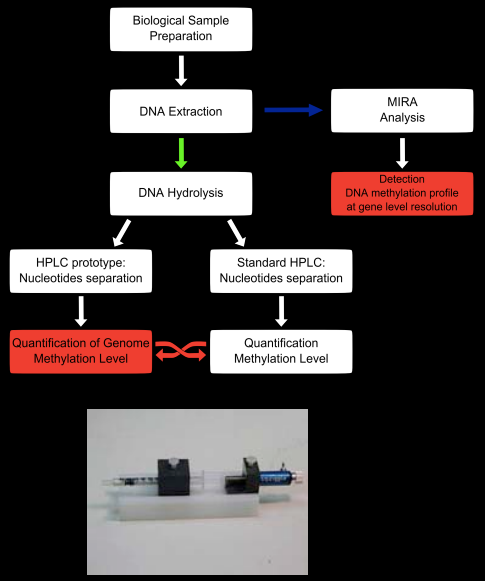
NASA Astrobiology Institute –
Focus Group: Thermodynamic, Disequilibrium and Evolution

Attività Spaziali

Analisi Campioni



Attività Tecnologica



OGGI

ASI: MarcoPolo - 170 K€ (2010-12)

ASI: LMC - 400 K€ (2010-14)

PRIN-MIUR 08: 61 K€ (2009-12)

1° dei 6 finanziati in ambito Astrofisica;
4° dei 58 finanziati dell'Area;
34° dei 986 finanziati in totale.

ASI + Horizon2020 K€ ?

PRIN-MIUR 11: ≈500 K€

ASI BioTech 11: 80 K€