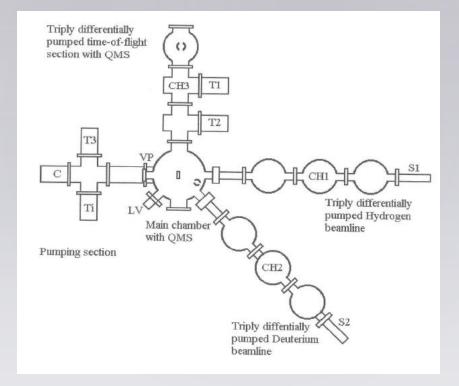
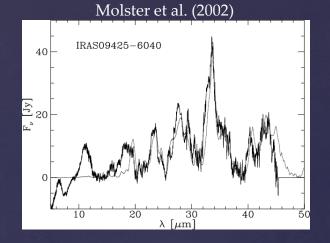
Role of Mineral Surfaces on Prebiotic Evolution of Organics in Space

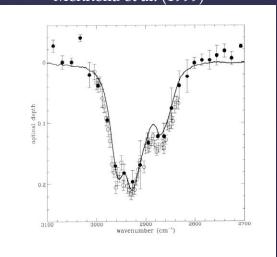
J.R. Brucato INAF-Arcetri Astrophysical Observatory, Firenze Italy jbrucato@arcetri.astro.it



Cristalline silicates in evolved stars

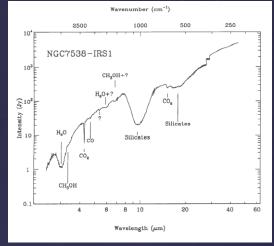


Hydrogenated a-Carbon in ISM Mennella et al. (1999)

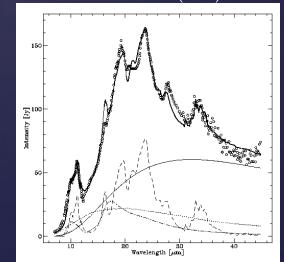


Amorphous silicates in ISM

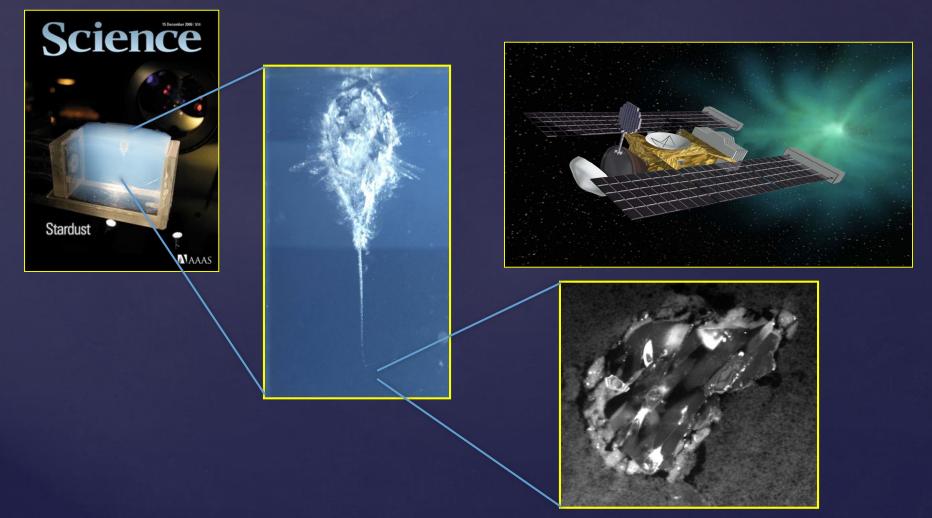
Strazzulla et al. (1998)



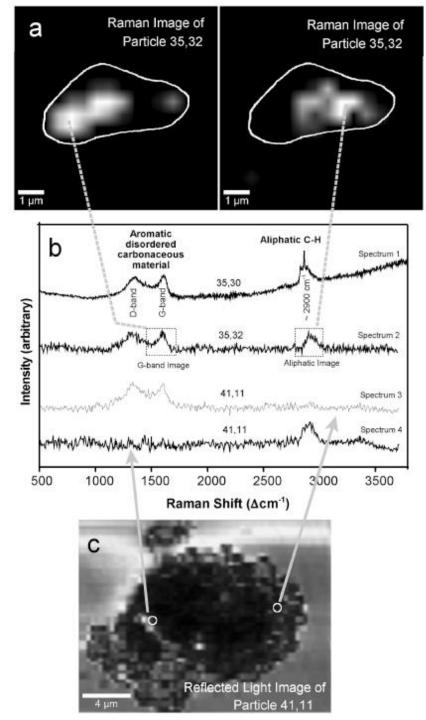
Silicate & a-carbon in comets Brucato et al. (1999)

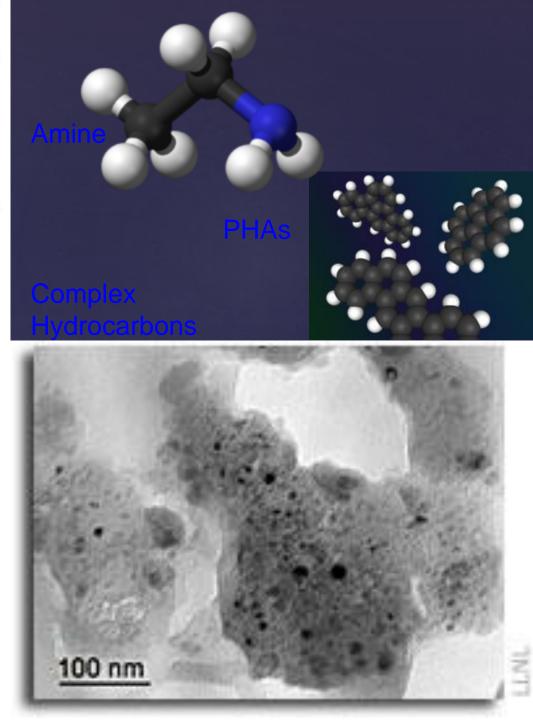


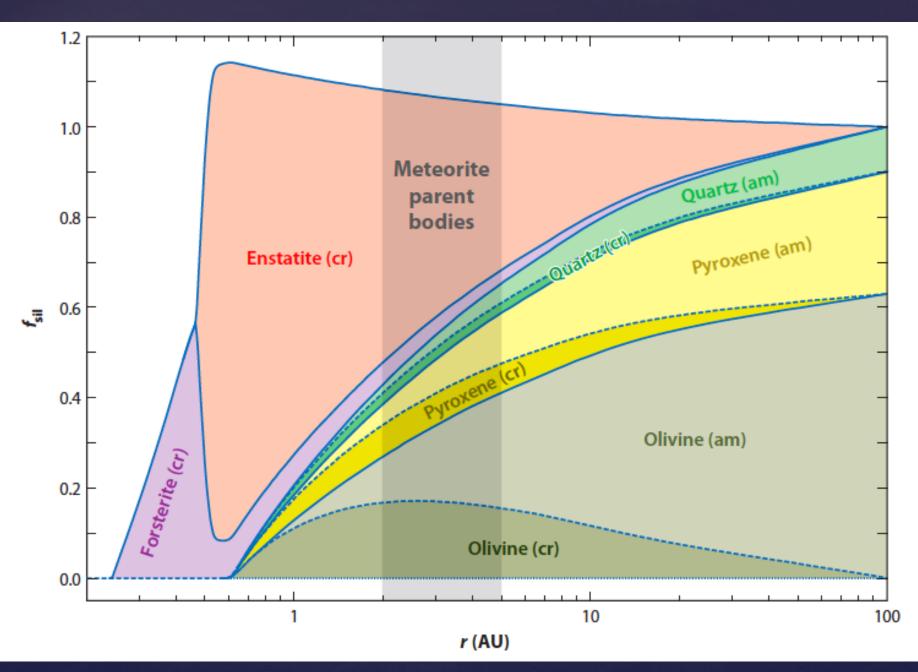
NASA STARDUST Mission returned on Earth dust grains collected by Wild 2 comet



Brownlee et al. Science 2006







Gail 2004

ISM, comets and Interplanetary Dust Particles inventory

Oxides: SiO₂, MgO, FeO, Fe₂O₃, TiO₂, ZrO₂, Al_xO_y

Silicon Carbide: SiC

a-Carbon

Sulfides: FeS, NiS

SilicatesOlivine: $(Mg,Fe)_2SiO_4$
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 (concentration effect)

• Minerals can act as catalytic environments, 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

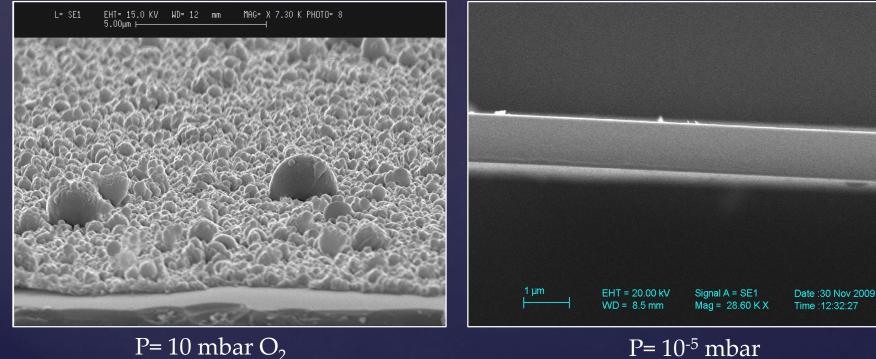
Talk Outline



Synthetic Silicate Produced in Laboratory

Amorphous olivine & pyroxene

Laser ablation



P= 10⁻⁵ mbar

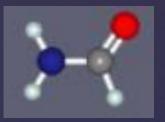
Electron Beam

ENERGY SOURCES IN SPACE

Environment	Ic	on Processir	ng	Pho	oton Process	ing
(ice residence time in years)	Flux, 1 MeV p ⁺ (eV cm ⁻² s ⁻¹)	Energy absorbed $(eV cm^{-2} s^{-1})^{a}$	Dose (eV molec ⁻¹)	Flux ($eV cm^{-2} s^{-1}$)	Energy absorbed (eV cm ⁻² s ⁻¹)	Dose (eV molec ⁻¹)
Diffuse ISM $(10^5 - 10^7)^b$	1 x 10 ⁷	$1.2 \ge 10^4$	<1 - 30	9.6 x 10 ⁸ at 10 eV ^b	5 x 10 ⁸ 0.02 μm ice	10 ⁴ - 10 ⁶
Dense cloud $(10^5 - 10^7)^{b}$	1 x 10 ⁶	$\begin{array}{c} 1.2 \text{ x } 10^{3} \\ 0.02 \mu\text{m ice} \end{array}$	<< 1 - 3	1.4 x 10 ⁴ at 10 eV	1.7 x 10 ³ 0.02 μm ice	< 1 - 4
Protoplanetary nebula $(10^5 - 10^7)^c$	1 x 10 ⁶	$\begin{array}{c} 1.2 \text{ x } 10^{3} \\ 0.02 \mu\text{m ice} \end{array}$	<< 1 - 3	2×10^{5} at 1-10 keV ^d	5 x10 ⁴ 0.02 μm ice ^e	2 - 240
Oort cloud (4.6 x 10 ⁹)	j _(E) ŕ	f	~150 (0.1 m) ~55-5 (1-5 m) <10 (5-15 m)	9.6×10^{4} at 10 eV	9.6 x 10 ⁸ 0.1 μm ice	$2.7 \ge 10^8$
Laboratory $(4.6 \times 10^{-4})^{g}$	8 x 10 ¹⁶	2 x 10 ¹⁵ 1 μm ice	10	2.2 x 10 ¹⁵ at 7.4 eV	2.2 x 10 ¹⁵ 1 μm ice	10

COMPLEX ORGANIC INTERSTELLAR MOLECULES

Species	Name	Source	Species	Name	Source
Hydrocarbons			N-Containing		
C ₂ H ₄	Ethene	circ	CH ₃ CN	Acetonitrile	cc, hc, of
HC ₄ H	Butadiyne	circ	CH ₃ NC	Methylisocyanide	hc
H ₂ C ₄	Butatrienylidene	circ, cc, lc	CH ₂ CNH	Keteneimine	hc
C₅H	Pentadiynyl	circ, cc	HC ₃ NH ⁺	Prot. cyanoacetylene	сс
CH ₃ C ₂ H	Propyne	cc, lc	C ₅ N	Cyanobutadiynyl	circ, cc
C ₆ H	Hexatriynyl	circ, cc, lc	HC ₄ N	Cyanopropynylidene	circ
C ₆ H ⁻	Hexatriynyl ion	circ, cc, lc	CH ₃ NH ₂	Methylamine	hc, gc
H ₂ C ₆	Hexapentaenylidene	circ, cc, lc	C ₂ H ₃ CN	Vinylcyanide	cc, hc
HC ₆ H	Triacetylene	circ	HC5N	Cyanodiacetylene	circ, cc
C ₇ H	Heptatriynyl	circ, cc	CH ₃ C ₃ N	Methylcyanoacetylene	cc
CH ₃ C ₄ H	Methyldiacetylene	сс	CH ₂ CCHCN	Cyanoallene	cc
CH ₃ CHCH ₂	Propylene	сс	NH ₂ CH ₂ CN	Aminoacetonitrile	hc
C ₈ H	Octatetraynyl	circ, cc	HC7N	Cyanotriacetylene	circ, cc
C_8H^-	Octatetraynyl ion	circ, cc	C ₂ H ₅ CN	Propionitrile	hc
CH ₃ C ₆ H	Methyltriacetylene	cc	CH ₃ C ₅ N	Methylcyanodiacetylene	cc
C ₆ H ₆	Benzene	circ	HC ₉ N	Cyanotetraacetylene	circ, cc
O-Containing			C ₃ H ₇ CN	N-propyl cyanide	hc
CH ₃ OH	Methanol	cc, hc, gc, of	HC ₁₁ N	Cyanopentaacetylene	circ, cc
HC ₂ CHO	Propynal	hc, gc	S-Containing		
c-C ₃ H ₂ O	Cyclopropenone	gc	CH ₃ SH	Methyl mercaptan	hc
CH ₃ CHO	Acetaldehyde	cc, hc, gc	N,O-Containing		
C ₂ H ₃ OH	Vinyl alcohol	hc	NH ₂ CHO	Formamide	
c-CH ₂ OCH ₂	Ethylene oxide	hc, gc	CH ₃ CONH ₂	Acetamide	he, ge
HCOOCH ₃	Methyl formate	hc, gc, of			
CH ₃ COOH	Acetic acid	hc, gc			
HOCH ₂ CHO	Glycolaldehyde	hc, gc			
C ₂ H ₃ CHO	Propenal	hc, gc			
C ₂ H ₅ OH	Ethanol	hc, of			
CH3OCH3	Methyl ether	hc, gc			
CH ₃ COCH ₃	Acetone	hc			
HOCH2CH2OH	Ethylene glycol	hc, gc			
C ₂ H ₅ CHO	Propanal	hc, gc			
HCOOC ₂ H ₅	Ethyl formate	hc			

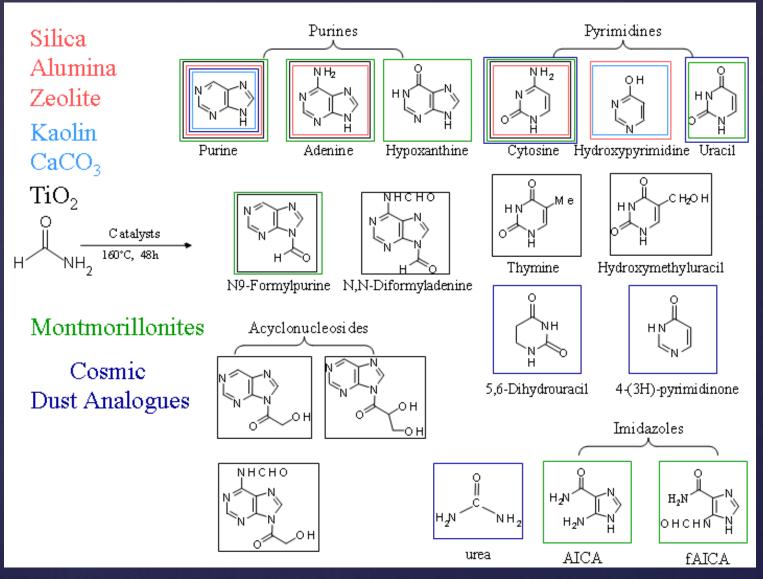


Why Formamide?

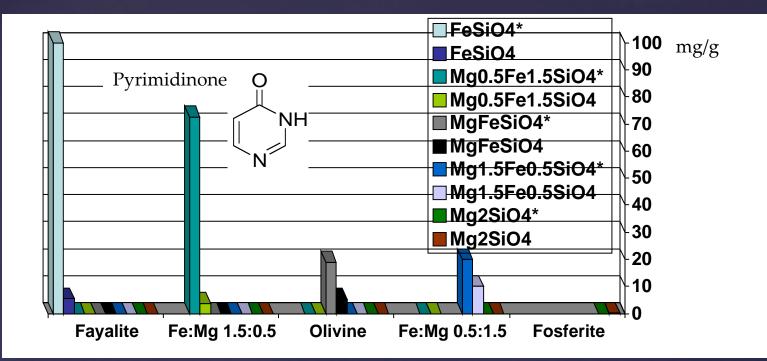


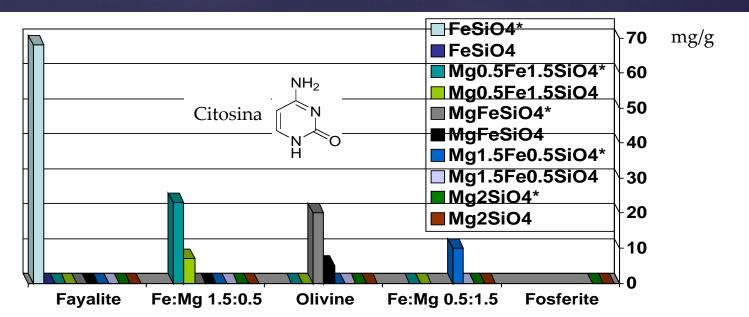
- It's a simple one C-bearing molecule.
- It's formed by hydrolysis of HCN.
- It's active in synthesis of nucleobases.
- It's active in selective degradation of DNA.
- It's observed in:
 - ✓ ISM (Millar 2005);
 - ✓ Hale-Bopp comet (Bockeleé-Morvan et al. 2000);
 - ✓ tentatively in young stellar object W33A (Schutte et al. 1999);
 - ✓ in dense ISM IRS9 (Raunier et al. 2000).

Thermal processing of *liquid* Formamide (160 °C) with & without dust

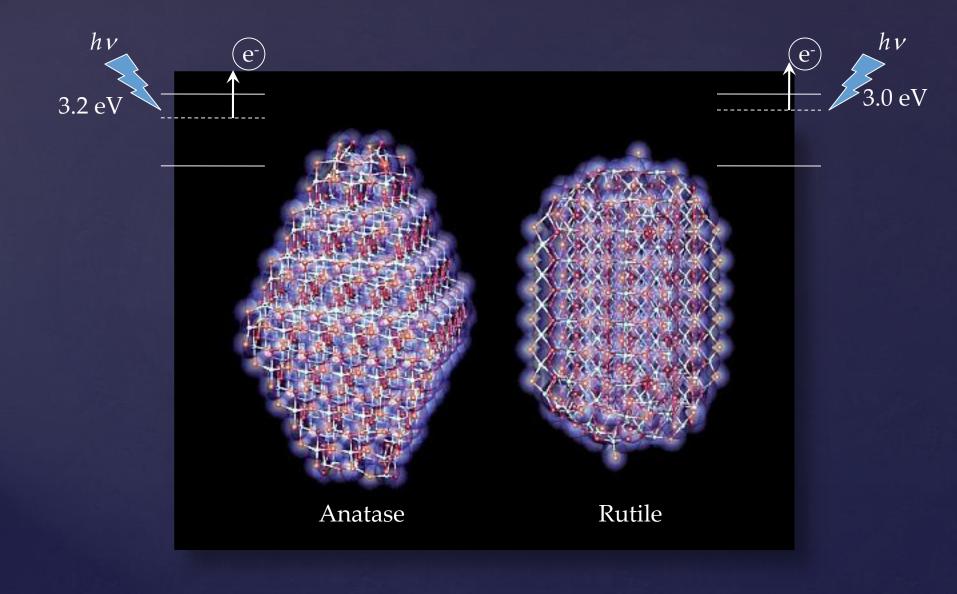


Saladino R., Crestini C., Neri C., Brucato J.R., Colangeli L. Ciciriello F., Di Mauro E., Costanzo G., *ChemBioChem* 6, 1, 2005

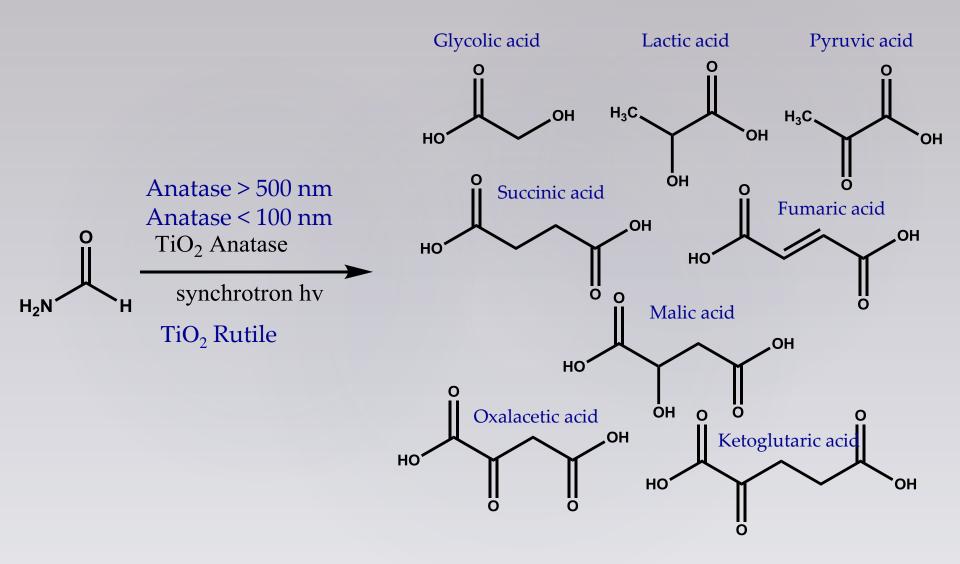




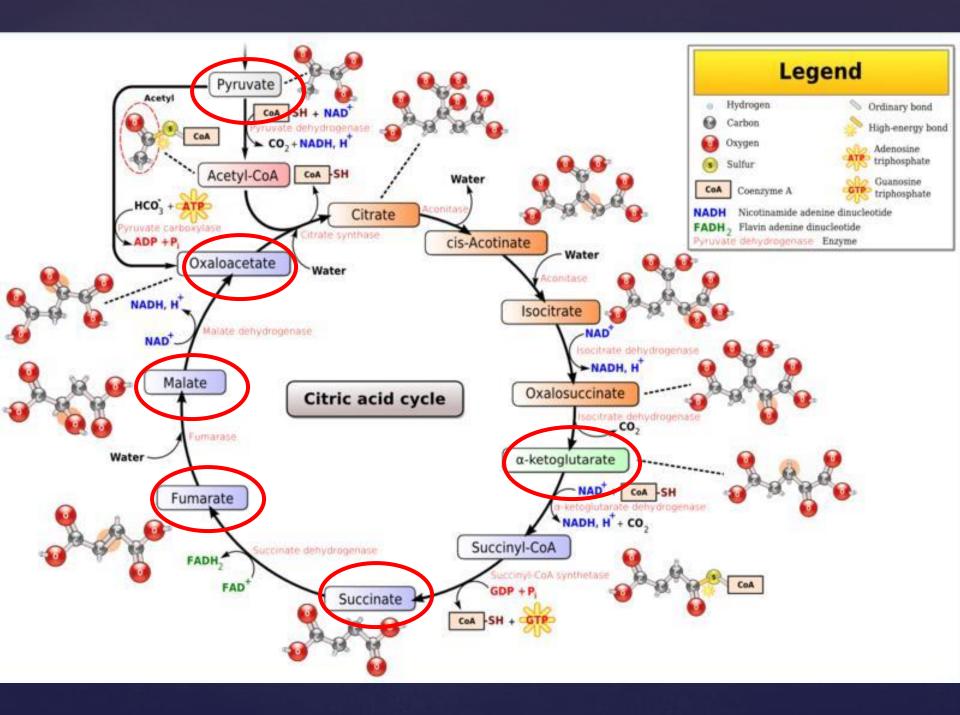
Titanium dioxide Photochemistry



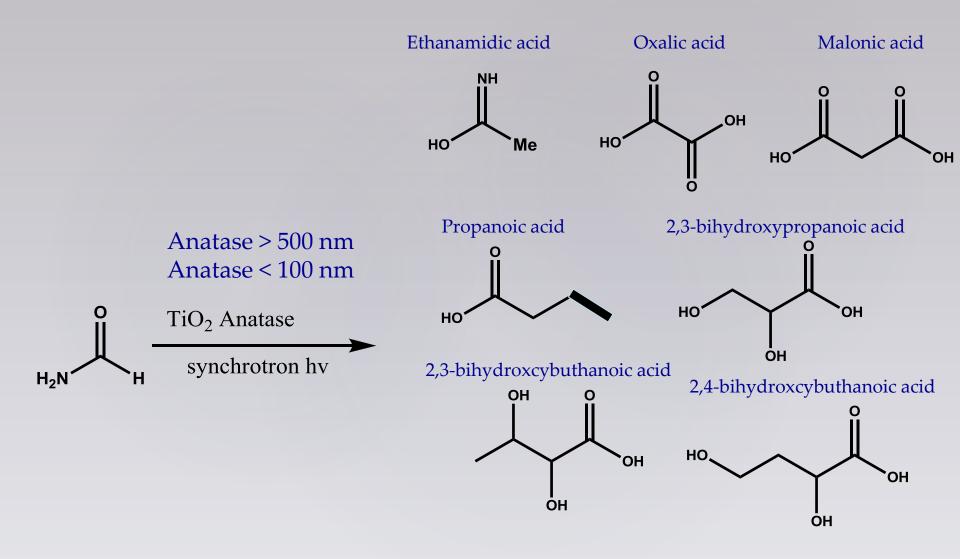
Biogenic Carboxylic Acids



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



Non-biogenic Carboxylic Acids

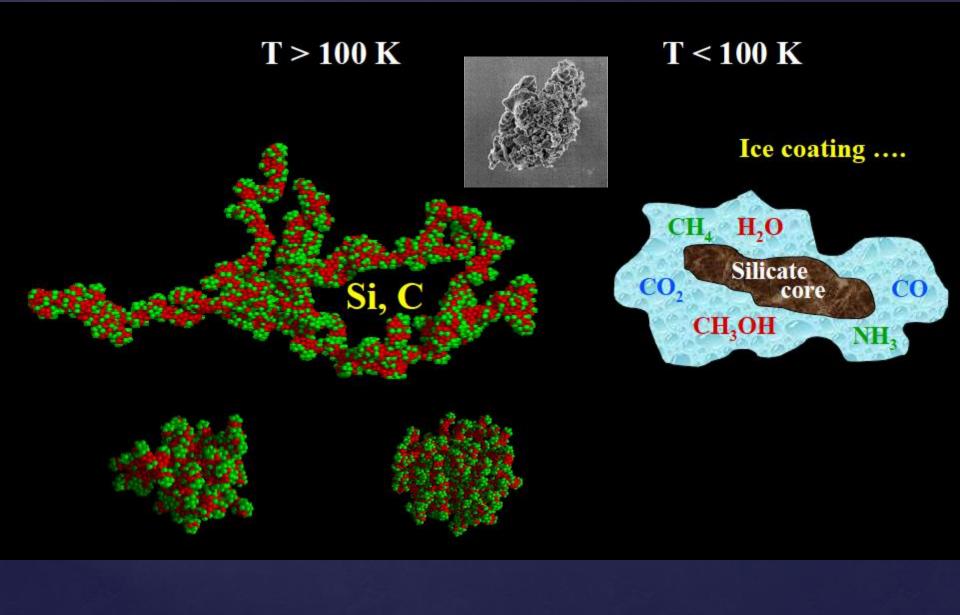


R. Saladino, J.R. Brucato, A. de Sio, E. Pace 2010

CONCLUSIONS

- Nucleic acid bases ARE NOT produced during the photochemical process
- Biogenic carboxylic acids are synthesized
- Six of ten key intermediates of the Krebs cycle are selectively obtained
- Anatase phase is more reactive than Rutile one

Dust particles: the seeds of planets and molecules



Type of Reactions

Type of process	Example	Number in model
Gas-grain interactions	$H + H + grain \rightarrow H_2 + grain$	14
Direct cosmic ray processes	$H_2 + \zeta \rightarrow H_2^+ + e$	11
Cation-neutral reactions	$\mathrm{H_2^+} + \mathrm{H_2} \rightarrow \mathrm{H_3^+} + \mathrm{H}$	2933
Anion-neutral reactions	$C^- + NO \rightarrow CN^- + O$	11
Radiative associations (ion)	$C^+ + H_2 \rightarrow CH_2^+ + b\nu$	81
Associative detachment	$C^- + H_2 \rightarrow CH_2 + e$	46
Chemi-ionization	$O + CH \rightarrow HCO^+ + e$	1
Neutral-neutral reactions	$\mathrm{C} + \mathrm{C}_2\mathrm{H}_2 \rightarrow \mathrm{C}_3 \ \mathrm{H} + \mathrm{H}$	382
Radiative association (neutral)	$C + H_2 \rightarrow CH_2 + b\nu$	16
Dissociative recombination	$N_2H^+ + e \rightarrow N_2 + H$	539
Radiative recombination	$H_2CO^+ + e \rightarrow H_2CO + bv$	16
Anion-cation recombination	$\rm HCO^+ + H^- \rightarrow H_2 + CO$	36
Electron attachment	$C_6H + e \rightarrow C_6H^- + bv$	4
External photo-processes ^a	$C_3N + b\nu \rightarrow C_2 + CN$	175
Internal photo-processes ^a	$CO + b\nu \rightarrow C + O$	192

1) $H + O_2 \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow H_2O + OH \rightarrow H_2O$

 H_2

H H H

(Ioppolo et al. 2008, 2010)



Η

(

(Tielens & Hagen 1982)

$(3) H + O \rightarrow OH \rightarrow H_2O$

(Dulieu et al. 2010)

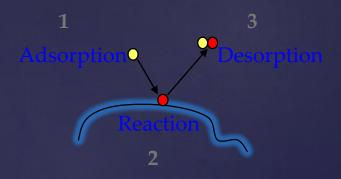
Some argues that species formed by these exotermic reactions will immediately desorb (Paoupular 2005). However, models predicts that most (99.1%) of OH and H_2O formed remain on surfaces (Cupper and Herbst 2007).

Η

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



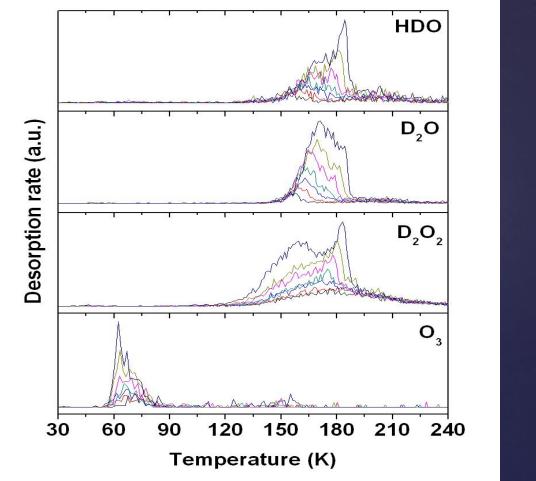
Langmuir-Hinshelwood



H & D beams irradiation of amorphous olivine silicate (Fe, Mg)SiO₄ (Perets et al. 2007)

Desorption Rate (arbitrary units 000 0000 0000 14 15 16 17 18 19 20 21 23 24 Temperature (K)

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



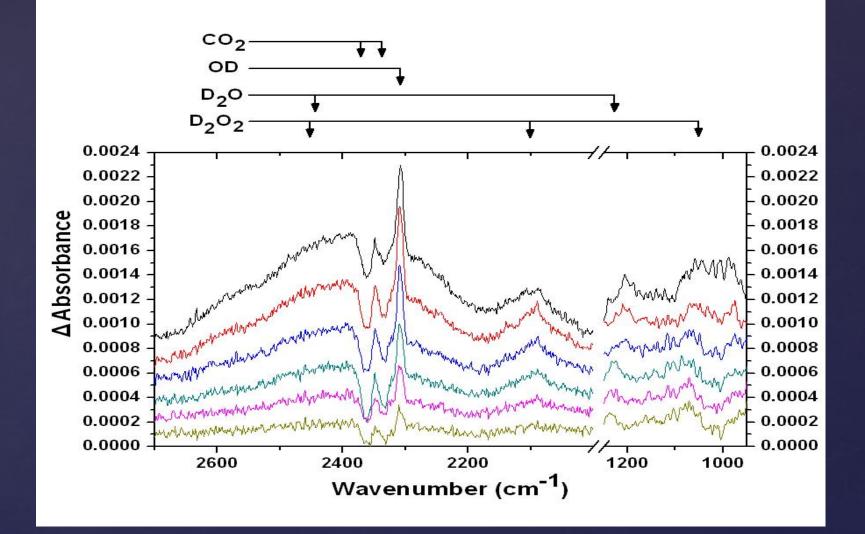
Ed=400 meV

Ed=390 meV

Ed=430 meV

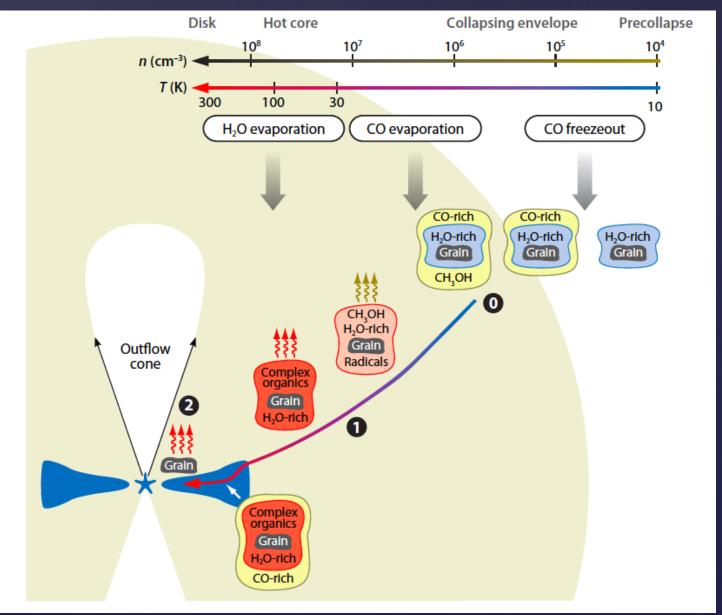
Ed=170 meV

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



The <u>formation of water</u> can follow hydrogenation of both O and O₂ pathways.

Conclusion



Conclusion

Interaction between protons & minerals.

- free protons in the interstitial space
- protons trapped in material defects chemical reactions with oxygen atoms in metal oxides (SiO₂, TiO₂, Al₂O₃) and <u>formation of hydroxyl groups</u>.

Interaction between hydrogen and minerals

• The <u>formation of water</u> can follow hydrogenation of both O and O_2 pathways.

Mars soil analogues

Kaolinite Smectite Montmorillonite Forsterite Nontronite Enstatite Illite Ferrosilite Albite Andesite Labradorite Anorthite Bytownite Oligoclase Anorthoclase Pyrrhotite Oligoclase Labradorite Nepheline

Natrolite Fayalite Jadeite Diopsite Augite Serpentine Apatite arsenate Troilite Pyrite Oxides

Biomarkers				
Extant	Extinct	Meteoritic		
ATP	Generic Isoprenoid	Napthalene		
Cyclic AMP Pyrimidine base	Pristane	Generic amino		
Purine base	Phytane	acid		
DNA		Isovaline		
Nicotinamide	Tetramethyl			
Quinones	benzenes	Generic aromatic		
ATP Synthase	Eatty A aids	carboxylic acid		
Phytane	Fatty Acids			
LPS	Quaternary carbon			
Squalene	alkane			

Biomarker Selection

Expectation of detection in Martian soils (likelihood of preservation and likelihood of existence)

Some Facts

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

- mediating the effects of electromagnetic radiation
- influencing the photostability of bio-molecules
- catalyzing important chemical reactions
- protecting molecules against degradation

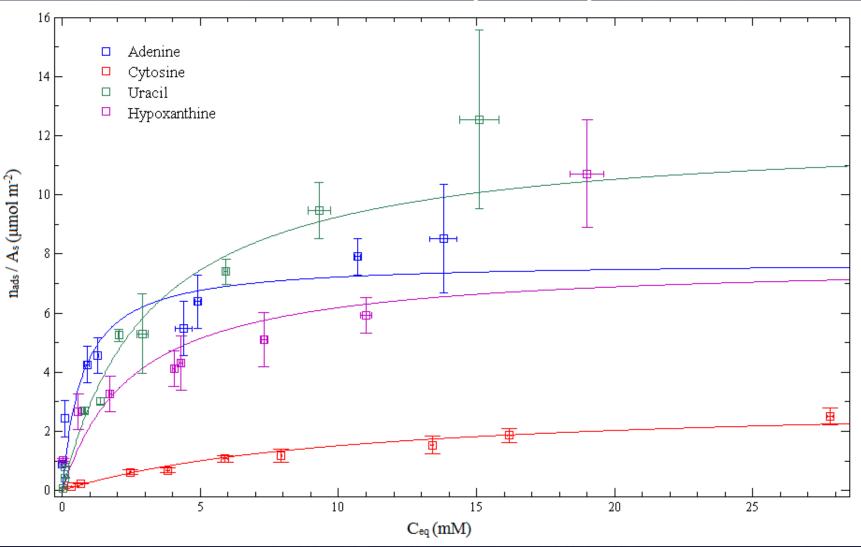
 \checkmark Study the photochemistry and the photophysics of nucleobases in the presence of mineral matrices, to investigate both the **survivability** when exposed to Mars surface and the **physical and chemical processes occurring in extraterrestrial environments.**



Adsorption properties of nucleobases on MgO

LANGMUIR ISOTHERMS OF NUCLEOBASES ONTO MgO AT 298 K

 $|\mathbf{n}_{ads}/\mathbf{m}_{mineral} = KbC_{eq} / (1 + KC_{eq})$



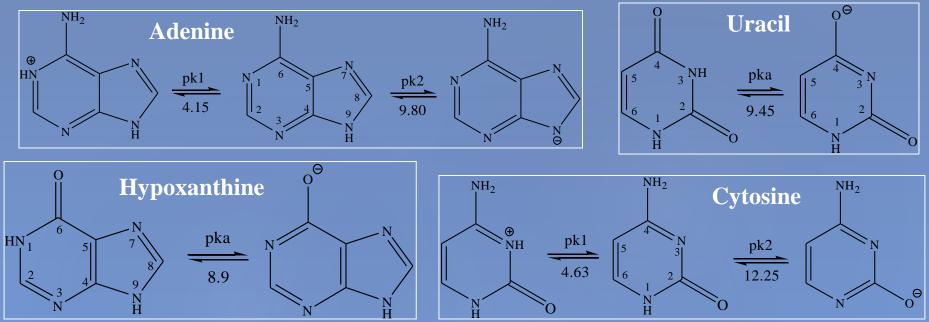
Adsorption properties of nucleobases on MgO LANGMUIR ISOTHERMS OF NUCLEOBASES ONTO MgO AT 298 K

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

Sample	$K(\mathbf{M}^{-1})$	<i>b</i> (mol g ⁻¹)
Adenine	$(1 \pm 1) \cdot 10^3$	$(4 \pm 7) \cdot 10^{-4}$
Uracil	$(3.0 \pm 0.9) \cdot 10^2$	$(4 \pm 2) \cdot 10^{-4}$
Hypoxanthine	$(3 \pm 5) \cdot 10^2$	$(3 \pm 8) \cdot 10^{-4}$
Cytosine	$(1.0 \pm 0.3) \cdot 10^2$	$(1.0 \pm 0.4) \cdot 10^{-4}$

Nucleobases adsorption order: adenine > uracil \geq hypoxanthine > cytosine

Interpretation of nucleobases adsorption on MgO

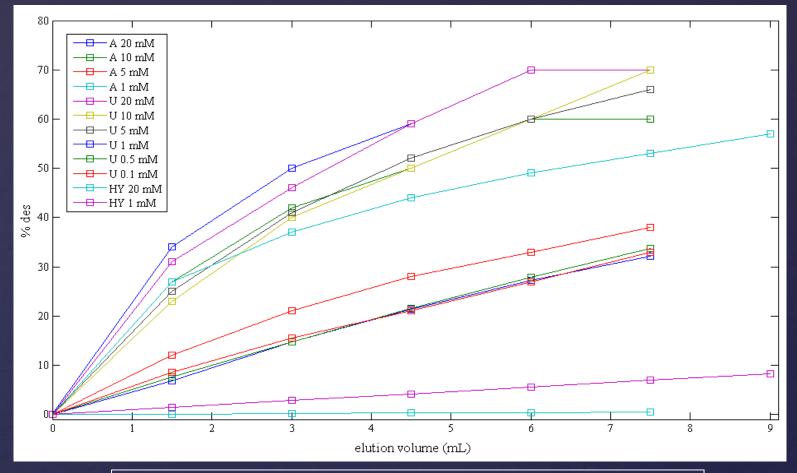


The basicity of MgO causes a pH \approx 10 at equilibrium

Adenine, uracil, hypoxanthine are largely anionic Cytosine is neutral

The efficient adsorption of adenine, uracil and hypoxanthine relative to cytosine suggests the involvement of ionic interactions with MgO

Desorption studies of nucleobases from MgO

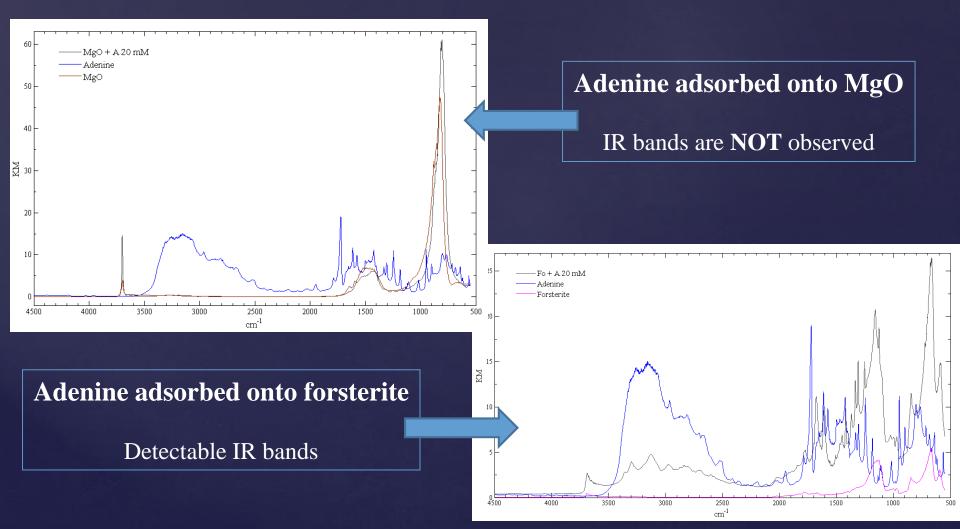


Nucleobases desorption order from MgO: cytosine >> uracil ≥ adenine > hypoxanthine

The high reversibility of the adsorption process and the decrease in adsorption with increasing temperature would suggest a physisorption

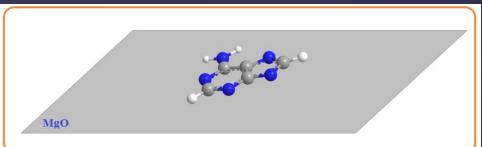
IR-spectroscopy studies of nucleobase-mineral complexes

To better understand, at molecular level, the kind of **interactions between nucleobases and minerals**, IR-spectroscopy studies were carried out, using the diffuse reflectance infrared Fourier transform spectroscopy technique (**DRIFTS**)

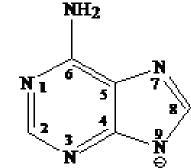


Interpretation of spectroscopic features



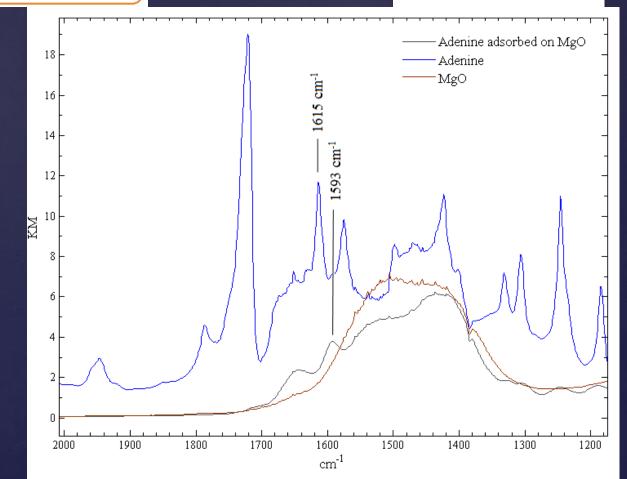




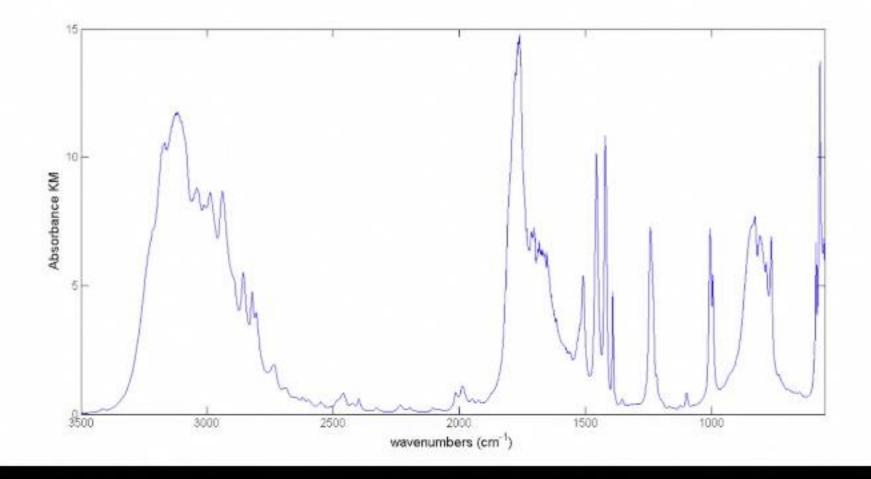


Low frequency shift (-22 cm⁻¹) of the Q_7 vibrational mode: N_3C_4 str, C_5C_6 str

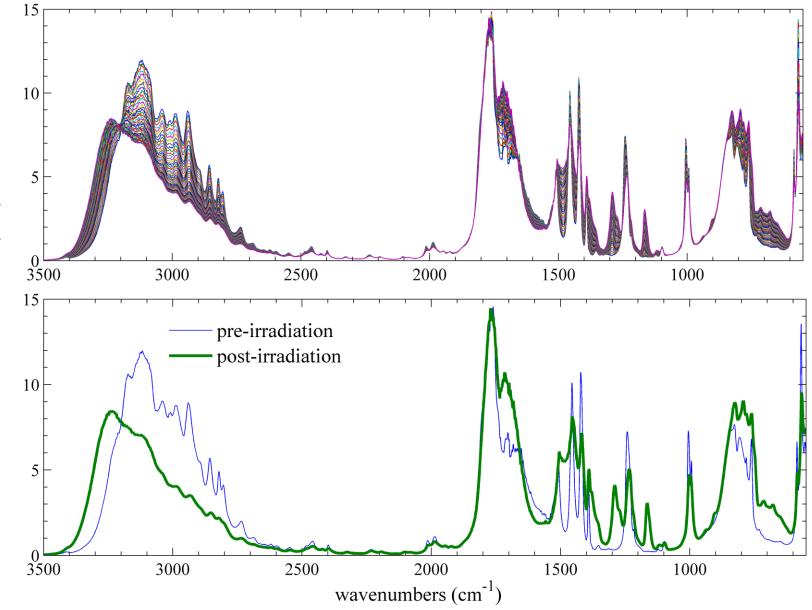
Distorted nearly planar arrangement



Mg0	Adenine on MgO Interaction with the $N_3C_4C_5C_6$ part of the molecule in a distorted nearly planar arrangement.
Forsterite	Adenine on forsterite Interaction with the NH_2 group in a tilted arrangement.
MgO / Forsterite	Cytosine on MgO and forsterite Face-to-face configuration.
MgD	Uracil on MgO Face-to-face configuration.
Forsterite	Uracil on forsterite Interaction with the $C_2=O$ and N_3H groups in a tilted arrangement.
MgO / Forsterite	Hypoxanthine on MgO and forsterite Face-to-face configuration.



UV degradation kinetics

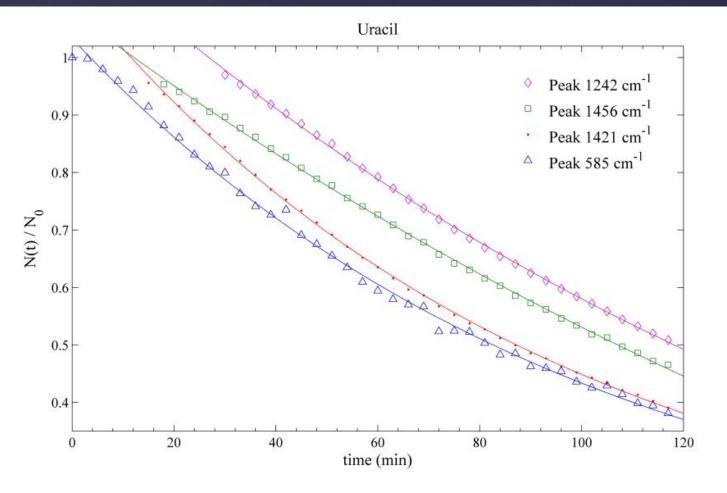


Absorbance (KM)

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

 $N(t)/N_0$ fraction of unaltered molecules

- N_0 initial number of molecules
- β degradation rate
- **B** fraction of interacting molecules
- *c* fraction of non-interacting molecules



peak (cm ⁻¹)	mode	σ (cm ²)	$t_{1/2 \text{ lab}}$ (min)	$\sigma_{\rm f}({\rm cm}^2)$
		Adenine		
1185	$Q_{17}\!\!:\delta_{rock}NH_2,\nu C_5N_7,\nu C_2N_3$	$(9\pm1)\cdot10^{-20}$	180 ± 20	
1017	$Q_{20}\!\!:\delta_{rock}NH_2,\nu N_1C_6$	$(1.4 \pm 0.1) \cdot 10^{-19}$	110 ± 10	
	Ado	enine adsorbed on MgO		
1247	$Q_{16}\!\!:\delta C_8H,\nu N_7C_8,\delta N_9H$	$(1.1 \pm 0.1) \cdot 10^{-18}$	36 ± 4	
	Aden	ine adsorbed on forsterite	:	
1675	Q_7 : νN_3C_4 , νC_5C_6	$(5 \pm 1) \cdot 10^{-20}$	310 ± 70	
1608	$Q_8:\delta_{sciss}NH_2,\nu C_4C_5,\nu C_5C_6$	$(6.9 \pm 0.7) \cdot 10^{-20}$	230 ± 20	
1420	Q_{11} : $\nu C_4 C_5$, $\nu C_4 N_9$, $\delta C_2 H$	$(1.2 \pm 0.1) \cdot 10^{-19}$	130 ± 10	
1334	Q_{13} : $\delta C_2 H$, $\nu C_8 N_9$, $\delta C_8 H$, $\nu C_6 N_6$	$(9\pm2)\cdot10^{-20}$	180 ± 30	
1309	Q_{15} : $\nu C_2 N_3$, $\nu N_1 C_2$	$(4 \pm 2) \cdot 10^{-20}$	400 ± 200	
1025	$Q_{20}\!\!:\delta_{rock}NH_2,\nu N_1C_6$	$(4.6 \pm 0.5) \cdot 10^{-19}$	35 ± 4	
		Uracil		
1242	Q ₁₂ : v ring	$(1.28 \pm 0.09) \cdot 10^{-19}$	124 ± 8	
1456	Q ₉ : ν ring, δN ₃ H	$(9.4\pm0.9){\cdot}10^{-20}$	170 ± 20	
1421	Q_{10} : $\delta N_3 H + \delta C H$	$(2.43\pm0.07){\cdot}10^{-19}$	65 ± 2	
1381				$(10 \pm 2) \cdot 10^{-20}$
1290				$(2.59\pm0.05){\cdot}10^{-19}$
1165				$(2 \pm 2) \cdot 10^{-21}$
585	Q ₂₃ : γNH	$(2.3 \pm 0.1) \cdot 10^{-19}$	69 ± 4	
	Ur	acil adsorbed on MgO		
1286	Q ₁₂ : v ring	$(1.77\pm0.06){\cdot}10^{-18}$	22.4 ± 0.7	
	Urac	cil adsorbed on forsterite		
1455	Q ₉ : ν ring, δN ₃ H	$(5.0 \pm 0.1) \cdot 10^{-19}$	31.7 ± 0.7	
1418	$Q_{10}\!\!:\delta N_3H+\delta CH$	$(5.4 \pm 0.1) \cdot 10^{-19}$	29.3 ± 0.7	
1287				$(1.60 \pm 0.07) \cdot 10^{-18}$
1240	Q ₁₂ : v ring	$(3.96\pm0.07){\cdot}10^{\text{-19}}$	40.1 ± 0.7	

• Cytosine and hypoxanthine have a greater photostability, both pure and adsorbed on MgO and forsterite.

• For **adenine** and **uracil** degradation was observed both pure and adsorbed onto MgO and forsterite.

• **Minerals** make degradation faster and more probable (the half-lifetimes of degradation decrease and the degradation cross sections increase), but do not promote the formation of new species.

• Comparing the measured cross sections with the molecular dimensions, a rather **low probability of interaction between UV radiation and nucleobases** was estimated (between 0.07 % and 0.0008 %), confirming the high intrinsic photostability of such molecules.

IN DUST WE TRUST