Heterogeneous Catalysis of Organic Molecules in Harsh Environments

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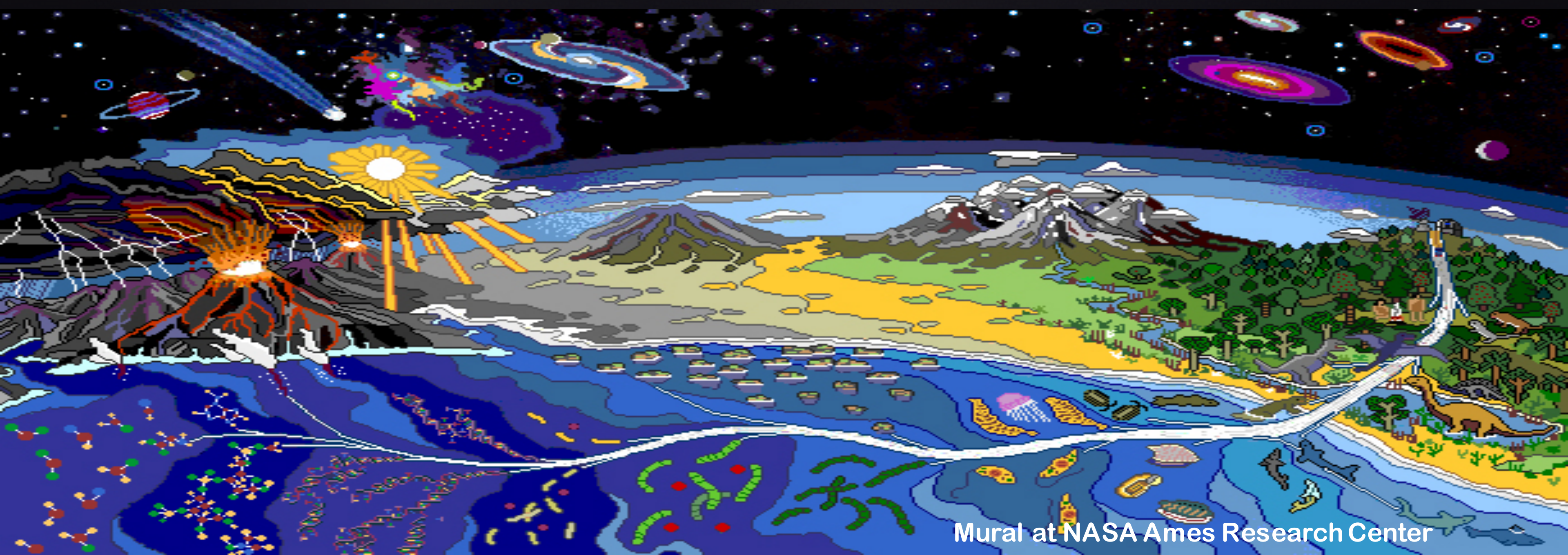
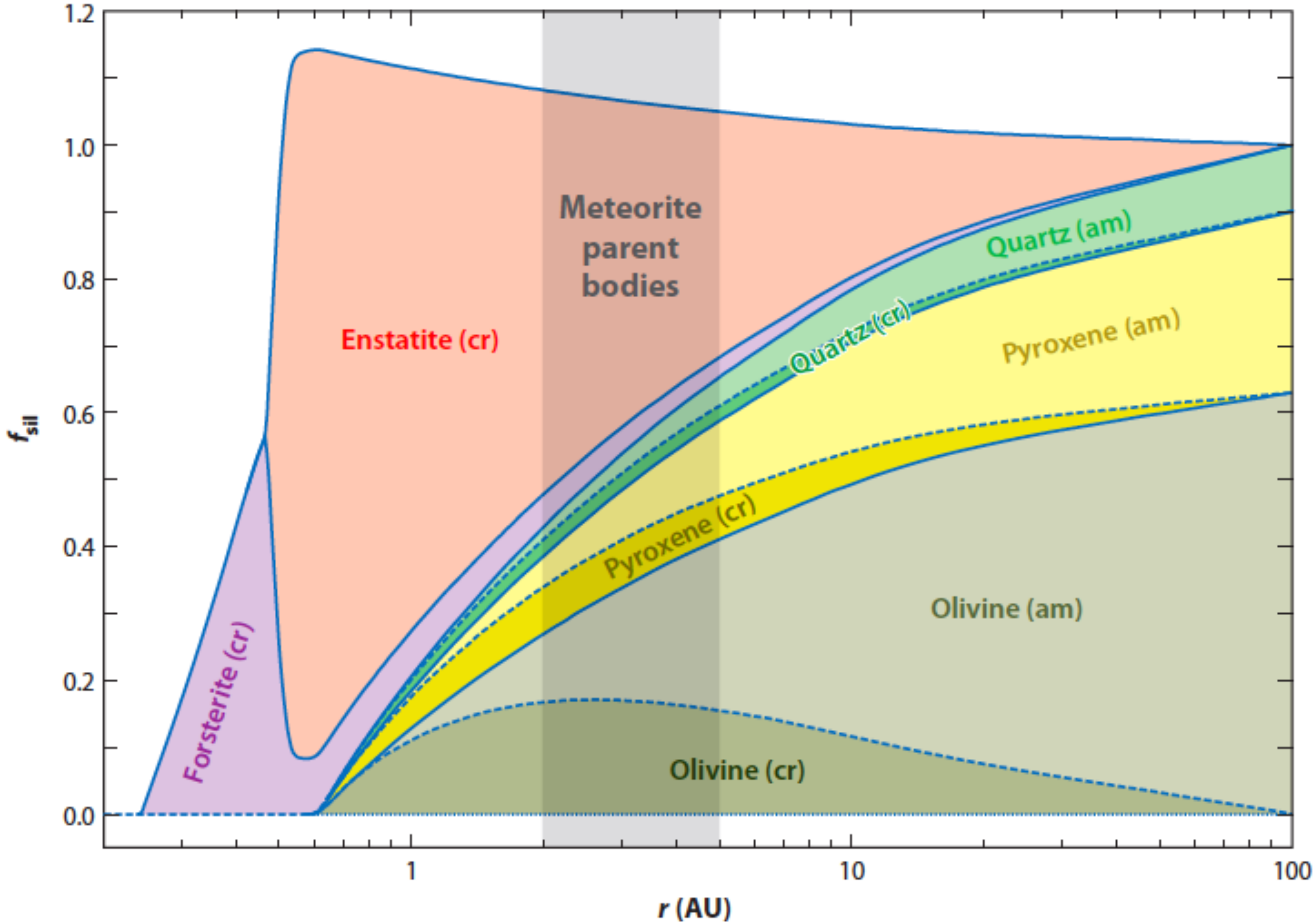
Cosmic Rays – the salt of the star formation recipe
2-4 May 2018, Firenze


Mural at NASA Ames Research Center

Talk Outline

- Gas
  - Atoms reaction
- Liquid
  - Thermal reaction
  - UV irradiation
- Solid
  - Ion & UV irradiation



1.2
1.0
0.8
0.6
0.4
0.2
0.0
f_{sil}
1
10
100
r (AU)
Meteorite parent bodies
Enstatite (cr)
Forsterite (cr)
Quartz (am)
Quartz (cr)
Pyroxene (am)
Pyroxene (cr)
Olivine (am)
Olivine (cr)

Gail 2004

ISM, Comets and Interplanetary Dust Particles inventory

Oxides: SiO_2, MgO, FeO, Fe_2O_3, TiO_2, ZrO_2, Al_xO_y

Silicon Carbide: SiC

a-Carbon

Sulfides: FeS, NiS

Silicates
- Olivine: $(Mg,Fe)_2SiO_4$
- Pyroxene: $(Mg,Fe)SiO_4$
- Spinel: $MgAl_2O_4$
- Diopsite: $CaMgSi_2O_4$
- Melilite: $(Ca,Na)_2(Al,Mg)[(Si,Al)_2O_7]$

Carbonates
- Calcite: $CaCO_3$
- Dolomite: $CaMg(CO_3)_2$

The role of minerals and metal oxides on prebiotic processes. A general overview

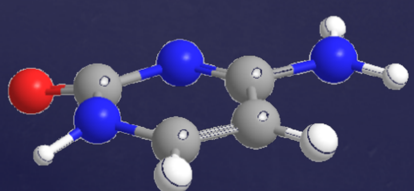
- Minerals can accumulate the prebiotic precursors;
- Minerals can act as catalyst, reducing the activation energy for the formation of products;
- Minerals can tune the selectivity of prebiotic syntheses;
- Minerals may act as a template;
- Minerals are benign environments to preserve newly formed biomolecules from degradation;

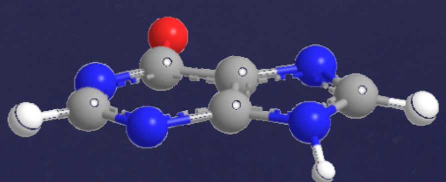
Some Facts

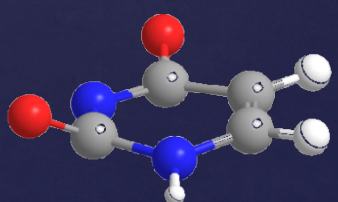
✓ **Minerals:** pivotal role in the prebiotic evolution of complex chemical systems by

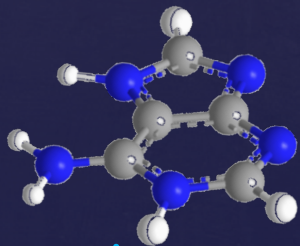
- **mediating** the effects of ion and photon radiation
- **influencing** the photostability of bio-molecules
- **catalyzing** important chemical reactions
- **protecting** molecules against degradation

✓ Study the photochemistry and the photophysics of **biomolecules** in the presence of mineral matrices, to investigate both the **survivability** when exposed to **physical and chemical processes occurring in extraterrestrial environments.**


Cytosine


Hypoxanthine


Uracil


Adenine

Minerals: Metal Oxides, Hydroxides and Silicates (am & cry)

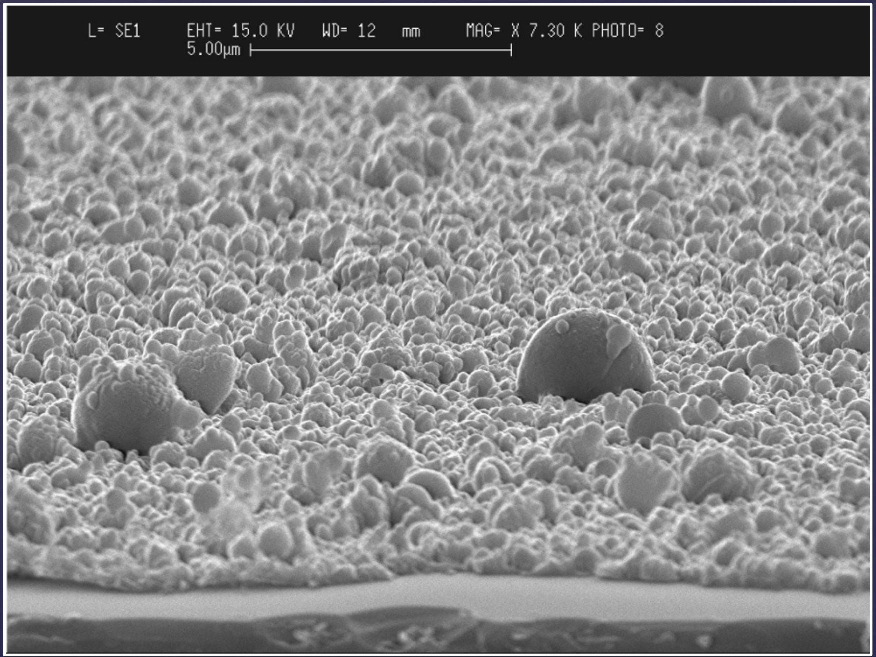
Molecules: Nucleobases, Nucleosites, Nucleotides, Aminoacids

	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					

Synthetic Silicate Produced in Laboratory

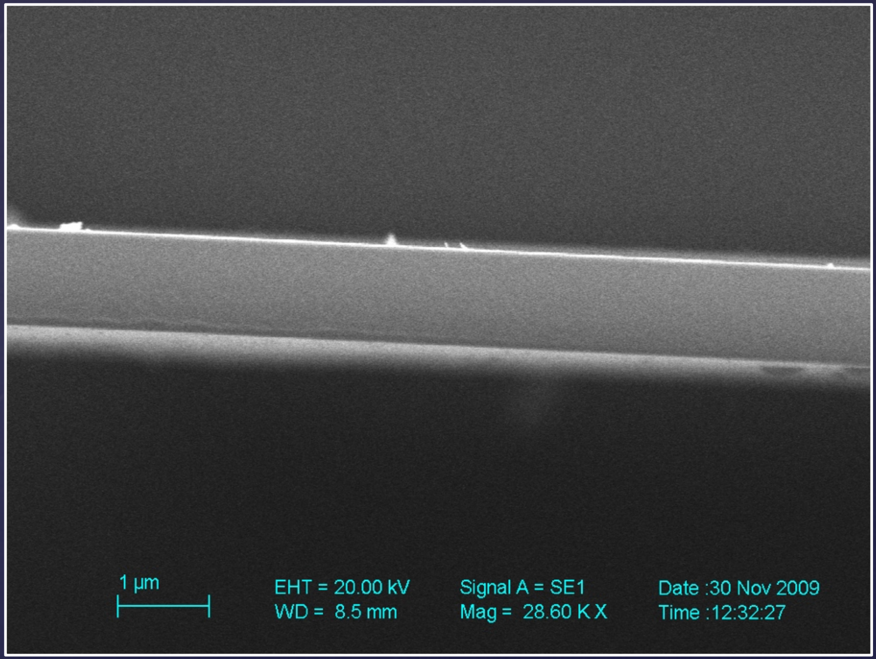
Amorphous silicates

Laser ablation



Fluffy

Electron Beam

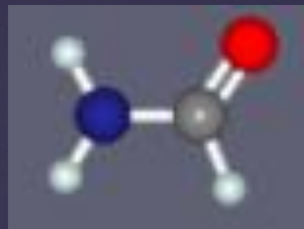


Thin film

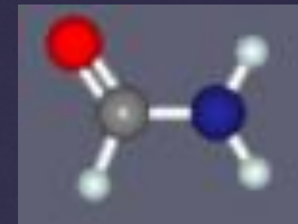
COMPLEX ORGANIC INTERSTELLAR MOLECULES

Herbst & van Dishoeck 2009

Species	Name	Source	Species	Name	Source
Hydrocarbons			**N-Containing**		
C_2H_4	Ethene	circ	CH_3CN	Acetonitrile	cc, hc, of
HC_4H	Butadiyne	circ	CH_3NC	Methylisocyanide	hc
H_2C_4	Butatrienylidene	circ, cc, lc	CH_2CNH	Keteneimine	hc
C_5H	Pentadiynyl	circ, cc	HC_3NH^+	Prot. cyanoacetylene	cc
CH_3C_2H	Propyne	cc, lc	C_5N	Cyanobutadiynyl	circ, cc
C_6H	Hexatriynyl	circ, cc, lc	HC_4N	Cyanopropynylidene	circ
C_6H^-	Hexatriynyl ion	circ, cc, lc	CH_3NH_2	Methylamine	hc, gc
H_2C_6	Hexapentaenylidene	circ, cc, lc	C_2H_3CN	Vinylcyanide	cc, hc
HC_6H	Triacetylene	circ	HC_5N	Cyanodiacetylene	circ, cc
C_7H	Heptatriynyl	circ, cc	CH_3C_3N	Methylcyanoacetylene	cc
CH_3C_4H	Methyldiacetylene	cc	CH_2CCHCN	Cyanoallene	cc
CH_3CHCH_2	Propylene	cc	NH_2CH_2CN	Aminoacetonitrile	hc
C_8H	Octatetraynyl	circ, cc	HC_7N	Cyanotriacetylene	circ, cc
C_8H^-	Octatetraynyl ion	circ, cc	C_2H_5CN	Propionitrile	hc
CH_3C_6H	Methyltriacetylene	cc	CH_3C_5N	Methylcyanodiacetylene	cc
C_6H_6	Benzene	circ	HC_9N	Cyanotetraacetylene	circ, cc
O-Containing			C_3H_7CN	N-propyl cyanide	hc
CH_3OH	Methanol	cc, hc, gc, of	$HC_{11}N$	Cyanopentaacetylene	circ, cc
HC_2CHO	Propynal	hc, gc	**S-Containing**		
$c\text{-}C_3H_2O$	Cyclopropenone	gc	CH_3SH	Methyl mercaptan	hc
CH_3CHO	Acetaldehyde	cc, hc, gc	**N,O-Containing**		
C_2H_3OH	Vinyl alcohol	hc	NH_2CHO	Formamide	
$c\text{-}CH_2OCH_2$	Ethylene oxide	hc, gc	CH_3CONH_2	Acetamide	hc, gc
$HCOOCH_3$	Methyl formate	hc, gc, of			
CH_3COOH	Acetic acid	hc, gc			
$HOCH_2CHO$	Glycolaldehyde	hc, gc			
C_2H_3CHO	Propenal	hc, gc			
C_2H_5OH	Ethanol	hc, of			
CH_3OCH_3	Methyl ether	hc, gc			
CH_3COCH_3	Acetone	hc			
$HOCH_2CH_2OH$	Ethylene glycol	hc, gc			
C_2H_5CHO	Propanal	hc, gc			
$HCOOC_2H_5$	Ethyl formate	hc			

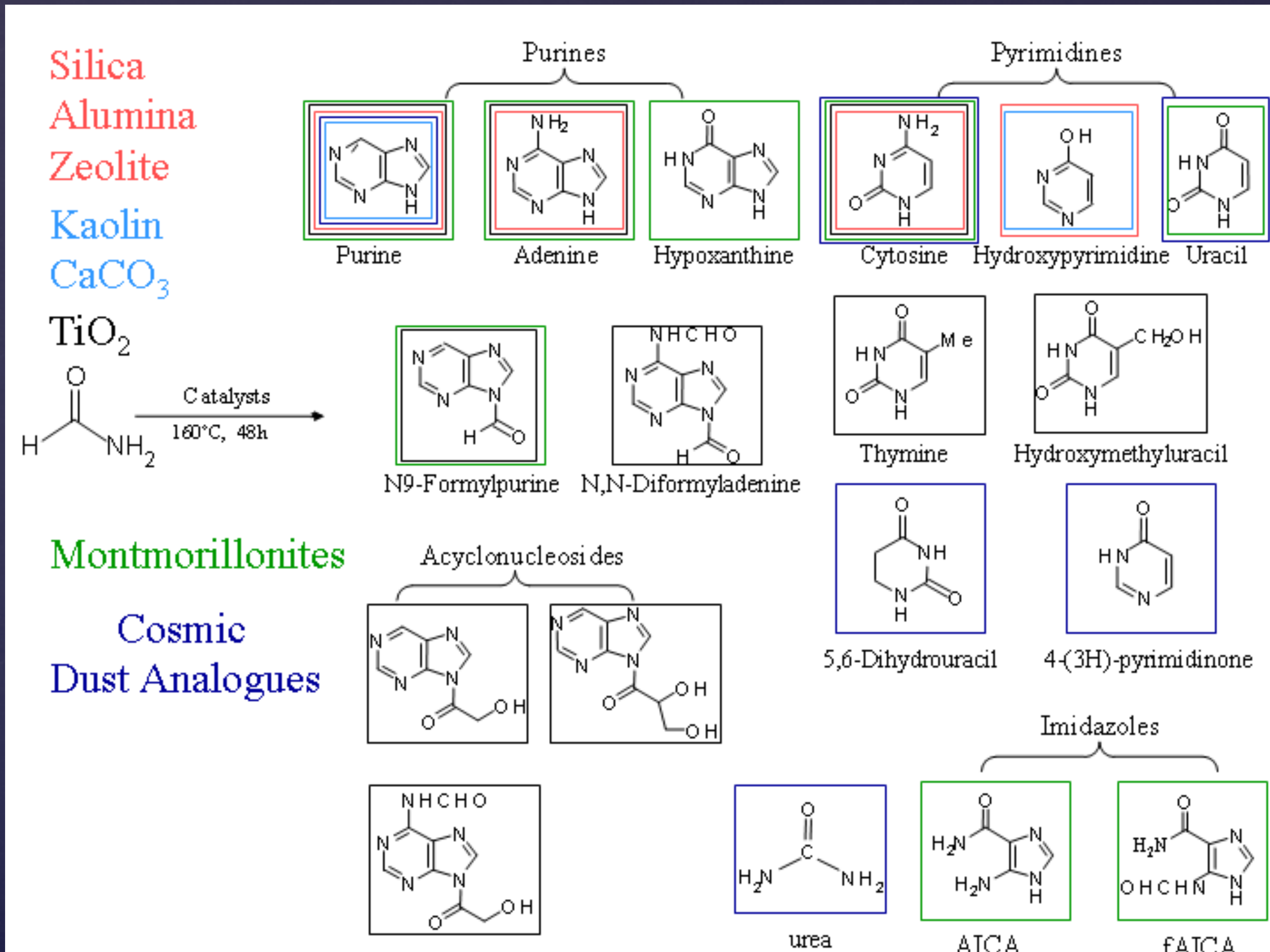


Why Formamide?

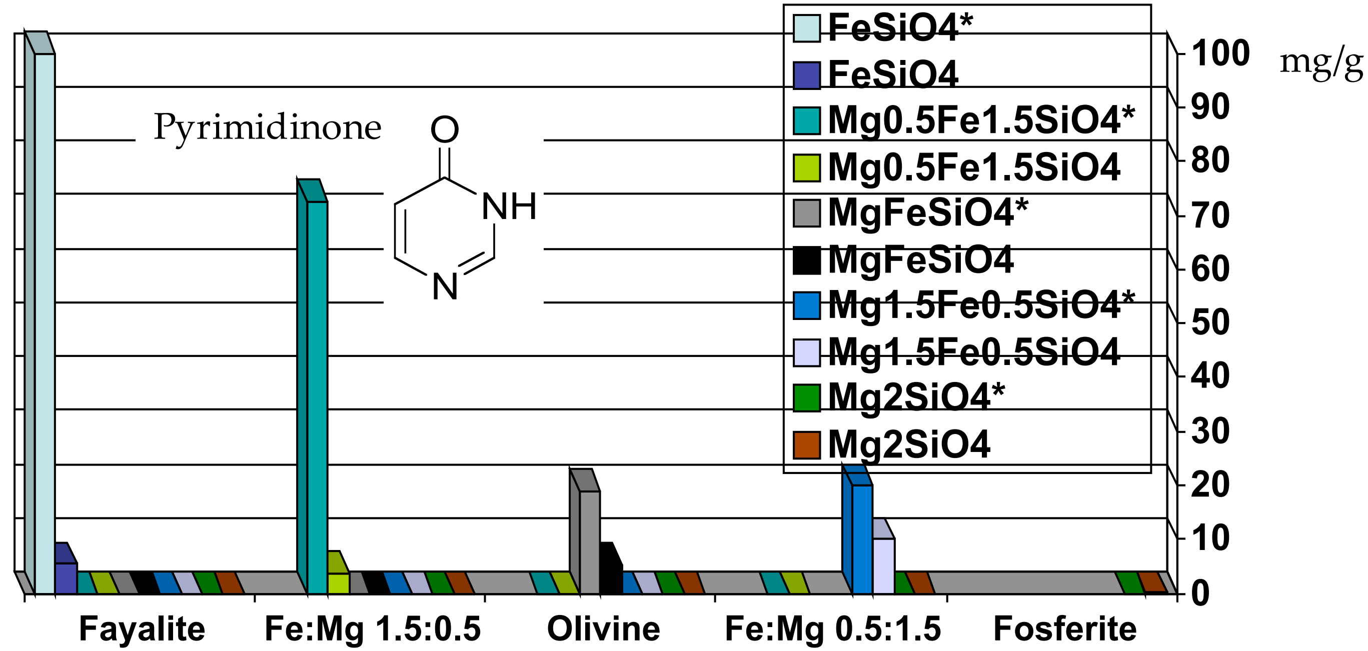


- It’s a simple one C-bearing molecule.
- It’s formed by hydrolysis of HCN.
- It’s active in synthesis of nucleobases.
- It’s observed in:
  - ✓ ISM (Millar 2005);
  - ✓ Hale-Bopp comet (Bockeleé-Morvan et al. 2000);
  - ✓ young stellar object W33A (Lopez-Sepulcre et al. 2015);
  - ✓ dense ISM IRS9 (Raunier et al. 2000)
  - ✓ Sun-like protostellar shock (Codella et al. 2017).

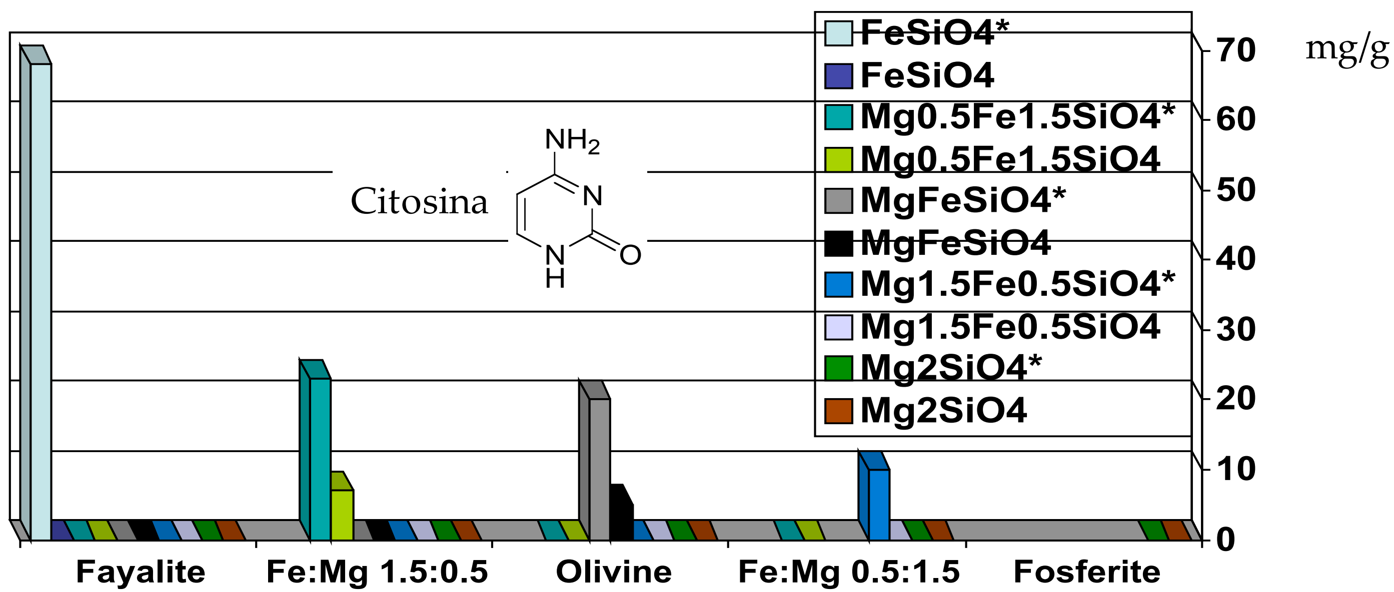
Thermal processing of *liquid* Formamide with & without dust



Saladino R., Crestini C., Neri C., Brucato J.R., Colangeli L. Ciciriello F., Di Mauro E., Costanzo G., *ChemBioChem* **6**, 1, 2005

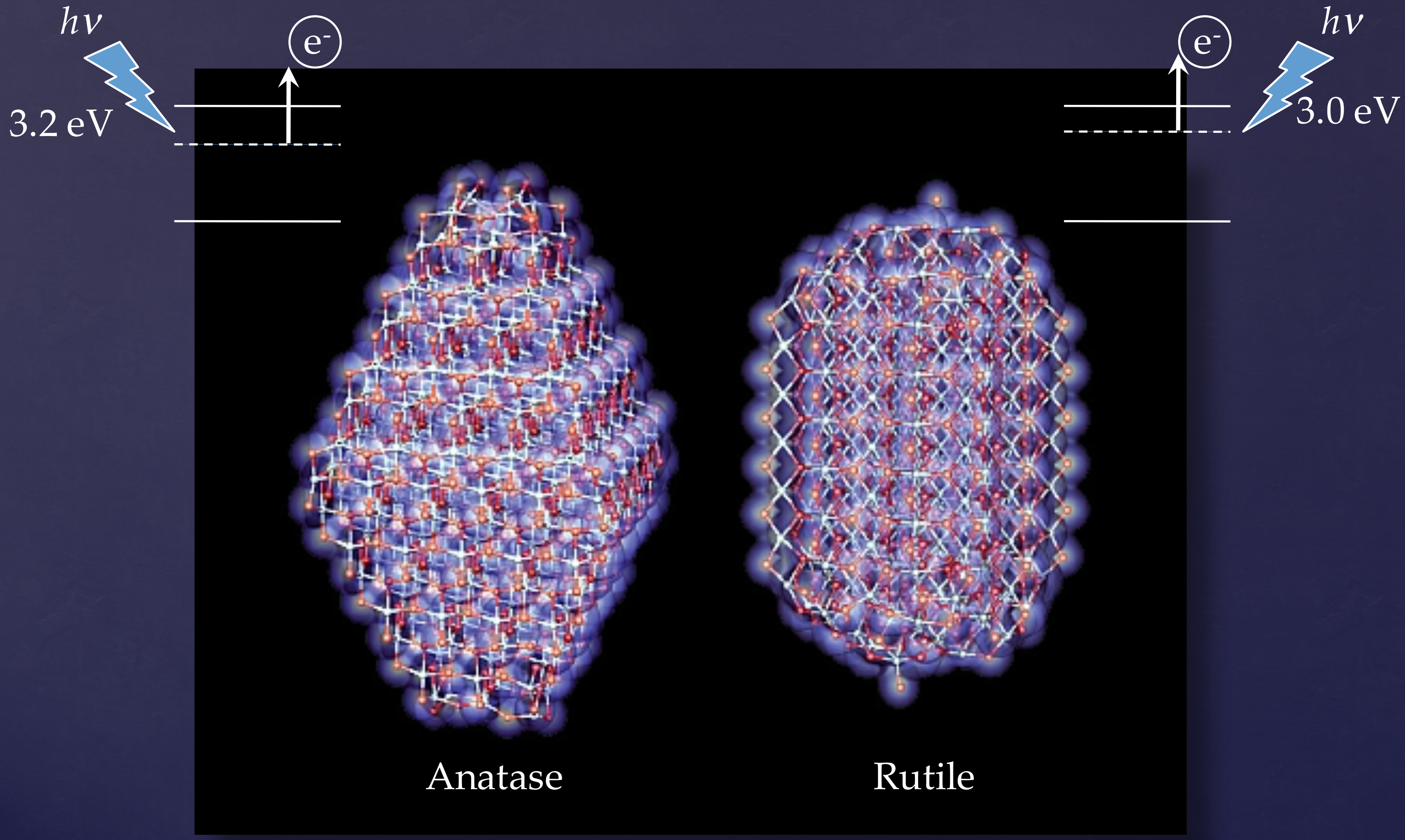


Pyrimidinone
O
NH
N
FeSiO4*
FeSiO4
Mg0.5Fe1.5SiO4*
Mg0.5Fe1.5SiO4
MgFeSiO4*
MgFeSiO4
Mg1.5Fe0.5SiO4*
Mg1.5Fe0.5SiO4
Mg2SiO4*
Mg2SiO4
100
90
80
70
60
50
40
30
20
10
0
mg/g
Fayalite
Fe:Mg 1.5:0.5
Olivine
Fe:Mg 0.5:1.5
Fosferite

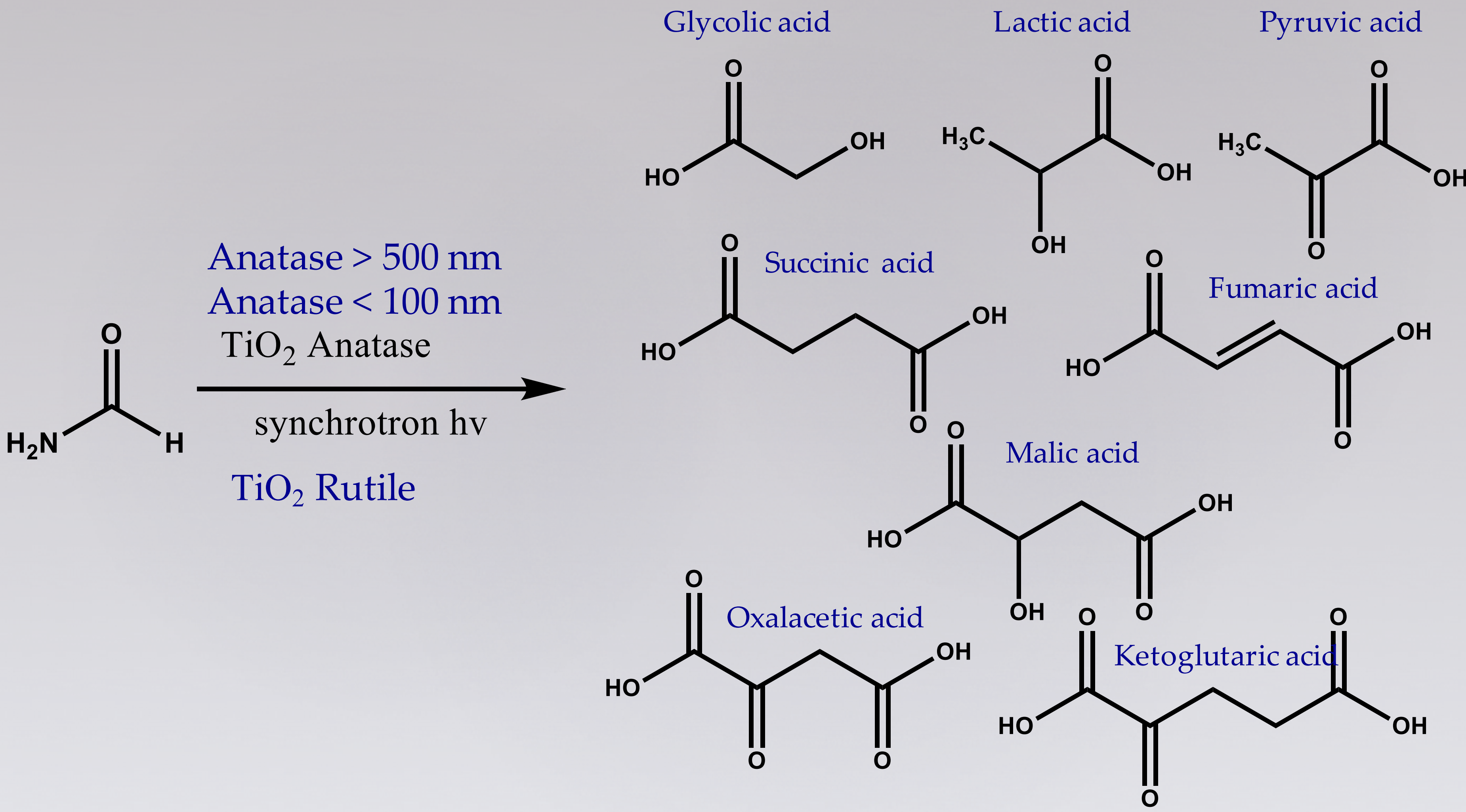


Citosina
NH2
N
N
H
O
FeSiO4*
FeSiO4
Mg0.5Fe1.5SiO4*
Mg0.5Fe1.5SiO4
MgFeSiO4*
MgFeSiO4
Mg1.5Fe0.5SiO4*
Mg1.5Fe0.5SiO4
Mg2SiO4*
Mg2SiO4
70
60
50
40
30
20
10
0
mg/g
Fayalite
Fe:Mg 1.5:0.5
Olivine
Fe:Mg 0.5:1.5
Fosferite

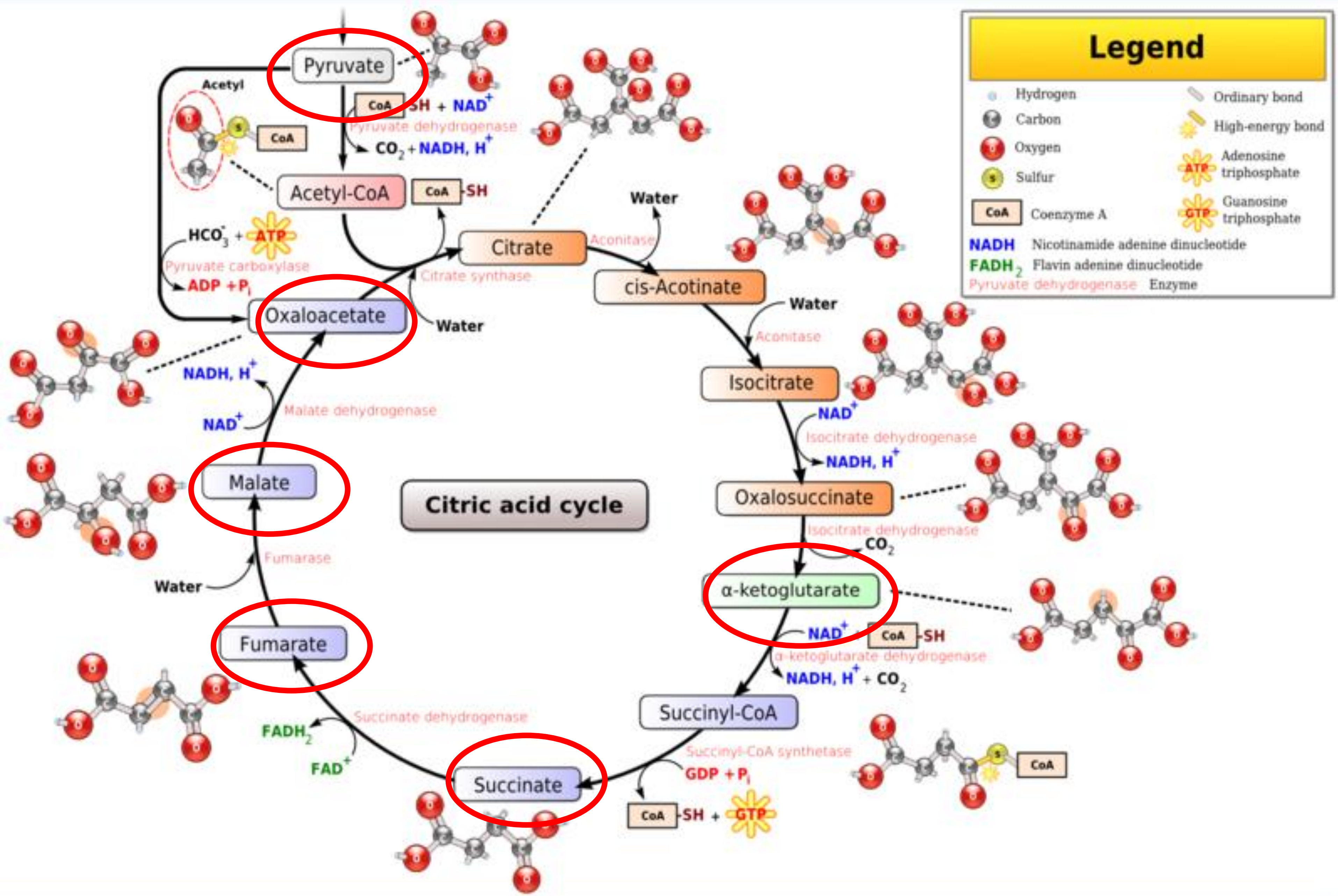
Titanium dioxide Photochemistry



Biogenic Carboxylic Acids

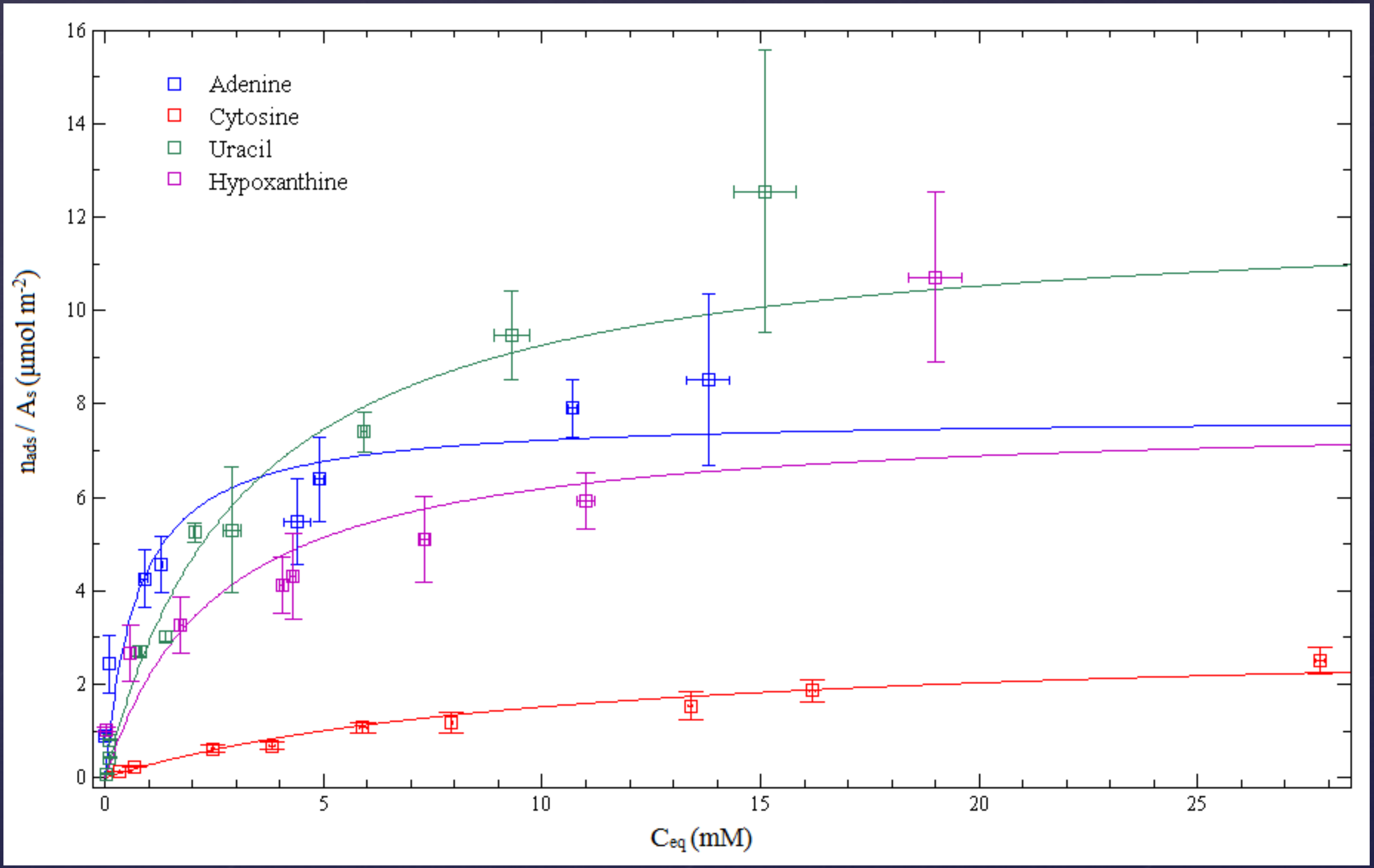


R. Saladino, J.R. Brucato, ASTROBIOLOGY 2011


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

Adsorption properties of nucleobases on minerals

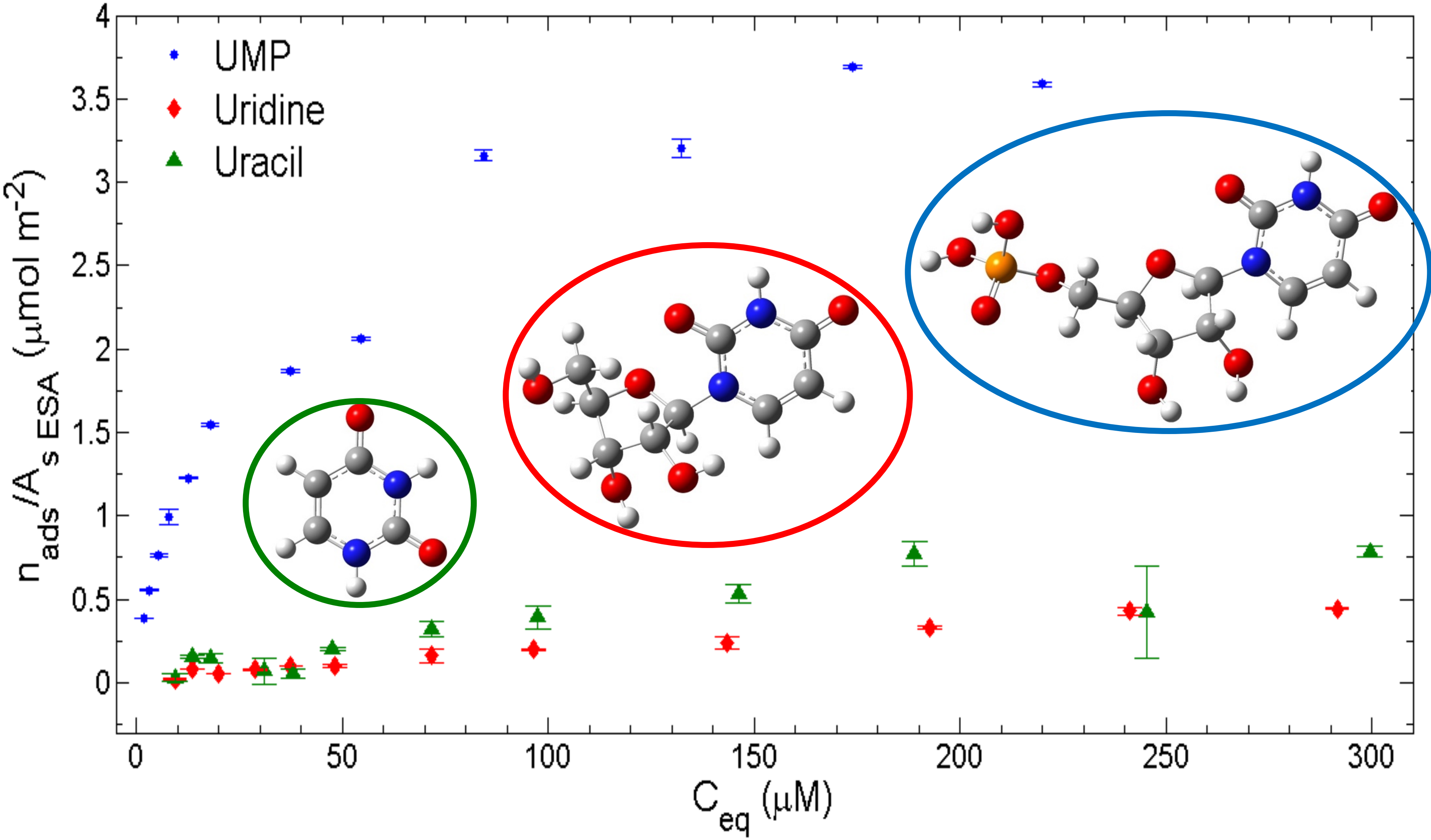
$$n_{ads}/m_{mineral} = KbC_{eq} / (1 + KC_{eq})$$



Nucleobases adsorption order:

adenine > uracil ≥ hypoxanthine > cytosine

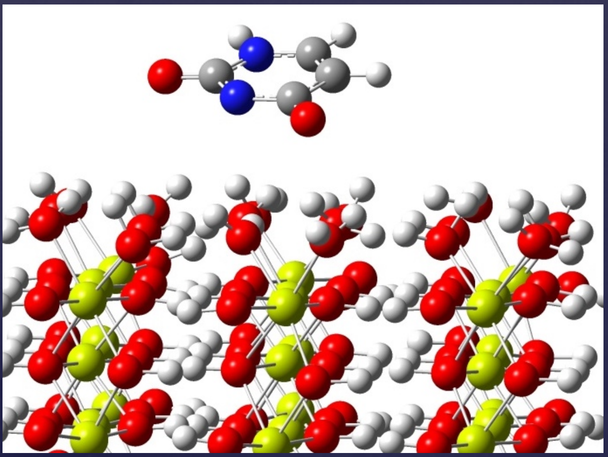
Adsorption of Uracil, Uridine and UMP on Brucite

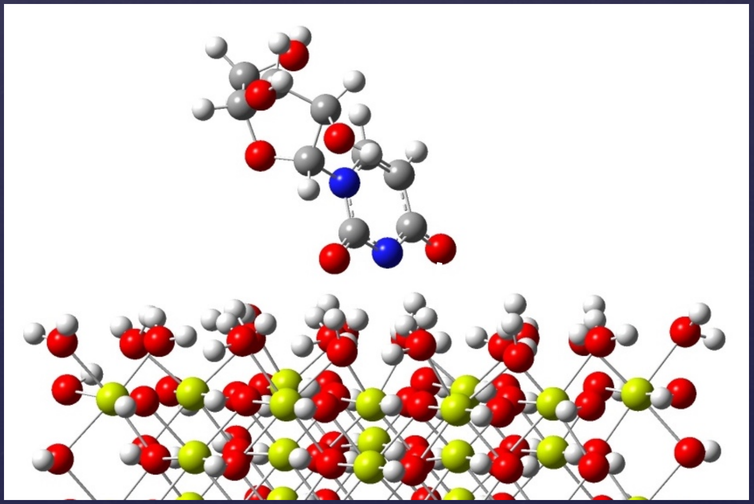


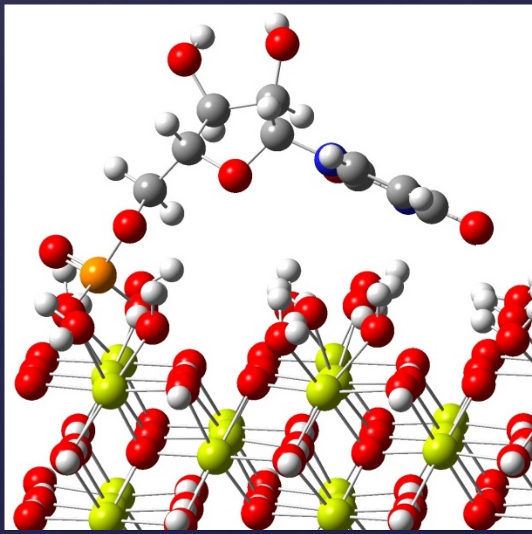
Ribose not involved in the adsorption (only weak outer-sphere interactions)
Strong interactions via Phosphate group

- 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

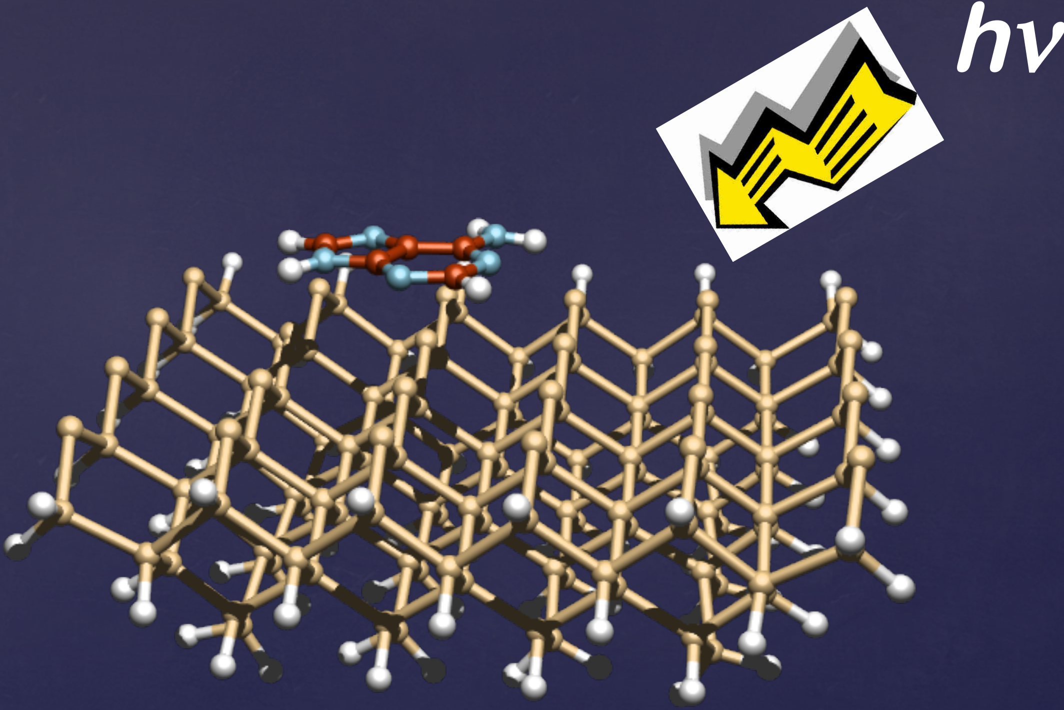




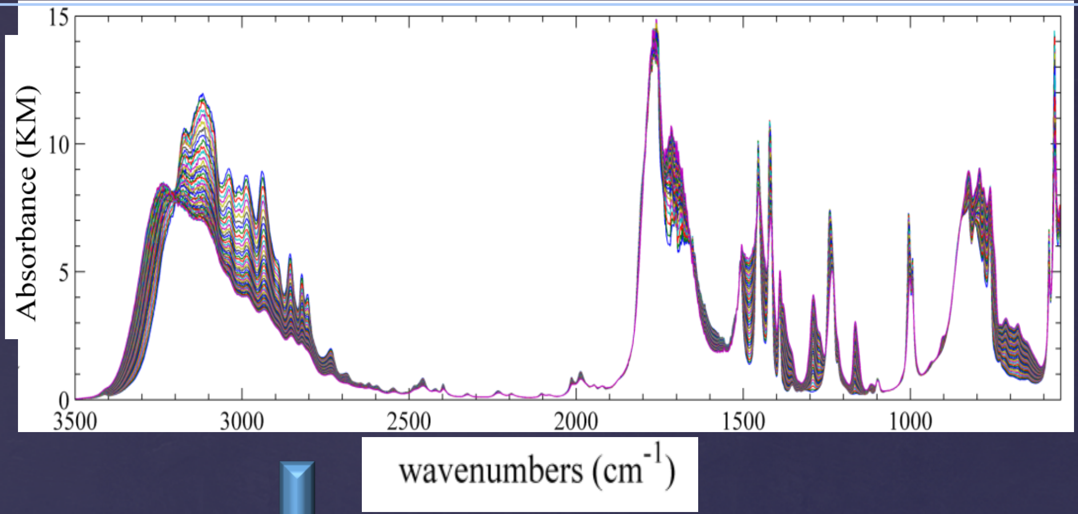


T. Fornaro, J. R. Brucato, C. Feuillie, D.A. Sverjensky, R. M. Hazen, R. Brunetto, M. D'Amore, V. Barone, *Astrobiology* 2018, in press

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

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

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

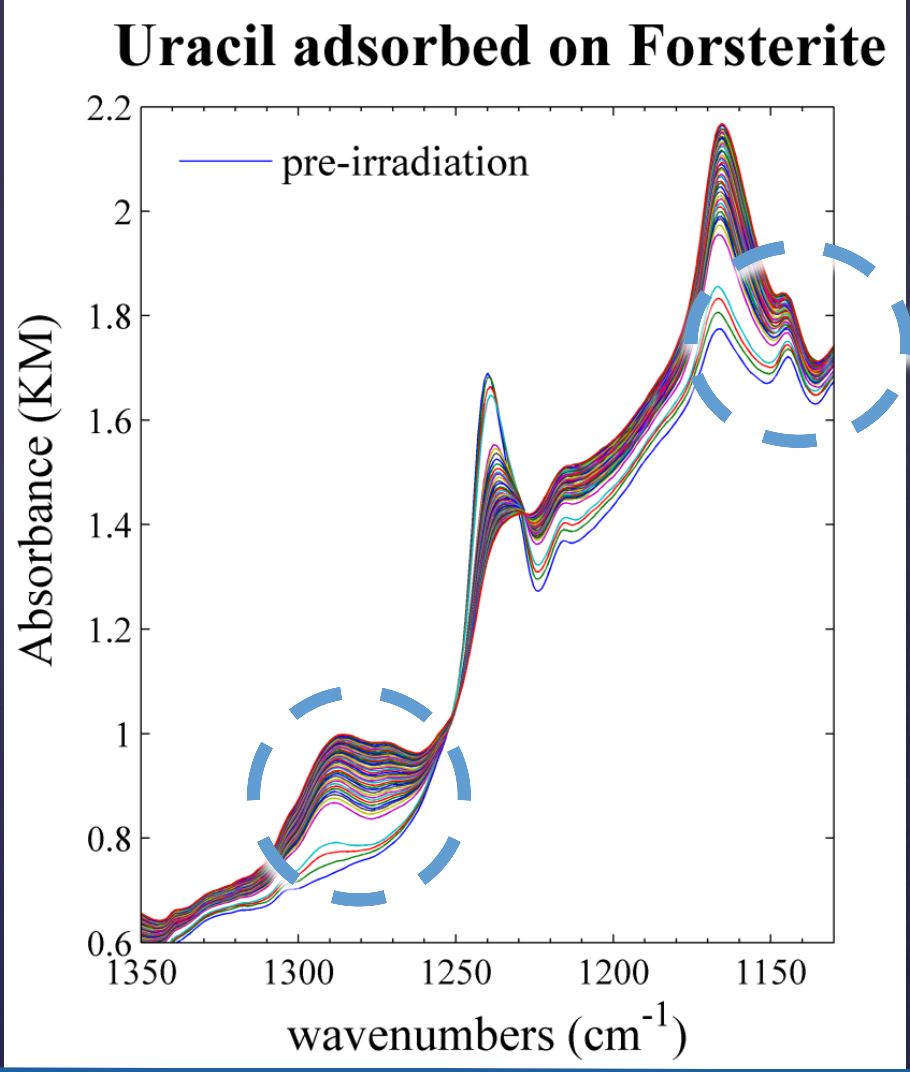
$t_{1/2}$ half-lifetime
σ UV destruction cross section
Φ_{tot} total focused incident UV flux
A_0 sample irradiated area

- **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.

peak (cm^{-1})	mode	σ (cm^2)	$t_{1/2\ lab}$ (min)	σ_f (cm^2)
		Adenine		
1185	Q_{17}: $\delta_{rock}NH_2$, νC_5N_7, νC_2N_3	$(9 \pm 1)\cdot10^{-20}$	180 ± 20	
1017	Q_{20}: $\delta_{rock}NH_2$, νN_1C_6	$(1.4 \pm 0.1)\cdot10^{-19}$	110 ± 10	
		Adenine adsorbed on MgO		
1247	Q_{16}: δC_8H, νN_7C_8, δN_9H	$(1.1 \pm 0.1)\cdot10^{-18}$	36 ± 4	
		Adenine adsorbed on forsterite		
1675	Q_7: νN_3C_4, νC_5C_6	$(5 \pm 1)\cdot10^{-20}$	310 ± 70	
1608	Q_8: $\delta_{sciss}NH_2$, νC_4C_5, νC_5C_6	$(6.9 \pm 0.7)\cdot10^{-20}$	230 ± 20	
1420	Q_{11}: νC_4C_5, νC_4N_9, δC_2H	$(1.2 \pm 0.1)\cdot10^{-19}$	130 ± 10	
1334	Q_{13}: δC_2H, νC_8N_9, δC_8H, νC_6N_6	$(9 \pm 2)\cdot10^{-20}$	180 ± 30	
1309	Q_{15}: νC_2N_3, νN_1C_2	$(4 \pm 2)\cdot10^{-20}$	400 ± 200	
1025	Q_{20}: $\delta_{rock}NH_2$, νN_1C_6	$(4.6 \pm 0.5)\cdot10^{-19}$	35 ± 4	
		Uracil		
1242	Q_{12}: ν ring	$(1.28 \pm 0.09)\cdot10^{-19}$	124 ± 8	
1456	Q_9: ν ring, δN_3H	$(9.4 \pm 0.9)\cdot10^{-20}$	170 ± 20	
1421	Q_{10}: $\delta N_3H + \delta CH$	$(2.43 \pm 0.07)\cdot10^{-19}$	65 ± 2	
1381				$(10 \pm 2)\cdot10^{-20}$
1290				$(2.59 \pm 0.05)\cdot10^{-19}$
1165				$(2 \pm 2)\cdot10^{-21}$
585	Q_{23}: γNH	$(2.3 \pm 0.1)\cdot10^{-19}$	69 ± 4	
		Uracil adsorbed on MgO		
1286	Q_{12}: ν ring	$(1.77 \pm 0.06)\cdot10^{-18}$	22.4 ± 0.7	
		Uracil adsorbed on forsterite		
1455	Q_9: ν ring, δN_3H	$(5.0 \pm 0.1)\cdot10^{-19}$	31.7 ± 0.7	
1418	Q_{10}: $\delta N_3H + \delta CH$	$(5.4 \pm 0.1)\cdot10^{-19}$	29.3 ± 0.7	
1287				$(1.60 \pm 0.07)\cdot10^{-18}$
1240	Q_{12}: ν ring	$(3.96 \pm 0.07)\cdot10^{-19}$	40.1 ± 0.7	

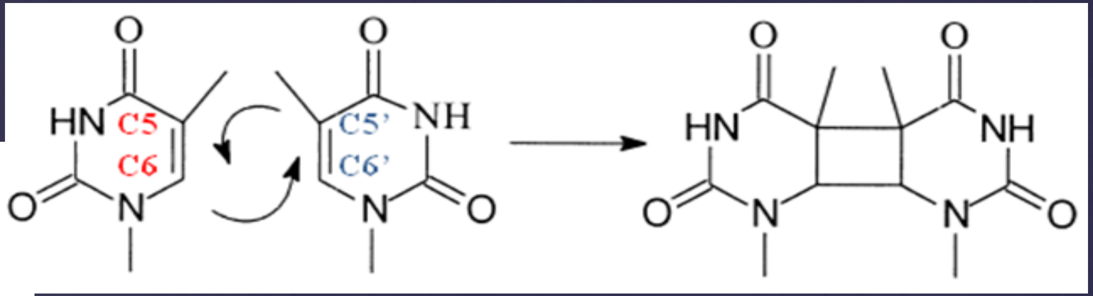
Photoproducts bonds

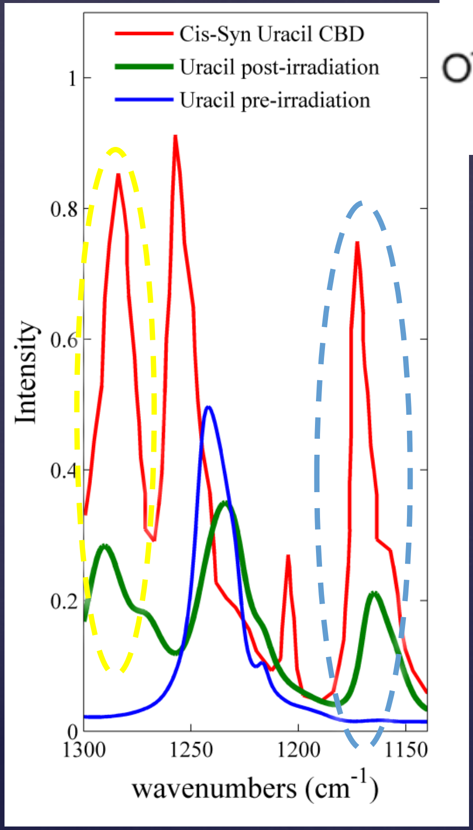


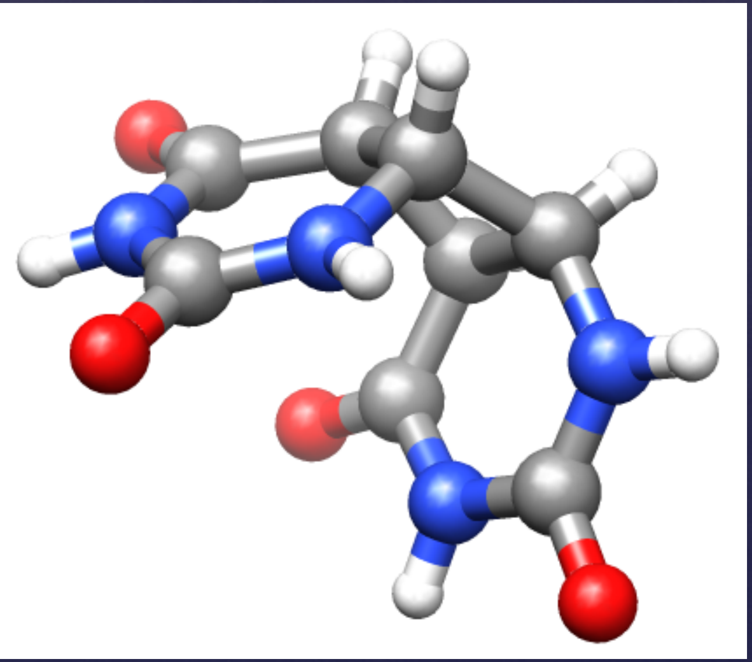
Fornaro, T.; Brucato, J. R.; Pace, E.; Guidi, M. C.; Branciamore, S.; Pucci, A. *Icarus* **2013**, *226*(1), 1068-1085.

Photoproducts

[2+2] Photocycloaddition





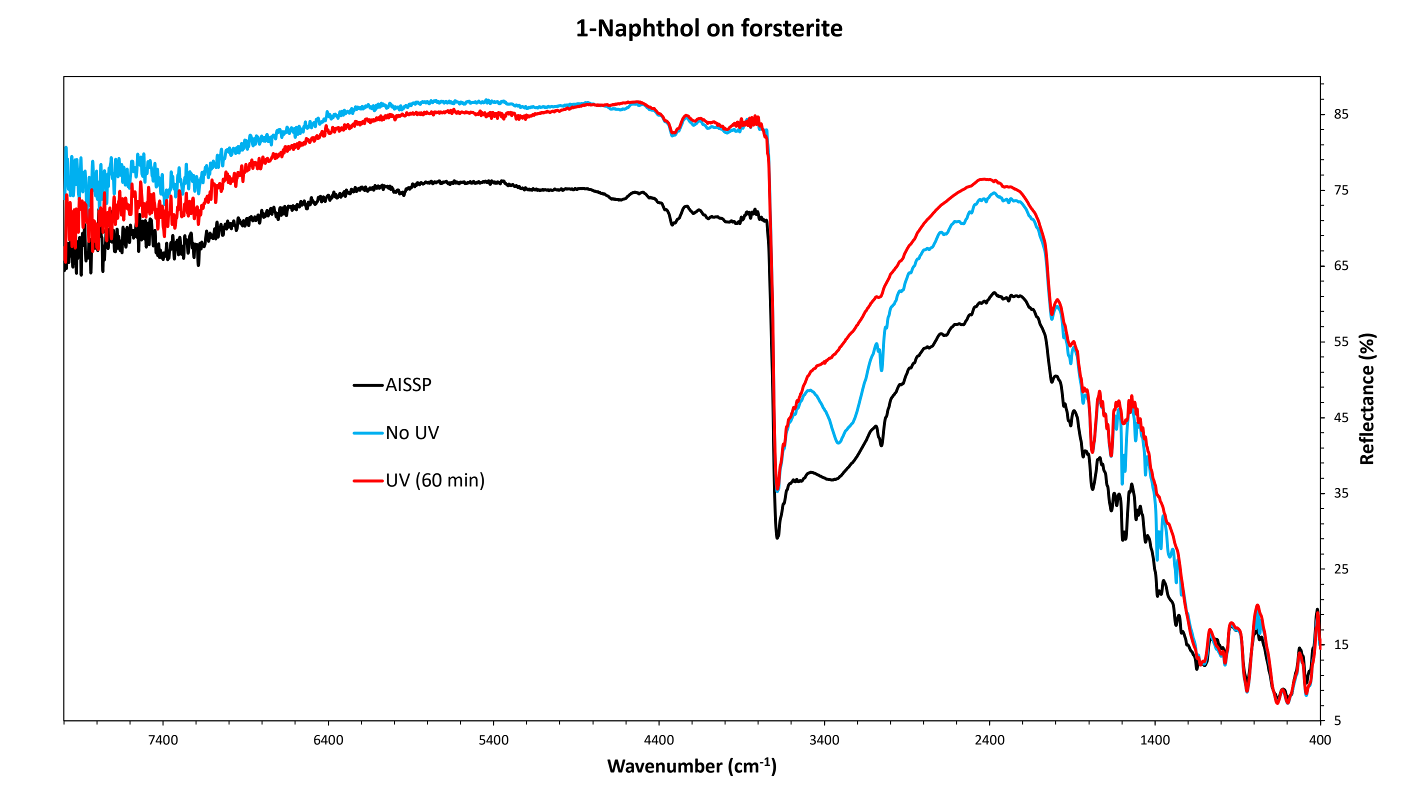


Main photoproduct:

Cyclobutane dimer (CBD)

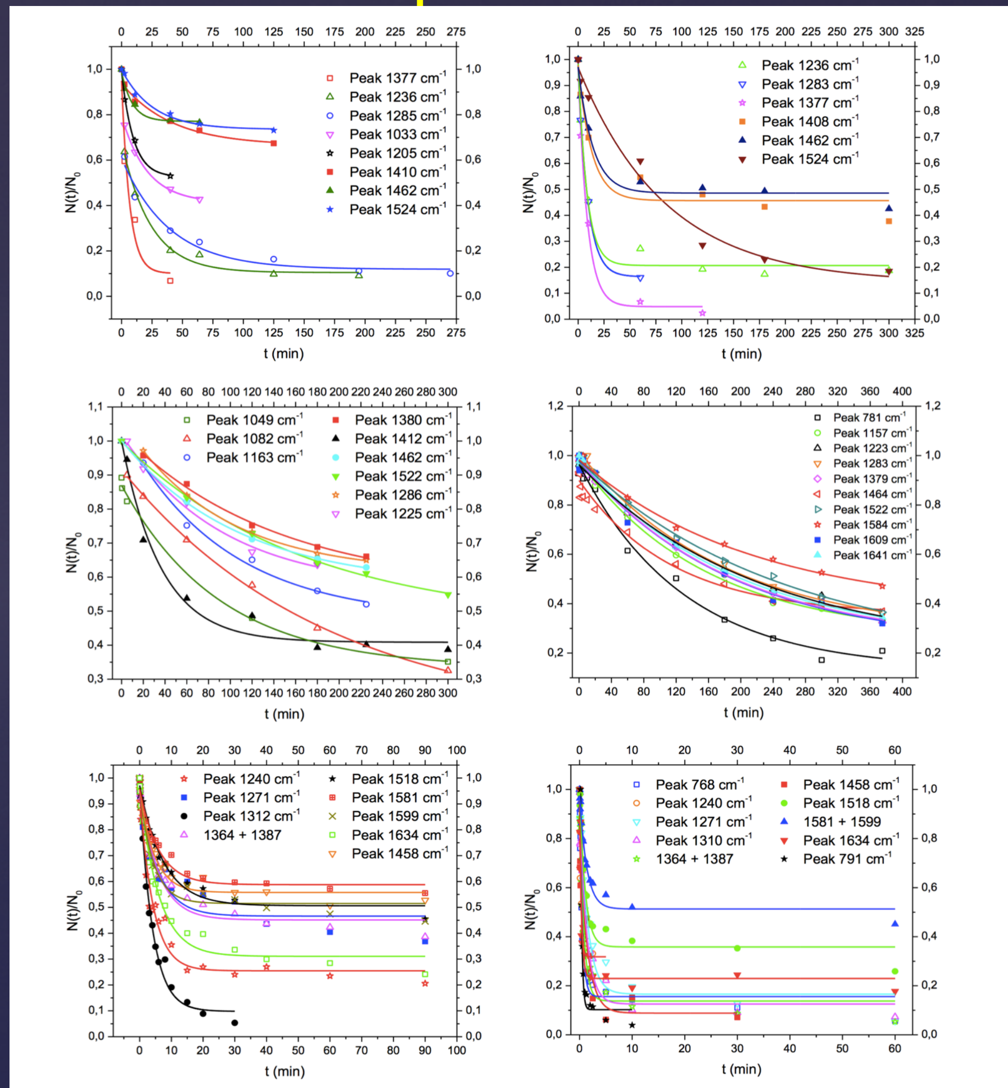
UV irradiation of Naphthol adsorbed on forsterite

UV irradiation at 80 K



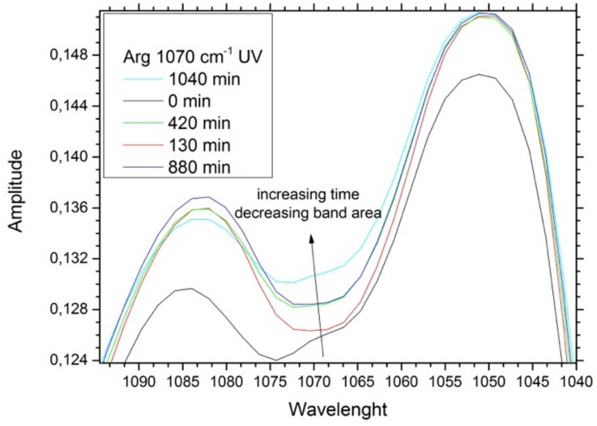
S. Potenti, P. Manini, T. Fornaro, G. Poggiali, O. Crescenzi, A. Napolitano, J. R. Brucato, V. Barone, M. d'Ischia , PCCP 2018, submitted

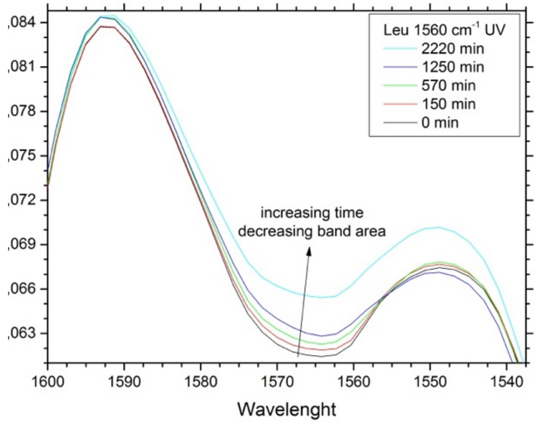
UV irradiation of Naphthol adsorbed on forsterite

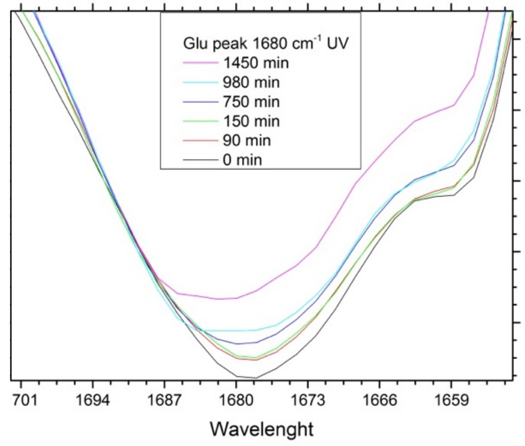


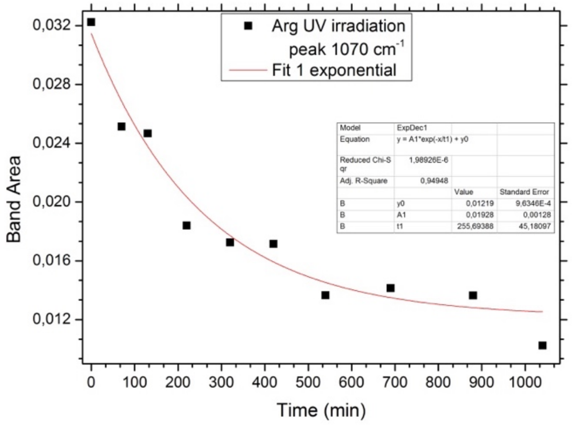
S. Potenti, P. Manini, T. Fornaro, G. Poggiali, O. Crescenzi, A. Napolitano, J. R. Brucato, V. Barone, M. d'Ischia , PCCP 2018, submitted

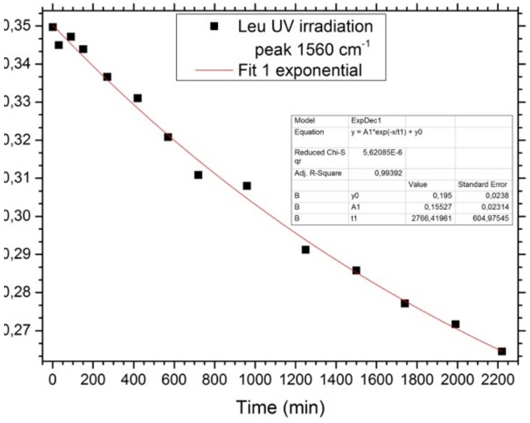
UV irradiation of aminoacids (Arg and Leu)

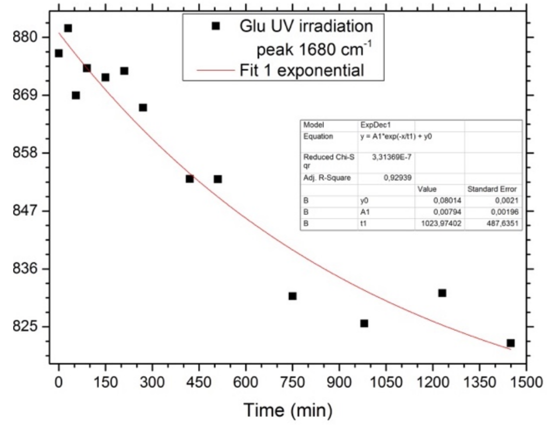












	Life-time (min)	Cross-section (m^2) x 10^{-26}
Glutamic acid 1680 cm^1	1.0 ± 0.5	2 ± 1
Glutamic acid 670 cm^1	0.6 ±0.1	3.6 ± 0.7
Glutamic acid 1267 cm^1	2.7 ± 3.5	0.8 ± 1.1
Leucine 1560 cm^1	2.8 ± 0.6	0.8 ± 0.2
Leucine 670 cm^1	2.8 ± 0.8	0.8 ± 0.3
Leucine 1530 cm^1	2.2 ± 0.9	1.0 ± 0.5
Arginine 1070 cm^1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

UV irradiation of Gly

Cross section and half-lifetimes at simulated space conditions

Peak (cm^{-1})	Mode	σ (cm^2)	$t_{1/2}(sec)$
Gly adsorbed on spinel			
2606	$\nu NH_3 + \nu CN$	$(3.6 \pm 0.4) \times 10^{-18}$	7.7 ± 0.8
2905	*unidentified*	$(2.4 \pm 0.8) \times 10^{-18}$	11 ± 4
3186	$\nu_{as} NH_3$	$(2 \pm 1) \times 10^{-18}$	17 ± 12
Gly adsorbed on pyrite			
2606	$\nu NH_3 + \nu CN$	$(7 \pm 2) \times 10^{-18}$	3.8 ± 0.8
3189	$\nu_{as} NH_3$	$(9.3 \pm 1.4) \times 10^{-18}$	3.0 ± 0.4

Parameters and cross section for bands formation process

Peak (cm^{-1})	α	χ^2_{dof}	σ_f (cm^2)	Mode
Gly adsorbed on pyrite in laboratory conditions				
2340	1.7 ± 0.3	0.923	$(6.8 \pm 1.3) \times 10^{-17}$	CO_2
Gly adsorbed on pyrite in simulated space conditions				
2045	0.09 ± 0.04	0.453	$(4 \pm 1) \times 10^{-18}$	C_xO_y
2343	0.3 ± 0.3	0.784	$(1.2 \pm 1.2) \times 10^{-17}$	CO_2

$$H_3NCH_2COO + h\nu \rightarrow H_3NCH_2 + COO$$

Cross section and half-lifetimes at laboratory conditions

Peak (cm^{-1})	Mode	σ (cm^2)	$t_{1/2}(h)$
Gly adsorbed on antigorite			
1333	ωCH_2	$(5 \pm 2) \times 10^{-21}$	1.4 ± 0.5
1412	$\nu_s COO^-$	$(7 \pm 2) \times 10^{-21}$	1.2 ± 0.4
1503	δNH_3	$(1 \pm 2) \times 10^{-21}$	7 ± 13
1584-1660	$\nu_{as} COO^-$	$(2.2 \pm 1.2) \times 10^{-21}$	3.5 ± 0.2
2116	$\nu NH_3 + \tau NH_3$	$(3 \pm 2) \times 10^{-21}$	2.3 ± 1.5
Gly adsorbed on forsterite			
1335	ωCH_2	$(1.3 \pm 0.3) \times 10^{-20}$	0.6 ± 0.1
1413	$\nu_s COO^-$	$(1.3 \pm 0.3) \times 10^{-20}$	0.6 ± 0.1
1523	δNH_3	$(2 \pm 1) \times 10^{-20}$	0.29 ± 0.12
1664	$\nu_{as} COO^-$	$(2 \pm 2) \times 10^{-20}$	0.3 ± 0.3
2134	$\nu NH_3 + \tau NH_3$	$(1.9 \pm 0.8) \times 10^{-20}$	0.4 ± 0.1
2615	$\nu NH_3 + \nu CN$	$(2.4 \pm 0.8) \times 10^{-20}$	0.4 ± 0.1
Gly adsorbed on spinel			
1333	ωCH_2	$(3 \pm 1) \times 10^{-21}$	2.3 ± 0.07
1412	$\nu_s COO^-$	$(1.1 \pm 1.1) \times 10^{-21}$	7 ± 6
1505	δNH_3	$(3.3 \pm 1.1) \times 10^{-21}$	2.3 ± 0.7
1584-1660	$\nu_{as} COO^-$	$(3 \pm 2) \times 10^{-21}$	2 ± 1
2117	$\nu NH_3 + \tau NH_3$	$(2 \pm 1) \times 10^{21}$	3 ± 1
Gly adsorbed on pyrite			
916	ρCH_2	$(5 \pm 2) \times 10^{-21}$	1.4 ± 0.5
1309	$tw CH_2$	$(2.4 \pm 0.4) \times 10^{-20}$	0.33 ± 0.05
1337	ωCH_2	$(2.2 \pm 0.6) \times 10^{-20}$	0.35 ± 0.08
1420	$\nu_s COO^-$	$(3 \pm 1) \times 10^{-20}$	0.23 ± 0.07
1521	δNH_3	$(1.6 \pm 0.5) \times 10^{-20}$	0.46 ± 0.09
Gly adsorbed on TiO_2			
1334	ωCH_2	$(3 \pm 4) \times 10^{-21}$	2.3 ± 0.7
1413	$\nu_s COO^-$	$(9 \pm 1) \times 10^{-21}$	0.9 ± 0.1
1506	δNH_3	$(1.0 \pm 0.2) \times 10^{-20}$	0.8 ± 0.2
1584-1660	$\nu_{as} COO^-$	$(1.0 \pm 0.1) \times 10^{-20}$	0.77 ± 0.07
3169	$\nu_{as} NH_3$	$(1.0 \pm 0.2) \times 10^{-20}$	0.8 ± 0.2

Summary

Photodegradation:

- We derived that the cross-section of photodegradation of adenine is very similar to that obtained in space experiment BIOPAN 6.
- Adenine and uracil are fragile at VUV irradiation ($t_{1/2}$ few hours).
- Changes in the photophysical behavior of nucleobases are highly dependent on the specific interactions with the mineral surface.
- Amino acids are photo-degradated faster in space simulated conditions.
- Minerals have no protective effect against the UV radiation, instead they may be catalytic speeding up the degradation kinetics.

Thermodynamics of adsorption:

- A physisorption process occurs predominantly;
- Hydroxyl plays a fundamental role in physisorption process.

IR spectroscopy analysis:

- Important shifts of the vibrational frequencies and changes of the IR intensities occur when biomolecules are adsorbed on minerals.
- Band assignments based on gas-phase data could be misleading.

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