Search for clues of life or habitability on Mars:

Laboratory simulation of organic molecules evolution at the surface of Mars

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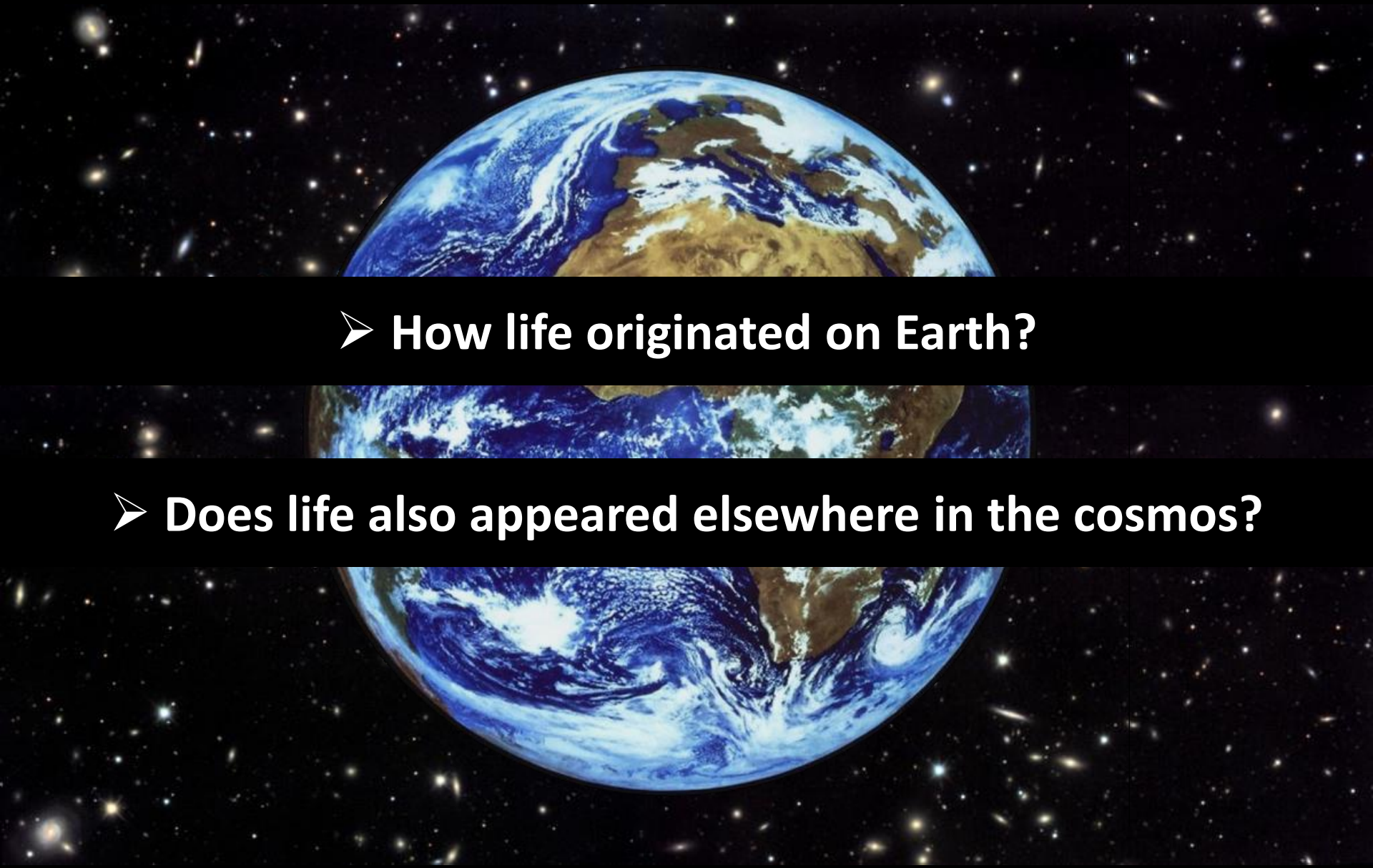
lisa

université PARIS DIDEROT PARIS 7

NASA/JPL-Caltech/D. Bouic

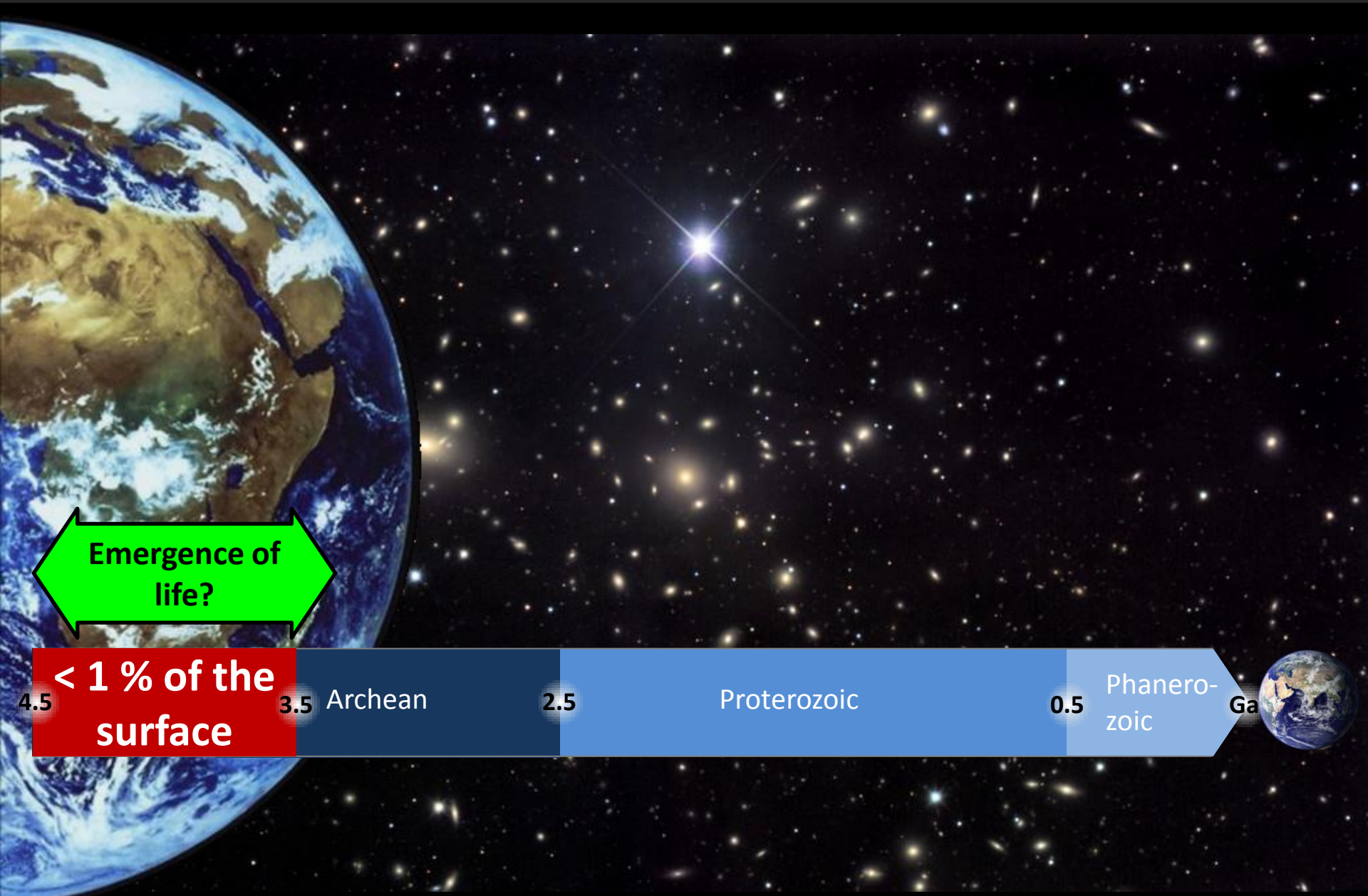
The question of the origin of life



- How life originated on Earth?
- Does life also appeared elsewhere in the cosmos?

images : NASA/ESA/OSIRIS/L.Bret pour C&E

Search for clues of life on Mars



images : NASA/ESA/OSIRIS/L.Bret pour C&E

Search for clues of life on Mars

If Mars has seen the emergence of life, can we find traces in the ancient land?

Search for organic molecules on Mars

Emergence of life?

< 1 % of the surface

4.5 — 3.5 Archean — 2.5 Proterozoic — 0.5 Phanero-zoic — Ga

50 % of the surface

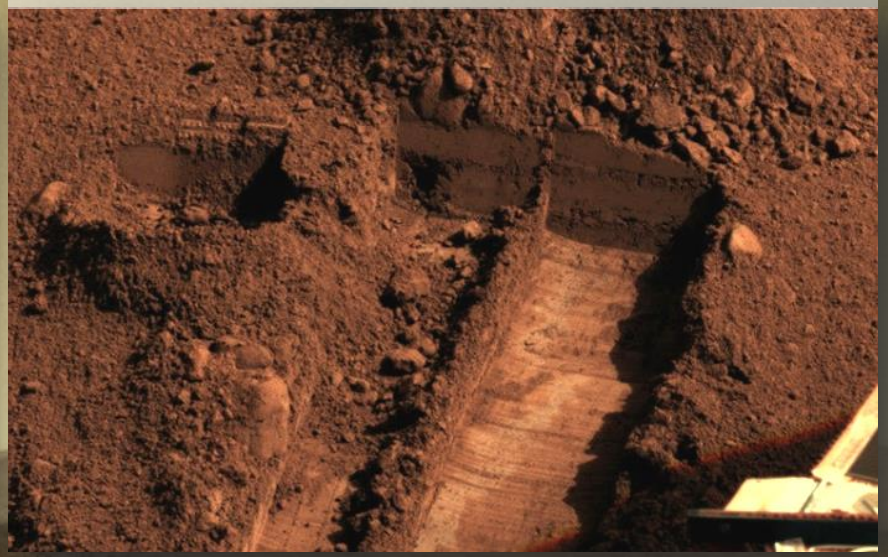
4.5 — 3.7 Hesperian — 3.0 Amazonian

images : NASA/ESA/OSIRIS/L.Bret pour C&E

Search for organic molecules on Mars

Viking 1 and 2 1976

Phoenix 2008



images : NASA/JPL/UA/T.Appéré

No definitive evidence of organic molecules in the soil

WHY?

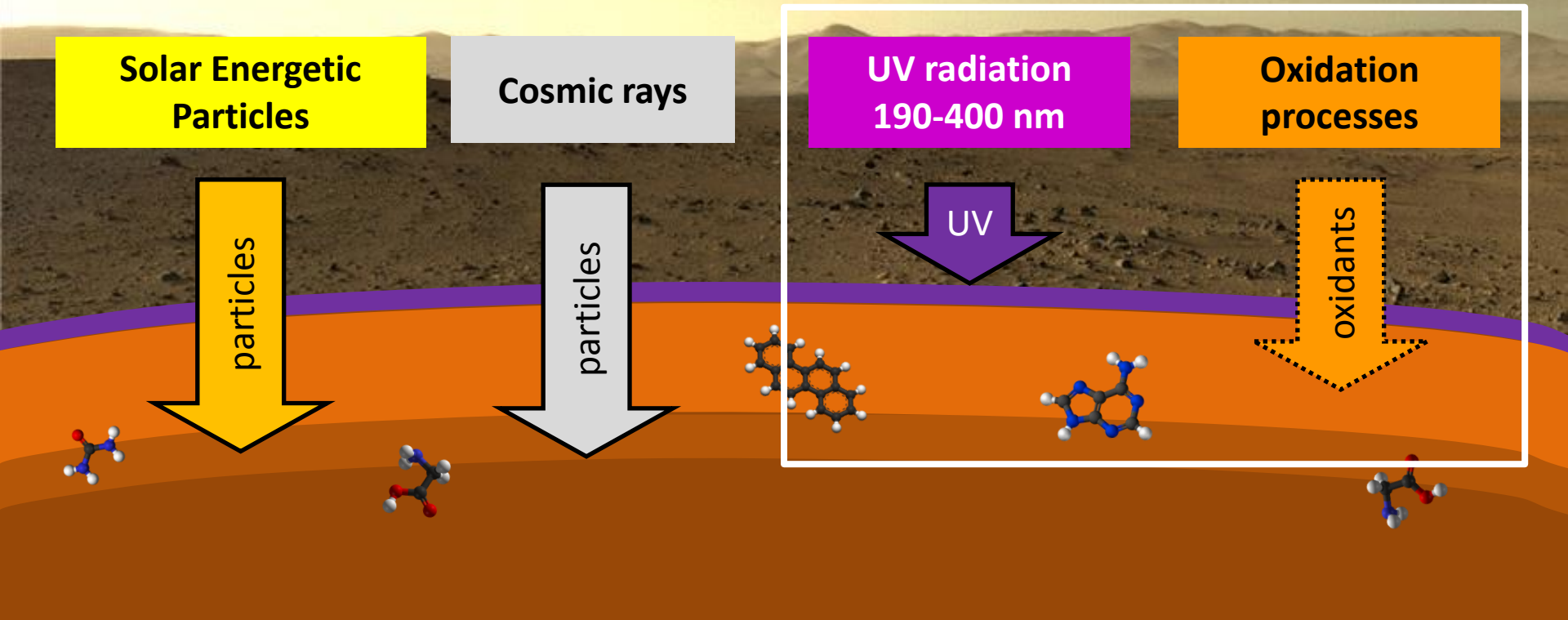
⇒ analytical limitations of the instruments?

⇒ choice of the landing sites?

⇒ evolution of the organic molecules on Mars?

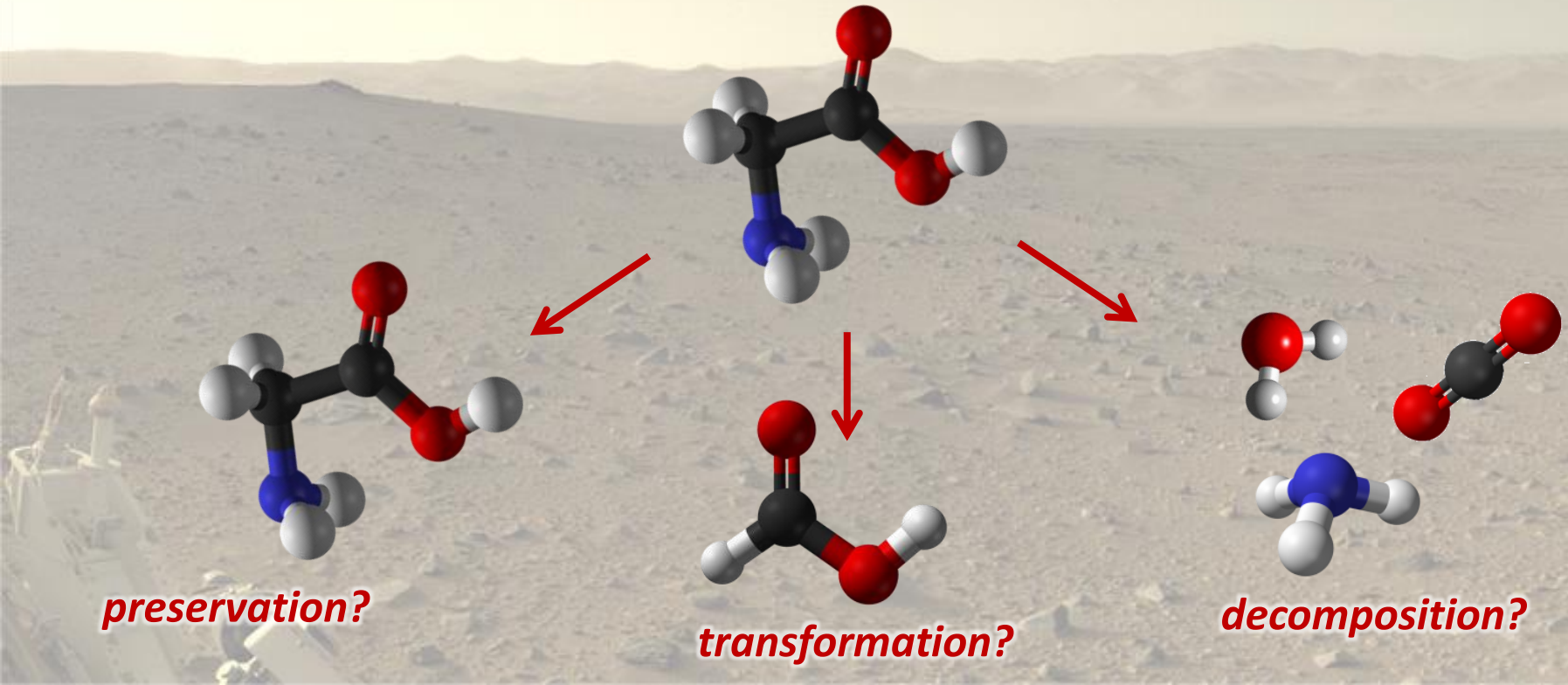
Current conditions at the surface of Mars

Environmental conditions likely to induce physico-chemical processes affecting organic matter at the surface of Mars:



My thesis

What is the evolution of selected organic molecules, in their mineral matrix, exposed to Martian UV and oxidation processes of the surface of Mars?



My thesis

What is the evolution of organic molecules in current Mars surface conditions?

Scientific issues:

It is essential to know the evolution of organic molecules on Mars in order to:

- **Guide the analyses performed *in situ*:**
  What molecules to search for?
- **Interpret the analyses performed *in situ*:**
  What is the origin of the detected molecule?

My thesis

What is the evolution of organic molecules in current Mars surface conditions?

Scientific issues:

- **Guide and discuss *in situ* analyses:**

Curiosity rover NASA/JPL

My thesis

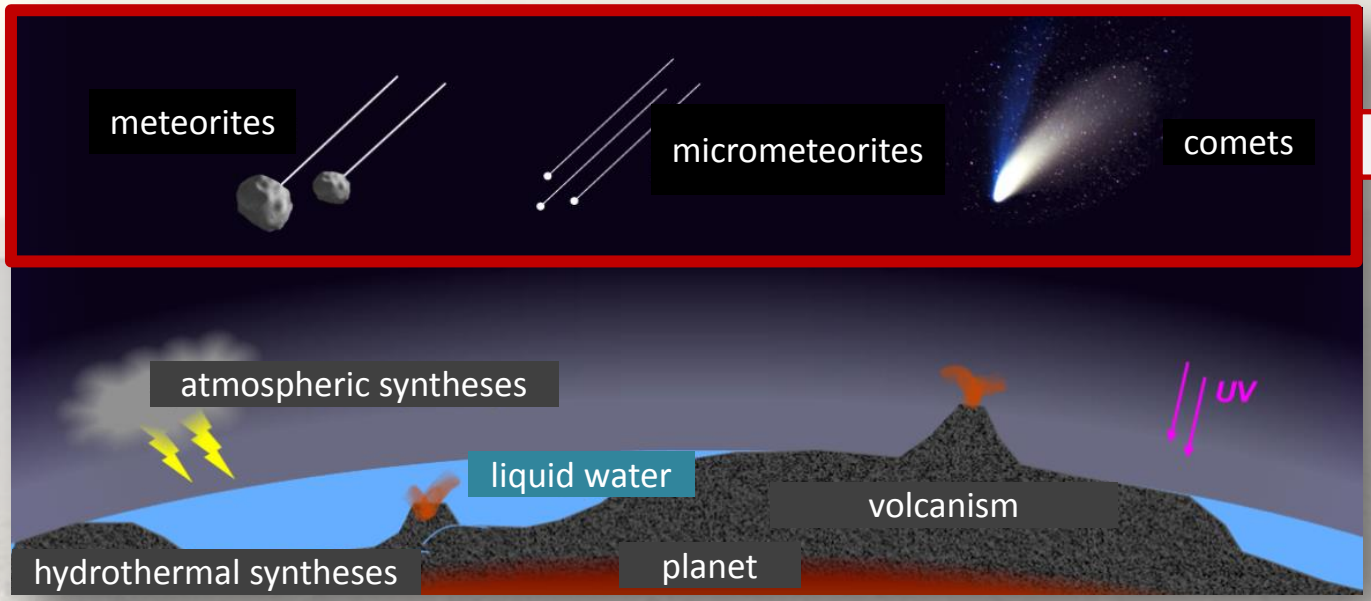
What is the evolution of organic molecules in current Mars surface conditions?

Adopted methodology:

Simulate in the laboratory the evolution of selected organic molecules, in a relevant mineral matrix, in the environmental conditions of the surface of Mars

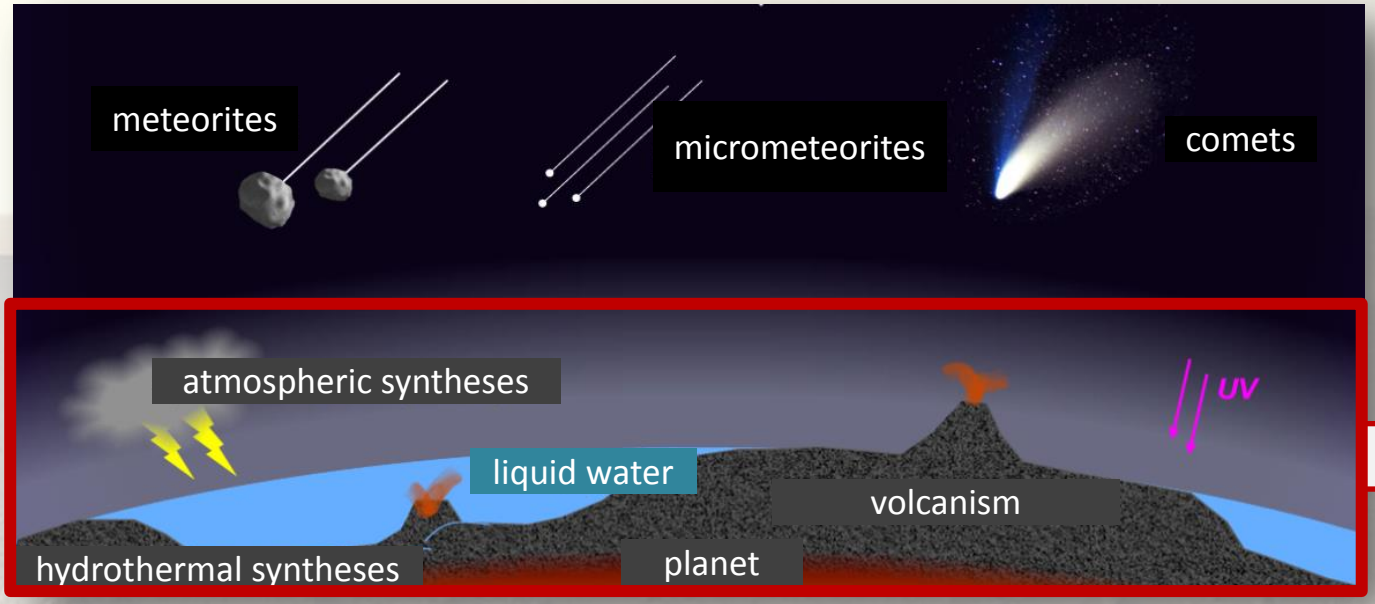
qualitative and quantitative data supporting the research of molecules on Mars.

Organic molecules selection



exogenous sources

Organic molecules selection



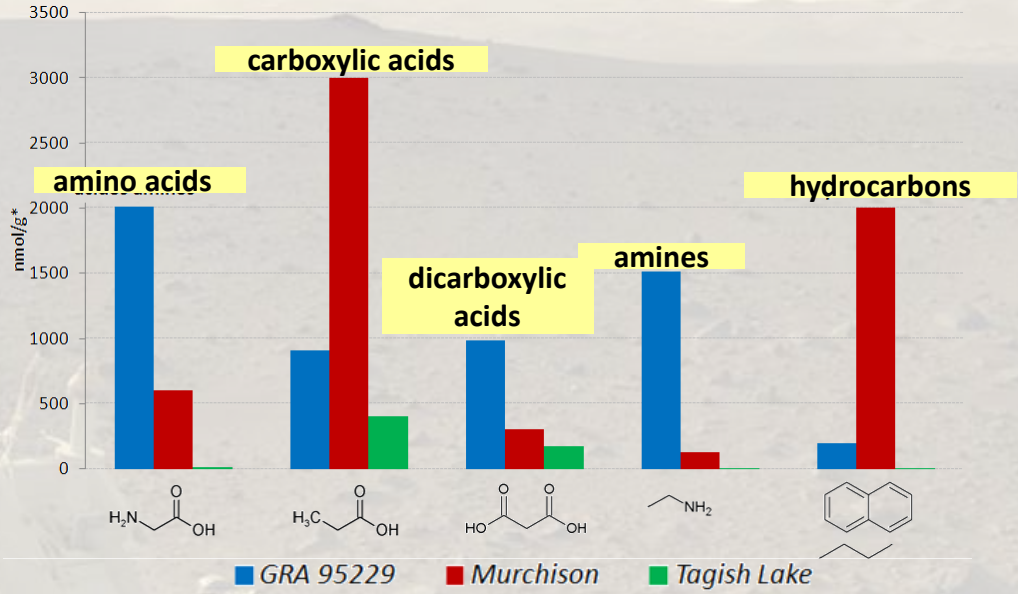
endogenous sources

Organic molecules selection

Organic molecules brought by exogenous sources:

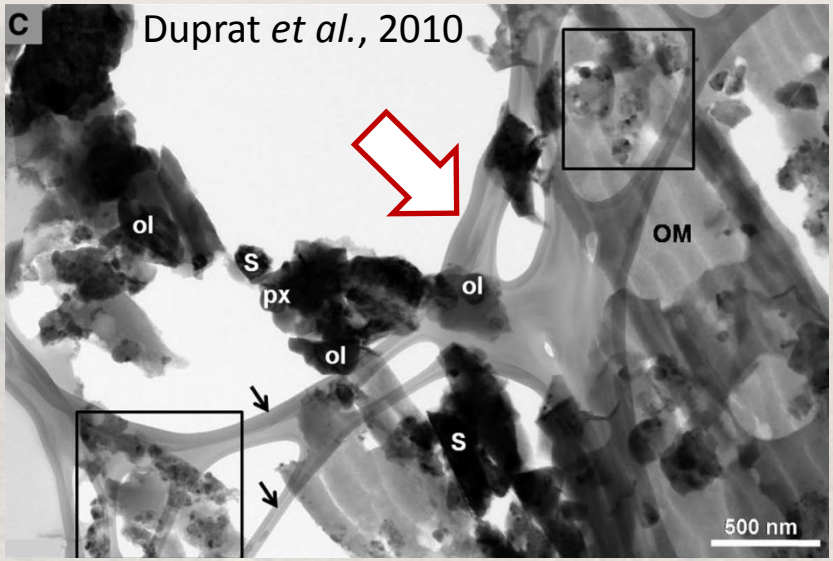
Carbon influx from micrometeorites estimated to **2,4 × 10^8 g an^{-1}** (Flynn 1996)

➢ *soluble phase (1-25%):*



Pizzarello 2006, 2008

➢ *insoluble phase (75-99%):*



Derenne *et al.*, 2010

Organic molecules selection

Bibliographic study of tracer molecules of the sources:

Sources →	Exogenous	Atmospheric	Hydrothermal	Magmatic	Biologic
glycine	✓	✓	✓		✓
urea	✓	✓	✓		✓
adenine	✓	✓	✓		✓
propanoic acid	✓	✓	✓		✓
dodecanoic acid	✓	✓	✓		✓
PAH (pyrene, phenanthrene, chrysene)	✓	✓	✓	✓	
linear hydrocarbons (octadecane)	✓	✓	✓	✓	✓
mellitic acid	✓	✓	✓	✓	✓
porphyrin		✓	✓		✓

✓ = tracer of this source ✓ = potential tracer of this source

Organic molecules selection

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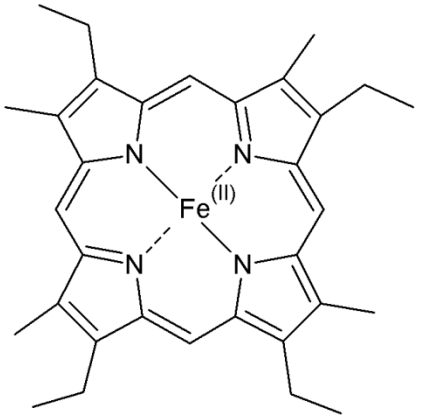
linear hydrocarbons (octadecane)	✓	✓	✓		
mellitic acid	✓	✓	✓		
porphyrin		✓	✓		✓

Porphyrin : a universal molecule in terrestrial life



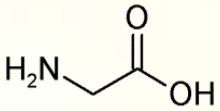
Suo *et al.*, 2007; Lindsey *et al.*, 2011

✓ = tracer of this source

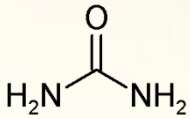
✓ = potential tracer of this source

Organic molecules selection

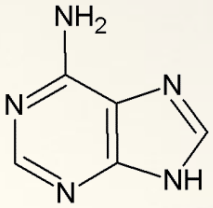
Organic molecules selected:



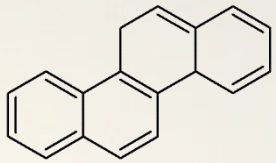
glycine



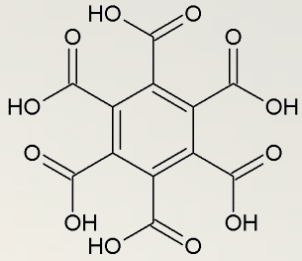
urea



adenine



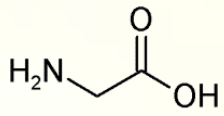
chrysene



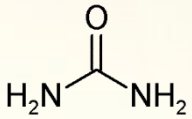
mellitic acid

Organic molecules selection

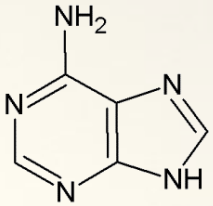
Organic molecules selected:



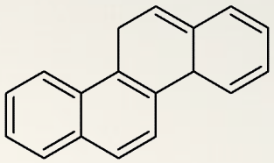
glycine



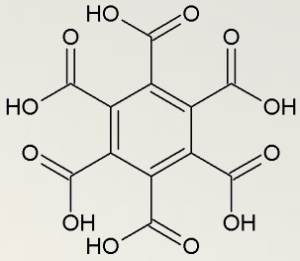
urea



adenine



chrysene



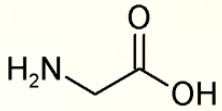
mellitic acid

- **The simplest amino acid**
- **Evolution under UV radiation well documented in the litterature**
- **Reference**

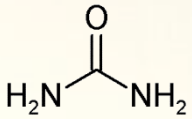
Stoker et Bullock 1997; ten Kate *et al.* 2005; Stalport *et al.* 2008

Organic molecules selection

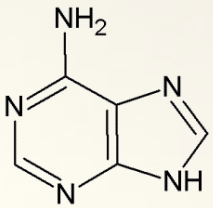
Organic molecules selected:



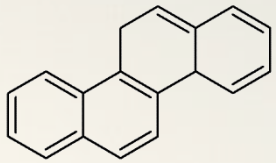
glycine



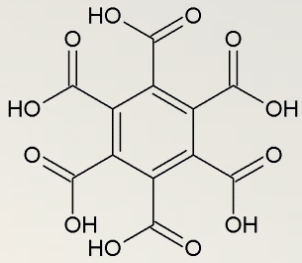
urea



adenine



chrysene



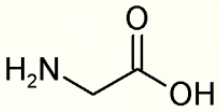
mellitic acid

- **Abundant** in exogenous and endogenous sources
- Key role in **prebiotic chemistry** and in **biology**
- **Resistant to oxidation**

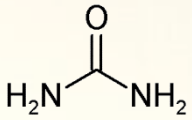
Navarro-Gonzalez *et al.*, 1981; Masuda 1980; Kenyon 1969

Organic molecules selection

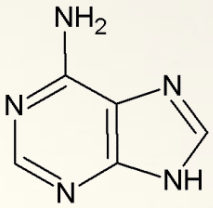
Organic molecules selected:



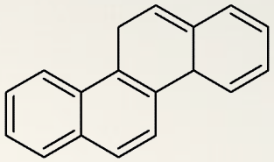
glycine



urea



adenine



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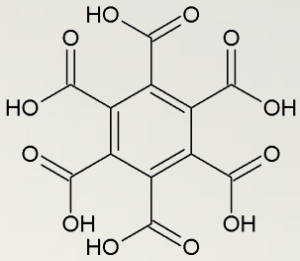


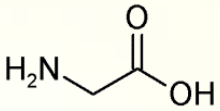
mellitic acid

- Tracer of the nucleobases (DNA/RNA)
- Purine base: potentially more resistant to UV

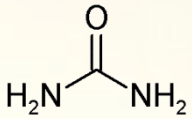
Wang 1976; Barbatti et Ullrich 2011

Organic molecules selection

Organic molecules selected:



glycine



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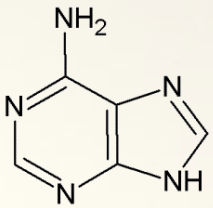

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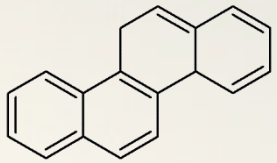

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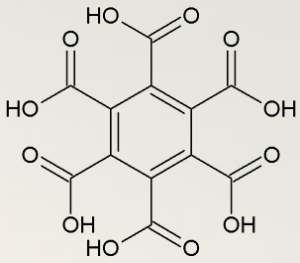


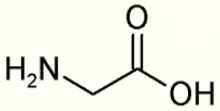
mellitic acid

- **Tracer of polycyclic aromatic hydrocarbons (PAH), abundant in exogenous and endogenous sources**

Botta et Bada 2002; Clemett et al., 1998; Steele et al., 2012

Organic molecules selection

Organic molecules selected:



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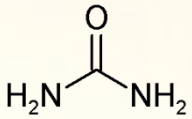

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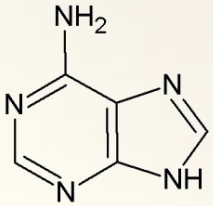

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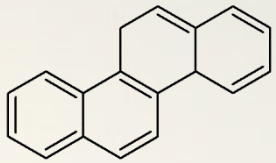

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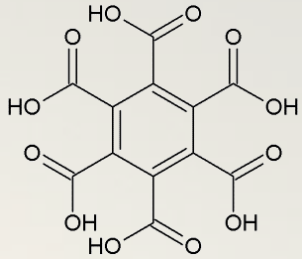


mellitic acid

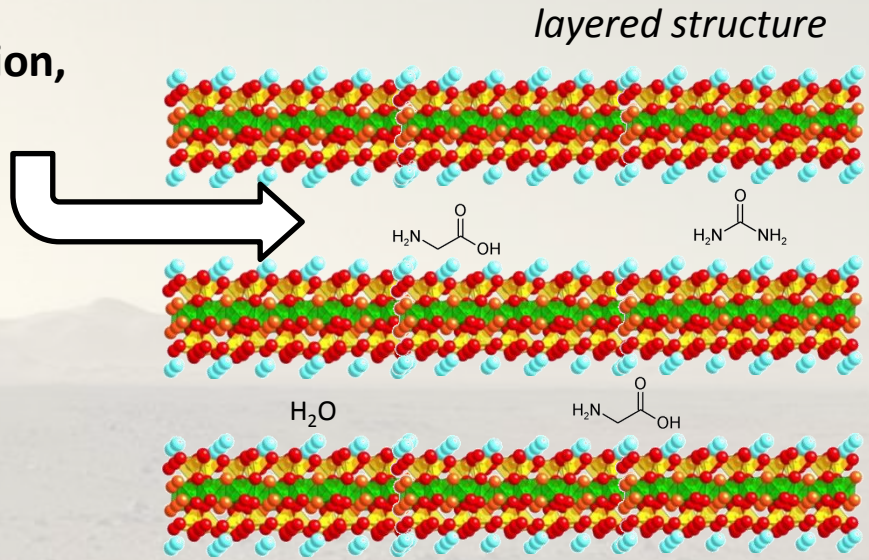
- **Oxidation product** of molecules having a benzene ring
- **Resistance** to oxidation and UV

Benner et al., 2000; Stalport et al., 2009; Archer 2010

Mineral matrix selection

Nontronite

- **A clay mineral: large surface of adsorption, layers → high preservation potential**
- **Detected several times on Mars** (Ehlmann *et al.*, 2012)
- **Found in Gale crater (Curiosity)** (Milliken *et al.*, 2010)
- **Possibility of production of pure organic-free nontronite via hydrothermal synthesis** (Andrieux et Petit, 2010)



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LRS
PARIS

Mineral matrix selection

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Gale crater

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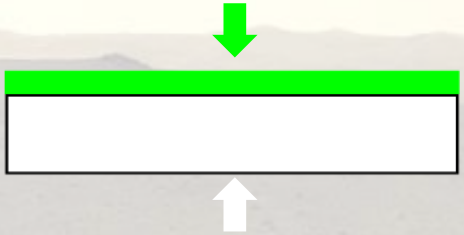
LRS
PARIS

Sample preparation

Type 1:
pure organic molecule

molecule deposit

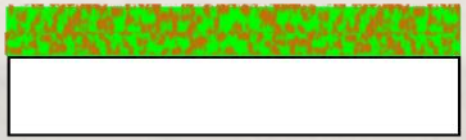


MgF_2 optical window

➢ **Deposited by sublimation/recondensation**

*thickness of **10 to 100 nm***

Type 2:
organic molecule with nontronite

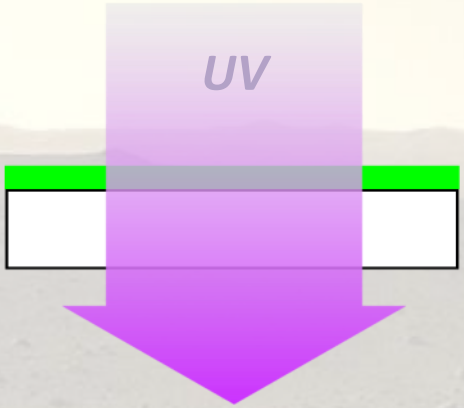


➢ **Deposited by evaporation/sedimentation** of a suspension of nontronite in an aqueous solution of the organic molecule

*thickness of **2 to 10 µm***

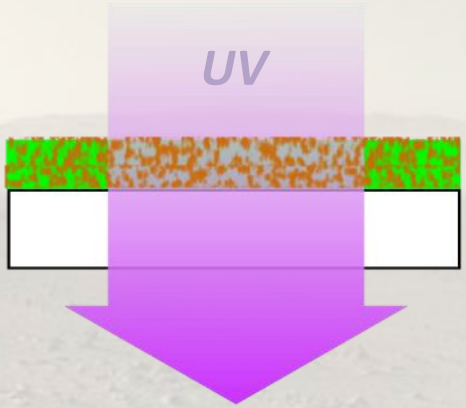
Evolution under simulated conditions

Type 1:
evolution of **pure organic molecules under UV**



Direct photolysis:
molecule + ***hv*** → products

Type 2:
evolution of **organic molecules with nontronite** under **UV** and **oxidation**

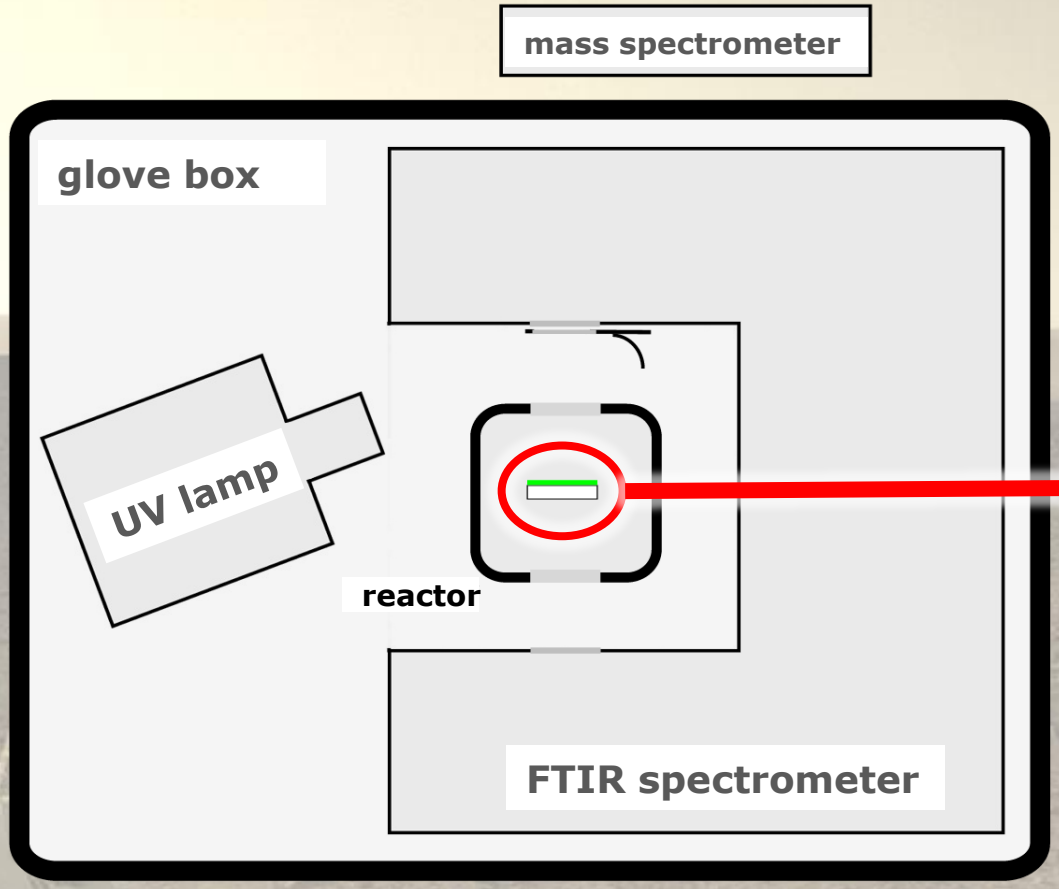


Effect of the nontronite:
- photoprotection?
- catalysis of the degradation?
- oxidation processes?

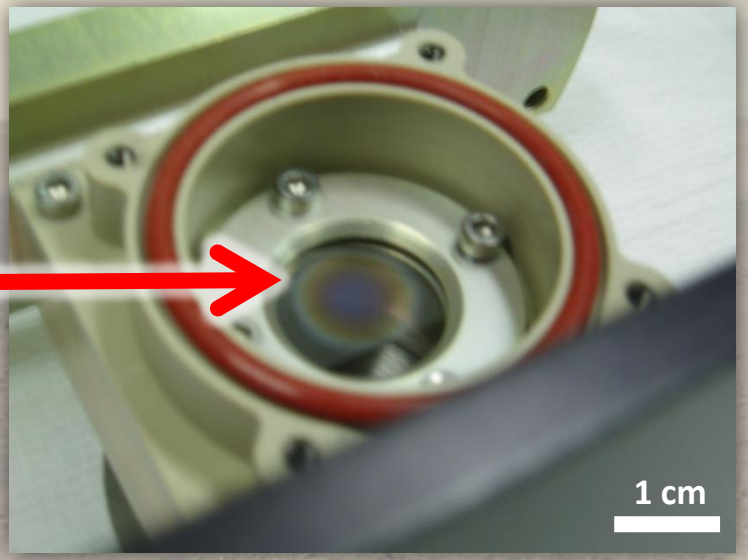
molecule + $OH^{\cdot}$ → products

The MOMIE experimental setup

scheme of the MOMIE setup:

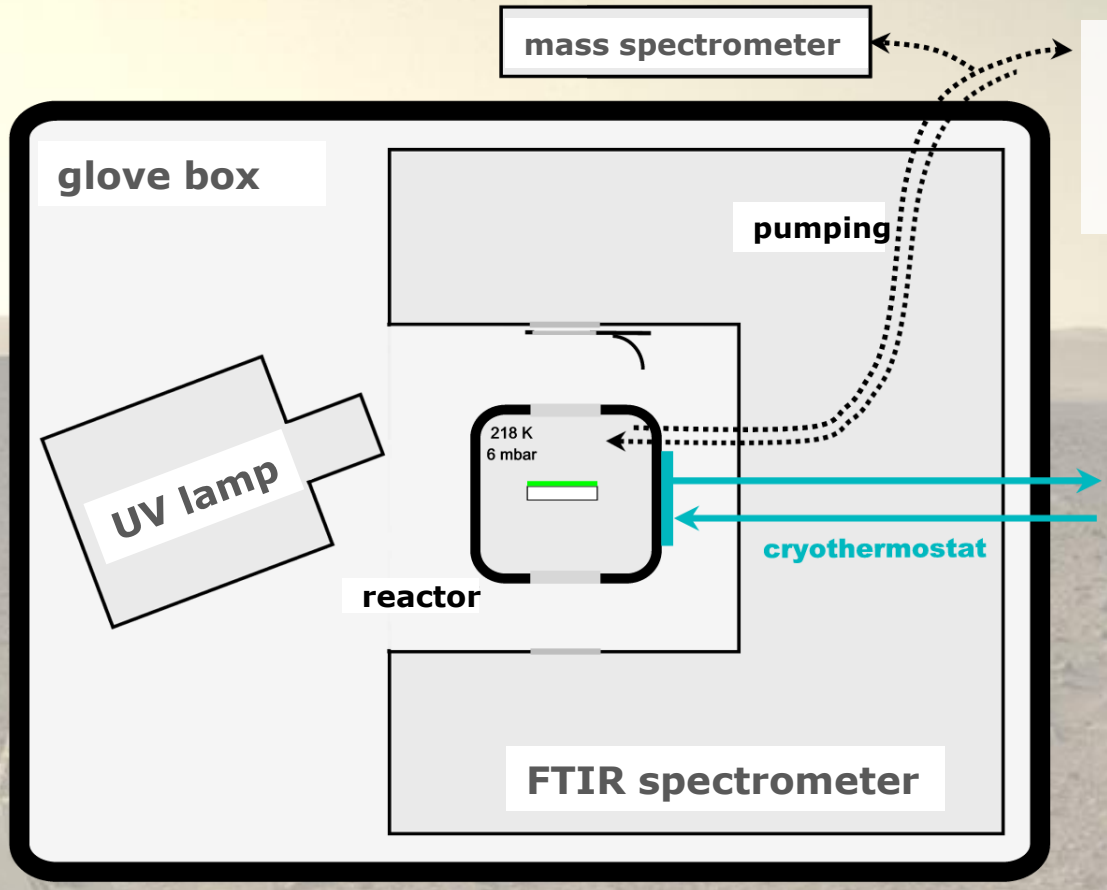


sample inside the reactor:

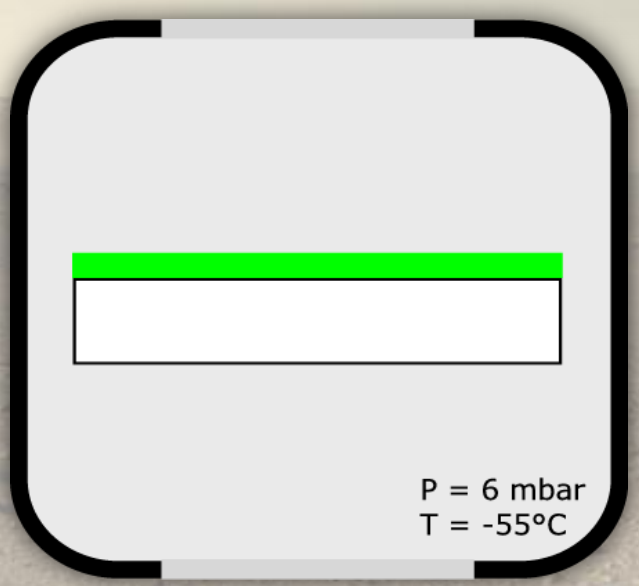


The MOMIE experimental setup

scheme of the MOMIE setup:



mean temperature and pressure of the surface of Mars -55°C and 6 mbar



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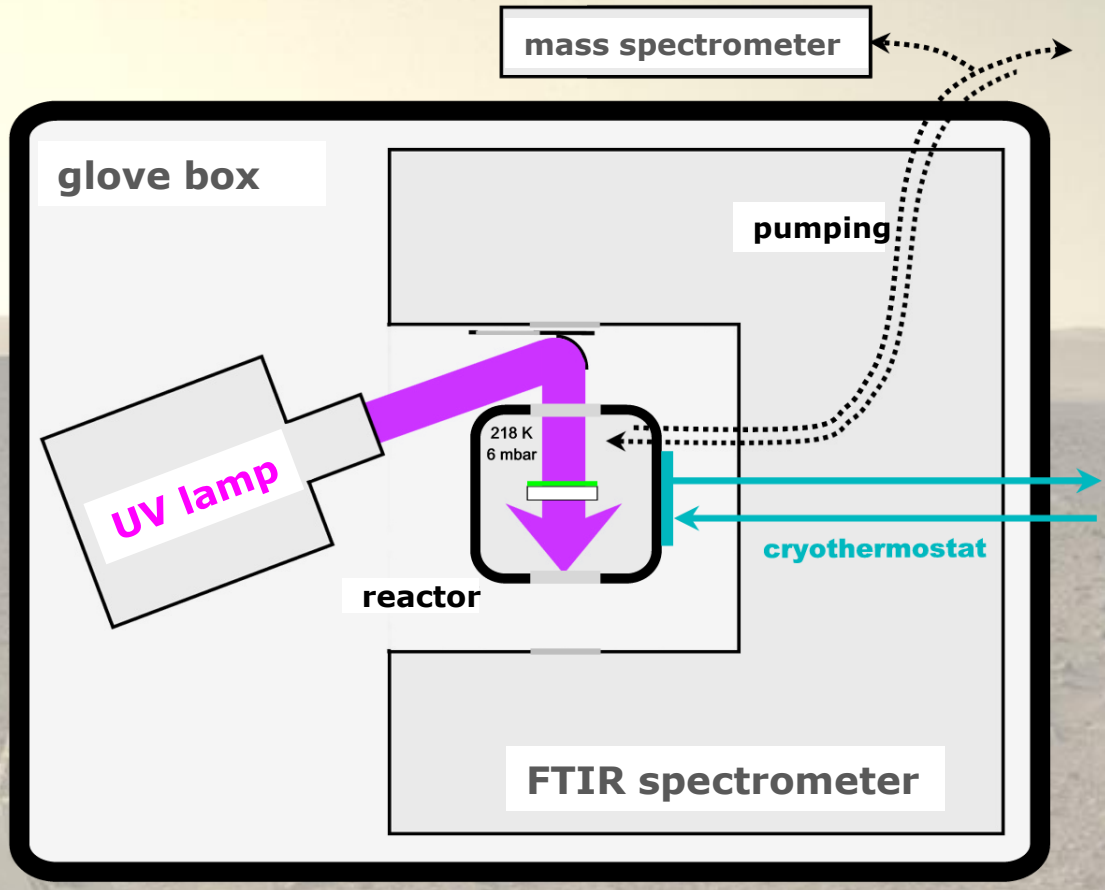

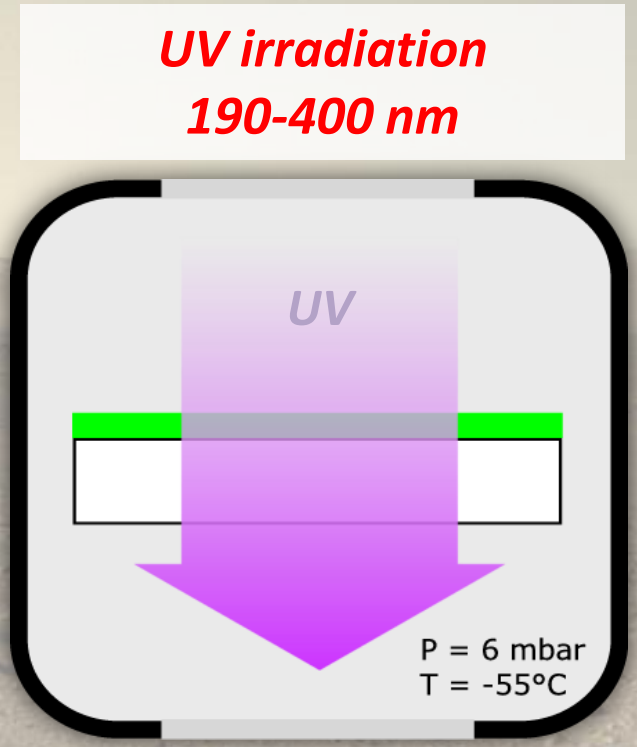

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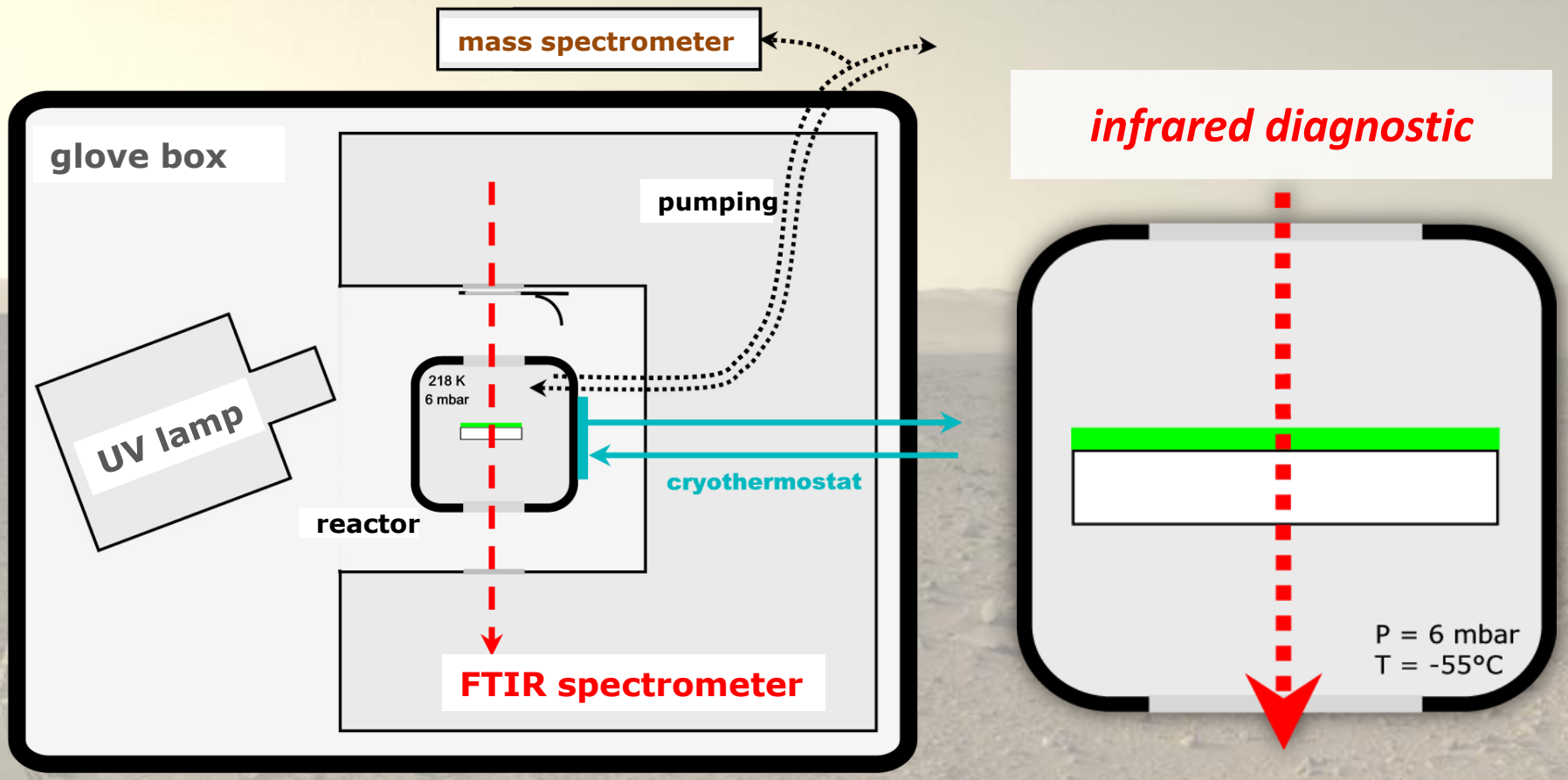

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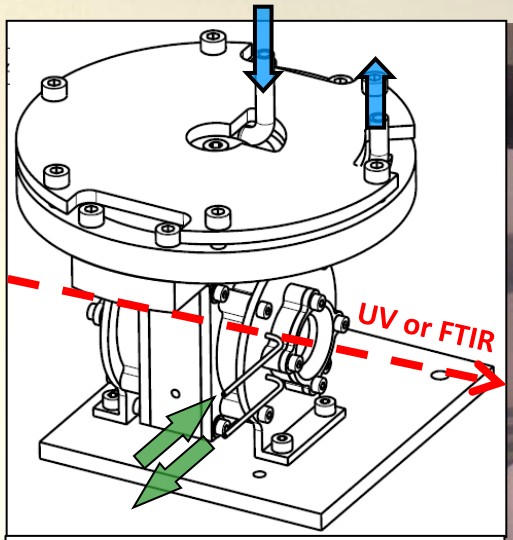


the MOMIE reactor

cryothermostat
-55°C

gas system
(pumping, MS)
6 mbar

Xenon arc lamp
UV 190-400 nm

FTIR spectrometer
4000-1000 cm^{-1}

Optimization of the MOMIE setup

- Limited duration of the simulations at **mean Martian temperature and pressure**

⇒ ***extension of the duration*** *of the simulations from 8h to 72h*

- ***In situ*** **qualitative and quantitative** analyses via FTIR.

⇒ *ex situ analysis of the* ***residue*** *via UV spectrometry and GC-MS*

⇒ *in situ analysis of the* ***gas phase*** *via a mass spectrometer*

- **UV irradiance variability** from one experiment to another.

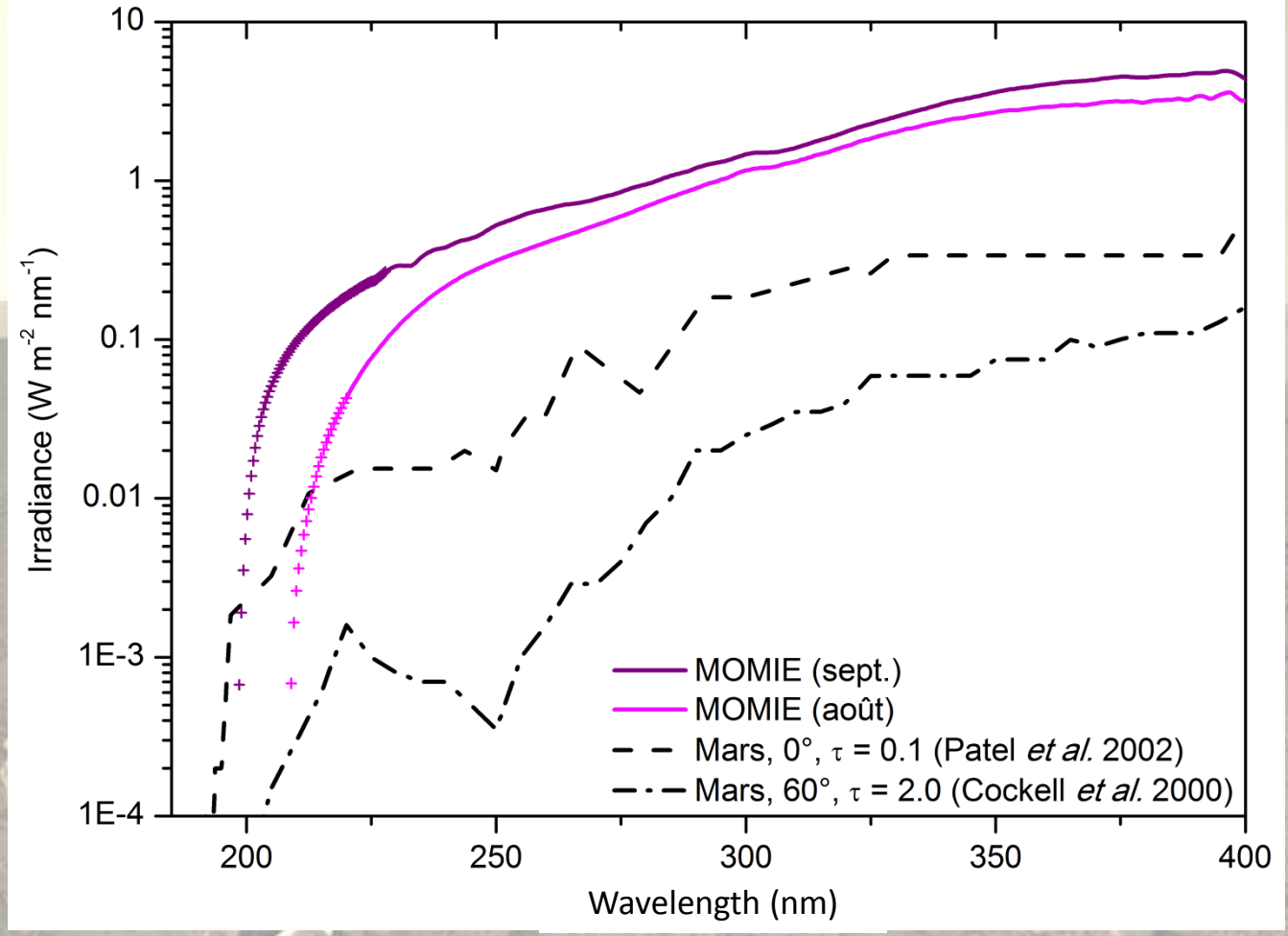
⇒ ***in situ measure of UV irradiance*** *with a spectroradiometer, taking into account all sources of variability of this irradiance*

⇒ ***improved extrapolation*** *of the data to the surface of Mars*

The most efficient experience to date
to simulate the evolution of organic molecules on Mars

Optimization of the MOMIE setup

Measurement of the **UV irradiance** reaching the sample



Integrated photon flux between 200 and 250 nm:

- MOMIE:
  $6{,}4 – 18 \times 10^{18}$ photon m^{-2} s^{-1}
- Mars (numerical model):
  $7{,}6 \times 10^{17}$ photon m^{-2} s^{-1}
  (Patel *et al.*, 2000)

extrapolation of the results to Mars

Scientific objective and expected results

What is the evolution of organic molecules in these simulated conditions of the surface of Mars?

⇒ **Photo-products analysis, solid and gaseous**

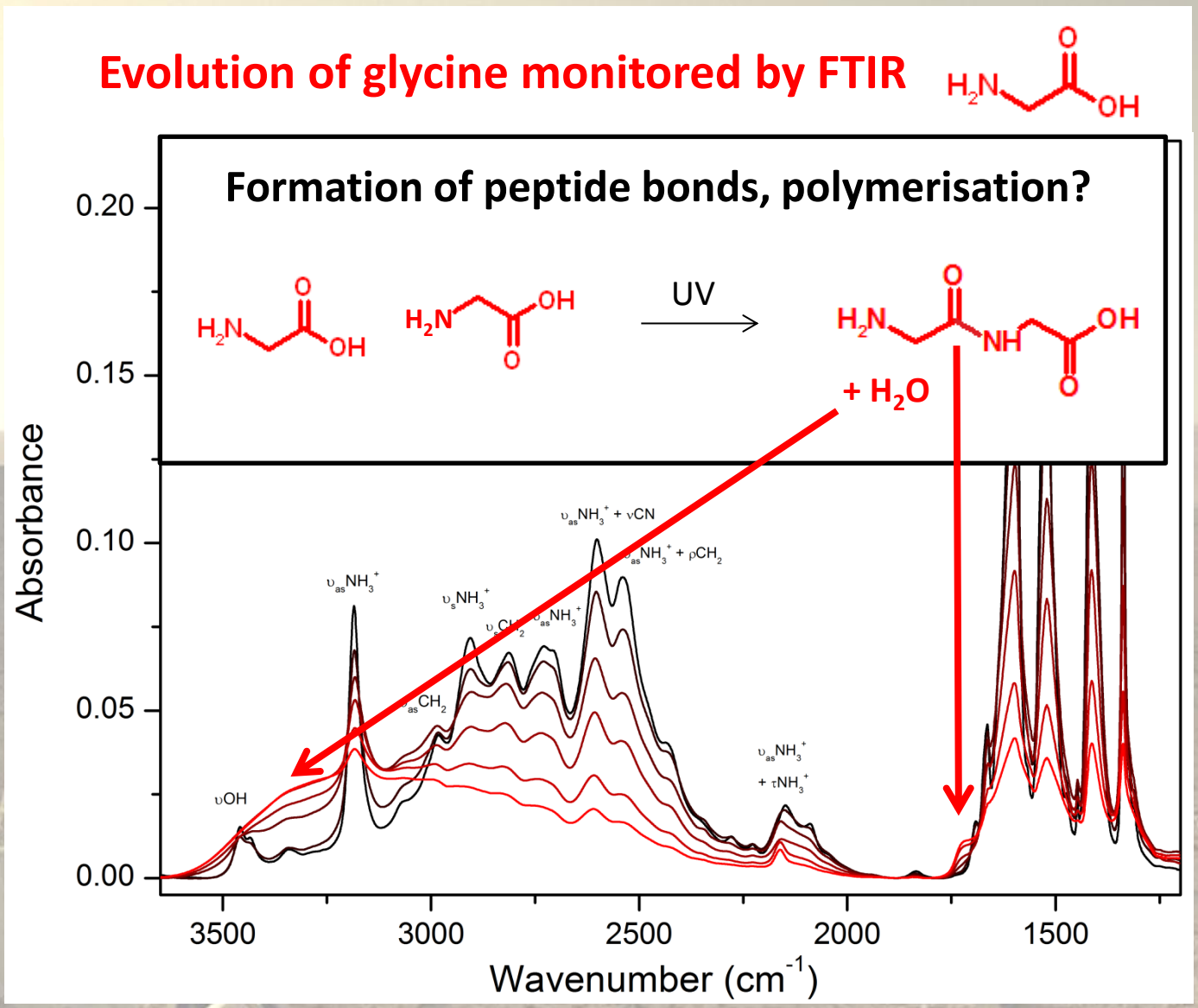
Suggestion of molecular targets to search for on Mars, in the atm.?

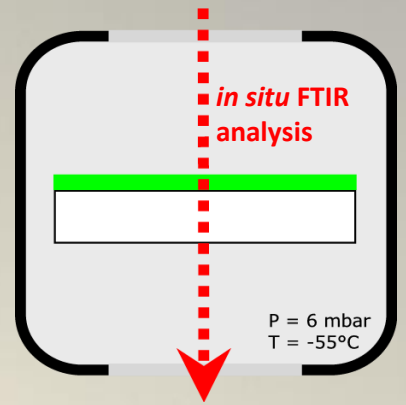
⇒ **Kinetics of degradation or evolution**

Stability in Martian environment? Extrapolated half-life?

Evolution of glycine under UV radiation

Evolution of glycine monitored by FTIR





Data prodution:

Qualitative : solid phase chemistry

Quantitative: kinetics of degradation

Poch *et al.*, *Planetary and Space Science* 85, 188-197, **2013**

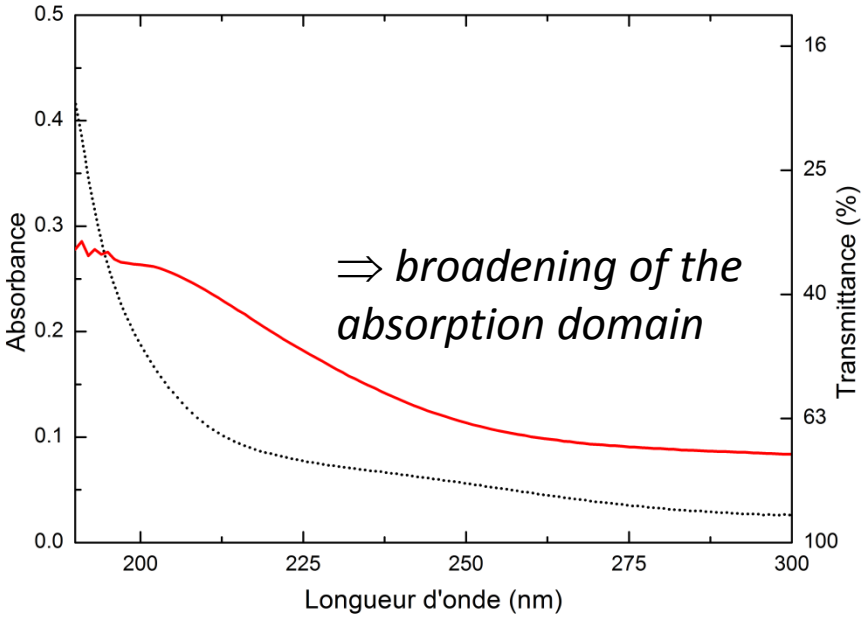
Evolution of glycine under UV radiation

ex-situ analyses of the residue before/after UV irradiation:

→ **Extraction/Derivatization (MTBSTFA) prior to GC-MS**

No glycylglycine detected → **Extraction?**
Cyclic polypeptide? other molecule?

→ **UV spectrum**

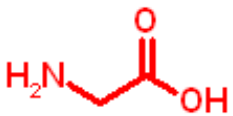


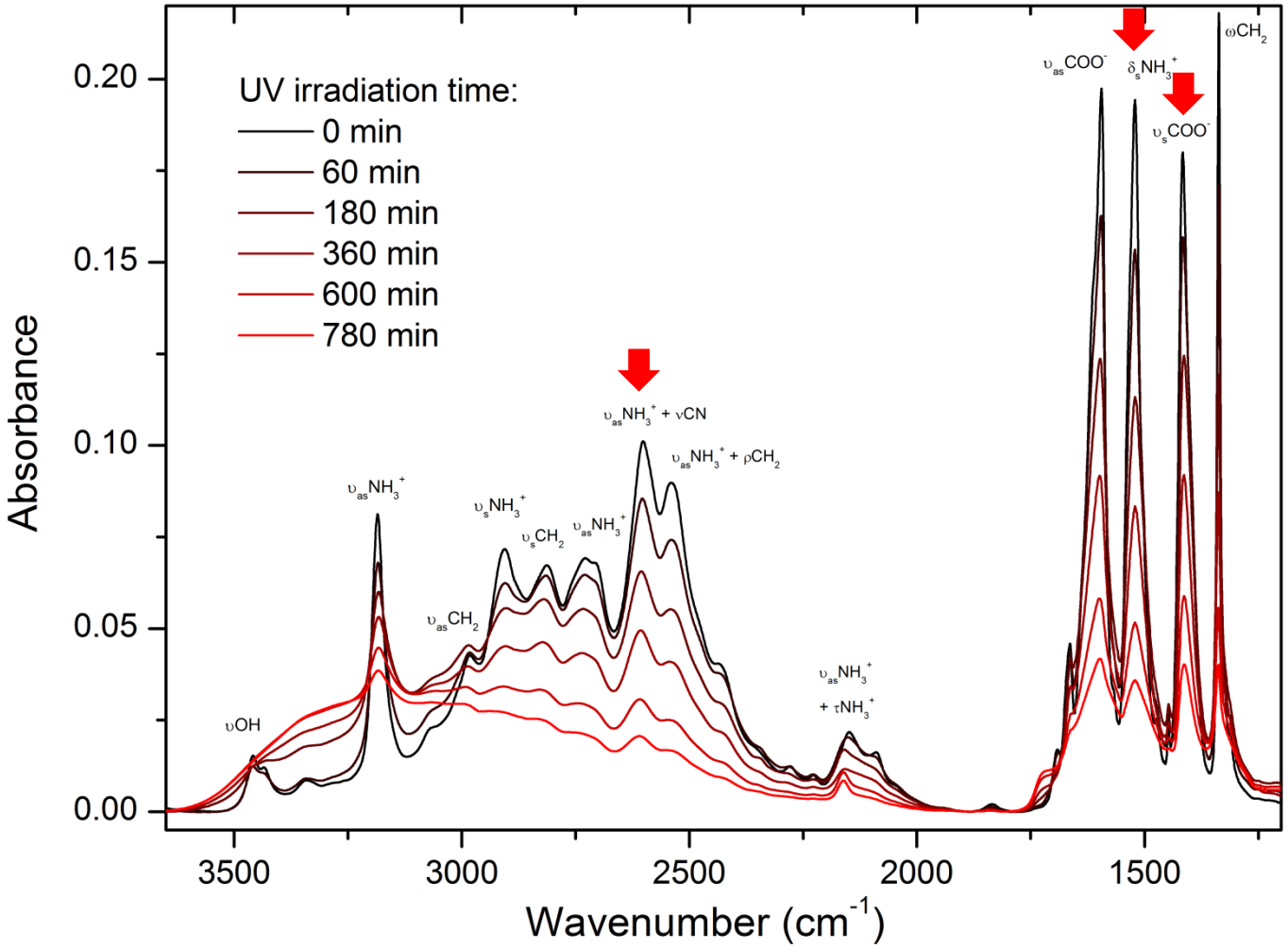
→ **Pictures of the sample**

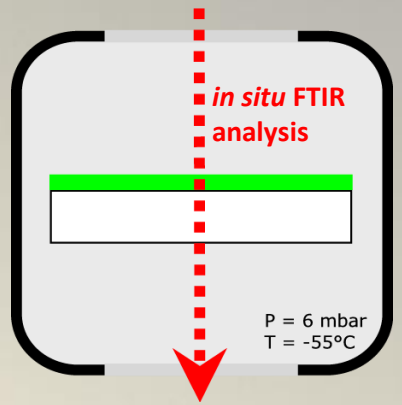
⇒ **change of the cristalline state** of glycine during the UV irradiation

Evolution of glycine under UV radiation

Evolution of glycine monitored by FTIR







Data production:

Qualitative : solid phase chemistry

Quantitative: kinetics of degradation

Poch *et al.*, *Planetary and Space Science* 85, 188-197, **2013**

Evolution of glycine under UV radiation

Photodissociation : considérations théoriques

Hypothesis: optically thin deposit

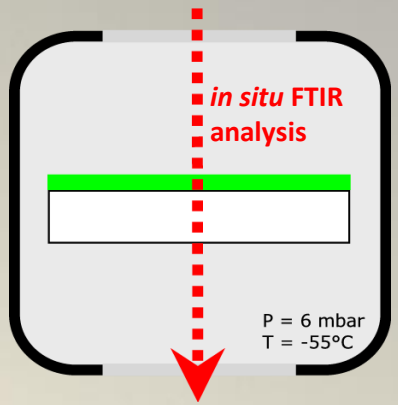
$$\Rightarrow dN = N.\mathbf{J}.dt$$

$$\Rightarrow \mathbf{N_{(t)} / N_{(t=0)} = e^{-J.t}}$$

Photolysis constant:

$$\mathbf{J} = \int_\lambda \Phi_\lambda \,.\, \sigma_\lambda \,.\, F_\lambda \,.\, d\lambda$$

Φ_λ : photodissociation quantum yield fo the molecule
σ_λ : absorption cross section of the molecule
F_λ : photon flux



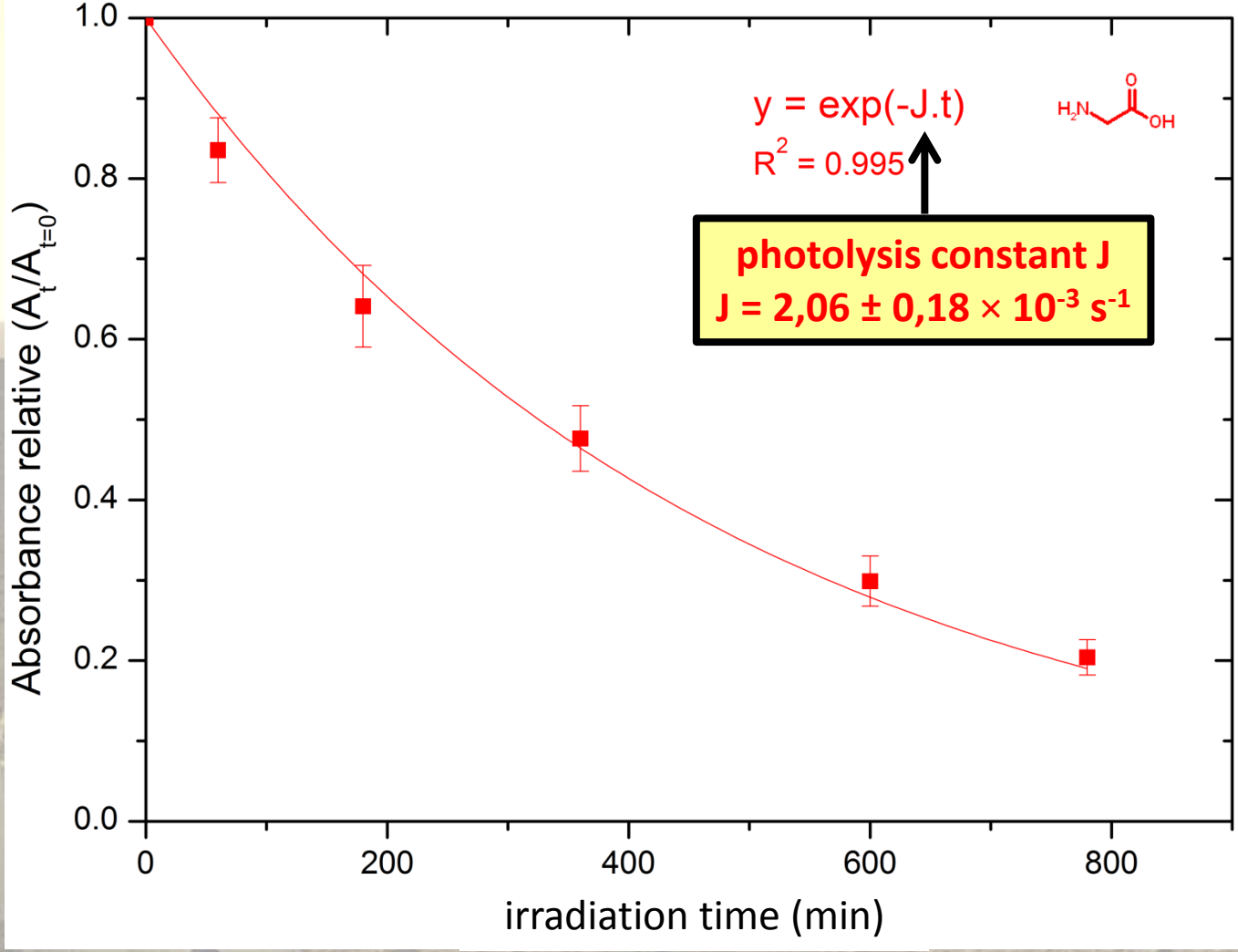
Data production:

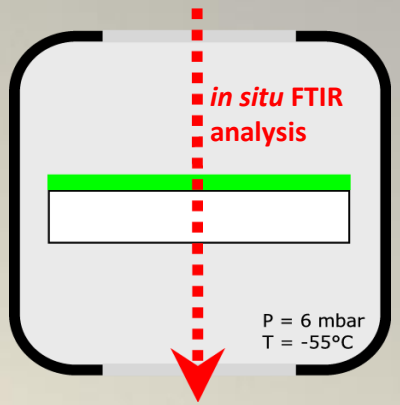
Qualitative :
solid phase chemistry

Quantitative:
kinetics of degradation

Evolution of glycine under UV radiation

Degradation kinetic of glycine monitored by FTIR



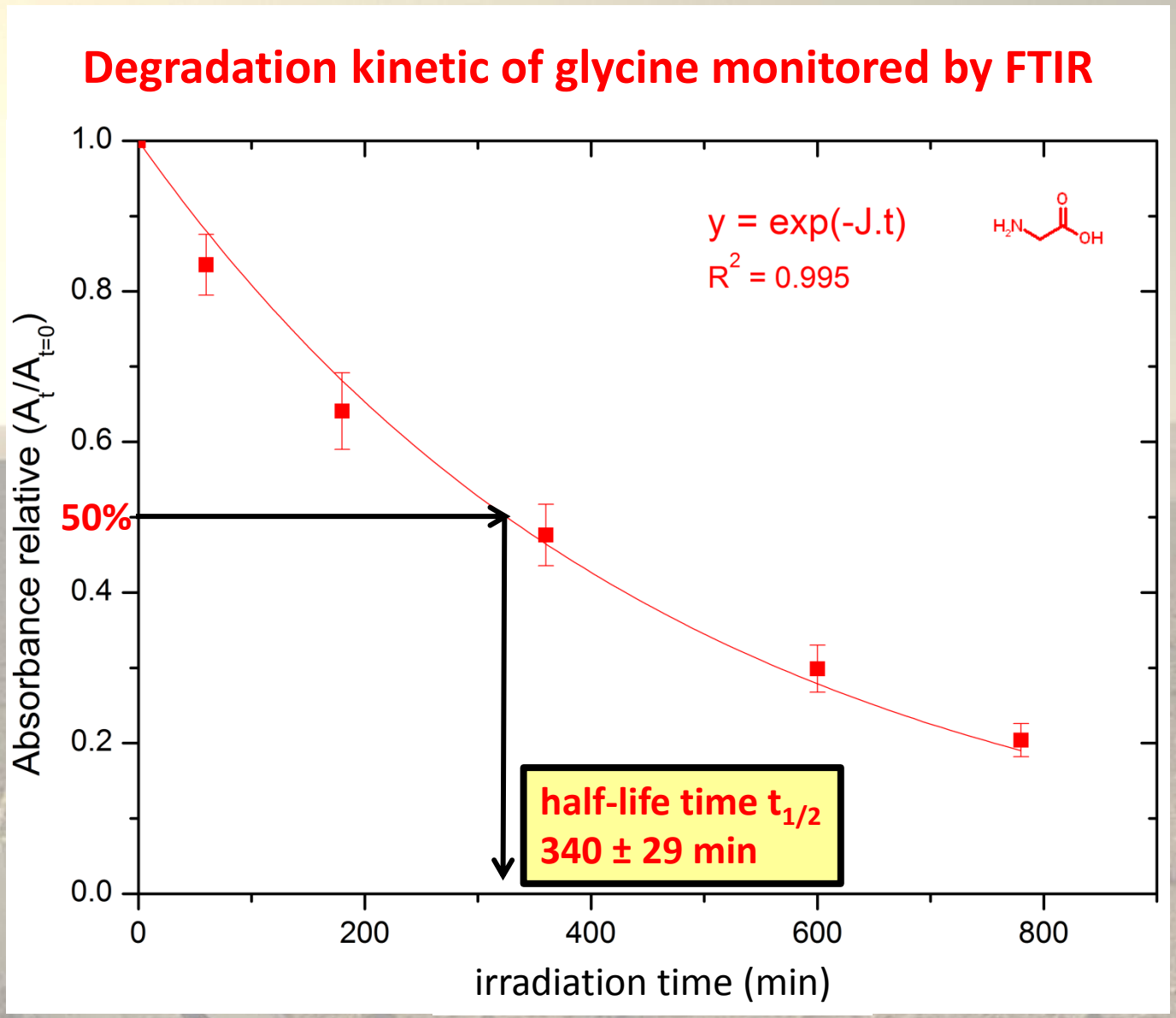


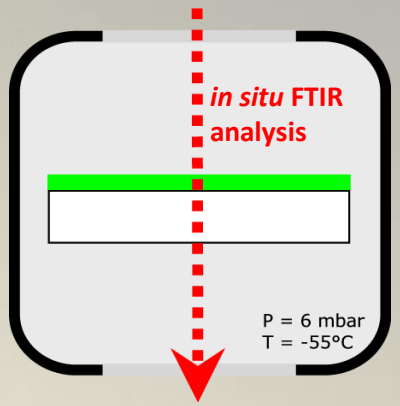
Data production:

Qualitative :
solid phase chemistry

Quantitative:
kinetics of degradation

Evolution of glycine under UV radiation





Data production:

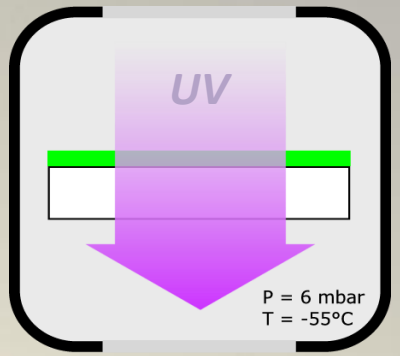
Qualitative : solid phase chemistry

Quantitative: kinetics of degradation

Evolution of glycine under UV radiation

Extrapolation of the temporal data to the photon flux at the surface of Mars:

	inside MOMIE:	*on Mars:*
Photons flux (200-250 nm) photons m^{-2} s^{-1}	$3,9 \pm 3,0 \times 10^{19}$	$7,6 \times 10^{17}$ (Patel *et al.*, 2002)
$t_{1/2}$	340 ± 29 min	**310 ± 240 h**
J	$2,06 \pm 0,18 \times 10^{-3}$ s^{-1}	**$1,7 \pm 1,3 \times 10^{-6}$ s^{-1}**



Data production:

Qualitative : solid phase chemistry

Quantitative: kinetics of degradation

Evolution of glycine under UV radiation

Determination of the photodecomposition efficiency

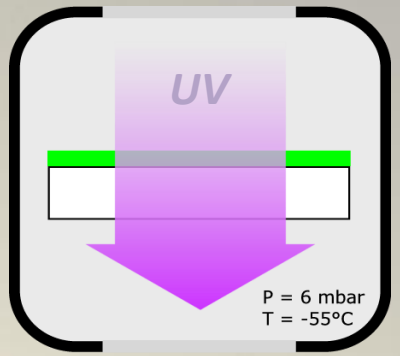
- degradation kinetics of the deposit
- measure of the deposit thickness

$$\Phi = \frac{\text{Number of transformed molecules}}{\text{Number of incident photons}} \quad \text{(molecule photon}^{-1}\text{)}$$

- measure of the UV irradiance (200-250 nm)

For glycine:

$\Phi = 6{,}3 \pm 5{,}2 \times 10^{-3}$ molecule photon^{-1} between 200 and 250 nm



Data production:

Qualitative :
solid phase chemistry

Quantitative:
photodissociation efficiency

Quantitative results

Molecule	Sample thickness (nm)	Photolysis constant J (s^{-1})	Half-life time $t_{1/2}$ (hours)	Photodissociation efficiency 200-250 nm (molecule photon^{-1})
Glycine	295 ± 19	$1.4 \pm 1.1 \times 10^{-6}$	310 ± 230	$4.6 \pm 3.4 \times 10^{-3}$
	295 ± 19	$1.7 \pm 1.3 \times 10^{-6}$	310 ± 240	$4.1 \pm 3.2 \times 10^{-3}$
	295 ± 19	$2.0 \pm 1.7 \times 10^{-6}$	330 ± 280	$9.0 \pm 7.6 \times 10^{-3}$
	295 ± 19	$1.8 \pm 1.5 \times 10^{-6}$	300 ± 240	$7.0 \pm 5.7 \times 10^{-3}$
	322 ± 80	$1.6 \pm 1.3 \times 10^{-6}$	330 ± 260	$7.1 \pm 6.2 \times 10^{-3}$
	499 ± 80	$9.1 \pm 7.1 \times 10^{-7}$	550 ± 430	$6.0 \pm 4.9 \times 10^{-3}$
Urea	119 ± 257	$1.5 \pm 1.1 \times 10^{-6}$	320 ± 250	$1.5 \pm 7.5 \times 10^{-3}$
	164 ± 257	$8.4 \pm 6.5 \times 10^{-7}$	590 ± 470	$1.1 \pm 4.5 \times 10^{-3}$
Adenine	27 ± 32	N.D.	380 ± 290 *	$8.2 \pm 27 \times 10^{-5}$
	70 ± 32	N.D.	1910 ± 1500 *	$1.1 \pm 1.0 \times 10^{-4}$
	100 ± 3	N.D.	4420 ± 3440 *	$1.10 \pm 0.9 \times 10^{-4}$
	1300	N.D.	N.D.	$1.0 \pm 0.9 \times 10^{-4}$
Chrysene	35 ± 7	$3.7 \pm 2.9 \times 10^{-7}$	1280 ± 990	$4.9 \pm 4.1 \times 10^{-5}$
Mellitic trianhydride	33 ± 70	$6.0 \pm 4.6 \times 10^{-7}$	780 ± 600	$4.7 \pm 24 \times 10^{-5}$

Poch *et al.*. in preparation

Extrapolated half-life times on Mars

Poch *et al.,* in preparation

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⇒ **Half-life times of the order of 10 to 1000 hours on Mars**

Extrapolated half-life times on Mars

Poch *et al.,* in preparation

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⇒ **Error bars of the order of ± 70 à 80 % due to uncertainties of the UV irradiance**

Extrapolated half-life times on Mars

Poch *et al.,* in preparation

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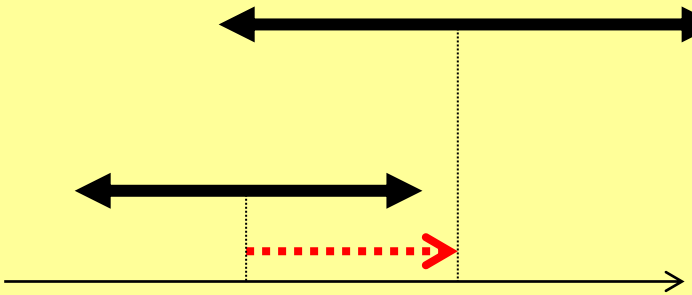
In order to compare two values of $t_{1/2}$, the error bars have to be read for the same photon flux

$t_{1/2}$ values for a high photon flux

$t_{1/2}$ values for a low photon flux



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Extrapolated half-life times on Mars

Poch *et al.,* in preparation

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⇒ **Measured half-life values depend on the initial thickness of the irradiated sample**

Extrapolated half-life times on Mars

Dependency of half-life times with the thickness of the deposits

- **May explain the differences between half-lives determined in the literature for similar molecules**

- Of interest in the context of the evolution of molecular layers on Mars

Extrapolated half-life times on Mars

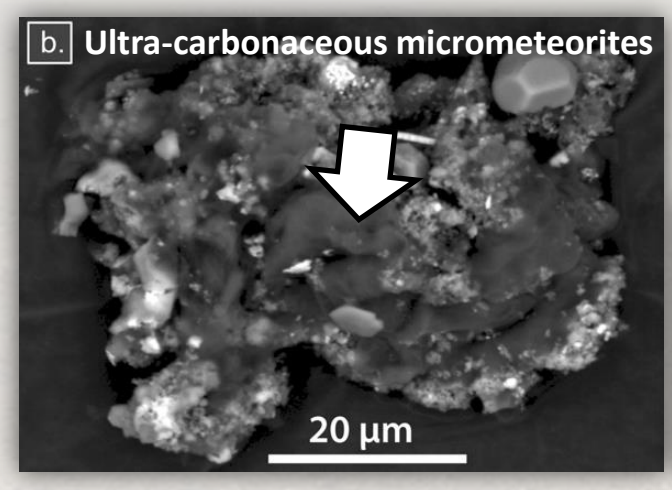
Dependency of half-life times with the thickness of the deposits

- May explain the differences between half-lives determined in the literature for similar molecules
- **Of interest in the context of the evolution of molecular layers on Mars**

Molecular layers might be formed in sedimentary? or evaporitic environements? on Mars

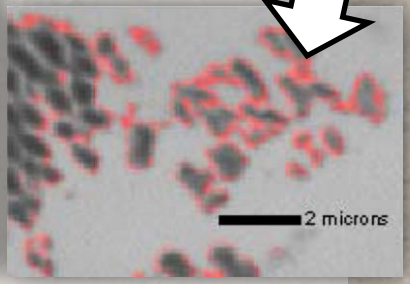
What is the evolution of these layers on Mars?

Molecular layers are found in micrometeorites:



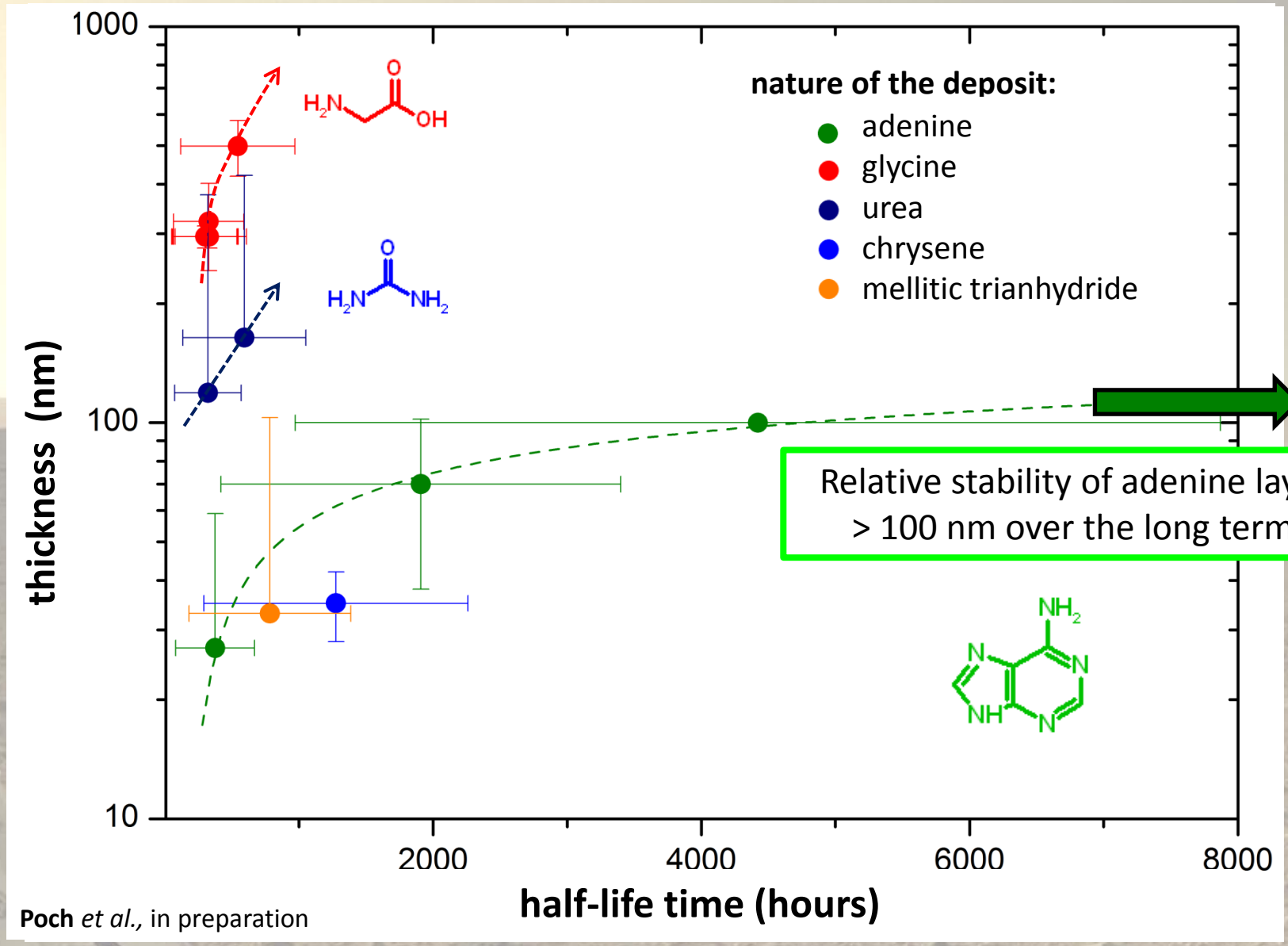
Dobrica *et al.*, 2012

IDP : ~100 nm around mineral grains



Flynn *et al.*, 2010

Photostability of organic layers on Mars



Poch *et al.,* in preparation

Photodissociation quantum yields

Poch *et al.,* in preparation

Molecule	Sample thickness (nm)	Photolysis constant J (s^{-1})	Half-life time $t_{1/2}$ (hours)	Photodissociation efficiency 200-250 nm (molecule $photon^{-1}$)
Glycine	295 ± 19	$1.4 \pm 1.1 \times 10^{-6}$	310 ± 230	$4.6 \pm 3.4 \times 10^{-3}$
	295 ± 19	$1.7 \pm 1.3 \times 10^{-6}$	310 ± 240	$4.1 \pm 3.2 \times 10^{-3}$
	295 ± 19	$2.0 \pm 1.7 \times 10^{-6}$	330 ± 280	$9.0 \pm 7.6 \times 10^{-3}$
	295 ± 19	$1.8 \pm 1.5 \times 10^{-6}$	300 ± 240	$7.0 \pm 5.7 \times 10^{-3}$
	322 ± 80	$1.6 \pm 1.3 \times 10^{-6}$	330 ± 260	$7.1 \pm 6.2 \times 10^{-3}$
	499 ± 80	$9.1 \pm 7.1 \times 10^{-7}$	550 ± 430	$6.0 \pm 4.9 \times 10^{-3}$
Urea	119 ± 257	$1.5 \pm 1.1 \times 10^{-6}$	320 ± 250	$1.5 \pm 7.5 \times 10^{-3}$
	164 ± 257	$8.4 \pm 6.5 \times 10^{-7}$	590 ± 470	$1.1 \pm 4.5 \times 10^{-3}$
Adenine	27 ± 32	N.D.	380 ± 290 *	$8.2 \pm 27 \times 10^{-5}$
	70 ± 32	N.D.	1910 ± 1500 *	$1.1 \pm 1.0 \times 10^{-4}$
	100 ± 3	N.D.	4420 ± 3440 *	$1.10 \pm 0.9 \times 10^{-4}$
	1300	N.D.	N.D.	$1.0 \pm 0.9 \times 10^{-4}$
Chrysene	35 ± 7	$3.7 \pm 2.9 \times 10^{-7}$	1280 ± 990	$4.9 \pm 4.1 \times 10^{-5}$
Mellitic trianhydride	33 ± 70	$6.0 \pm 4.6 \times 10^{-7}$	780 ± 600	$4.7 \pm 24 \times 10^{-5}$

Photodissociation quantum yields

Poch *et al.,* in preparation

Molecule	Sample thickness (nm)	Photolysis constant J (s^{-1})	Half-life time $t_{1/2}$ (hours)	Photodissociation efficiency 200-250 nm (molecule $photon^{-1}$)
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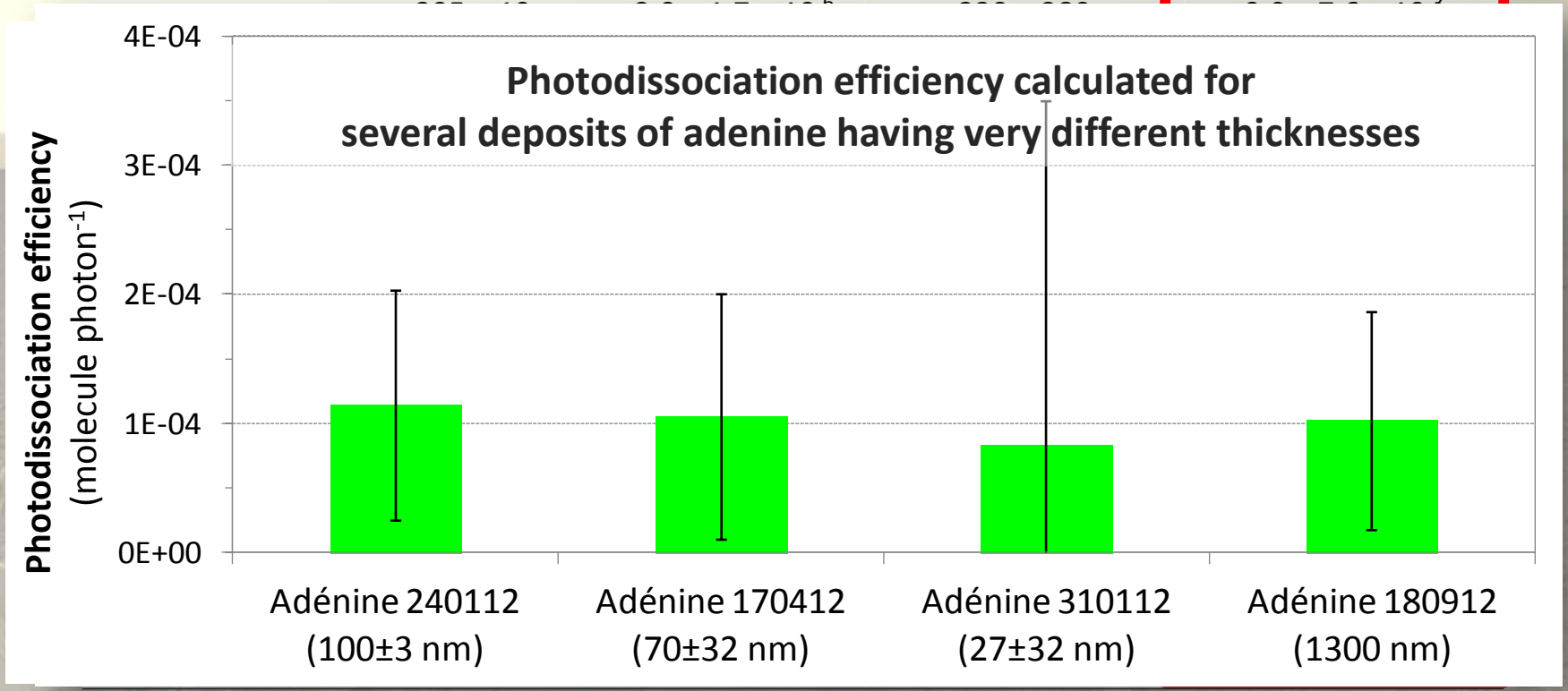


⇒ **The calculated photodissociation quantum yields are molecular values**

Photodissociation quantum yields

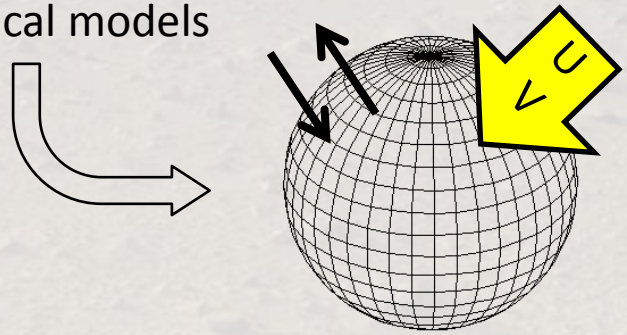
Interest of these photodissociation quantum yields in the search for organic molecules on Mars:

- **Molecular values:**

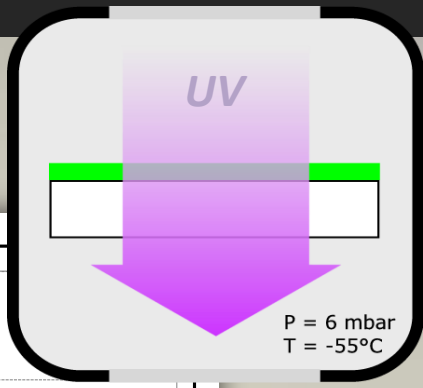
  indicate the chemical **potential of resistance to UV** radiation for each molecular structure, can be applied to isolated molecules

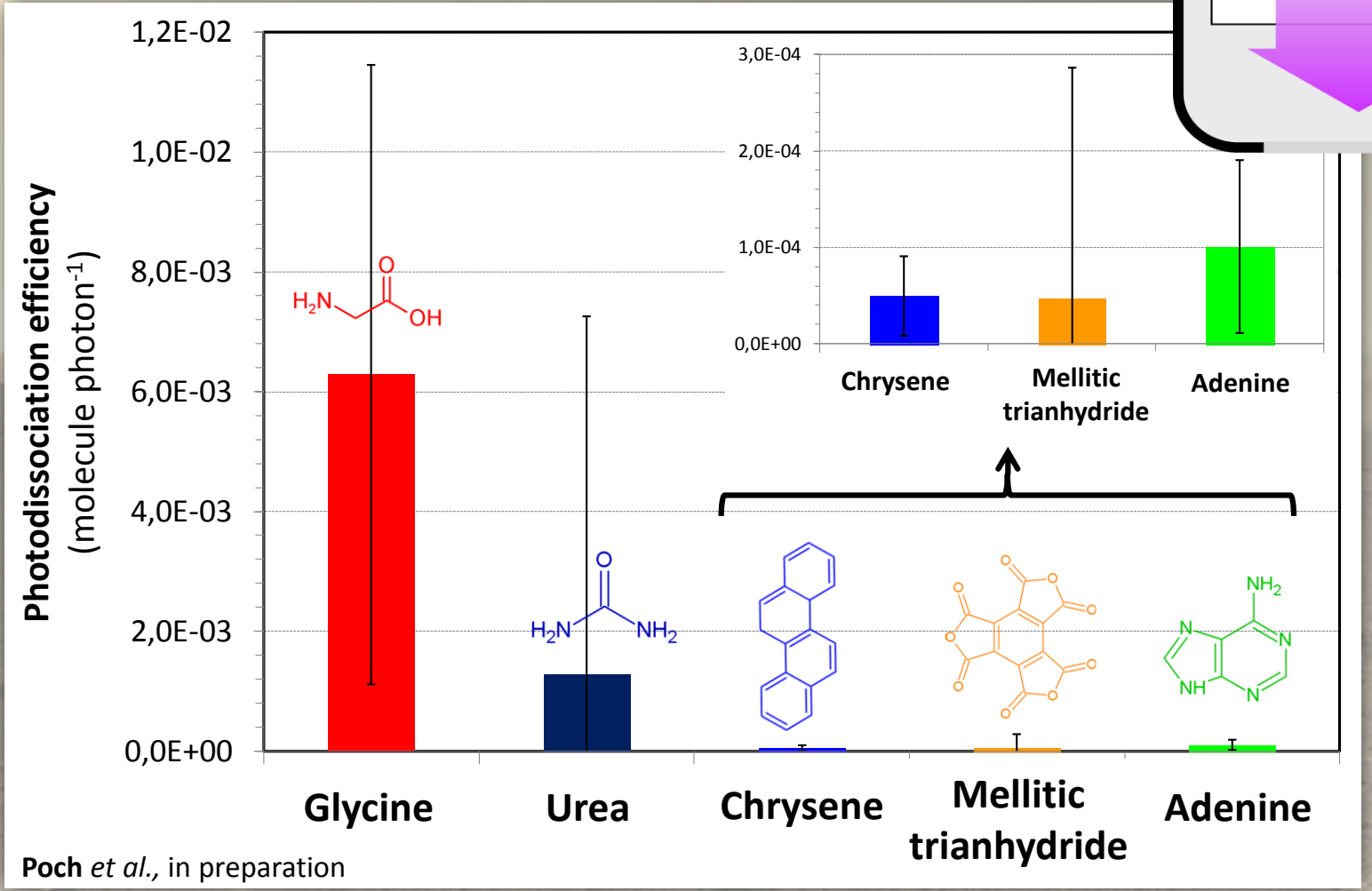
- **Values independent of the photon flux:**

  extrapolation of the life times of organics at the **scale of the Martian globe** via numerical models



Photodissociation quantum yields

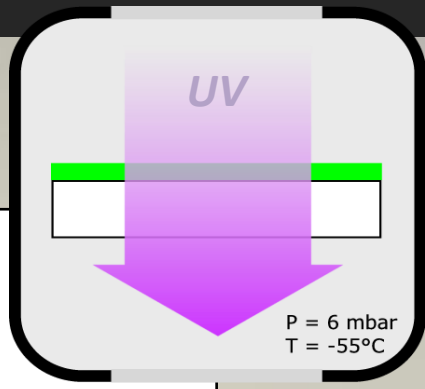


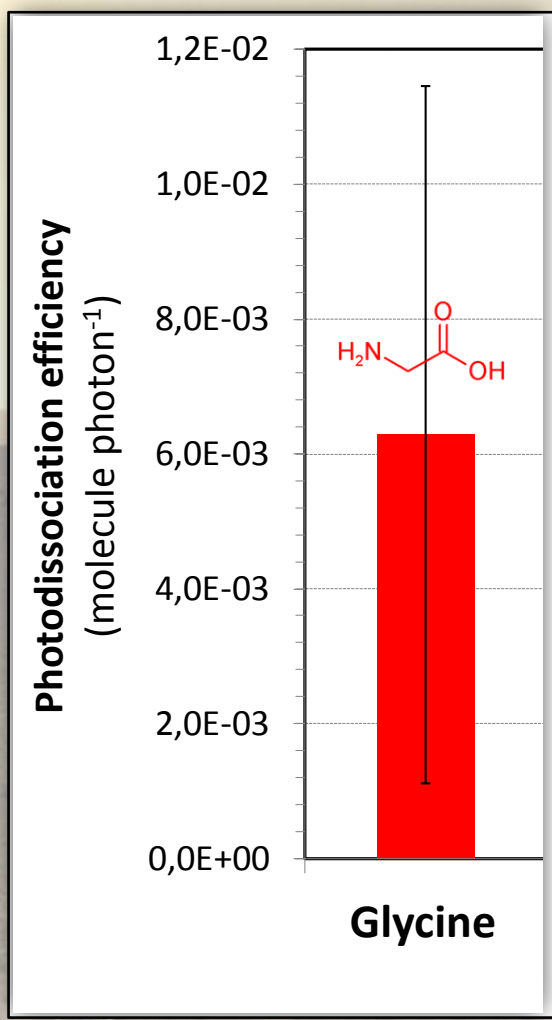


Poch *et al.,* in preparation

⇒ **Aromatic structures are 10 to 100 times more resistant to UV at the surface of Mars**

Photodissociation quantum yields





This work:

6,3 ± 5,2 × 10^{-3} molecule/photons

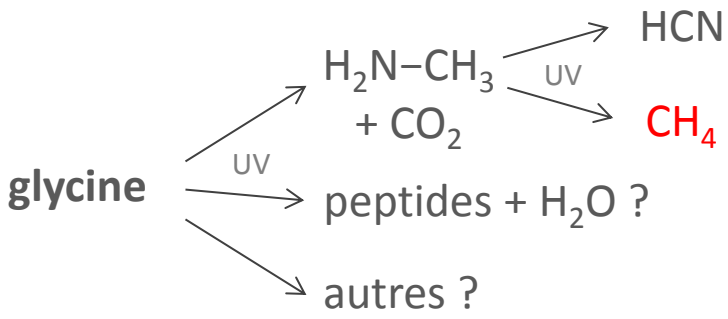
via measure of the relative abundance of glycine

Stoker and Bullock (1997) :

1,46 ± 1,00 × 10^{-6} molecule/photons

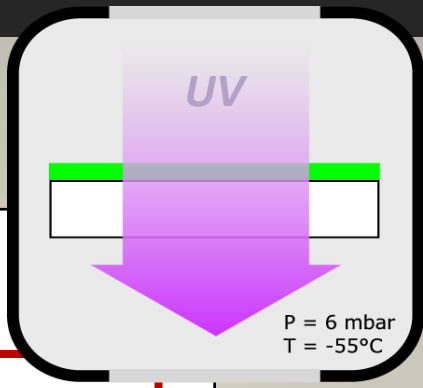
via measure of the methane emission

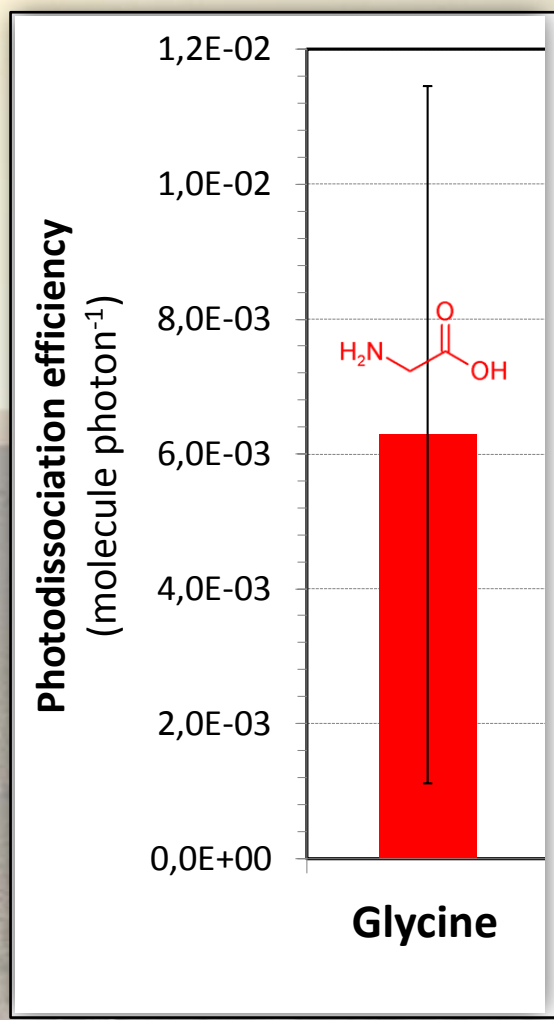
Underestimation of the photo-dissociation yield



Ehrenfreund *et al.*, 2001; Johnson *et al.*, 2012

Photodissociation quantum yields





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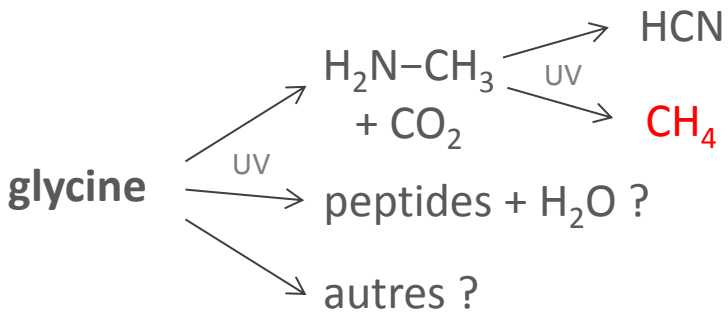
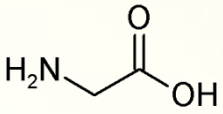


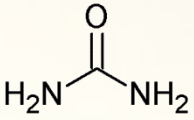
Ehrenfreund *et al.*, 2001; Johnson *et al.*, 2012

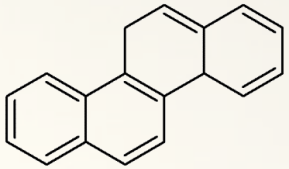
⇒ **Determination of a new value of the photodissociation efficiency of glycine**

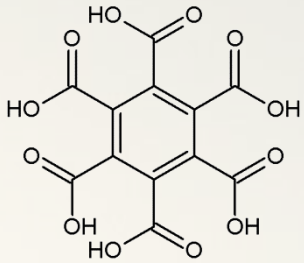
What are the products of evolution?

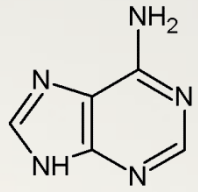
In which products are processed these molecules when exposed to UV from the surface of Mars?

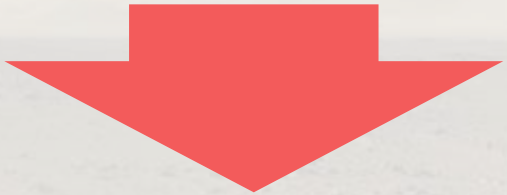


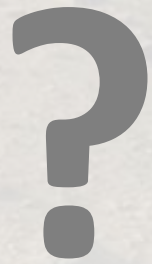






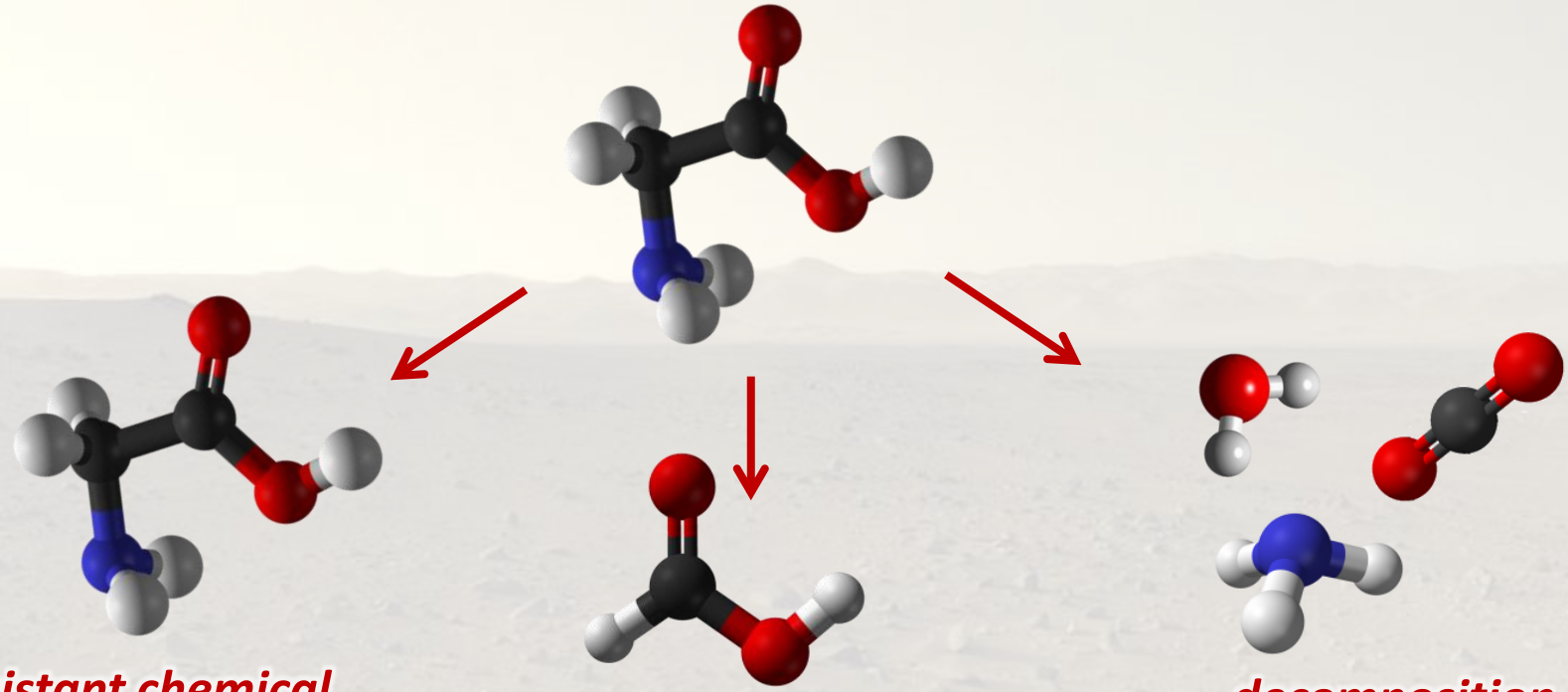






What are the products of evolution?

In which products are processed these molecules when exposed to UV from the surface of Mars?



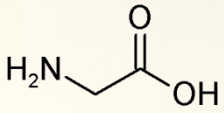
resistant chemical structures?

transformation products?

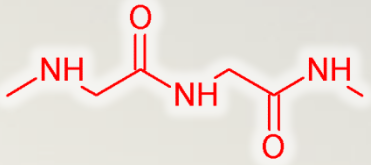
decomposition products?

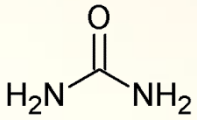
What are the products of evolution?

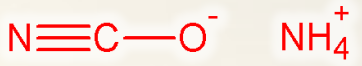
organic molecule → **UV** *200-400 nm* → **fragmentation** et / ou **polymerization**

glycine 

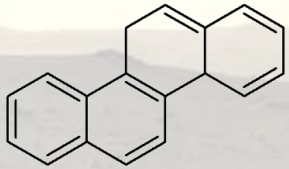
CO_2 CH_4 HCN ? NH_3 ?



urea 

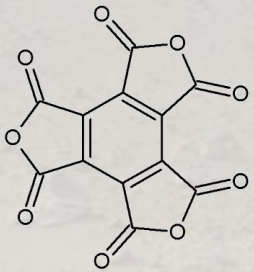


to be clarified

chrysene 

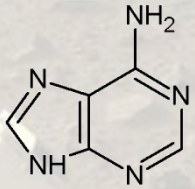
CH_4 C_xH_y ?

not detected

mellitic trianhydride 

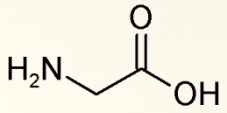
CO ? CO_2 ?

not detected

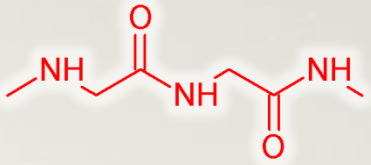
adenine 

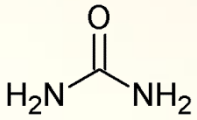
What are the products of evolution?

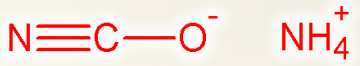
organic molecule → **UV** *200-400 nm* → **fragmentation** et / ou **polymerization**

glycine 

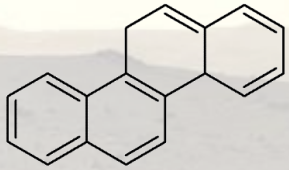
CO_2 CH_4 HCN ? NH_3 ?



urea 

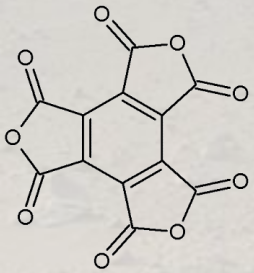


to be clarified

chrysene 

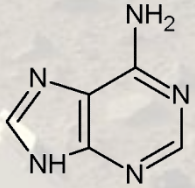
CH_4 C_xH_y ?

not detected

mellitic trianhydride 

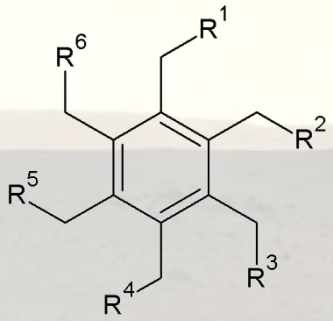
CO ? CO_2 ?

not detected

adenine 

Compounds resistant to UV at the surface of Mars

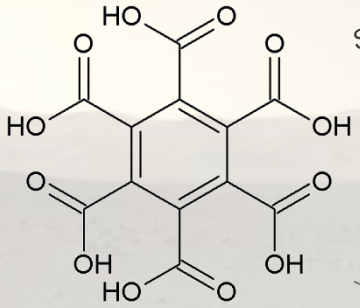
Production of a photoproduct resistant to UV via dehydratation of mellitic acid



aromatic compound

oxidation

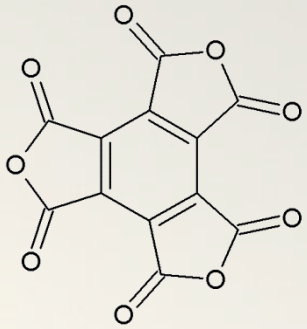
Benner et al. 2000



mellitic acid

UV

Stalport et al. 2009

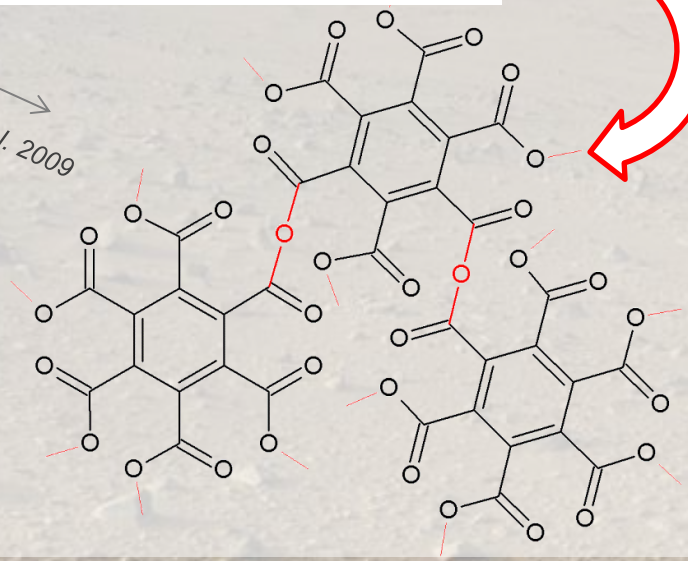


intra- or inter-molecular dehydratation

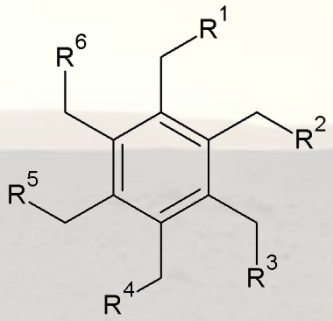
?

UV

Stalport et al. 2009

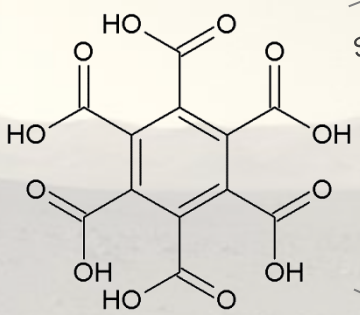


Compounds resistant to UV at the surface of Mars



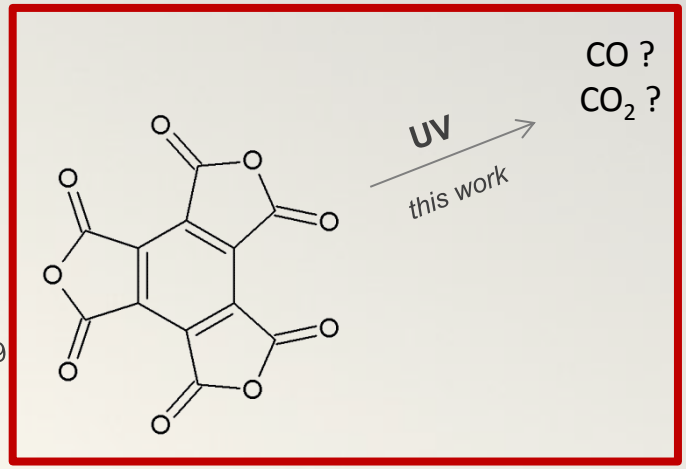
oxidation

Benner et al. 2000



UV

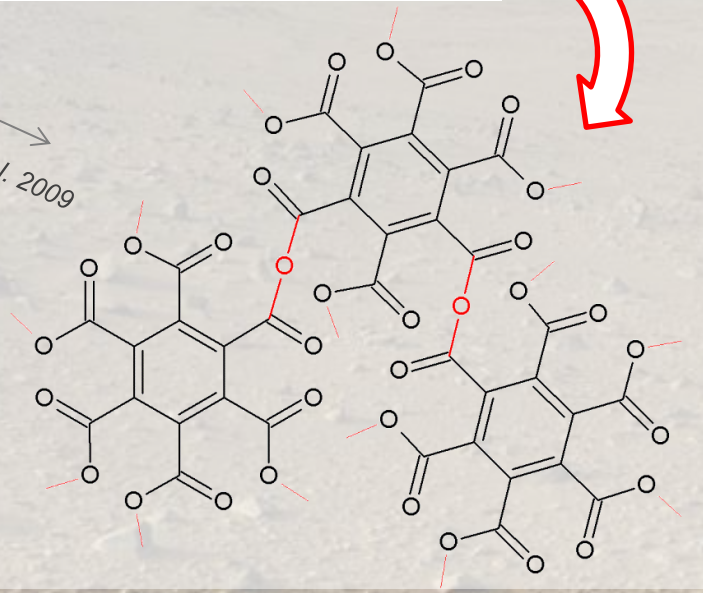
Stalport et al. 2009



inter-molecular dehydratation

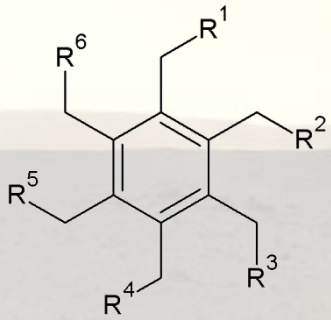
UV

Stalport et al. 2009



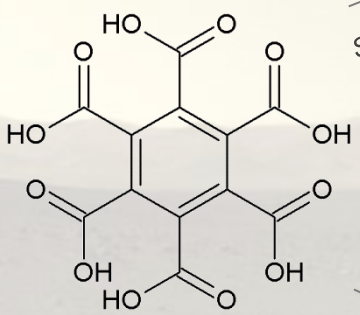
Compounds resistant to UV at the surface of Mars

endogenous and exogenous sources



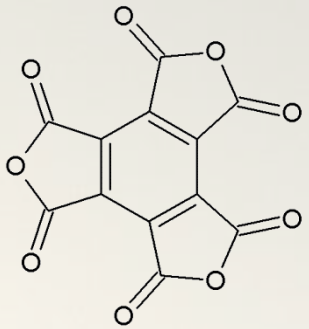
oxidation

Benner et al. 2000



UV

Stalport et al. 2009



UV

this work

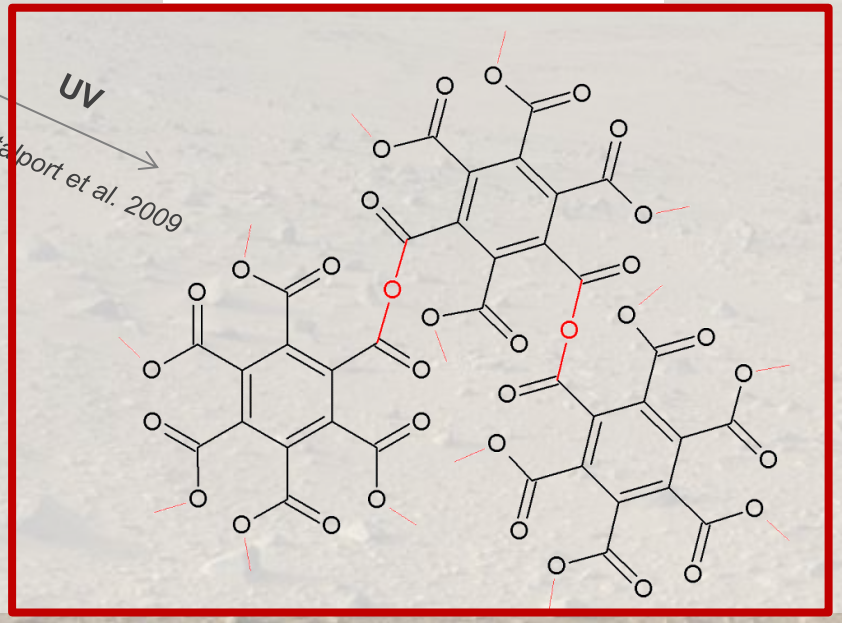
CO ?

CO_2 ?

Photoresistant product

UV

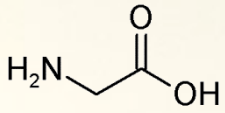
Stalport et al. 2009



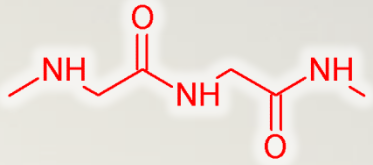
accumulation in the Martian soil?

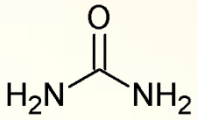
What are the products of evolution?

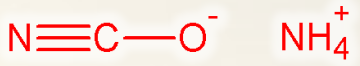
organic molecule → **UV** *200-400 nm* → **fragmentation** et / ou **polymerization**

glycine 

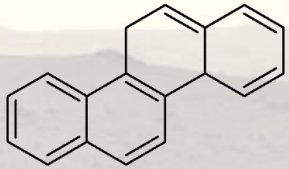
CO_2 CH_4 HCN ? NH_3 ?



urea 

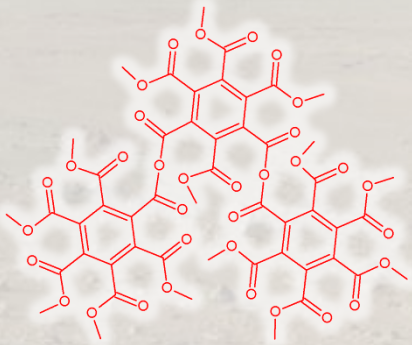


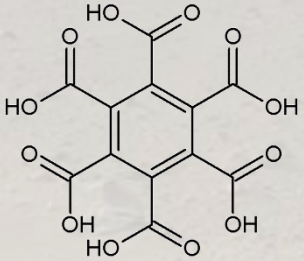
to be clarified

chrysene 

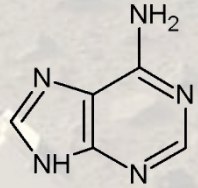
CH_4 C_xH_y ?

not detected

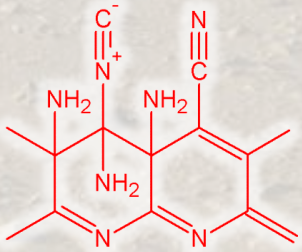


mellitic acid 

H_2O CO ? CO_2 ?

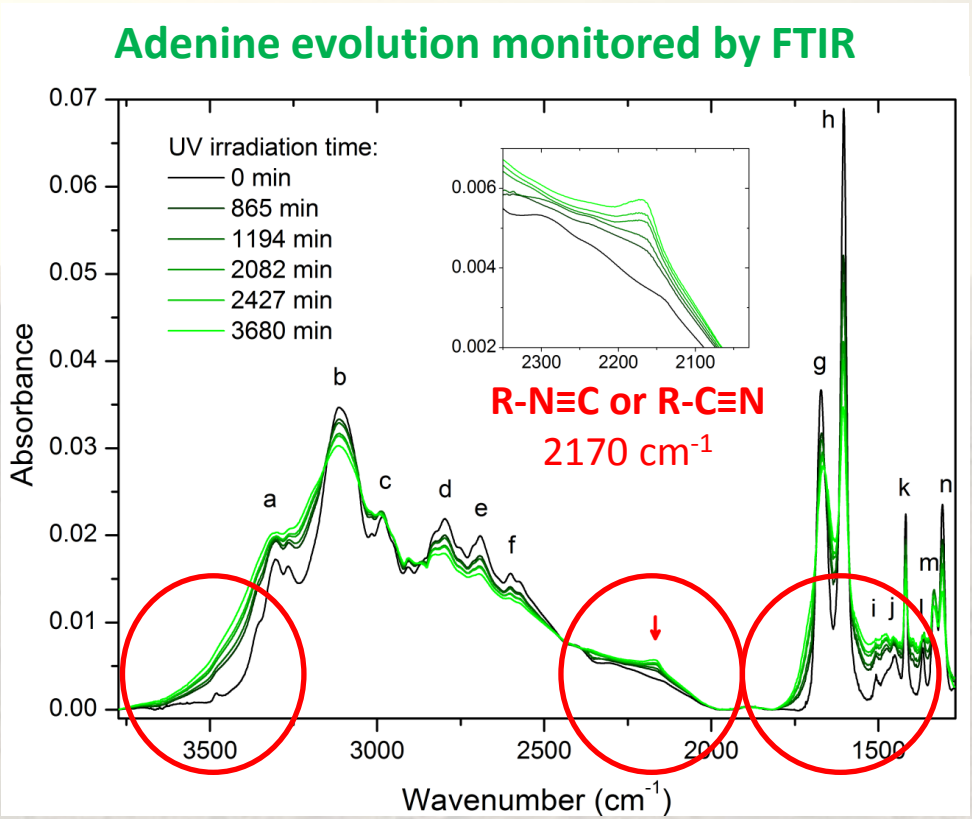
adenine 

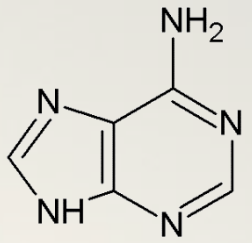
CH_4 HCN ? NH_3 ?



Compounds resistant to UV at the surface of Mars

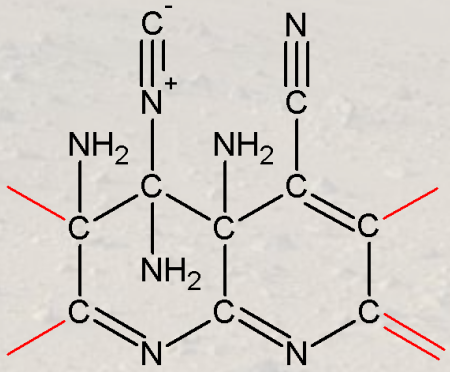
Production of a photoresistant compound observed during the UV irradiation of adenine





adenine

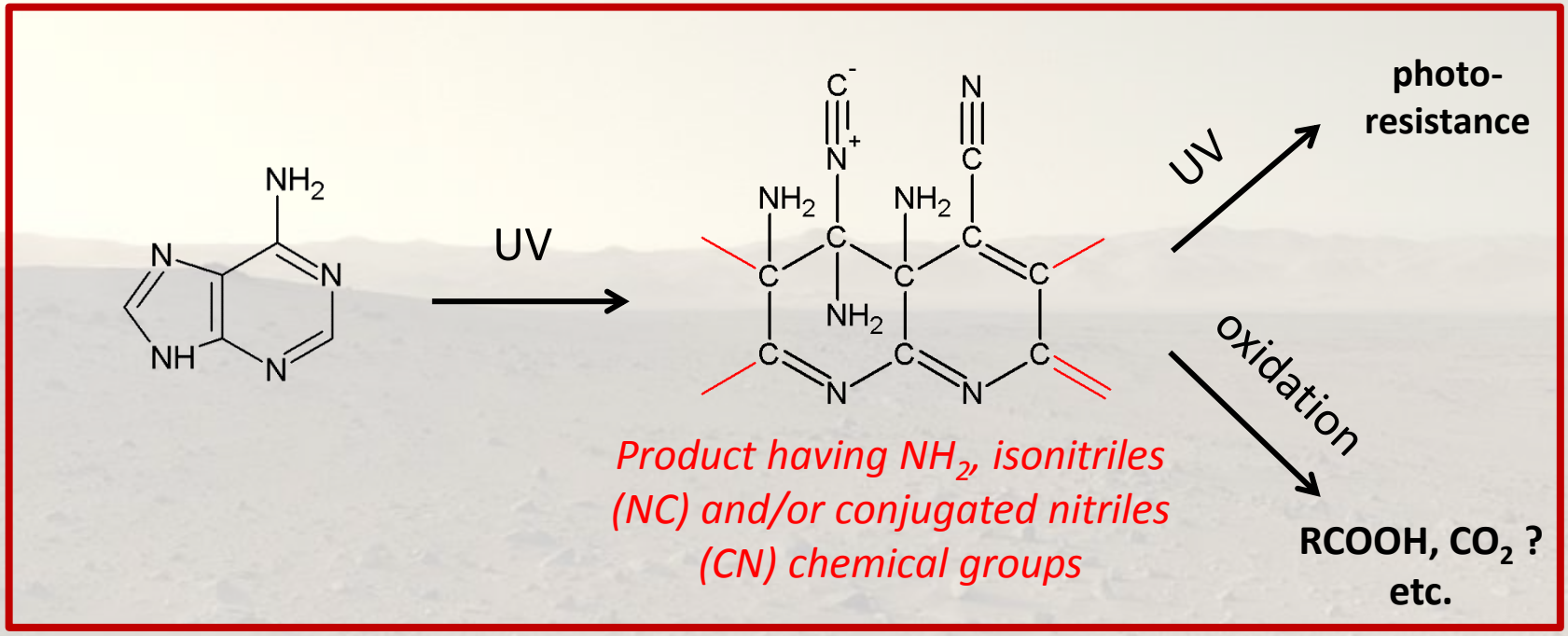
UV



H,C,N macromolecule

Compounds resistant to UV at the surface of Mars

Production of a photoresistant compound observed during the UV irradiation of adenine



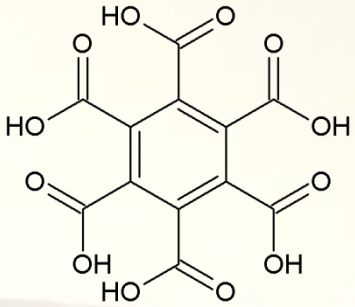
C, N, H photoresistant macromolecule

Similar to HCN polymers or Titan's tholins?

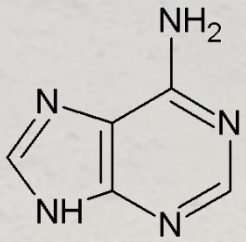
Völker, 1960

Qualitative evolution of aromatic molecules

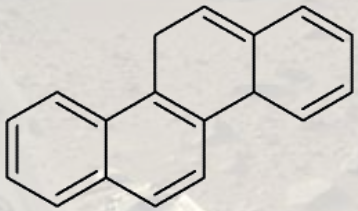
Chemical pathways of aromatic molecules under UV radiation of the surface of Mars ?



UV



UV



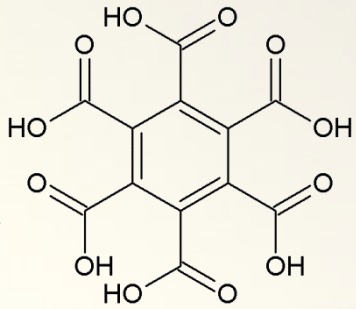
UV

Formation of macromolecular compounds resistant to UV

Photodecomposition in volatile fragments (hydrocarbons, CH_4?)

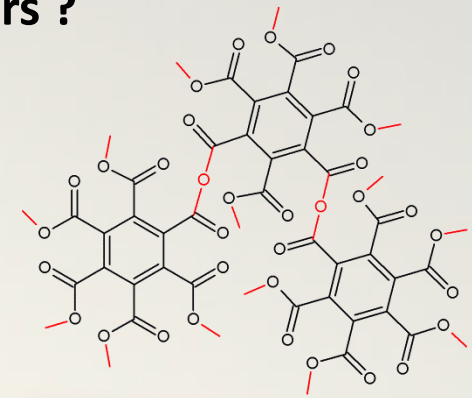
Qualitative evolution of aromatic molecules

Chemical pathways of aromatic molecules under UV radiation of the surface of Mars ?

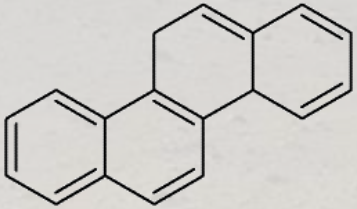


1 oxidation

2 UV



solid residue



1 UV

volatile hydrocarbons, CH_4

2 oxidation

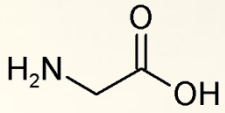
gases

CO, CO_2

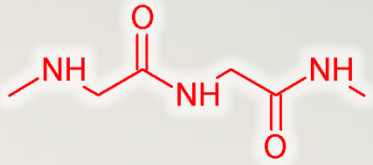
importance of the order of succession of the weathering process?

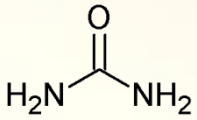
Summary of the qualitative evolutions

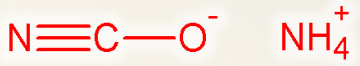
organic molecule → **UV** *200-400 nm* → **fragmentation** et / ou **polymerization**

glycine 

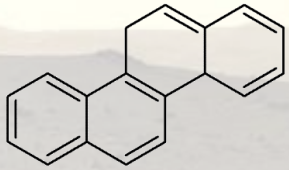
CO_2 CH_4 HCN ? NH_3 ?



urea 

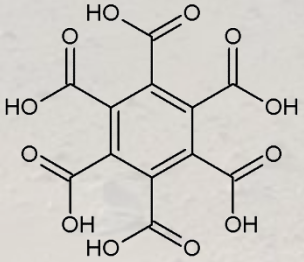


to be clarified

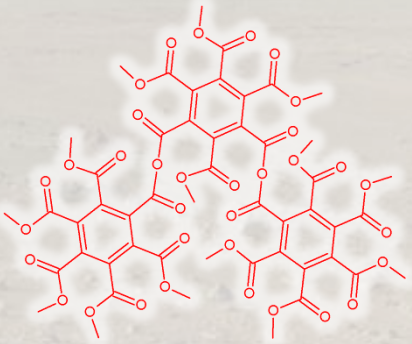
chrysene 

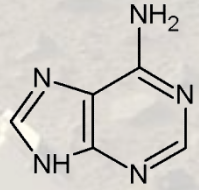
CH_4 C_xH_y ?

not detected

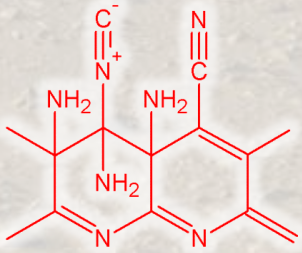
mellitic acid 

H_2O CO ? CO_2 ?



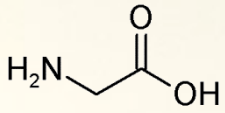
adenine 

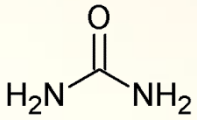
CH_4 HCN ? NH_3 ?

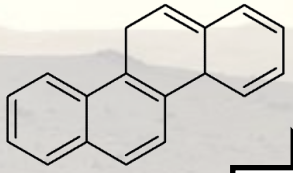


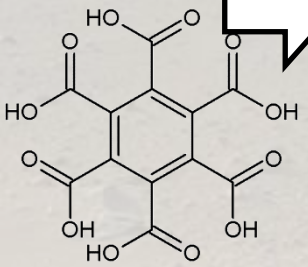
Summary of the qualitative evolutions

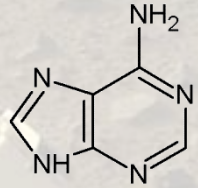
organic molecule → **UV** *200-400 nm* → **fragmentation** et / ou **polymerization**

glycine 

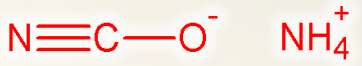
urea 

chrysene 

mellitic acid 

adenine 

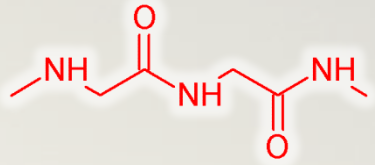
CO_2 CH_4 HCN ? NH_3 ?



CH_4 C_xH_y ?

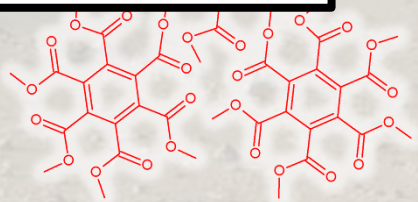
H_2O CO ? CO_2 ?

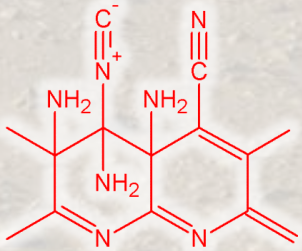
CH_4 HCN ? NH_3 ?



to be clarified

not detected



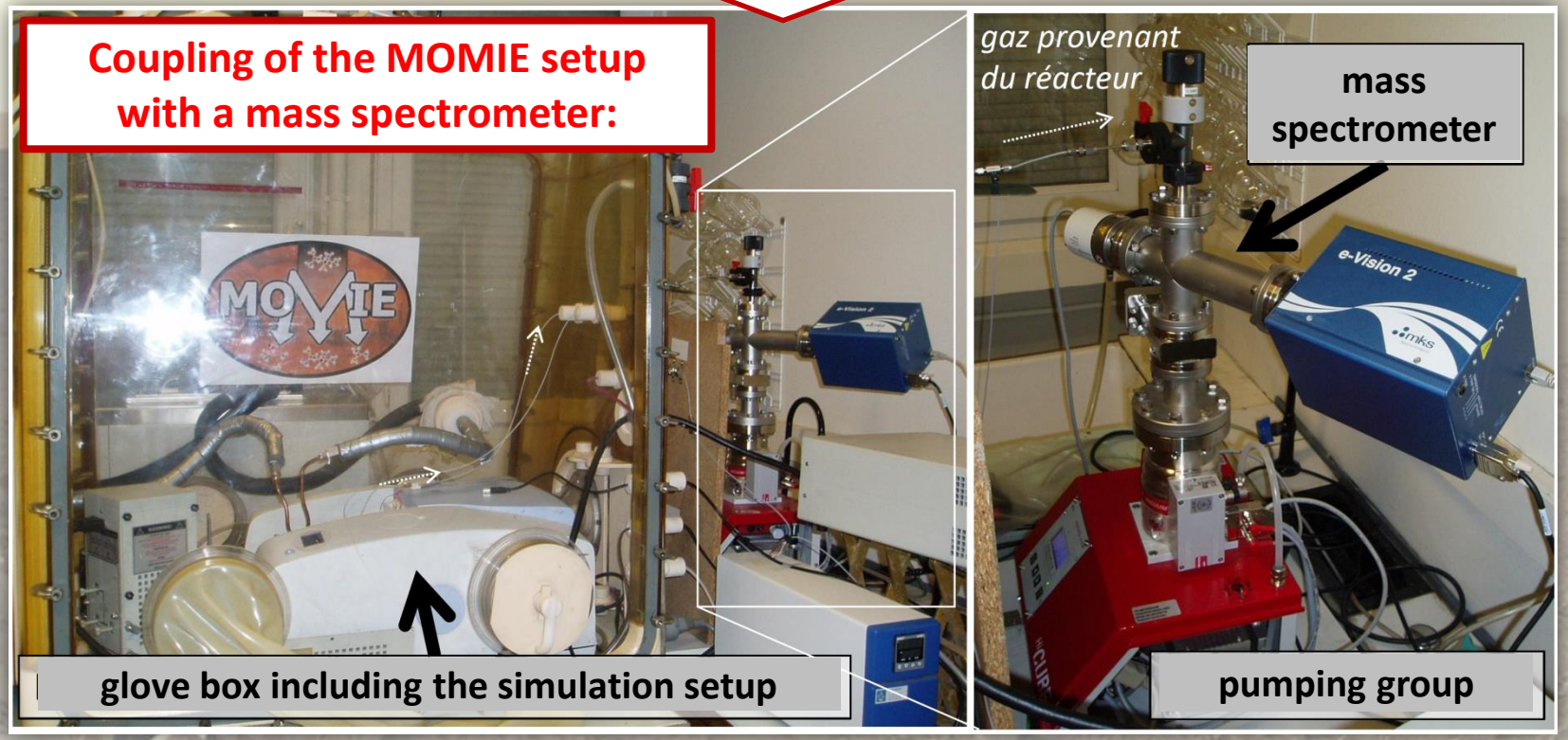


Need to clarify the nature of the gaseous products

Identification of the gaseous products

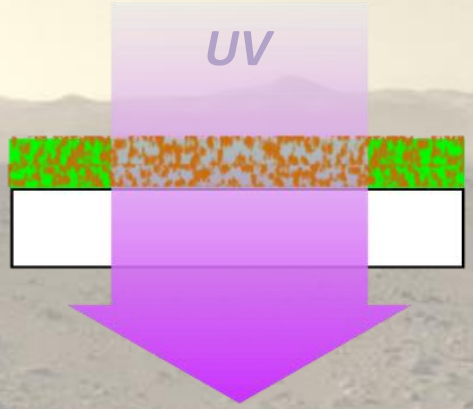
Issues:

- Clarify the chemical pathways, the mass balances
- Source of gases in the near surface atmosphere of Mars?



Effect of the nontronite on the evolution

What is the effect of nontronite clay on the evolution of organic molecules?



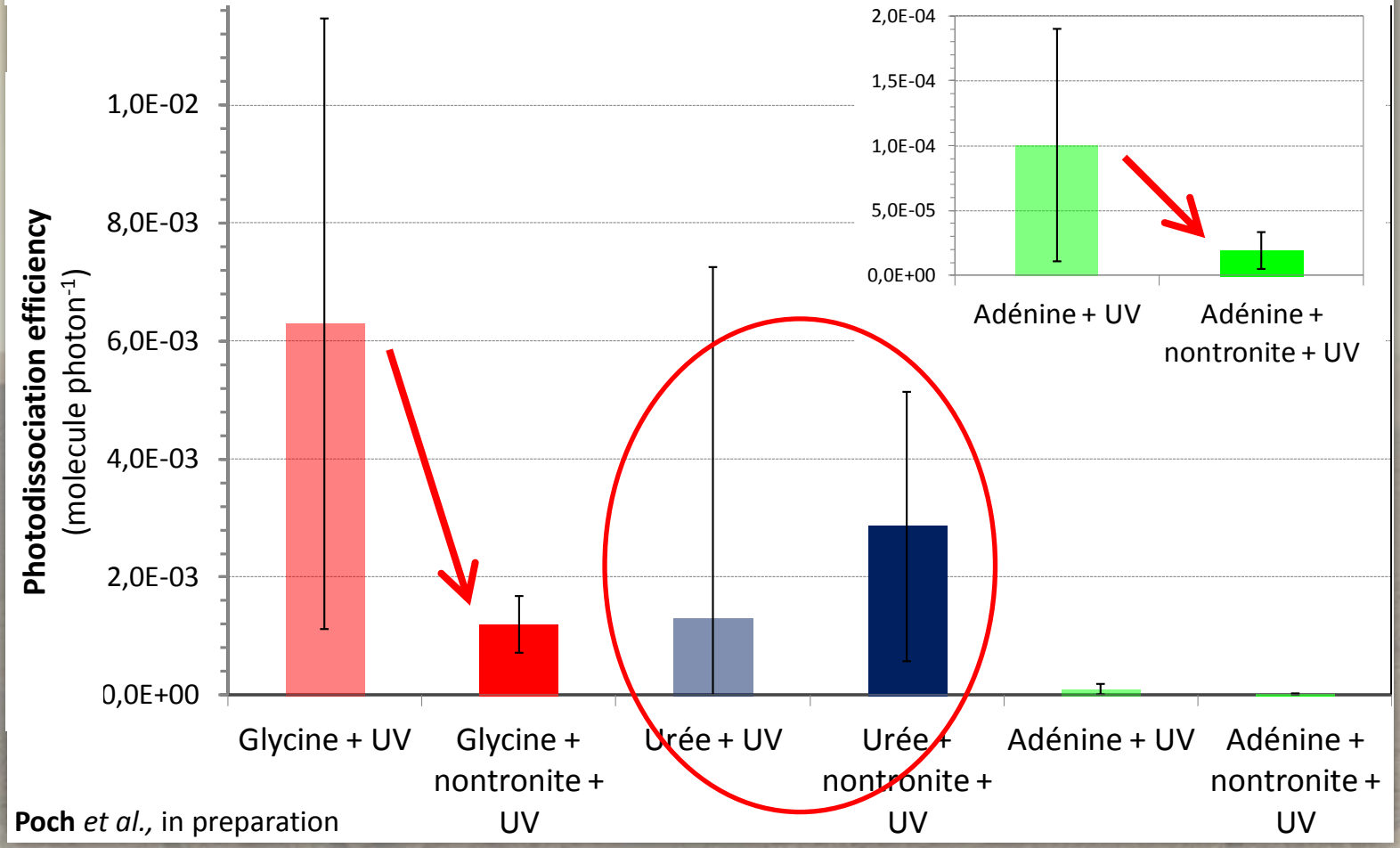
⇒ **protection** of the molecules?

⇒ or **catalysis** of the degradation processes?

⇒ **new products?**

What is the effect of nontronite on the evolution?

Comparison of the photodissociation efficiency without / with nontronite



Poch *et al.*, in preparation

⇒ **Effect of nontronite: photoprotection for glycine and adenine, catalysis of the decomposition of urea?**

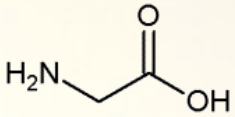
What is the effect of nontronite on the evolution?

New product(s) detected in presence of nontronite?

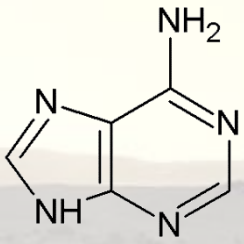
	NO	MAYBE	YES
Glycine	FTIR, GC-MS		
Adenine	FTIR	GC-MS	
Urea		GC-MS	FTIR

- **interaction of OCN^- or $O=C=N-H$ with Fe^{3+} or nontronite**
- **no NH_4^+ detected**

Effect of nontronite on the evolution

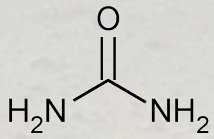


nontronite + UV



nontronite + UV

Photoprotective effect of nontronite

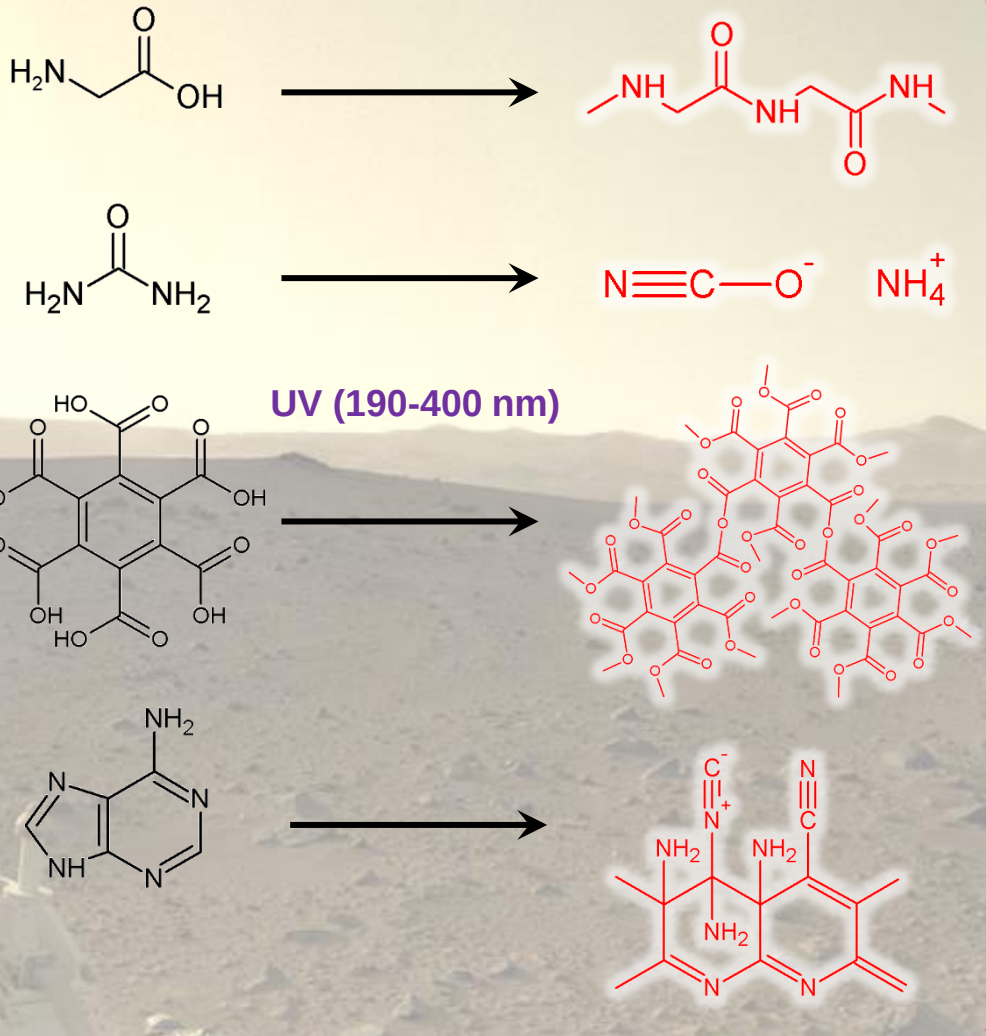


nontronite + UV

Possible accelerating effect of the degradation caused by the nontronite

Selective protection of organic molecules by nontronite on Mars?

Summary of the results



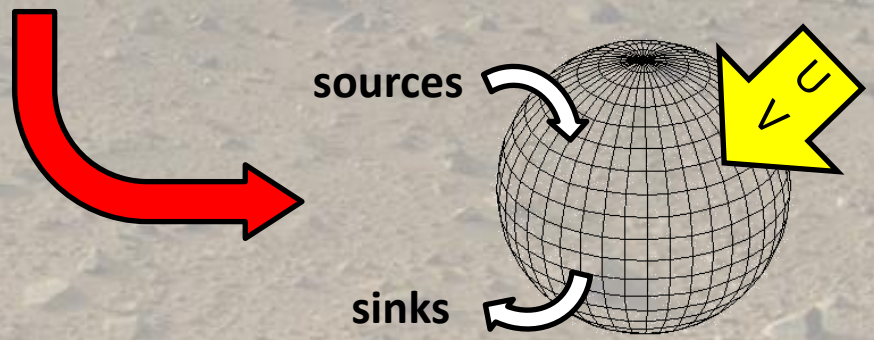
Chemical evolution on Mars,
Molecular targets to search for

Summary of the results

Extrapolated Half-life times on Mars and photodissociation efficiencies:

molecule	➢ pure molecule + UV: $t_{1/2}$ on Mars (h)	yields (molecule/photon)	➢ molecule + nontronite + UV : yields (molecule/photon)
glycine	310 ± 230	$6{,}3 \pm 5.2 \times 10^{-3}$	$1.2 \pm 0.5 \times 10^{-3}$
urea	320 ± 250	$< 7.3 \times 10^{-3}$	$3.0 \pm 2.3 \times 10^{-3}$
adenine	380 ± 290	$1.0 \pm 0.9 \times 10^{-4}$	$2.0 \pm 1.4 \times 10^{-5}$
chrysene	1280 ± 990	$4.9 \pm 4.1 \times 10^{-5}$	N.D.

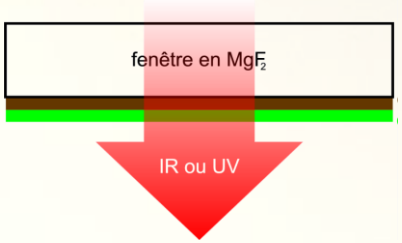
No catalytic effect observed during the degradation of glycine and adenine in presence of nontronite clay

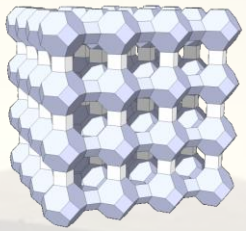


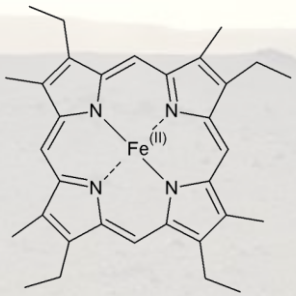
⇒ **input data for global modeling of the evolution of organic matter on Mars**

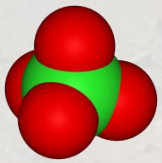
Perspectives of this work

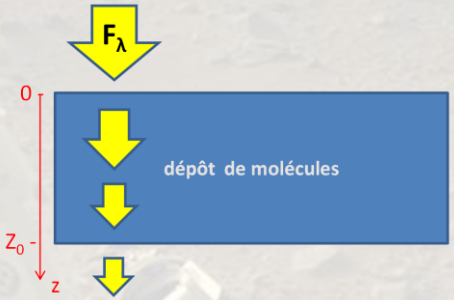
Experimental perspectives:







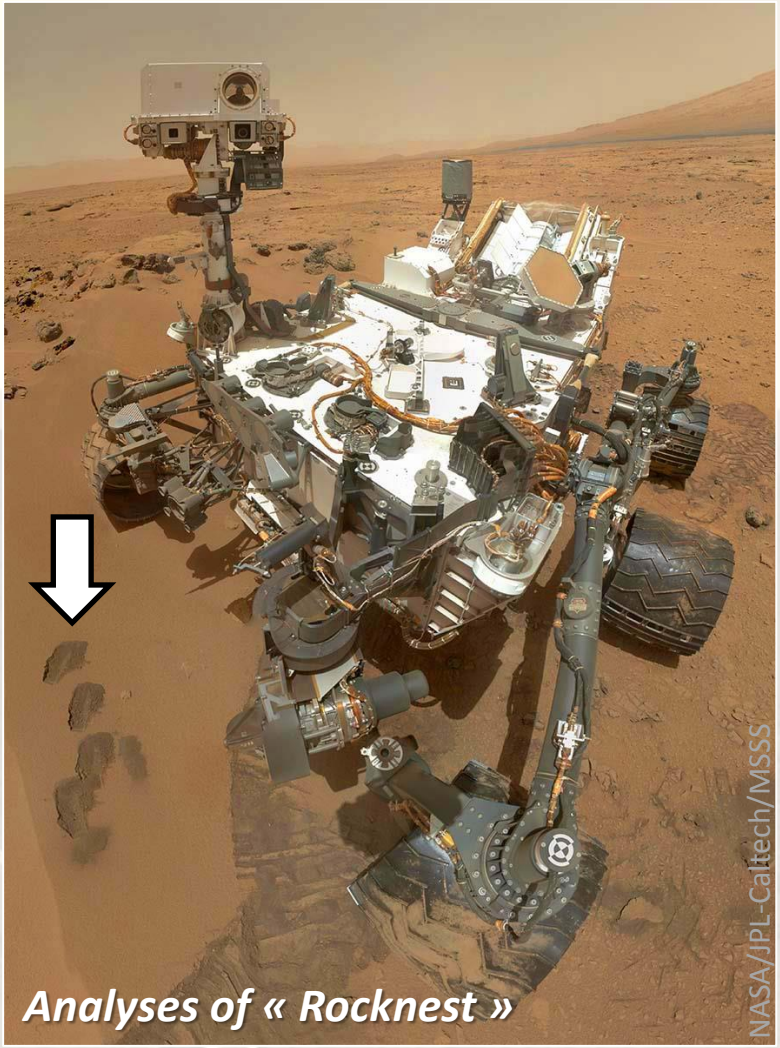




- Clarify the **effect of nontronite**: why a photoprotective effect? selective protection?
- New **molecule+mineral couples**: urea+montmorillonite, urea+zeolithe, sulfates etc.
- Study **organic molecules**: hydrocarbons, fatty acids, porphyrins.
- Influence of **perchlorates** (ClO_4^-) on the evolution of organic molecules under UV radiation?
- Clarify the dependency of the **half-life time of the deposits with their thickness**: simulations, numerical model.

Perspectives of this work

Search for organic molecules on Mars



Analyses of « Rocknest »

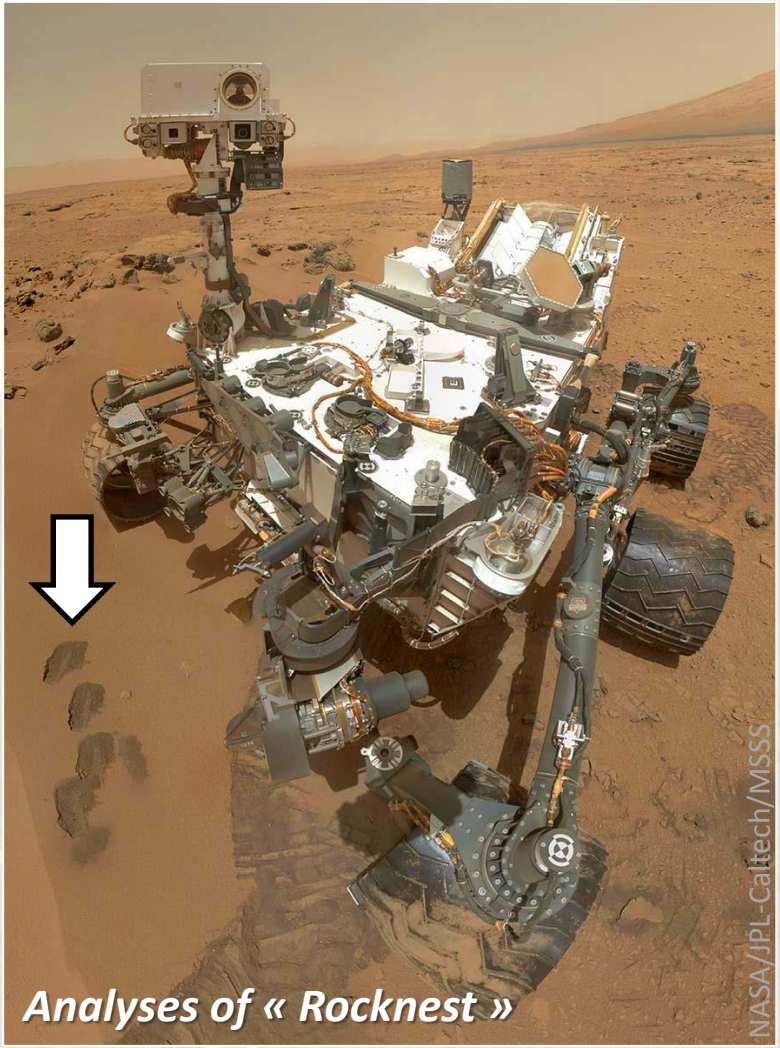
Preliminary results of the search for organic molecules on Mars by the Curiosity rover :

- Organic matter in not abundant in the Rocknest dune,
- **No-detection of polycyclic aromatic hydrocarbons (PAH),**
- **Detection of HCN and C_2H_3N.**

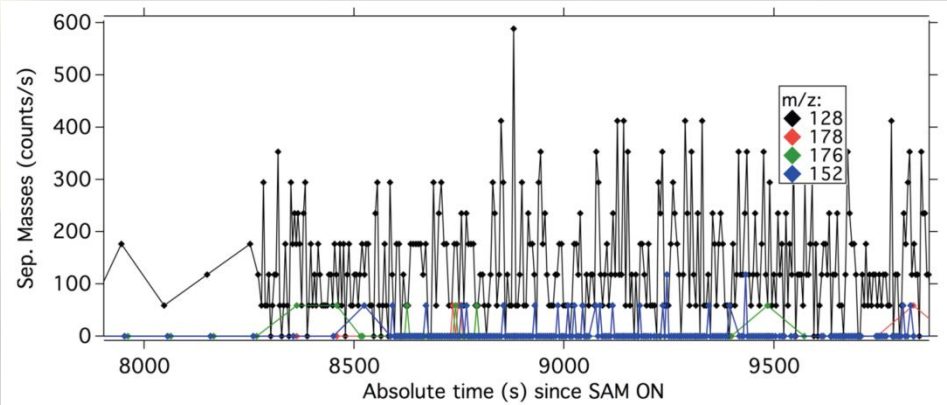
Leshin *et al.*, 2013; Mahaffy *et al.*, 2013

Perspectives of this work

Search for organic molecules on Mars

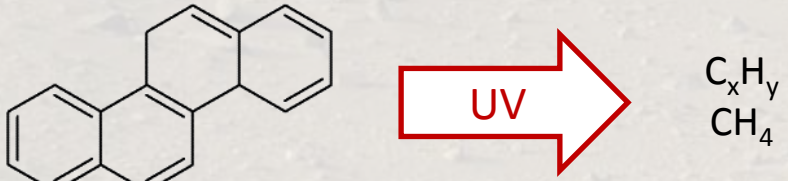


➢ **No-detection of polycyclic aromatic hydrocarbons (PAH)**



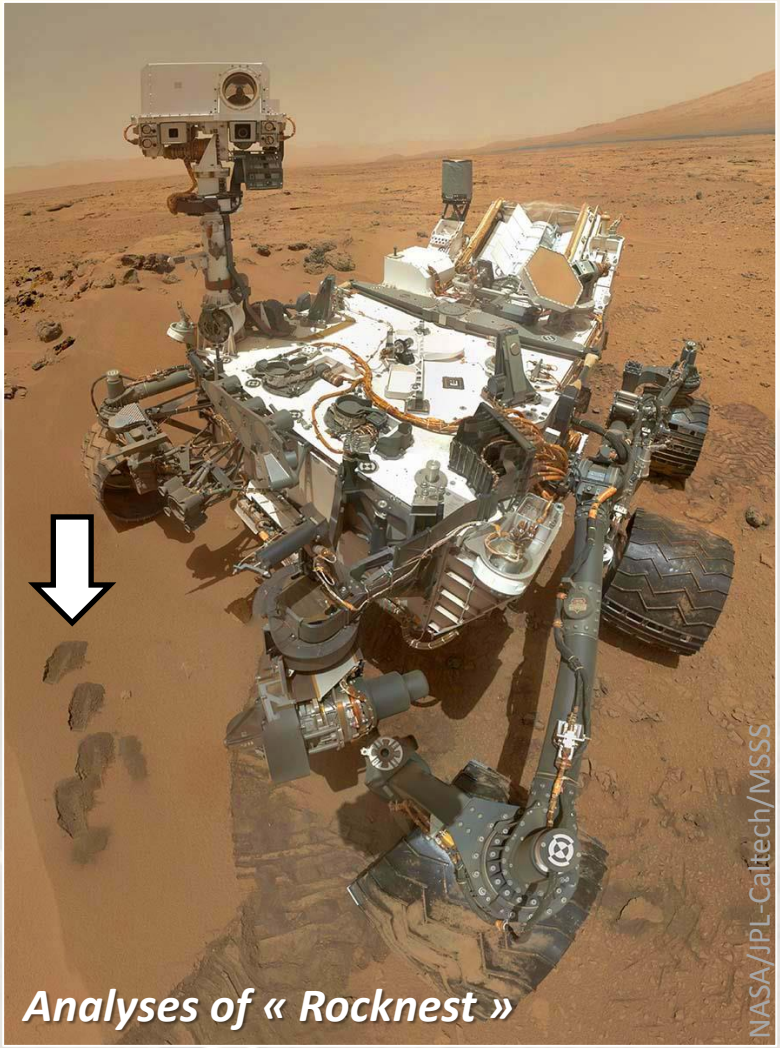
Cabane *et al.*, 2013

➢ **This work:**

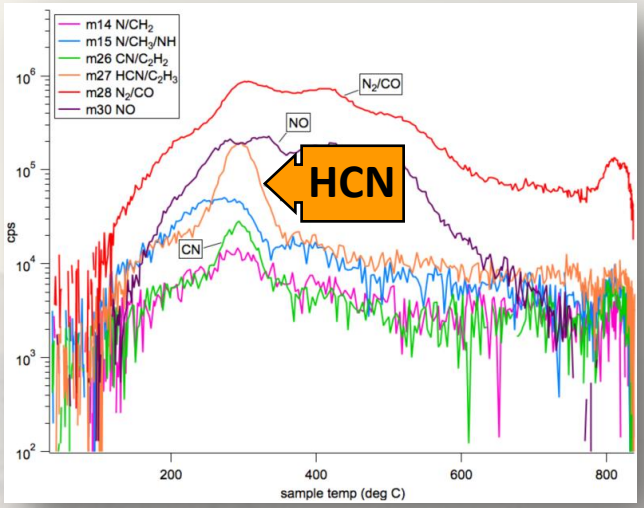


Perspectives of this work

Search for organic molecules on Mars



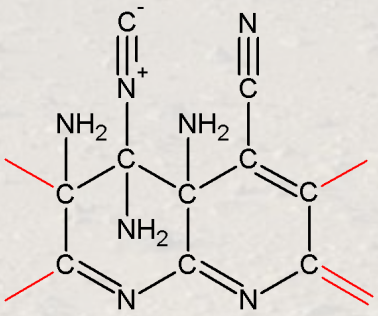
➢ **Detection of HCN and C_2H_3N**



Stern *et al.*, 2013

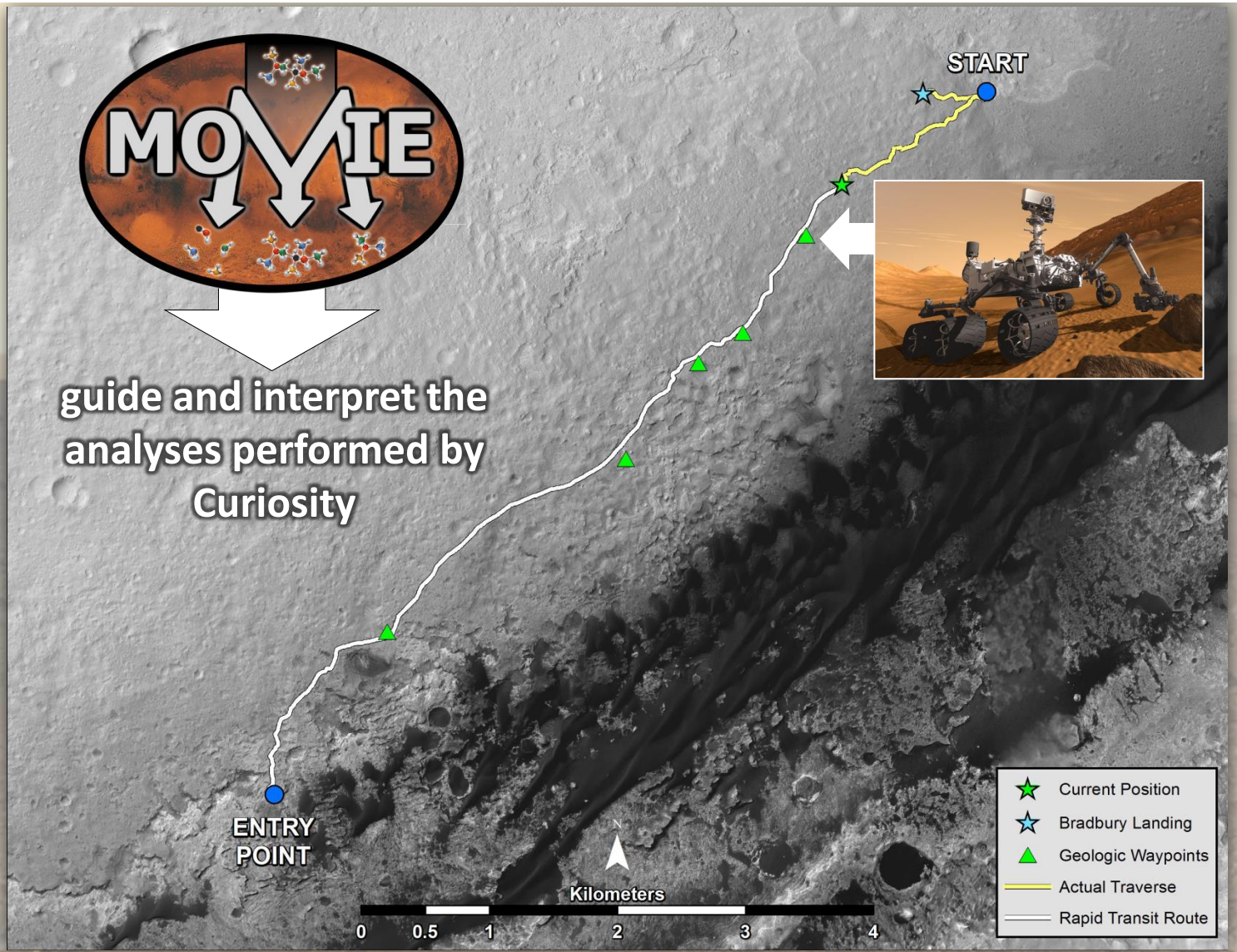
➢ **This work:**

Resistance of C,H,N macromolecules to Martian UV photons



Perspectives of this work

The search for organic molecules on Mars continue!



images : NASA/JPL-Caltech/Univ. of Arizona

Perspectives of this work

The search for organic molecules on Mars continue!

⇒ Curiosity will soon expore nontronite outcrops in the Gale crater!

Terrains at the base of Mount Sharp (*Aeolis Mons*)

NASA/JPL/MSSS/Ronald pour UMSF