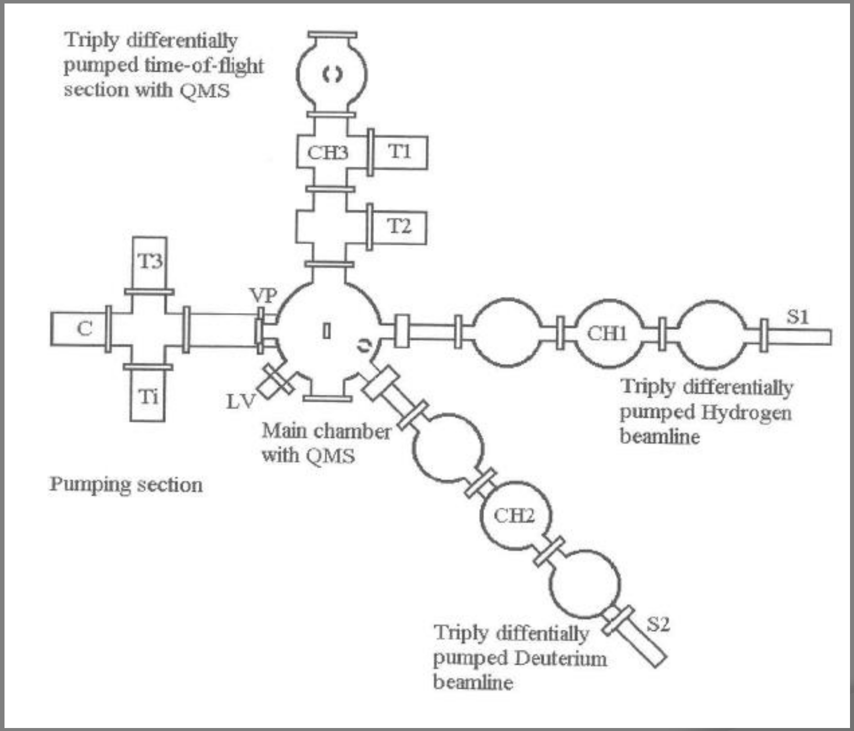
Mineral-biomolecules interactions: detect organic compounds in space

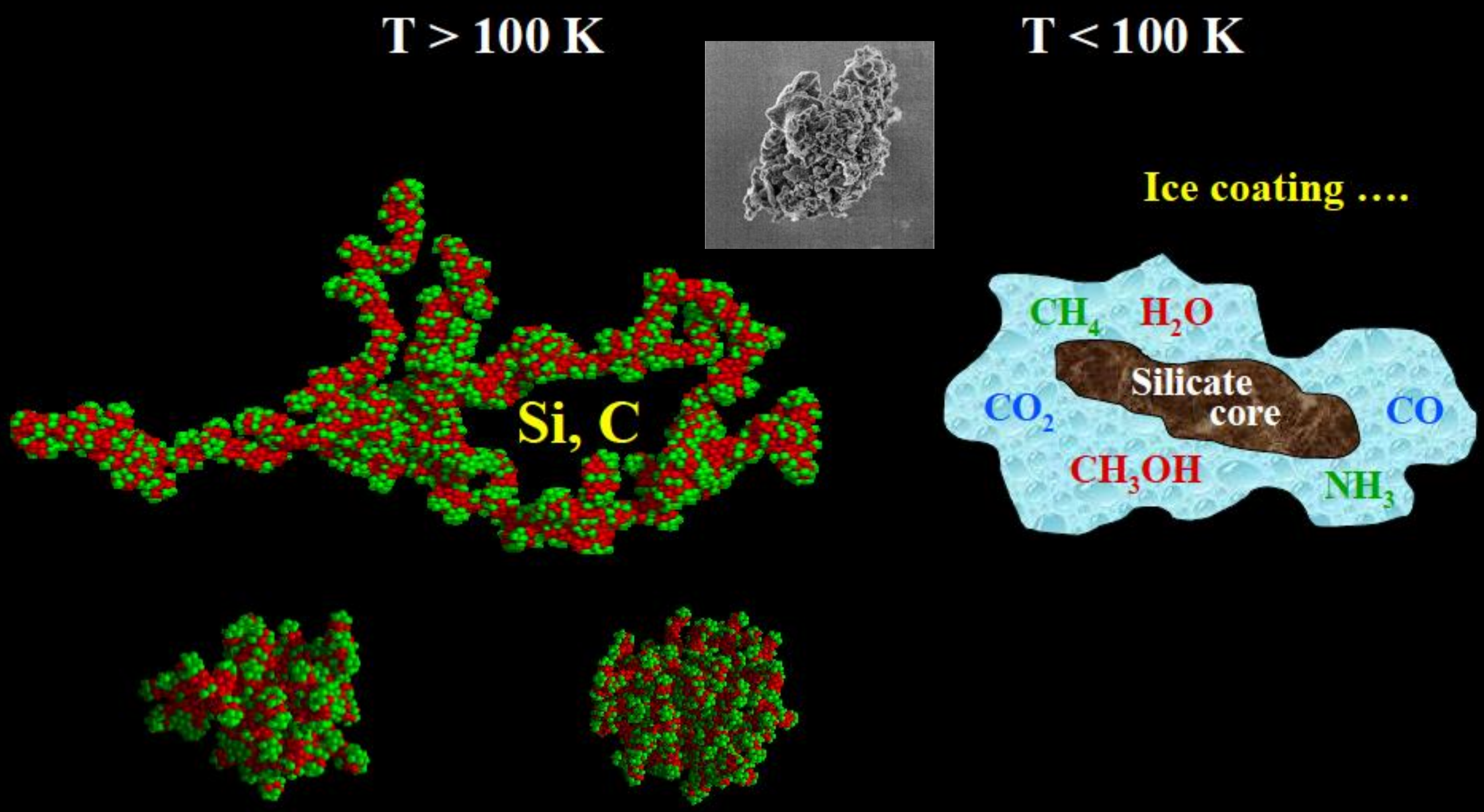
J.R. Brucato INAF-Arcetri Astrophysical Observatory, Firenze Italy
jbrucato@arcetri.astro.it



There are a number of space processes that can produce significant organic complex products:

- Gas phase ion-molecule interactions;
- Low-temperature gas-grain reactions;
- Gas phase unimolecular photodissociation;
- Ultraviolet photolysis and photodesorption in ice mantles
- Isotopic substitution due to ion irradiation.

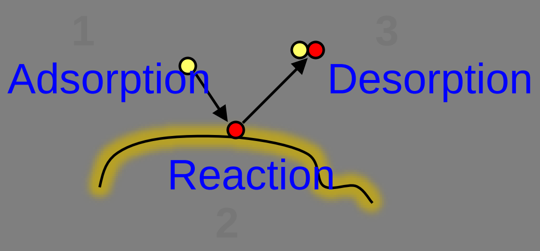
Dust particles: the seeds of planets and molecules



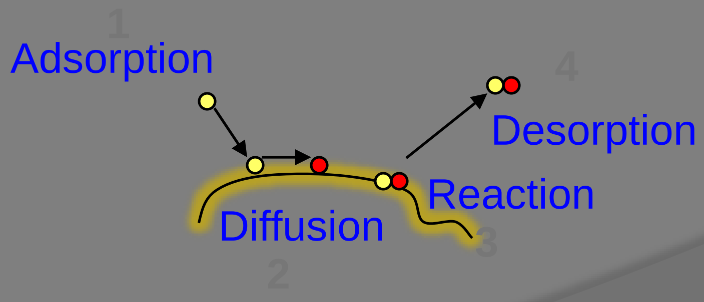
Surface catalysis

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

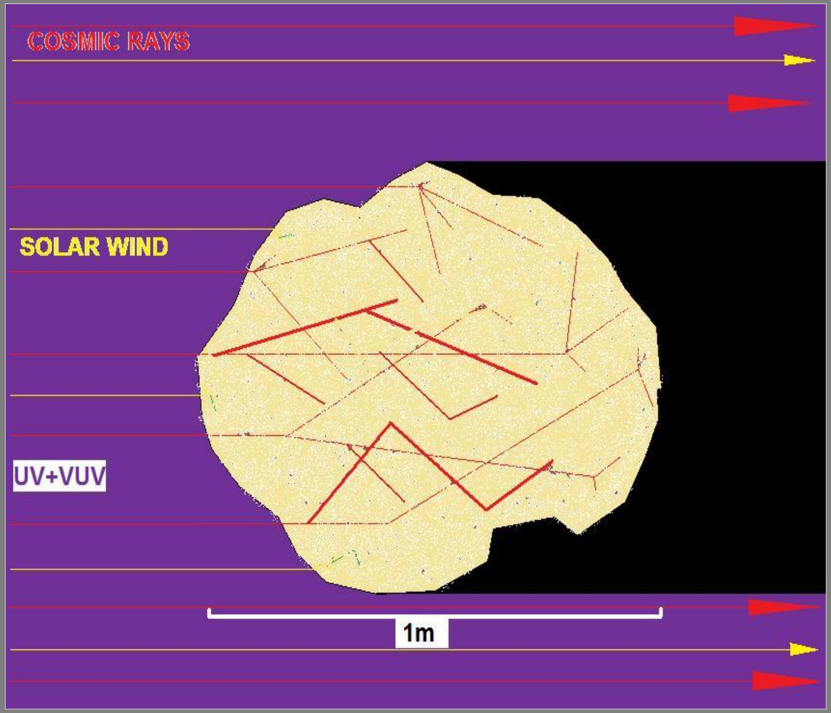
Eley-Rideal mechanism



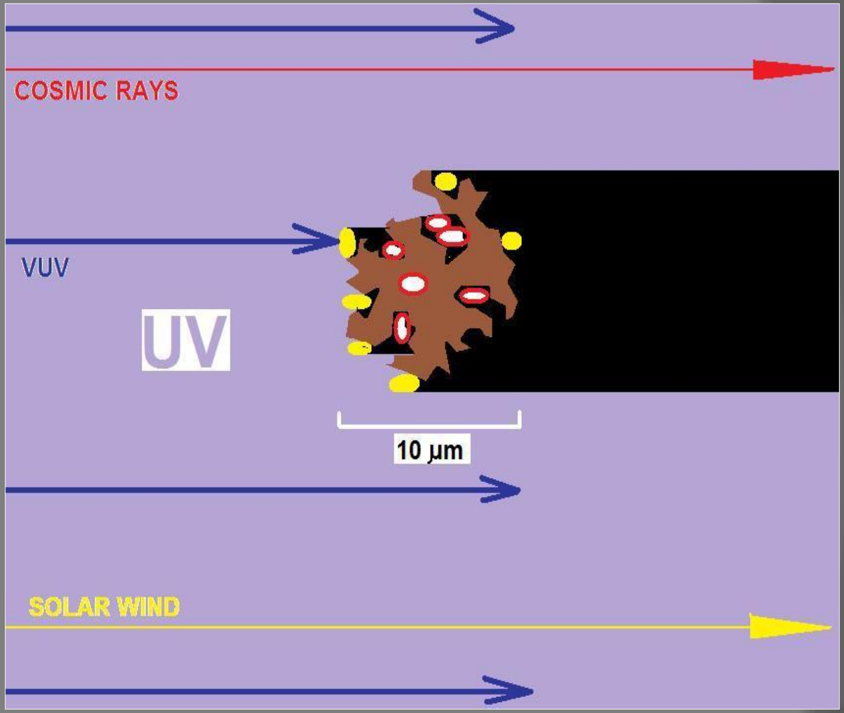
Langmuir-Hinshelwood mechanism



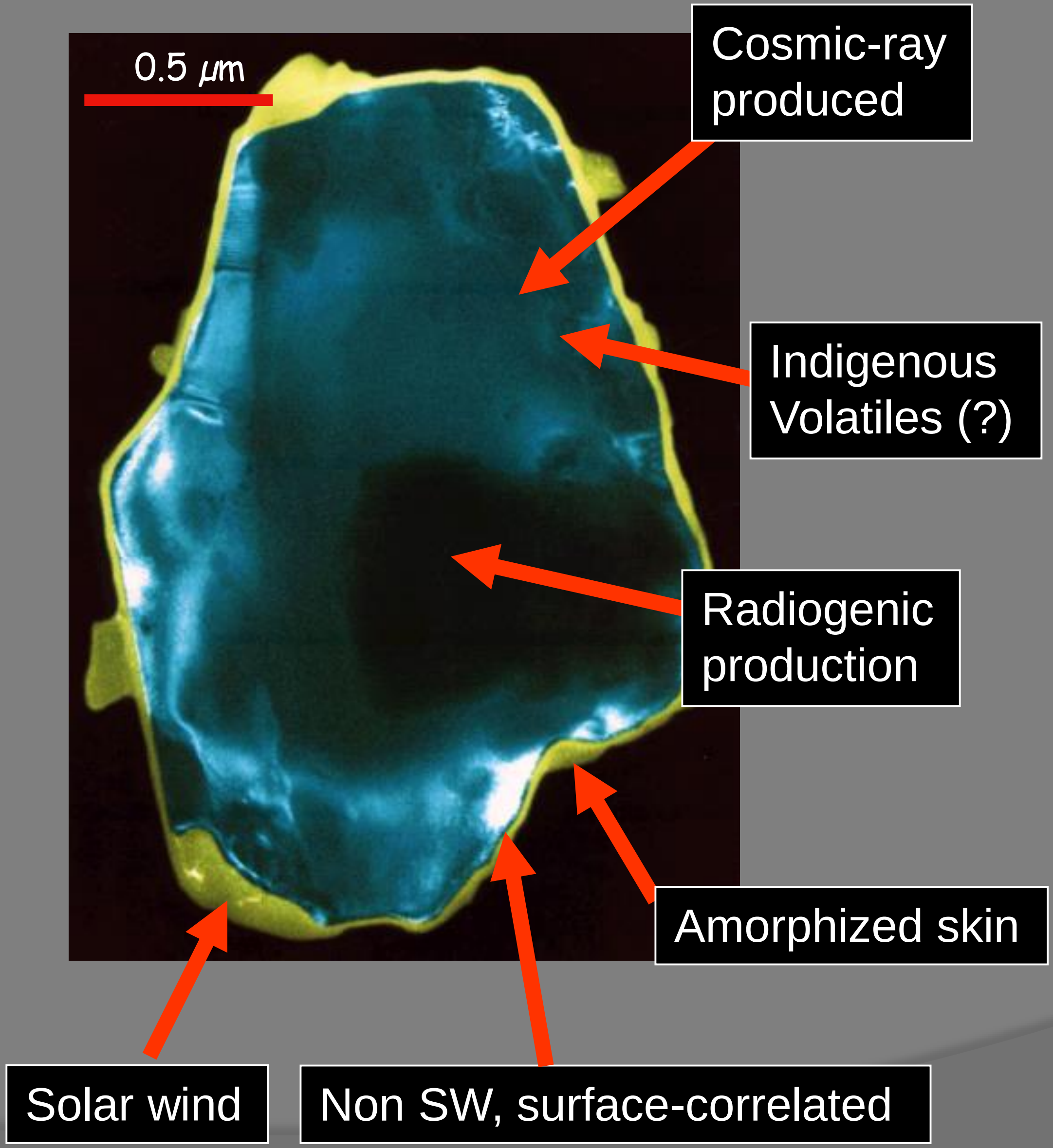
Big Rocks



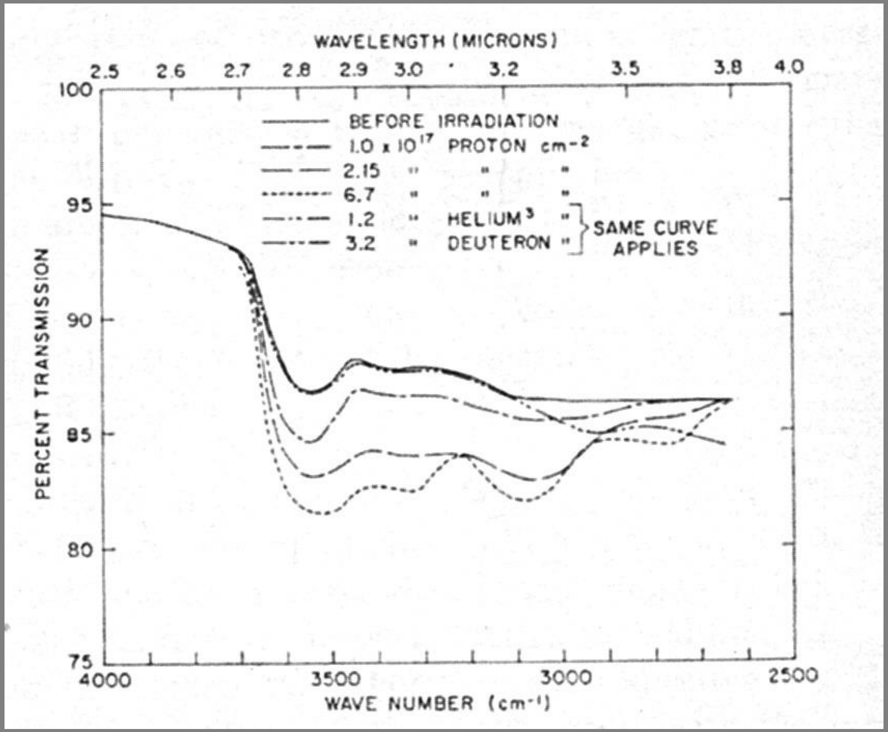
Small grains

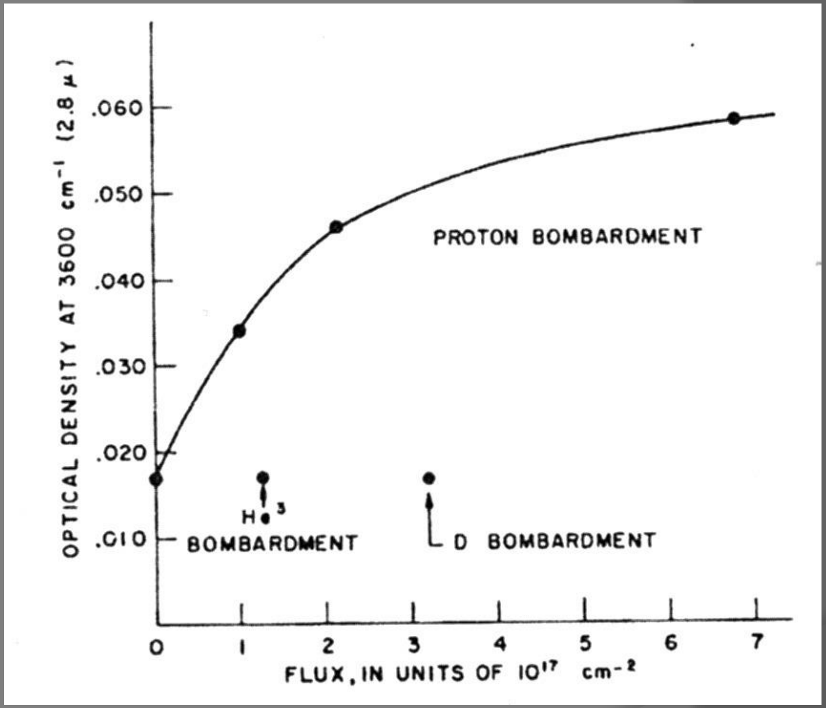


			Energy inputs (%) and Fluxes ($cm^{-2}\ s^{-1}$)
Solar Photons	2 eV	Visible (50%)	$2.0 \cdot 10^{17}$
	4 eV	NUV (10%)	$1.5 \cdot 10^{16}$
	6 eV	FUV (0.02%)	$3.0 \cdot 10^{13}$
Solar Wind (1 AU)	1keV	H^+ (95%)	$3.0 \cdot 10^{8}$
	4keV	He^{2+} (5%)	
Solar Flares (1 AU)	>1 MeV	H^+(95%)	10^{10} ($cm^{-2}\ yr^{-1}$)
	>1 MeV	He^{2+} (5%)	
Galactic cosmic rays	>1 MeV	H^+ (87%)	10^{1}
	>1 MeV	He^{2+} (12%)	


0.5 μm
Cosmic-ray produced
Indigenous Volatiles (?)
Radiogenic production
Amorphized skin
Solar wind
Non SW, surface-correlated

Proton-induced hydroxyl formation

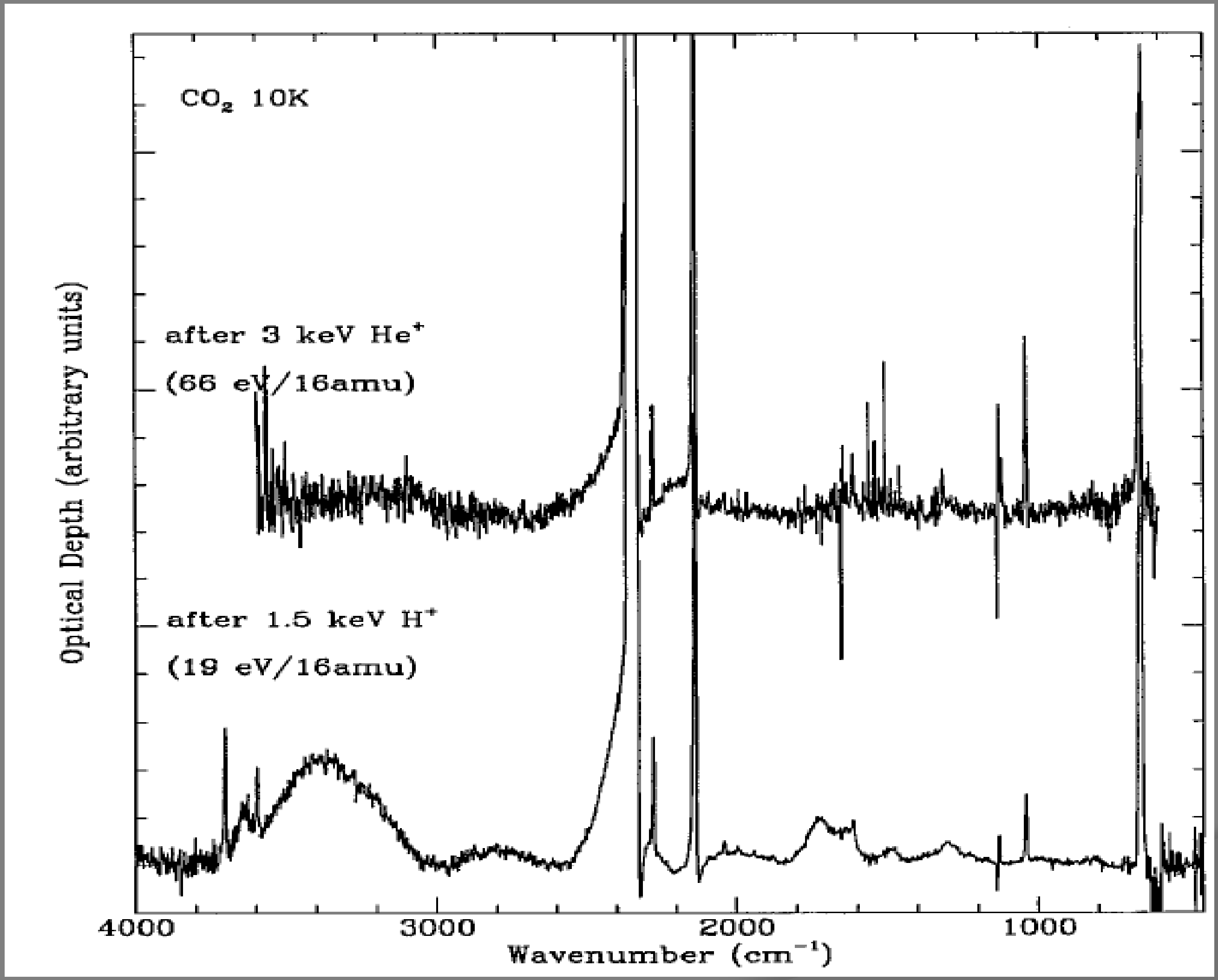




Estimate of the OH produced in the upper centimeter of the lunar surface material by proton bombardment: $4x10^{16}$ OH cm^{-3}

(Zeller et al. 1966)

Water formation by ice irradiation



Brucato et al. 1997

1) $H + O_2 \xrightarrow{H} HO_2 \xrightarrow{H} H_2O_2 \xrightarrow{H} H_2O + OH \xrightarrow{H} H_2O$ (Ioppolo et al. 2008, 2010)

2) $O + O_2 \rightarrow O_3 \xrightarrow{H} O_2 + OH \xrightarrow{H_2} H_2O + H$ (Tielens & Hagen 1982)

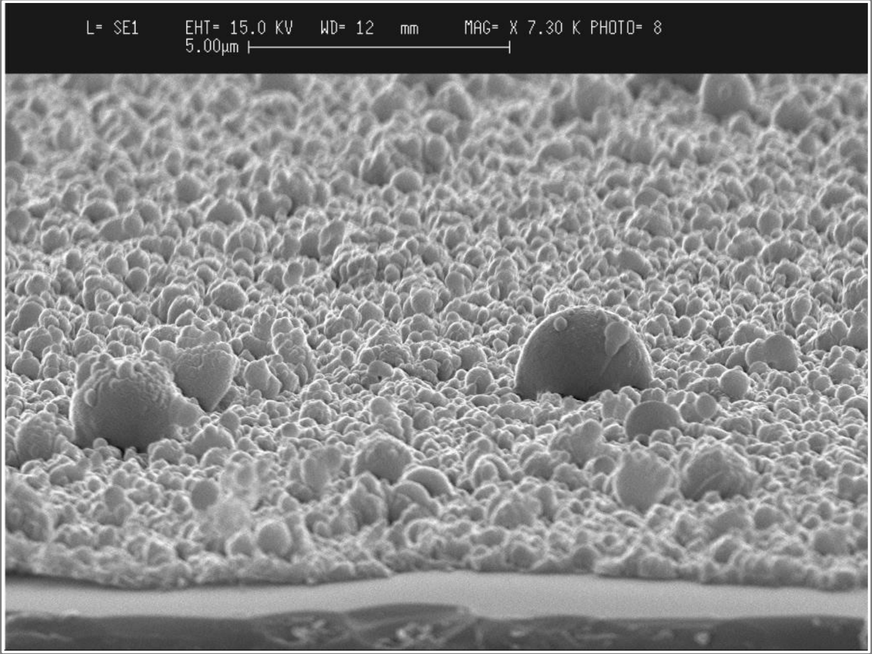
3) $H + O \rightarrow OH \xrightarrow{H} H_2O$ (Dulieu et al. 2010)

Some argues that species formed by these exotermic reactions will immediately desorb (Paoupular 2005). However, models predicts that most (99.1%) of OH and H_2O formed remain on surfaces (Cupper and Herbst 2007).

Silicate production in laboratory

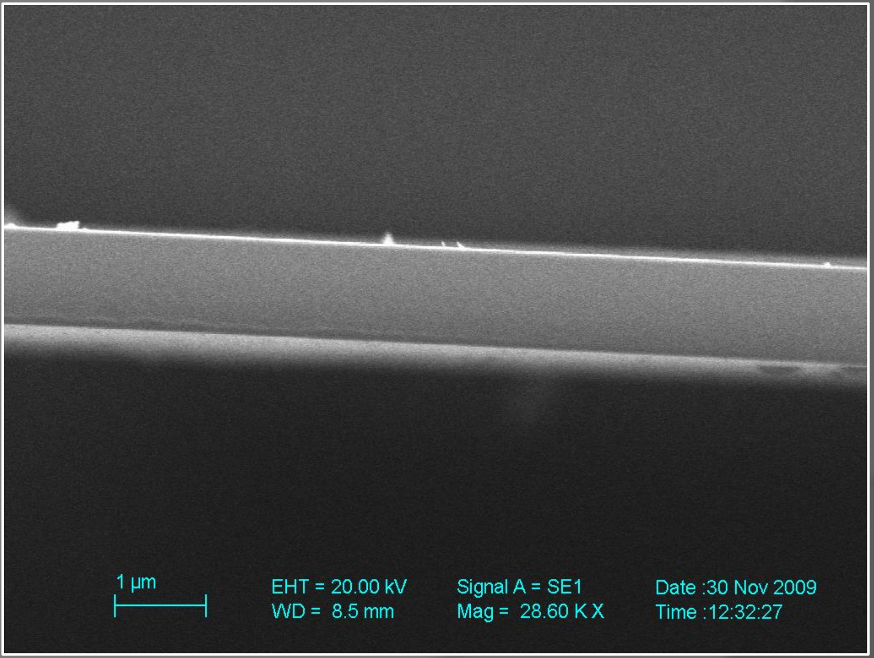
Amorphous olivine & pyroxene

Laser ablation

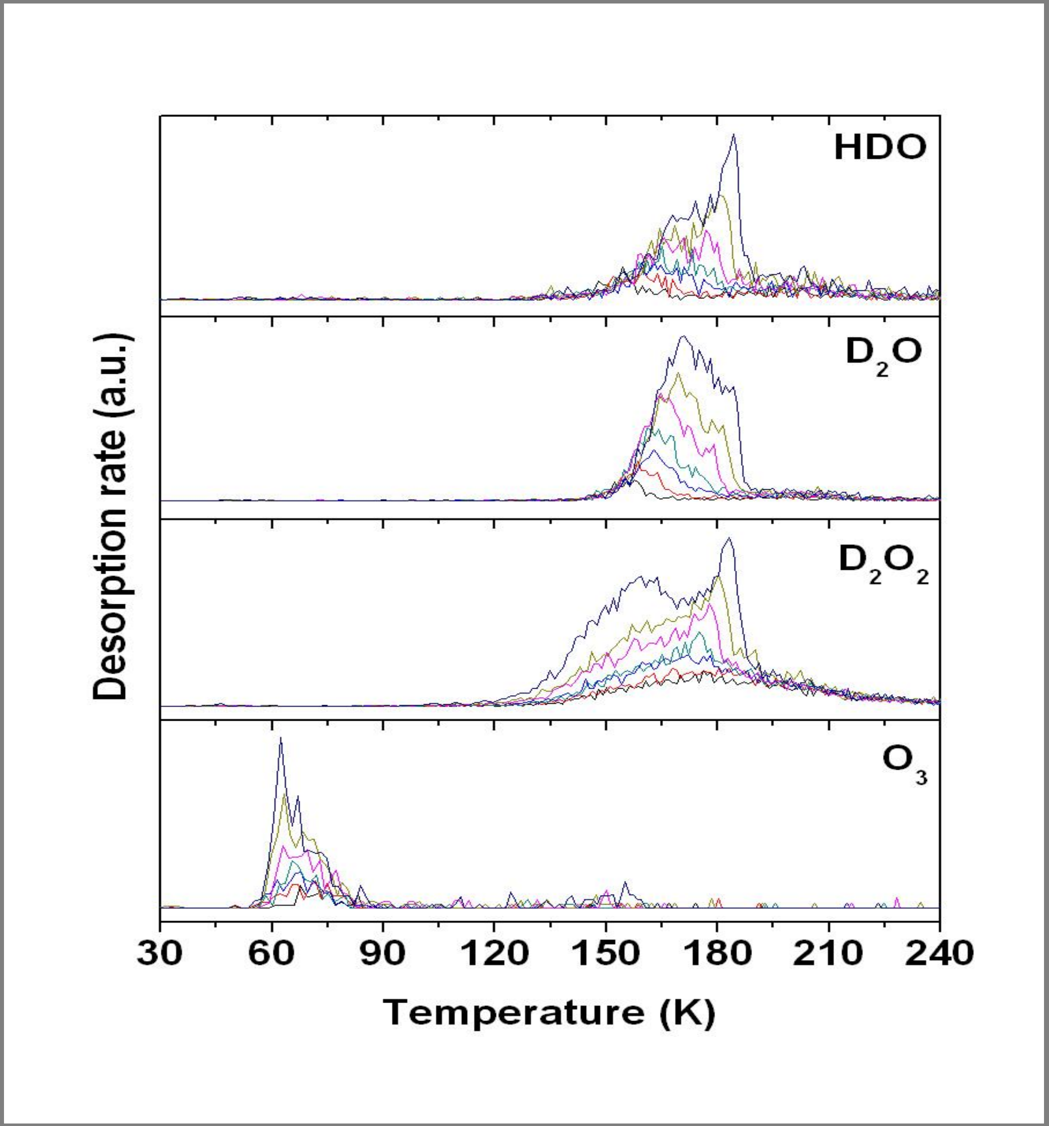


P= 10 mbar O_2

Electron Beam

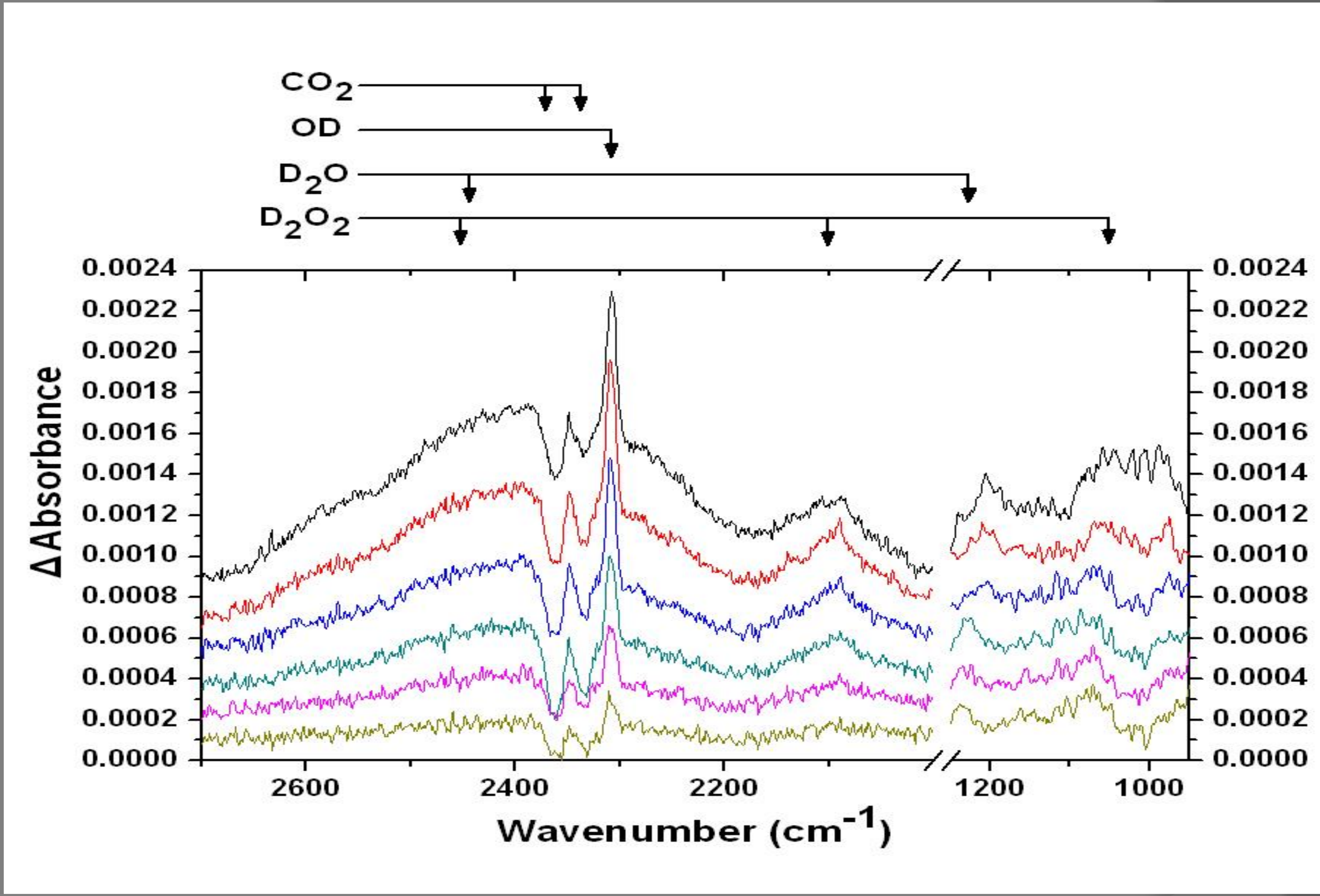


P= 10^{-5} mbar



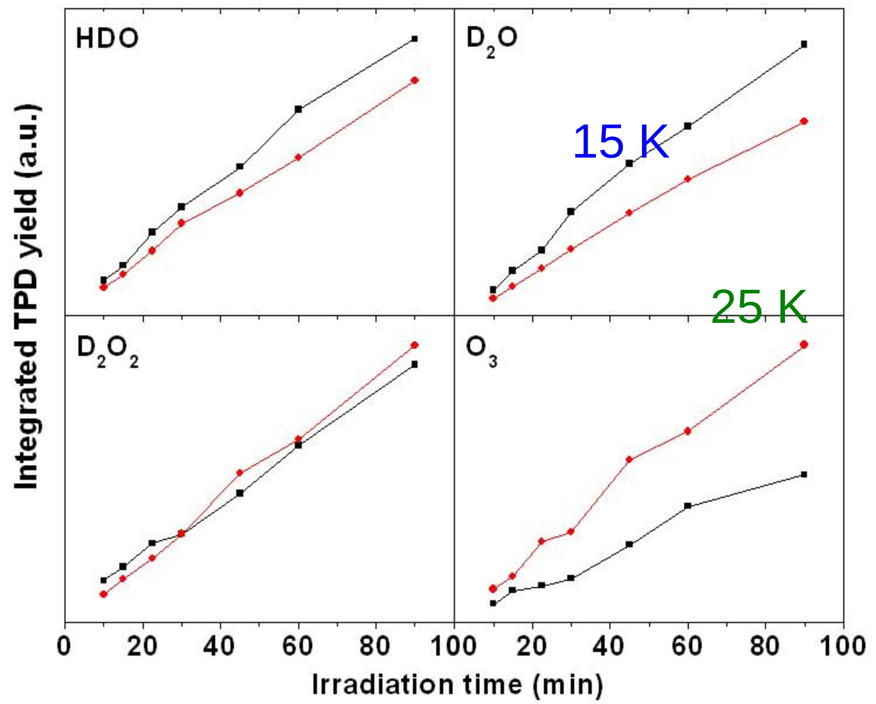
Desorption peaks for various species after D and O co-exposure. From bottom to top: 10 min, 15 min, 22.5 min, 30 min, 45 min, 60 min and 90 min.

Jing et al. 2011



RAIR spectra of D and O co-exposure for (from bottom to top) 1 hour, 2 hours, 3 hours, 4 hours, 5 hours and after annealing the sample at 70 K for 5 min after exposure. The spectra are displaced on the vertical axis for clarity.

Jing et al. 2011



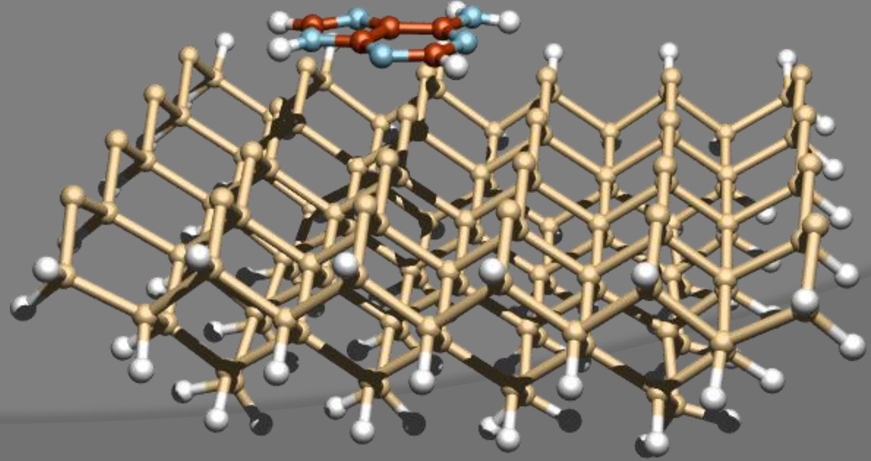
Binding energy

HDO 390 meV
D2O 400 meV
H2O 170 meV
D2O2 430 meV

	HDO	D_2O	D_2O_2	O_3
15 K Slope ($cm^{-2}min^{-1}$)	1.5×10^{13}	4.2×10^{13}	7.6×10^{13}	2.6×10^{12}
25 K Slope ($cm^{-2}min^{-1}$)	1.2×10^{13}	3.0×10^{13}	8.9×10^{13}	4.9×10^{12}
15 K Formation efficiency	0.043	0.12	0.22	0.007
25 K Formation efficiency	0.034	0.087	0.26	0.014

Crucial transition from inanimate matter to biological systems probably occurred through selection, concentration and organization of organic precursors, yielding to the essential macromolecules of life

? MINERALS ?



Interaction of Nucleic Acid Components with Mg-containing Minerals in two different Astrobiologically Relevant Environments:

1. Serpentinite-hosted Hydrothermal Vents

Lost City Hydrothermal Field

SERPENTINIZATION

$(Mg,Fe)_2SiO_4 + H_2O + C$ - - → $Mg_3SiO_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2 + CH_4 + C_2–C_5$

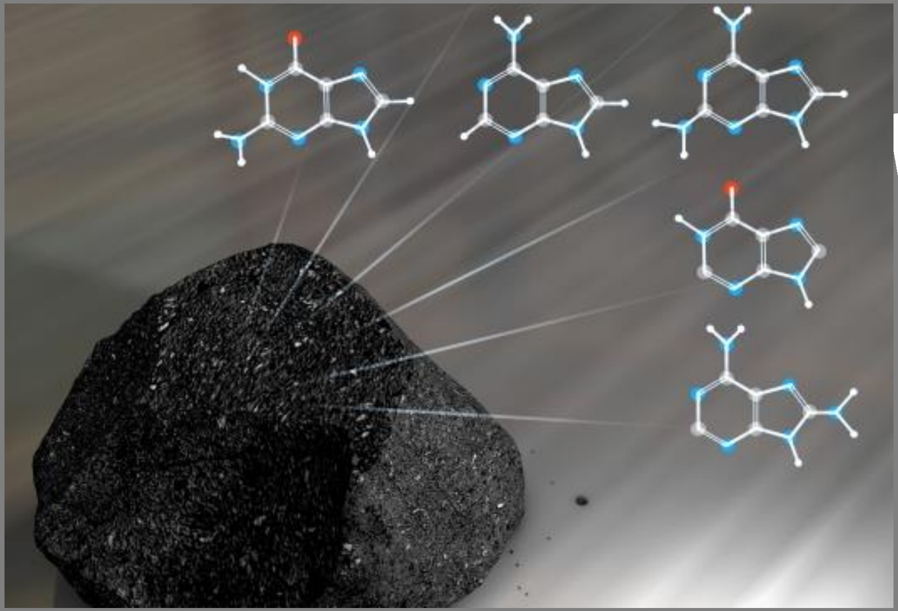
✓ **Disequilibria, redox gradient potentially catalyze formation of prebiotic molecules**

✓ **Lower temperatures typical of the Lost City hydrothermal fluids favor biosynthesis**

Barge L. M., Branscomb, E., Brucato, J. R., Cardoso, S. S. S., Cartwright, J. H. E., Danielache, S. O., Galante, D., Kee, T. P., Miguel, Y., Mojzsis, S., Robinson, K. J., Russell, M. J., Simoncini E, Sobron, P. *OLEB* **2016**

Interaction of Nucleic Acid Components with Mg-containing Minerals in two different Astrobiologically Relevant Environments:

2. High UV Irradiation and Space-like Environments



hν

Magnesium oxide (MgO);

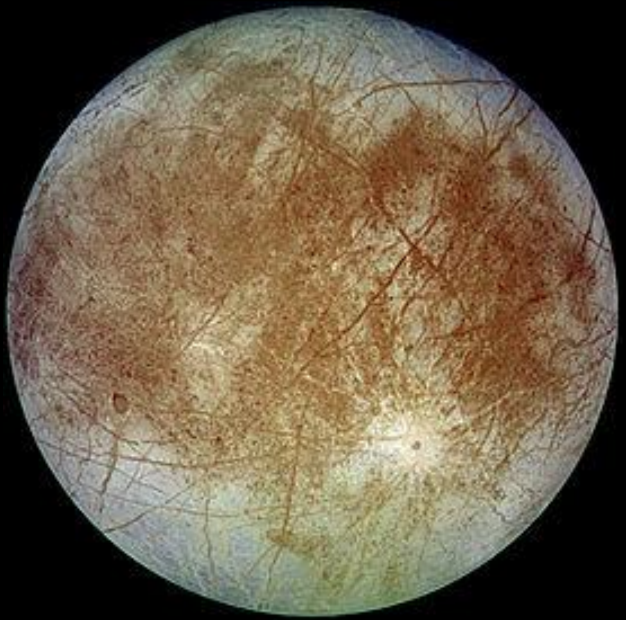
Forsterite (Mg_2SiO_4)

…

Weinbruch et al. *Meteoritics & Planetary Science* **2000**; Barber and Scott *PNAS* **2002**; Messenger et al. *Science* **2005**; Ming et al. *Journal of Geophysical Research* **2006**; Chevrier and Mathé *Planetary and Space Science* **2007**; Poteet et al. *The Astrophysical Journal Letters* **2011**.

POSSIBLE PRESENCE OF HYDROTHERMAL ACTIVITY

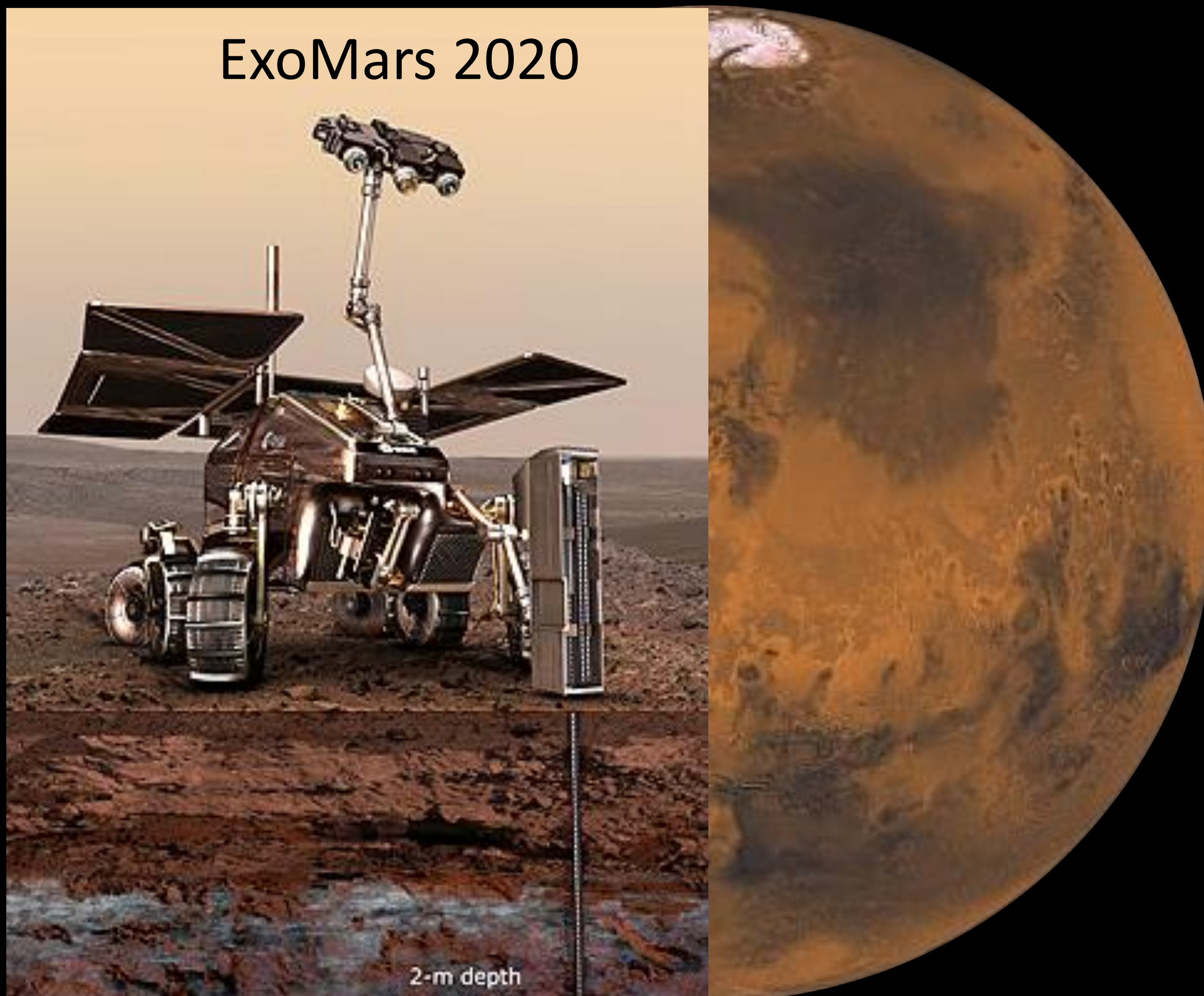
Jupiter’s moon Europa

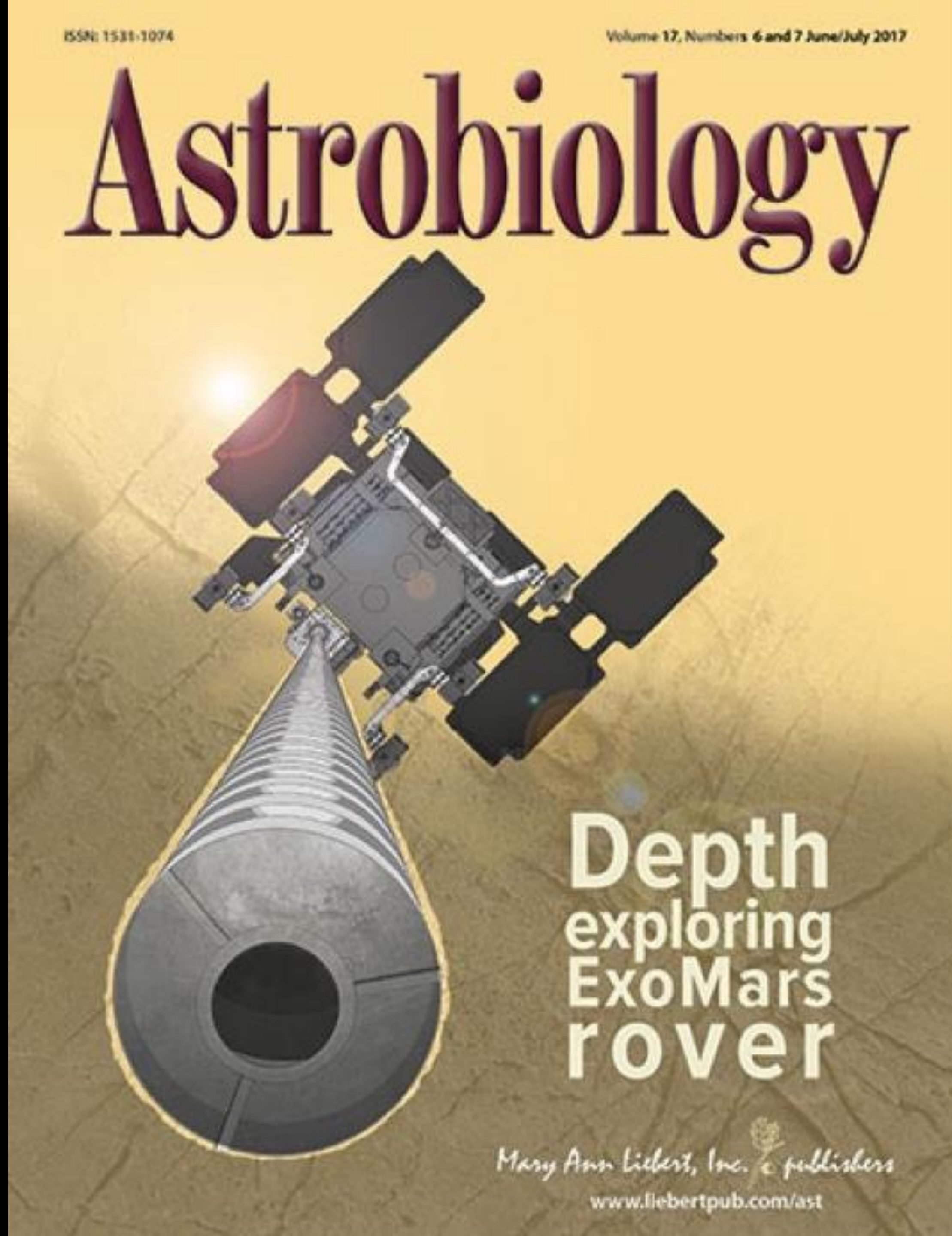


Saturn’s moon Enceladus

Past Mars (maybe Noachian era ~ 4.1 to 3.7 Gyr)

ExoMars 2020

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Astrobiology
Depth exploring ExoMars rover
Mary Ann Liebert, Inc. publishers
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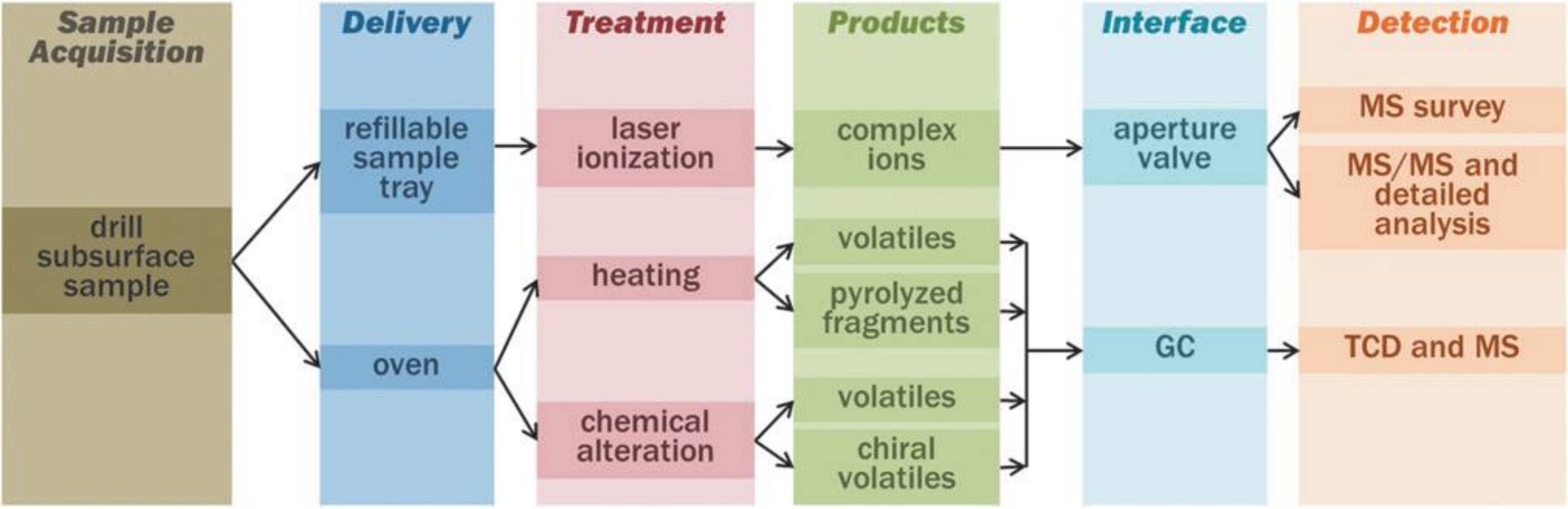
Mars Organic Molecule Analyzer (MOMA)
ExoMars 2020

O1. Detect and characterize organic molecular species in solid samples with high (ppb) sensitivity.
O2. Analyze patterns of, and interrelationships among, a variety of organic molecules over a wide range of molecular weights and volatilities.
O3. Analyze for the presence and degree of ee in detected chiral organics.
O4. Characterize the inorganic geochemical context of the organic analyses.

R1. MOMA shall be able to detect organic molecules at concentrations as low as 10 ppb.
R2. MOMA shall be able to identify organics with chainbased or ring-based structures.
R3. MOMA shall be able to characterize molecular weight distribution patterns in organic molecules over mass-to-charge ratio as high as 1000 u.
R4. MOMA shall be able to detect compounds of low stability (e.g. , formaldehyde)
R5. MOMA shall investigate the biotic or abiotic origin of organic chiral molecules by analyzing their enantiomers at molecular concentrations as low as 1 ppmw.
R6. MOMA shall be able to detect light volatile organics at concentrations as low as 1 ppmw.
R7. MOMA shall be able to detect refractory organics (e.g. , heavy PAHs, kerogen-like material) with molecular weights up to 1000 u at concentrations as low as 10 ppmw.

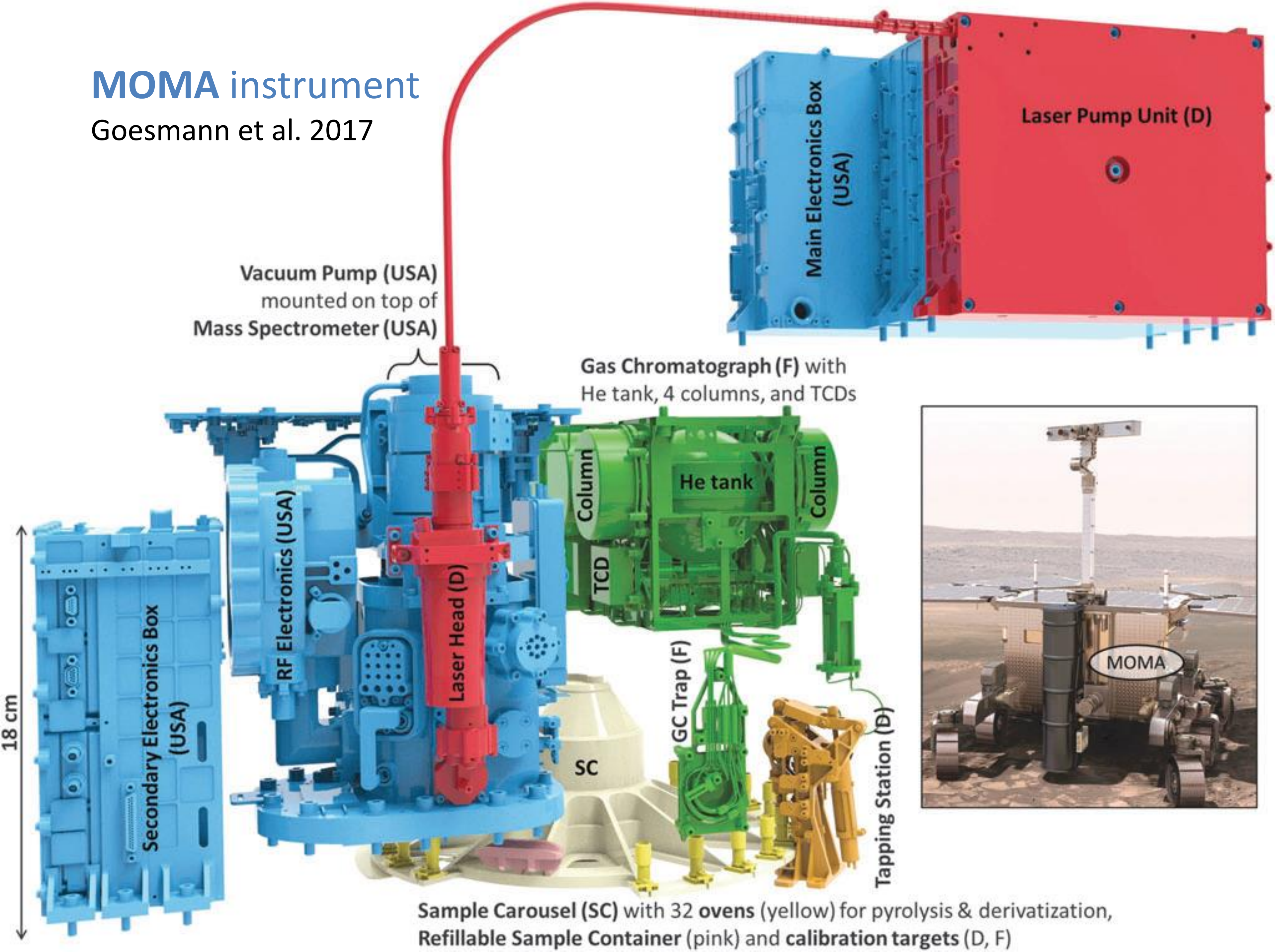
Mars Organic Molecule Analyzer (MOMA)
ExoMars 2020



Goesmann et al. 2017

MOMA instrument

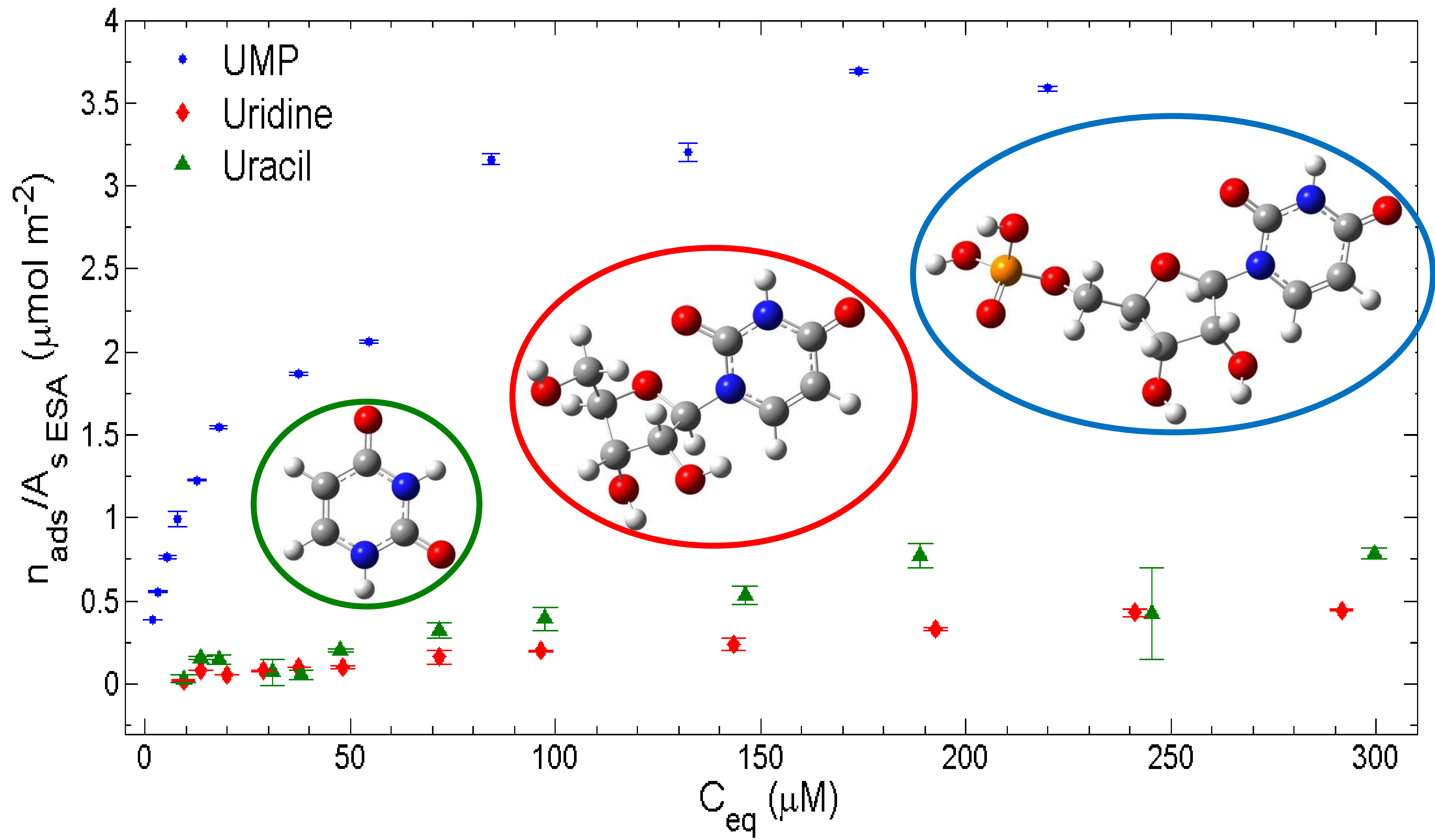
Goesmann et al. 2017



Minerals: **Metal Oxides, Hydroxides and Silicates**
Molecules: **nucleobases, nucleosites, nucleotides, aminoacids**

	DHN	Glu	Arg	Leu	Gly	Isoval	Nucleobeses	Nucleosites	Nucleotides
Oligoclasio							X	X	X
Lizardite	X				X		X	X	X
Pirite	X				X			X	X
Mimetite						X	X	X	X
Natrolite	X					X	X	X	X
Serpentinite	X				X	X	X	X	
Brucite	X				X	X	X	X	
Olivine	X				X		X	X	X
SiO2		X	X	X					

Adsorption of Uracil, Uridine and UMP on Brucite in Water

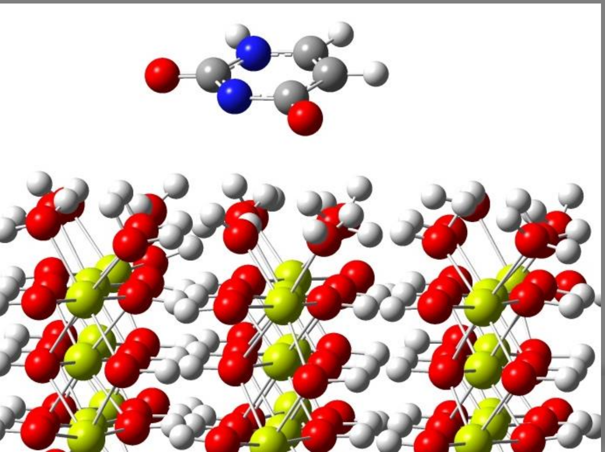


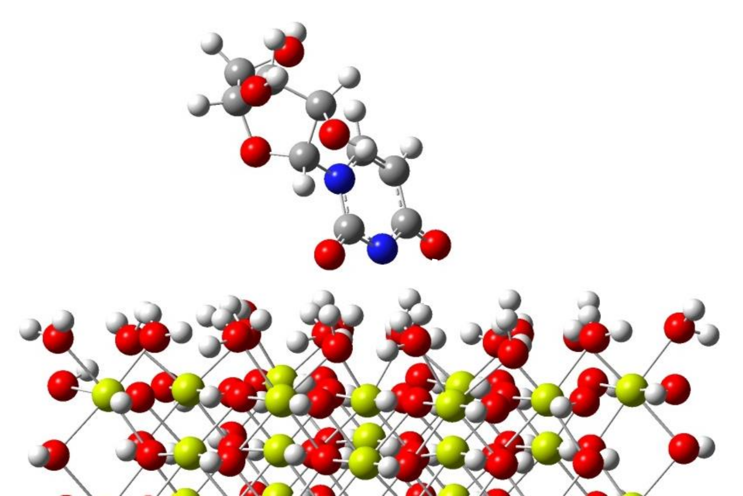
Ribose not involved in the adsorption (only weak outer-sphere interactions)
Strong interactions via Phosphate group

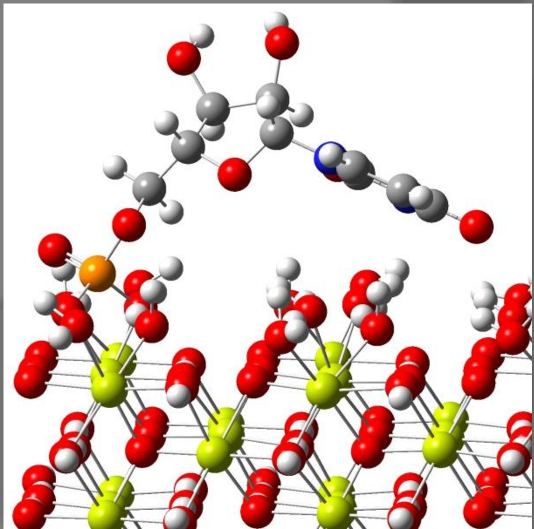
SERPENTINITE-HOSTED HYDROTHERMAL MINERALS

- Brucite selectively adsorbs nucleic acid components from dilute aqueous environments, suggesting a role in concentrating biomolecules in prebiotic conditions

- Brucite surface induces well-defined orientations of the molecules through specific molecule-mineral interactions, suggesting a role in assisting prebiotic self-organization, increasing molecular complexity and promoting chemical reactions towards more complex species

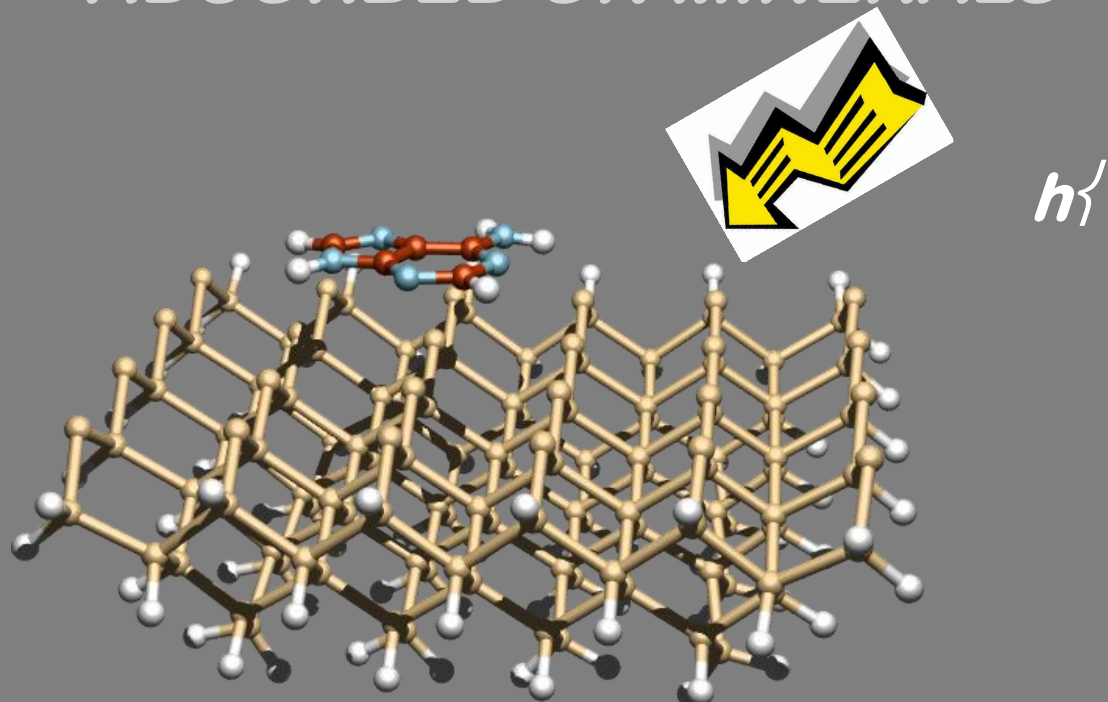




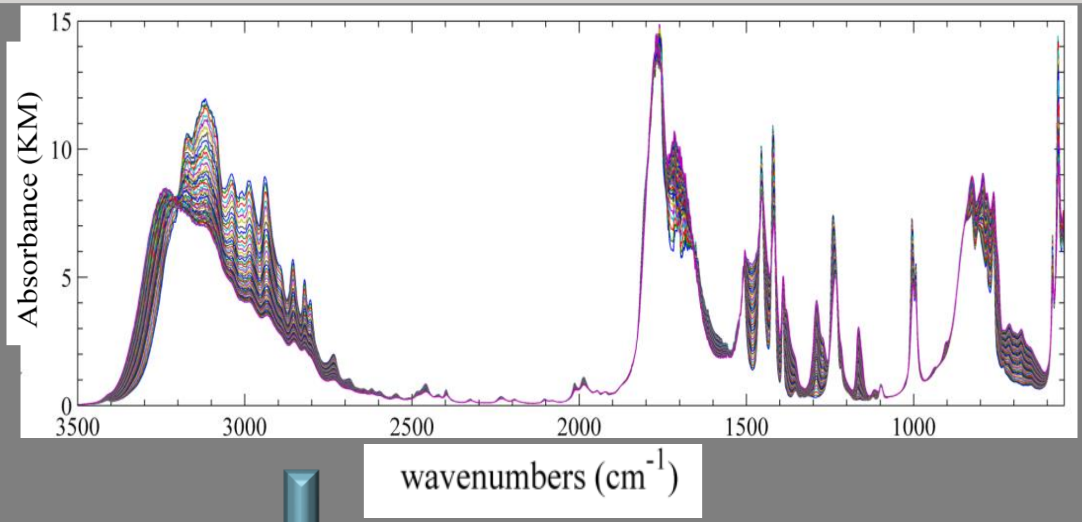


HIGH UV IRRADIATION AND SPACE-LIKE ENVIRONMENTS

UV IRRADIATION OF "BUILDING BLOCKS OF LIFE" ADSORBED ON MINERALS



UV degradation kinetics



$$N(t)/N_0 = Be^{-\beta t} + c$$

$N(t)/N_0$ fraction of unaltered molecules
β degradation rate
B fraction of interacting molecules
c fraction of non-interacting molecules

$$t_{1/2} = \ln 2 / \beta$$

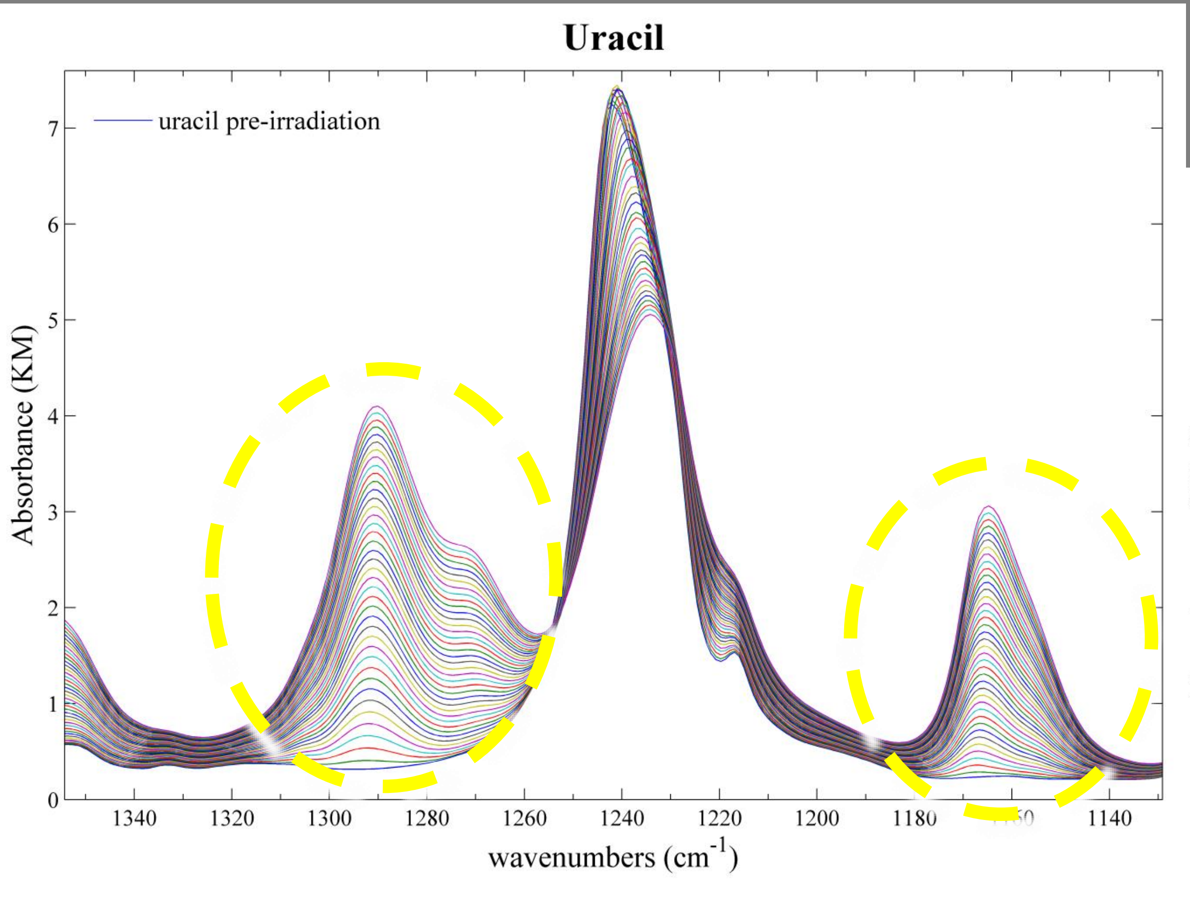
$$\beta = \sigma \Phi_{tot} / A_0$$

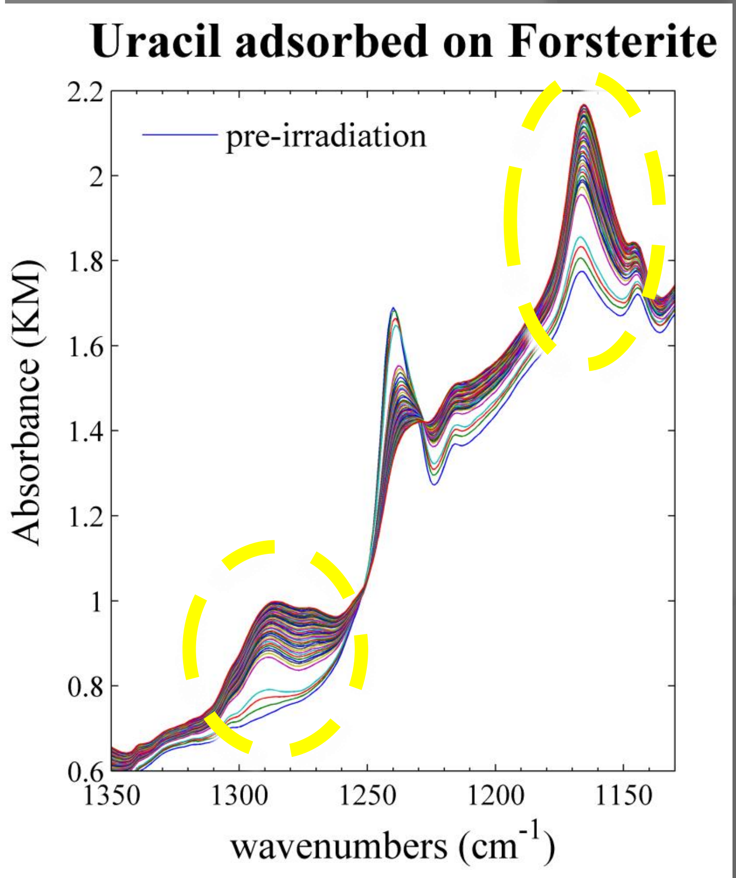
$t_{1/2}$ half-lifetime
σ UV destruction cross section
Φ_{tot} total focused incident UV flux
A_0 sample irradiated area

- **Cytosine** and **hypoxanthine** have a greater photostability
- For **adenine** and especially **uracil** degradation was observed both pure and adsorbed onto MgO and forsterite
- **Minerals** make degradation faster and more probable

Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*(1), 1068-1085.

Photoproducts marker bands

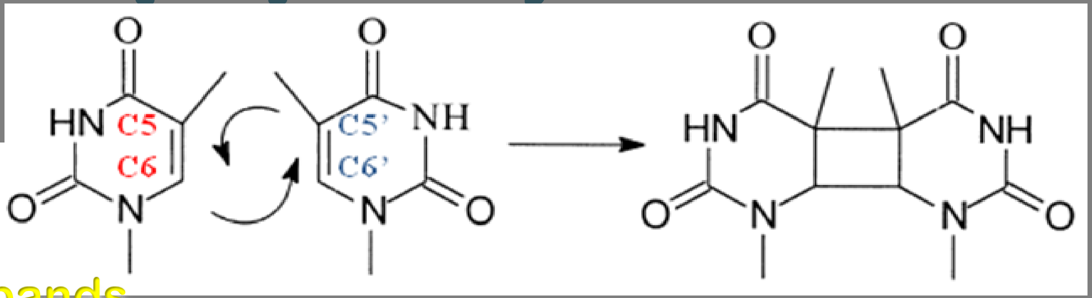


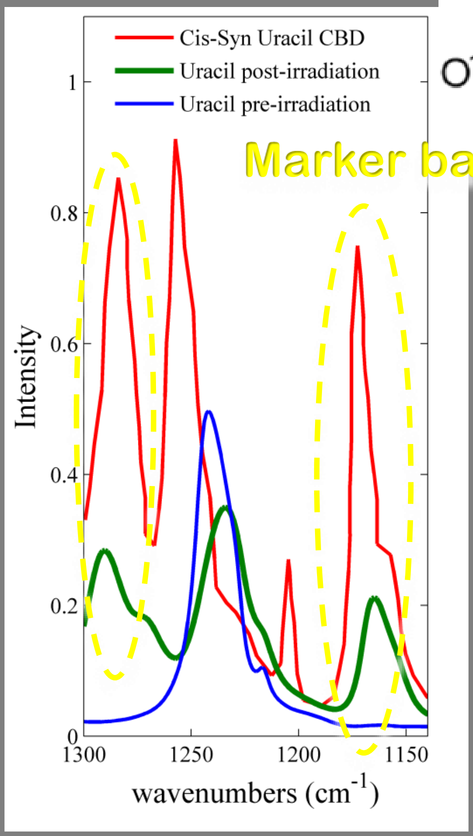


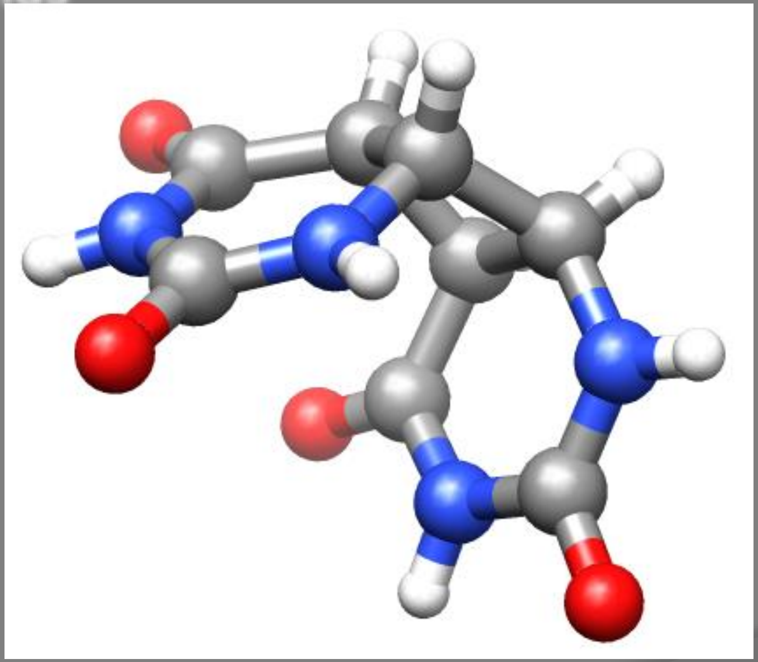
Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*(1), 1068-1085.

Photoproducts

[2+2] Photocycloaddition





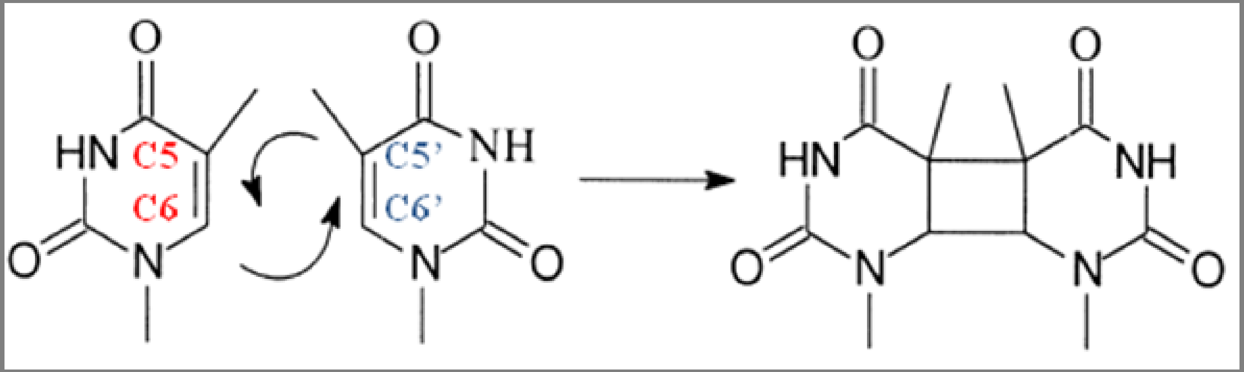


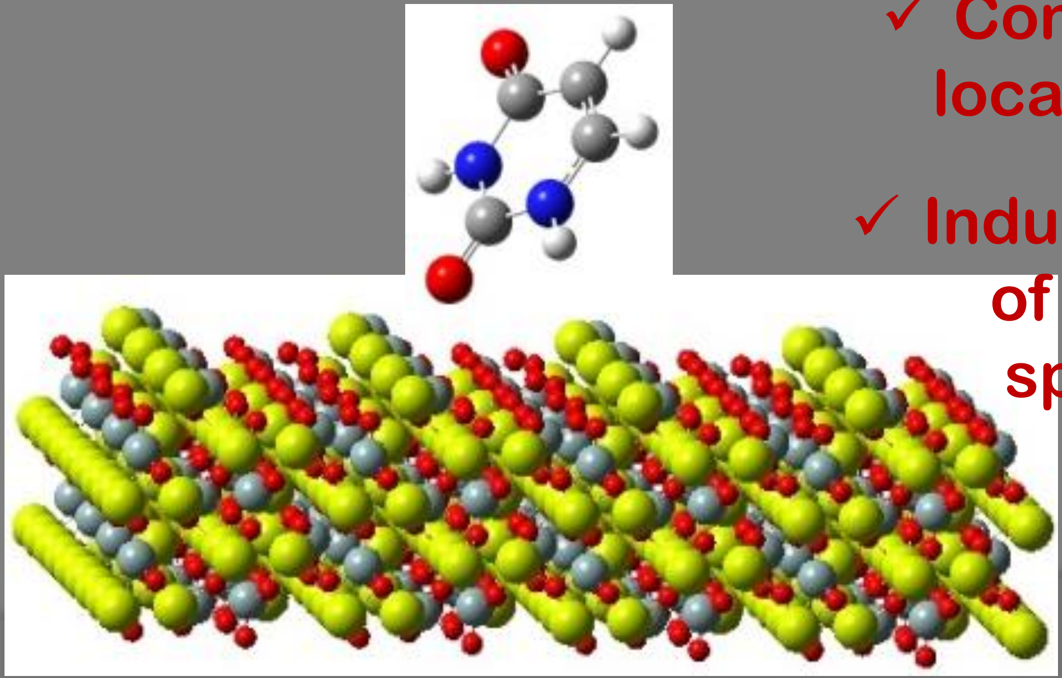
Main photoproduct:

Cis-syn cyclobutane dimer (CBD)

Catalytic Effect of Forsterite

[2+2] Photocycloaddition

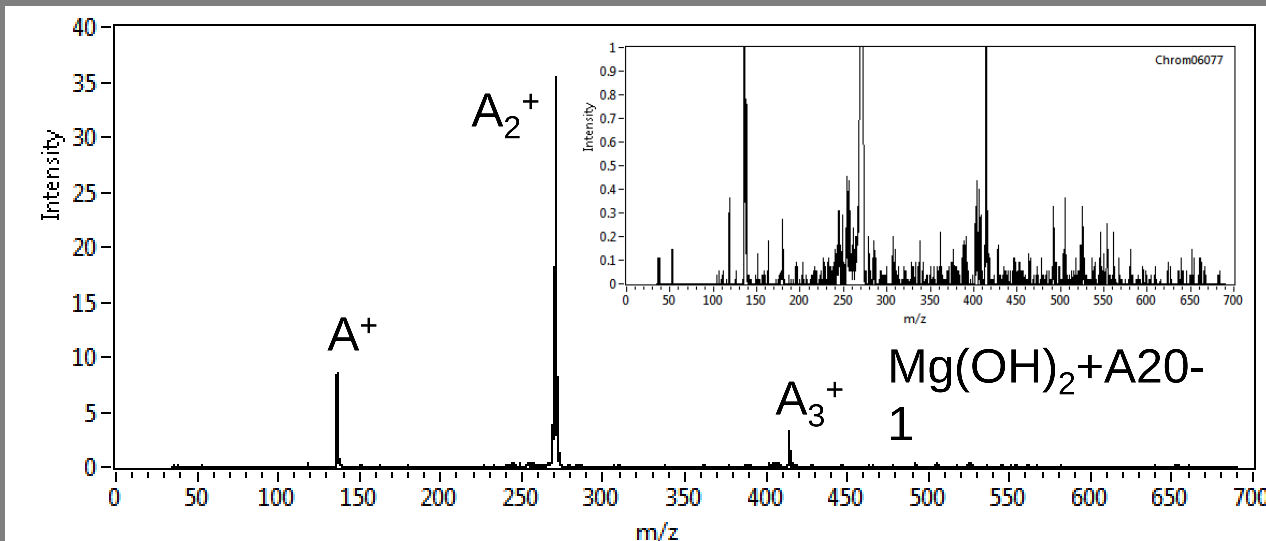


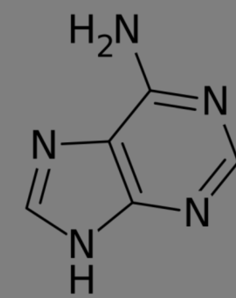


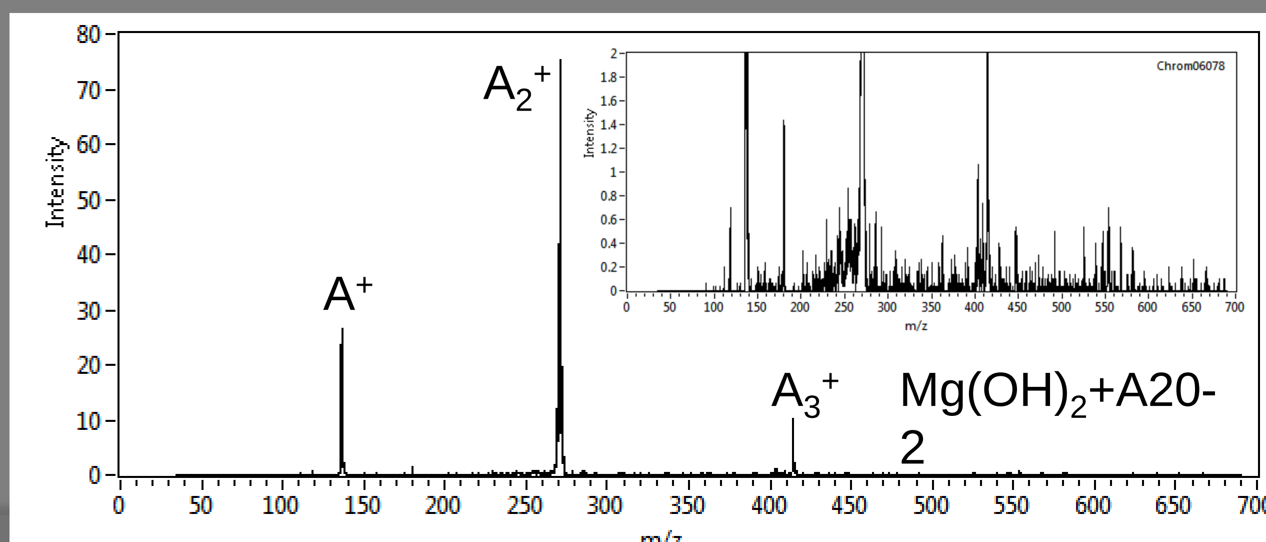
- ✓ Concentrates molecules on a local scale through adsorption
- ✓ Induces the correct orientation of reactive groups through specific molecule-mineral interactions

MOMA LDI Tests

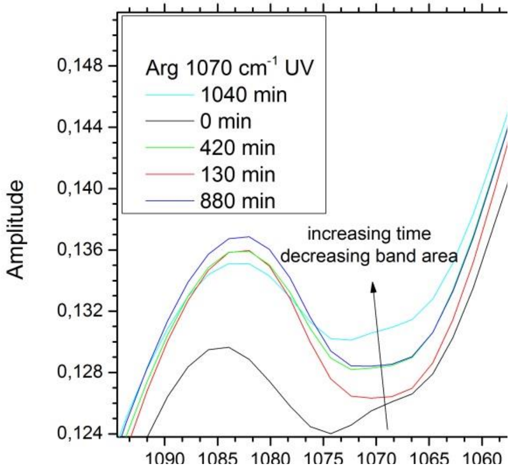
20 mM Adenine on Brucite

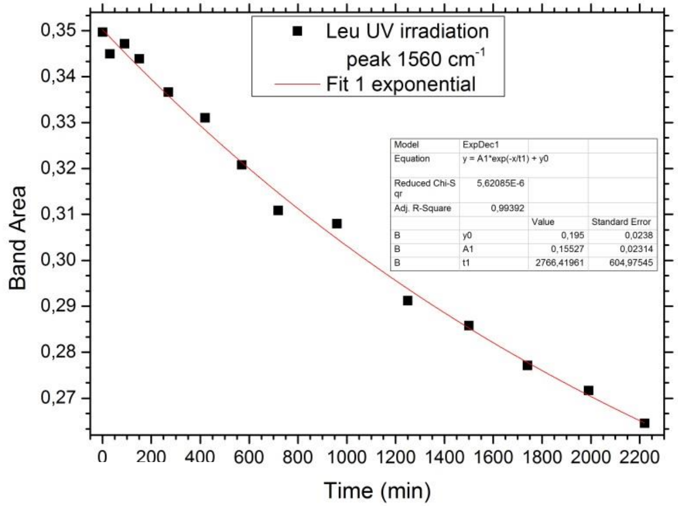




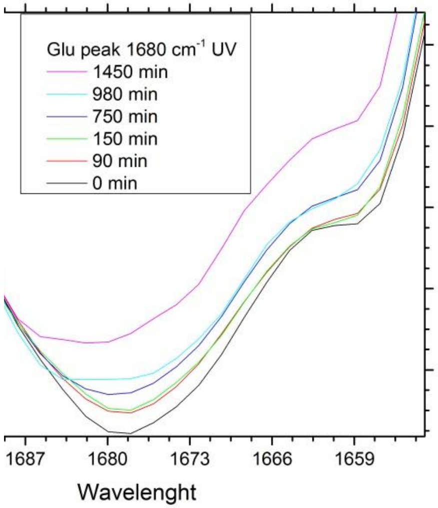


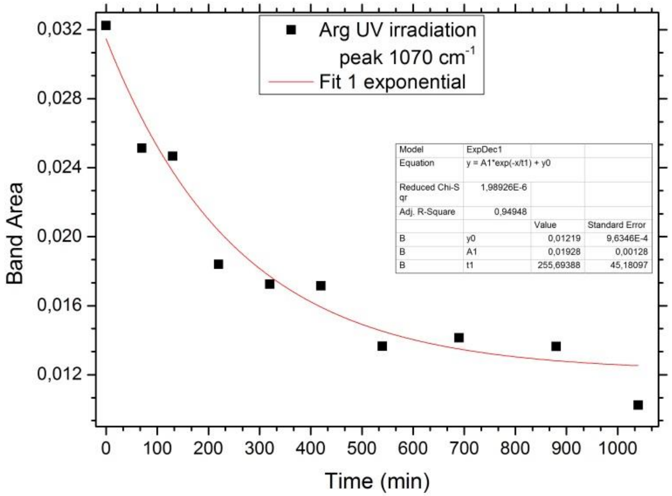
Arg and Leu UV irradiation



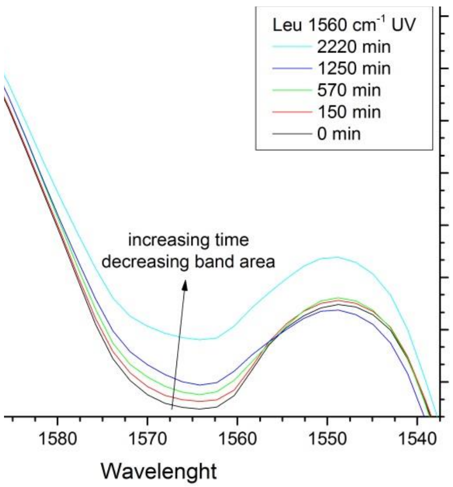


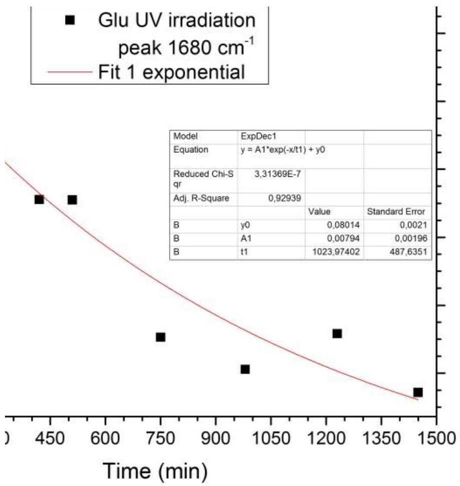
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	5,62085E-6		
Adj. R-Square	0,99392		
		Value	Standard Error
B	y0	0,195	0,0238
B	A1	0,15527	0,02314
B	t1	2766,41961	604,97545





Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1,98926E-6		
Adj. R-Square	0,94948		
		Value	Standard Error
B	y0	0,01219	9,6346E-4
B	A1	0,01928	0,00128
B	t1	255,69388	45,18097

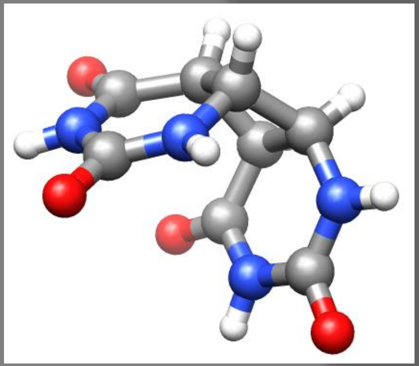




Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	3,31369E-7		
Adj. R-Square	0,92939		
		Value	Standard Error
B	y0	0,08014	0,0021
B	A1	0,00794	0,00196
B	t1	1023,97402	487,6351

	Life-time (min)	Cross-section (m^2) x 10^{-26}
Glutamic acid 1680 cm^{1}	1.0 ± 0.5	2 ± 1
Glutamic acid 670 cm^{1}	0.6 ±0.1	3.6 ± 0.7
Glutamic acid 1267 cm^{1}	2.7 ± 3.5	0.8 ± 1.1
Leucine 1560 cm^{1}	2.8 ± 0.6	0.8 ± 0.2
Leucine 670 cm^{1}	2.8 ± 0.8	0.8 ± 0.3
Leucine 1530 cm^{1}	2.2 ± 0.9	1.0 ± 0.5
Arginine 1070 cm^{1}	0.26 ± 0.05	9 ± 2

HIGH UV IRRADIATION AND SPACE-LIKE ENVIRONMENTS



- **Uracil is the most photoreactive, probably forming cyclobutane dimers**

- **MgO and Forsterite have no protective effect, instead they may be catalytic potentially triggering chemical processes towards more complex species**

Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*, 1068-1085.
Fornaro T.; Brucato, J. R.; Branciamore, S.; Pucci, A. *International Journal of Astrobiology* **2013**, *12* (1), 78-86.

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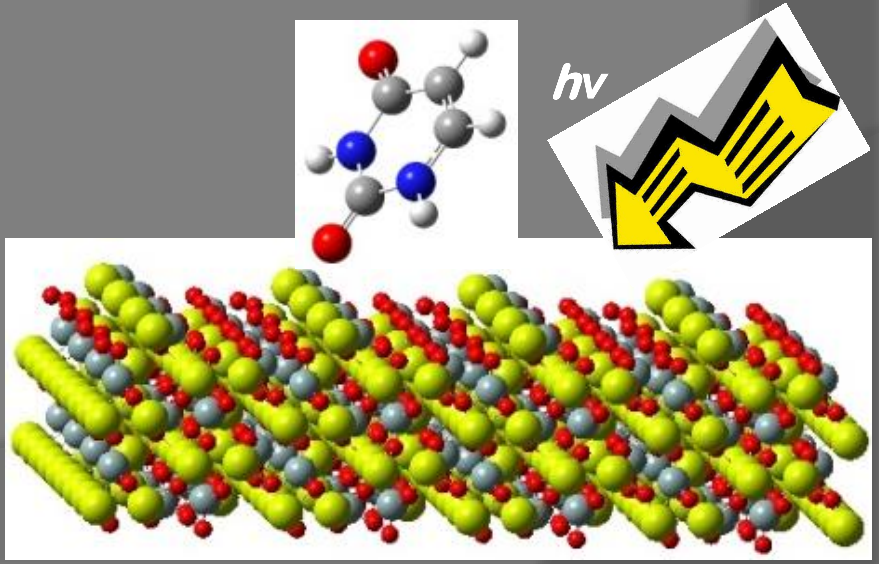
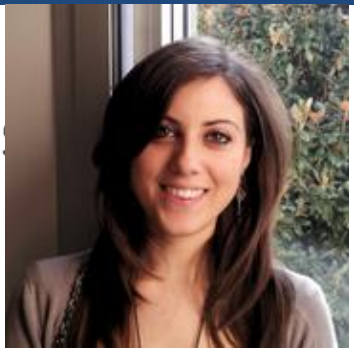
Mineral surfaces have the ability to selectively adsorb and concentrate organic molecules on a local scale, removing key organics from aqueous environments, promoting self-organization through specific molecule- mineral interactions

Minerals can act as photocatalysts promoting reactions towards more complex species



Acknowledgements



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