LABORATORY SIMULATIONS OF MARTIAN CONDITIONS: HINTS FOR DETECTION OF MOLECULAR BIOMARKERS ON MARS

Teresa Fornaro[1,*], **John. R. Brucato**[2], **Inge Loes ten Kate**[3], **Andrew Steele**[1], **George D. Cody**[1] and **Robert M. Hazen**[1]

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[2]INAF-Astrophysical Observatory of Arcetri, Firenze, Italy
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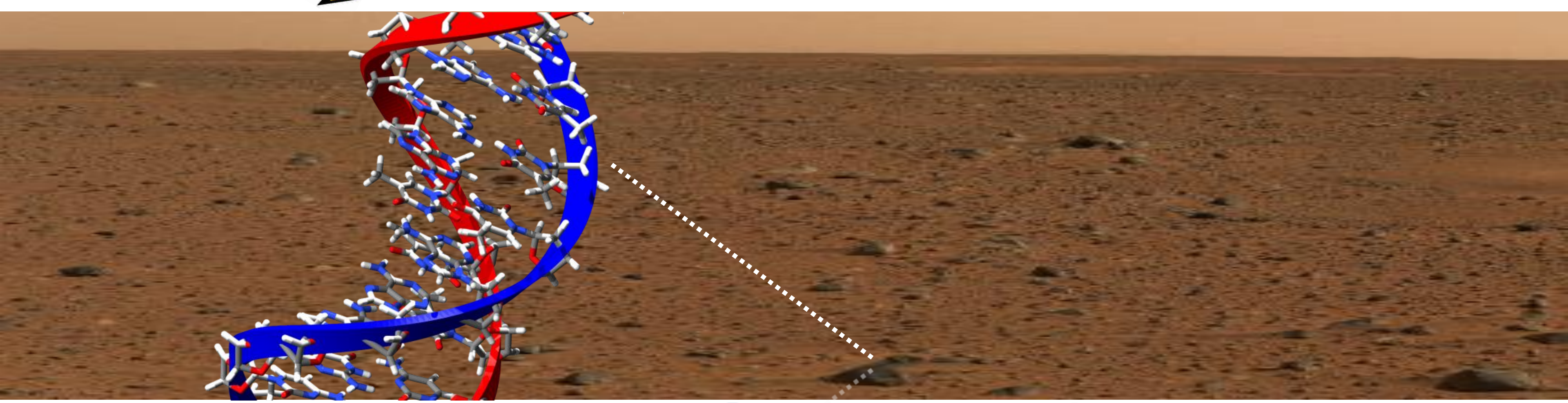


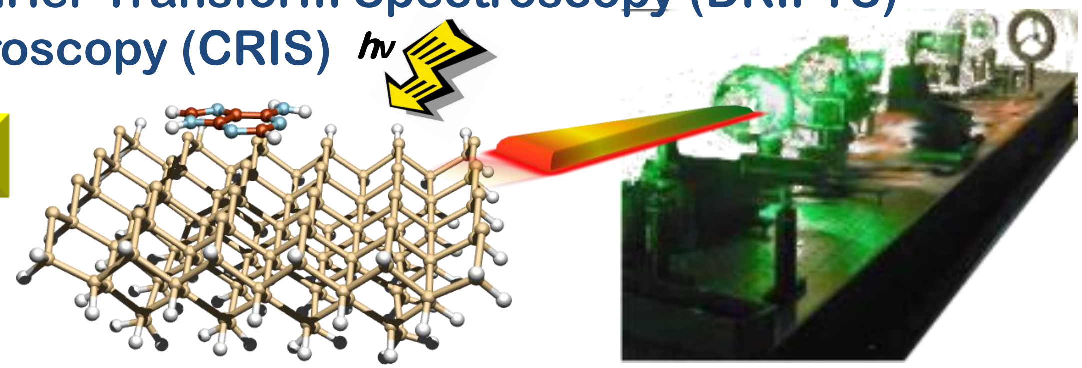
Laboratory Studies

1. Preparation of Mars soil analogues doped with biomarkers

- Biomarkers of extant life: AMP and UMP
- Minerals: forsterite, natrolite, labradorite, hematite, apatite, lizardite, antigorite

2. Characterization of Mars soil analogues

- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
- Confocal Raman Imaging Spectroscopy (CRIS)



3. UV irradiation processing

- Terrestrial ambient conditions
- Martian simulation chamber

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

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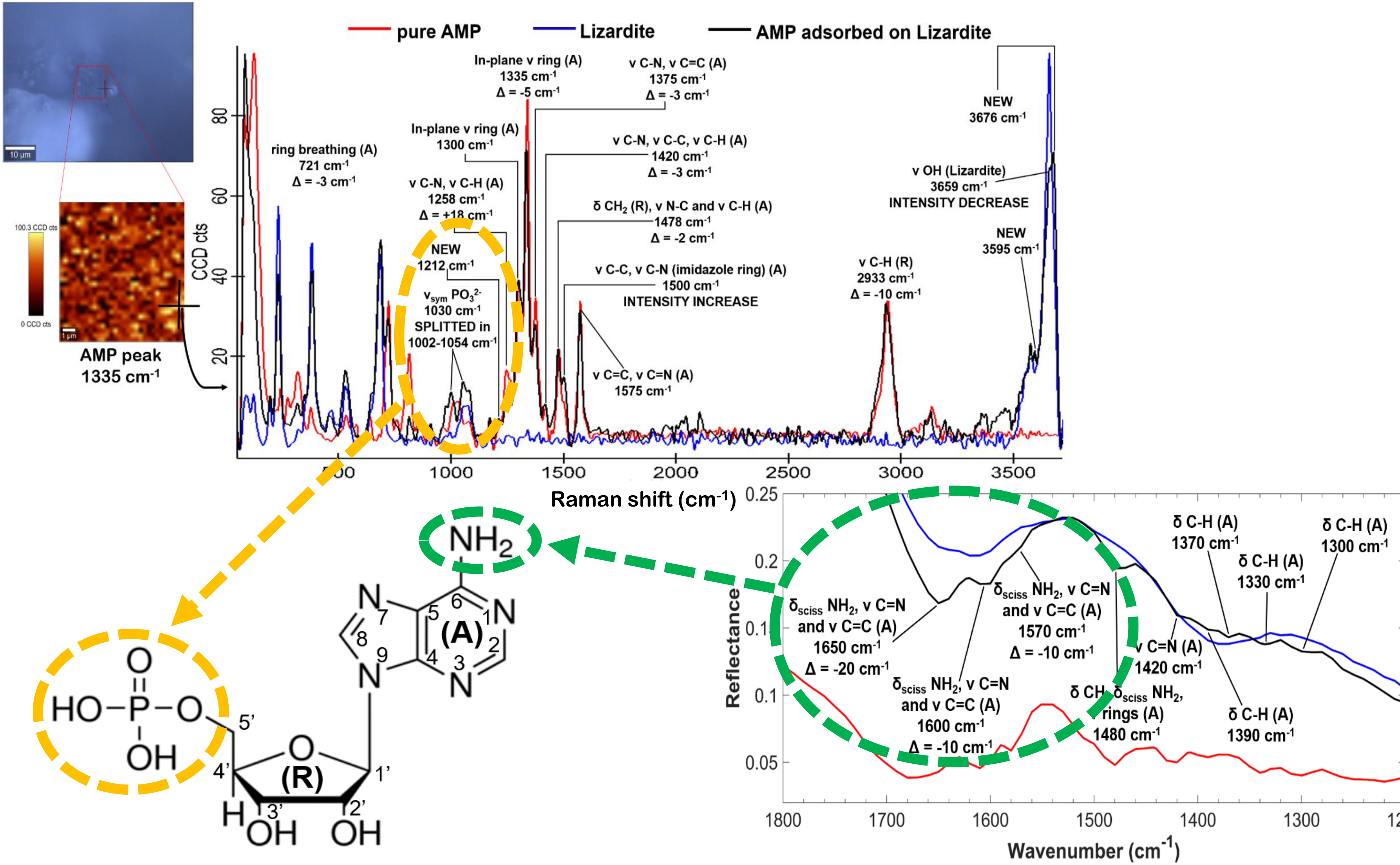
2. Characterization of Mars Soil Analogues

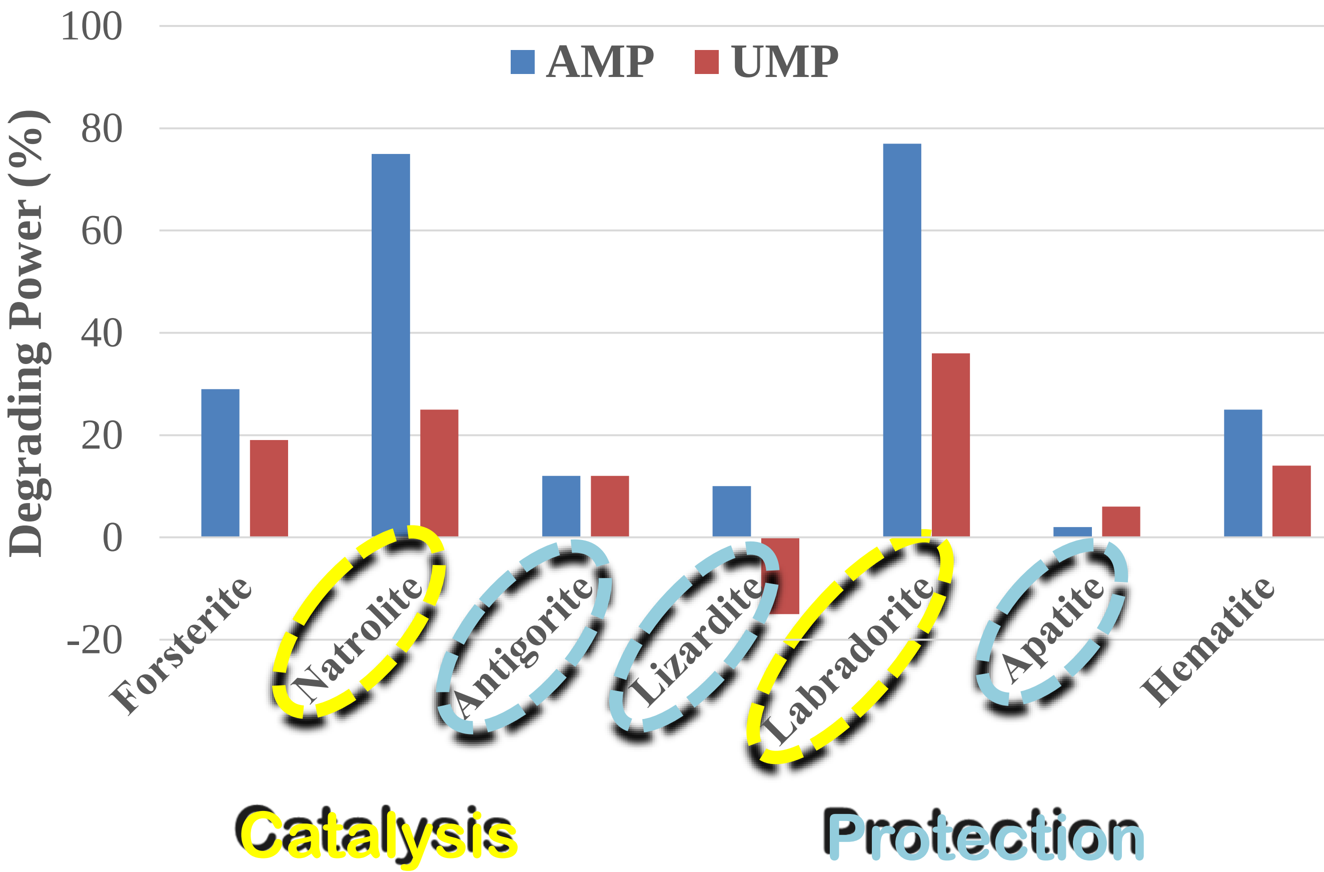
Raman and Infrared spectroscopies are very sensitive complementary techniques to investigate molecule-mineral interactions and for detection of biomarkers features



3. UV Irradiation inside Martian Chamber

Comparison of the catalytic/protective properties of a variety of minerals relevant to Mars mineralogy:

- Develop models for degradation of biomarkers
- Predict the mineral deposits with the highest preservation potential



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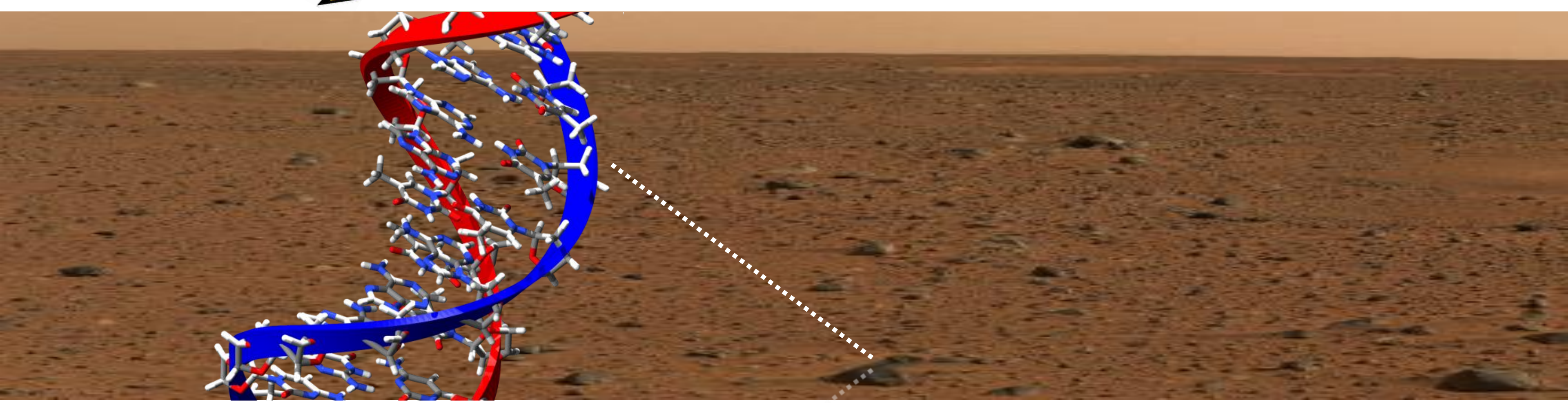
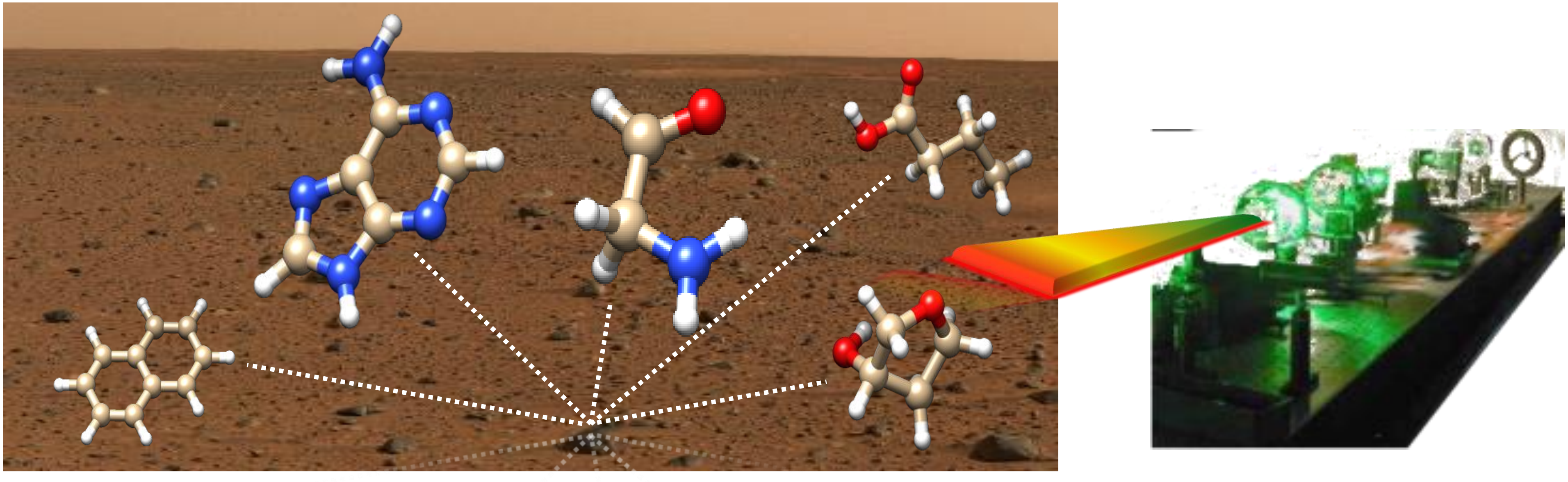


Scientific Relevance → Laboratory Studies → Summary of the Results → Acknowledgements

SCIENTIFIC RELEVANCE

Characterization of Mars soil analogues through various techniques:

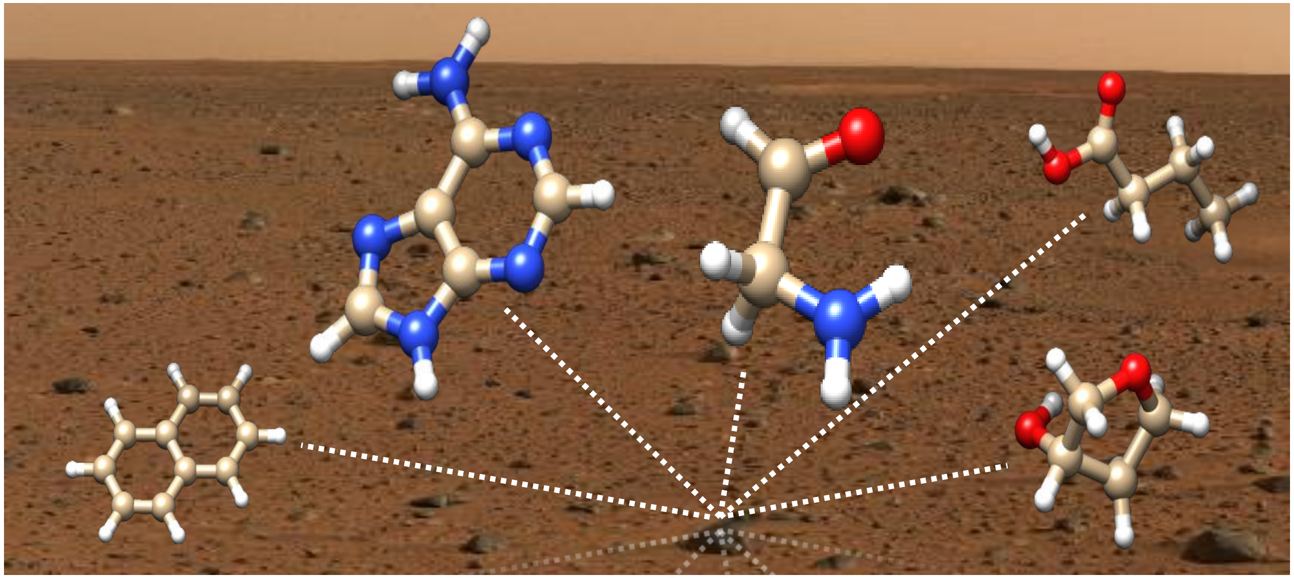
- Assay the sensitivity of different laboratory instruments to detect diagnostic features of molecular biomarkers
- Support development of flight instruments and life detection methods
- Interpretation of data obtained by remote sensing



Scientific Relevance

Study of the transformation of potential biomarkers adsorbed on a variety of mineral matrices under Martian-like conditions:

- **Establish habitability of the planet**
- **Identify potential biomarkers**
- **Select landing sites**
- **Interpret data collected on the ground**



LABORATORY STUDIES

1. Preparation of Mars soil analogues doped with biomarkers

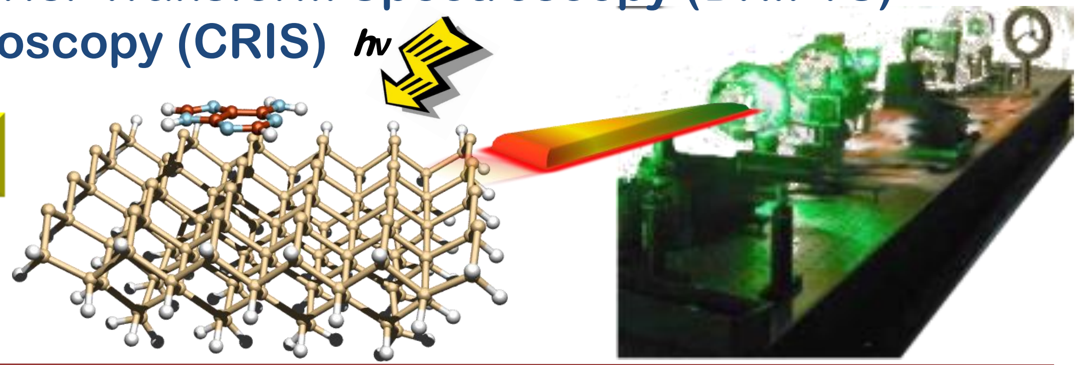
-Equilibrium adsorption

-Water deposition

2. Characterization of Mars soil analogues

-Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

-Confocal Raman Imaging Spectroscopy (CRIS)



3. UV irradiation processing

-Terrestrial ambient conditions

-Martian simulation chamber

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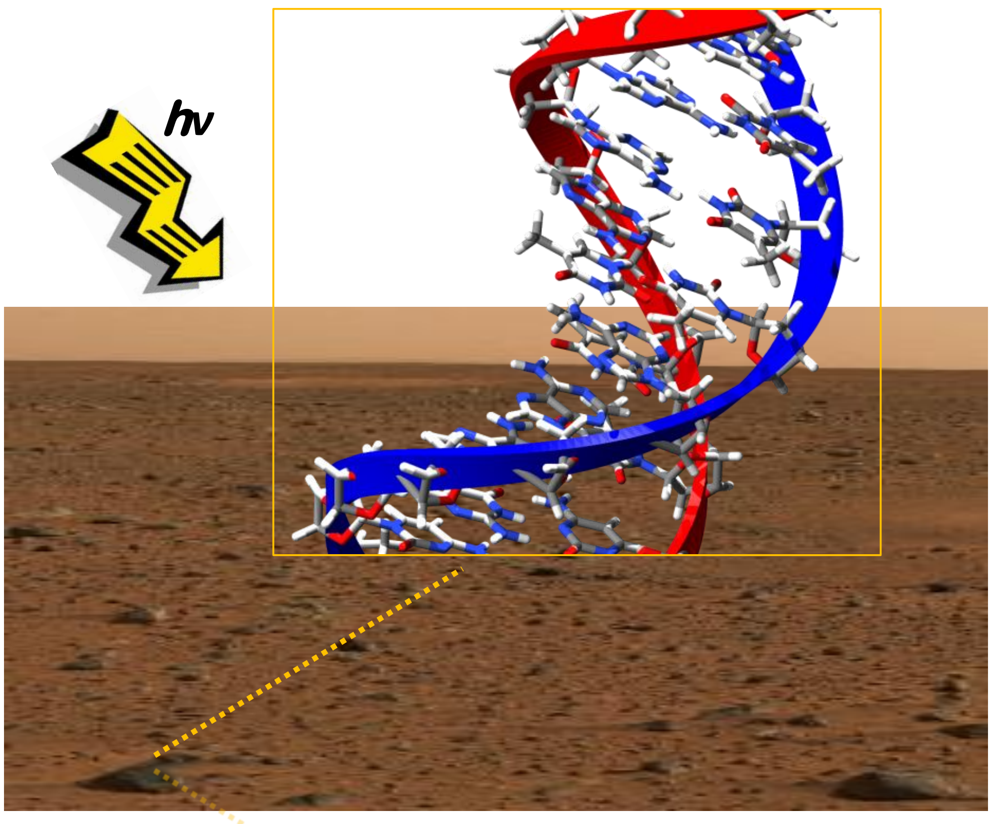
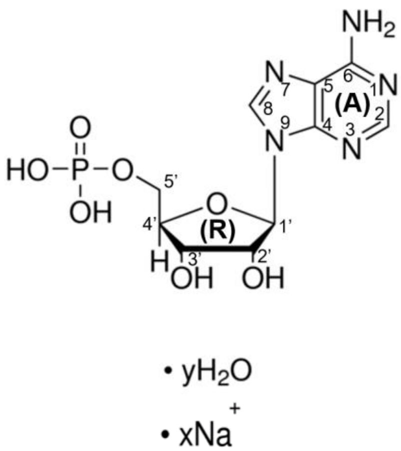
1. PREPARATION OF MARS SOIL ANALOGUES

Systems under study

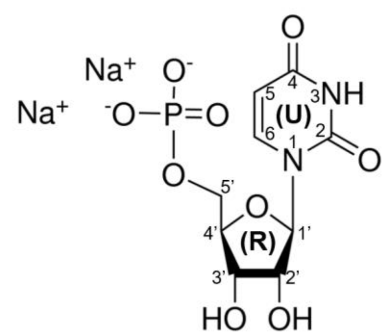
- **Biomarkers of extant life:** nucleotides adenosine and uridine monophosphate **AMP** and **UMP**
- **Minerals:** **forsterite** [Mg_2SiO_4], **natrolite** [$Na_2Al_2Si_3O_{10}\cdot 2H_2O$], **labradorite** [$(Ca,Na)(Al,Si)_4O_8$], **hematite** [$Fe_2O_3$], **apatite** [$Ca_{10}(PO_4)_6(OH)_2$], **lizardite** and **antigorite** [$(Mg,Fe)_3Si_2O_5(OH)_4$]



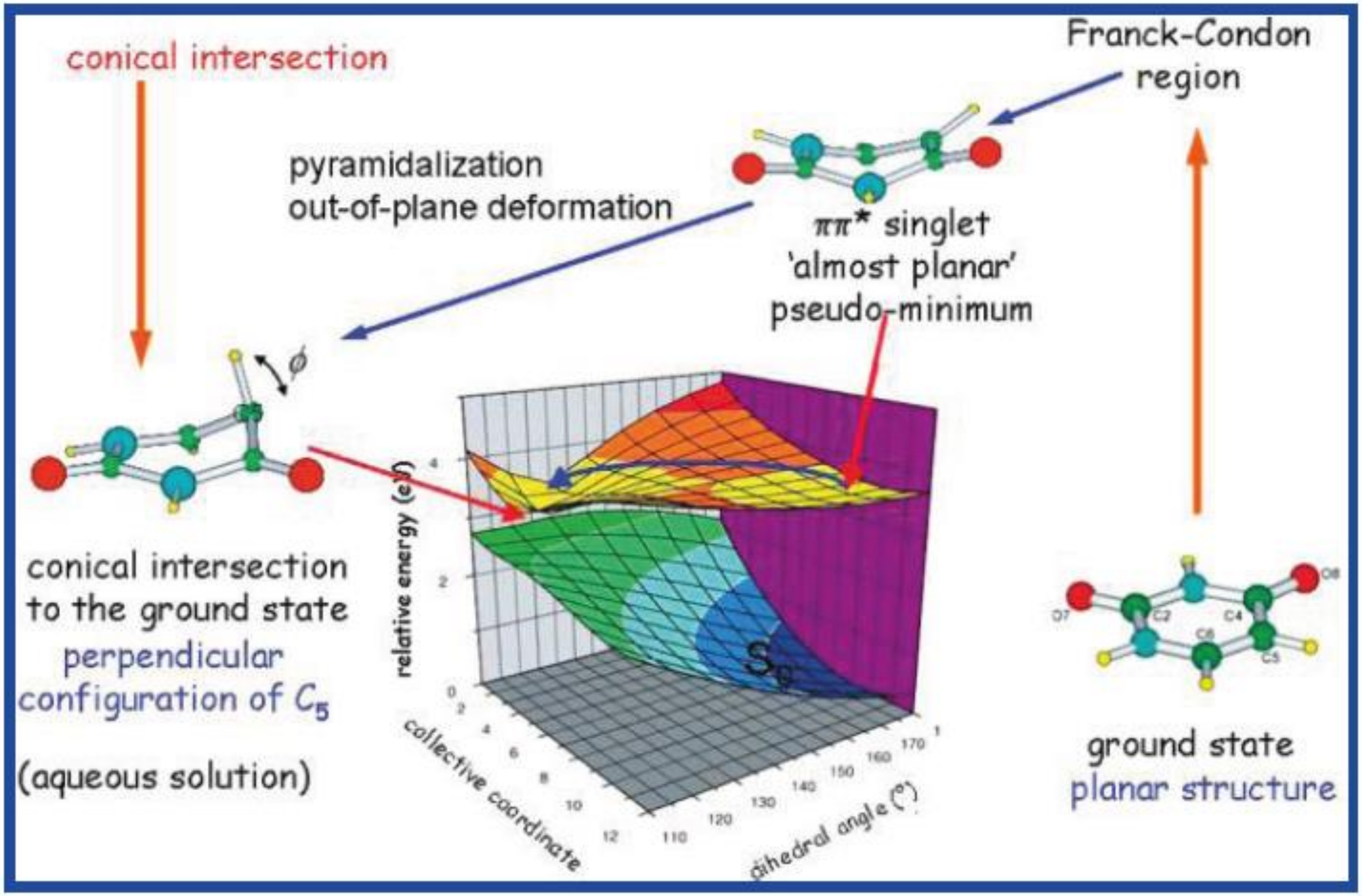
AMP



UMP



Photoprotective properties of nucleobases: ultrafast internal conversion



Gustavsson, T. *et al.*, *J. Am. Chem. Soc.* **2006**, *128*, 607–619;
Gustavsson, T.; Improta, R.; Markovitsi, D. *J. Phys. Chem. Lett.* **2010**, *1*, 2025–2030.

1. Preparation of Mars soil analogues

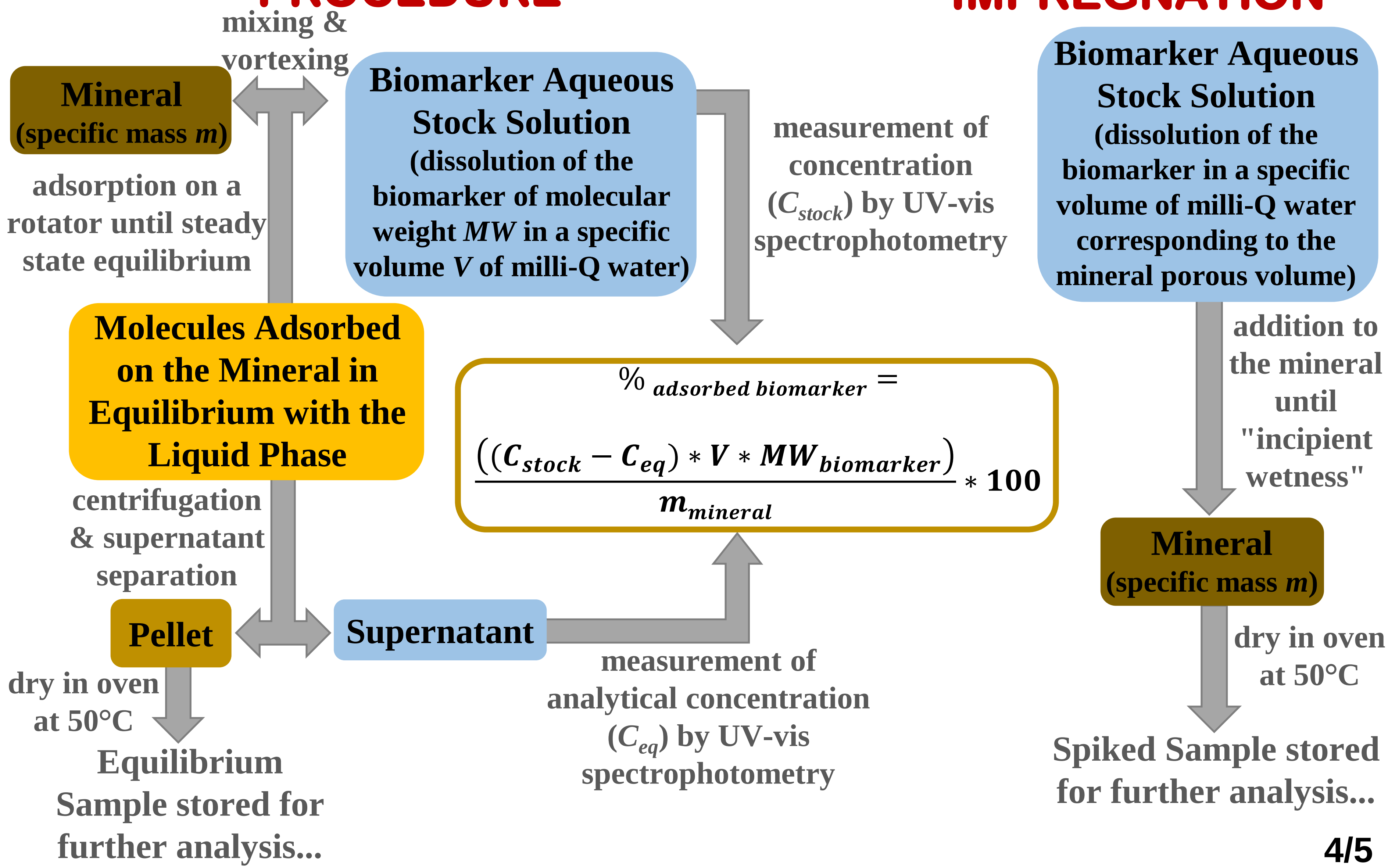
Mineral treatments to remove possible organic and biological contaminations:

- Crush and grind rock samples with a Planetary Ball Mill
- Sieve mineral powder in different grain size ranges - 500, 250, 100, 50, <20 μm – using a Vibratory Sieve Shaker
- Sterilization in autoclave
- Washing cycles with polar/non-polar solvents (e.g. chloroform, toluene, acetonitrile, methanol, water) and sonication
- H_2O_2 oxidation
- Heating at 550°C for 3 hours

1. Preparation of Mars Soil Analogues

EQUILIBRIUM ADSORPTION PROCEDURE

INCIPIENT WETNESS IMPREGNATION



1. Preparation of Mars soil analogues

Water deposition *vs.* Equilibrium adsorption

	Water deposition	Equilibrium adsorption
➢ Control of the amount of molecules adsorbed on the solid support	✓	✓
➢ Control on experimental conditions and degree of coverage	✗	✓
➢ Study of physico-chemical interactions establishing between molecules and mineral surface	✗	✓
➢ Simulated environment on Mars	Evaporation of warm little ponds of liquid water / desiccation of liquid water bodies	Adsorption processes in dilute aqueous environments like those presumably present on Noachian Mars

2. Characterization of Mars Soil Analogues

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

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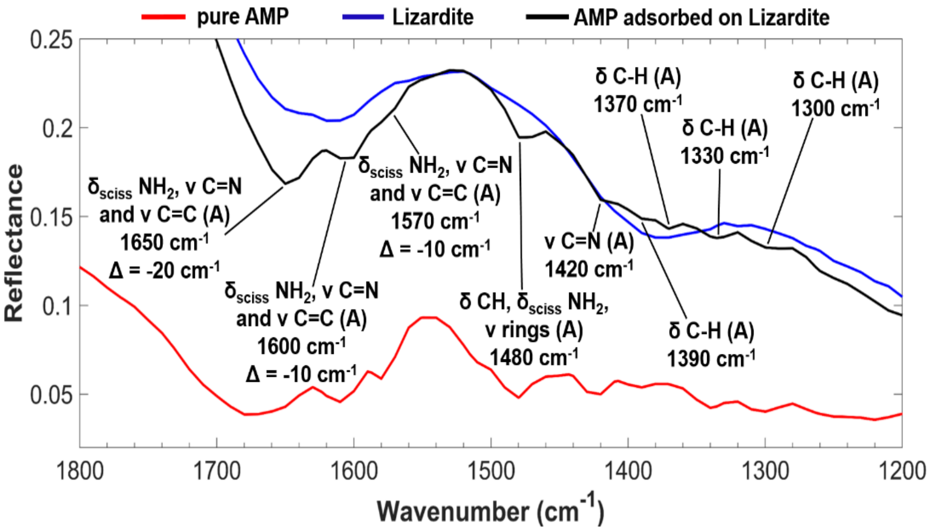

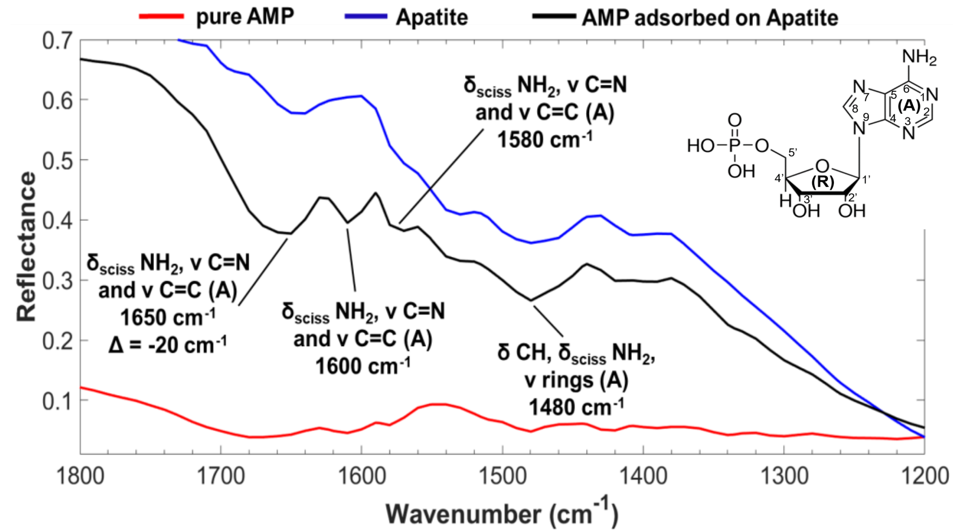

Assignment of vibrational modes: v = stretching; δ = bending; sciss = scissoring.
Δ indicates the shift of vibrational frequencies of AMP adsorbed on the mineral with respect to pure AMP.

- **Red-shift of NH_2 scissoring indicates that AMP molecules interact with the mineral surface through the nucleobase amino group**
- **No new bands indicative of formation of covalent bonds through the nucleobase amino group (maybe only physical interactions)**

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2. Characterization of Mars Soil Analogues

Confocal micro-Raman Imaging Spectroscopy (CRIS)

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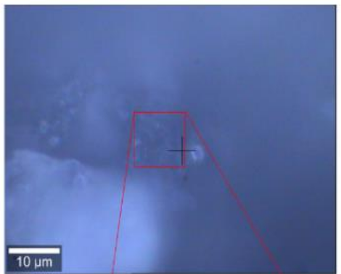
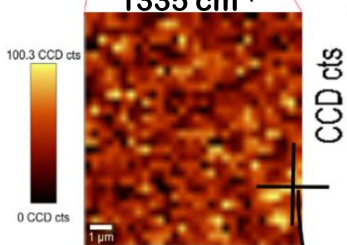
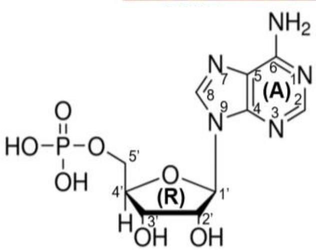
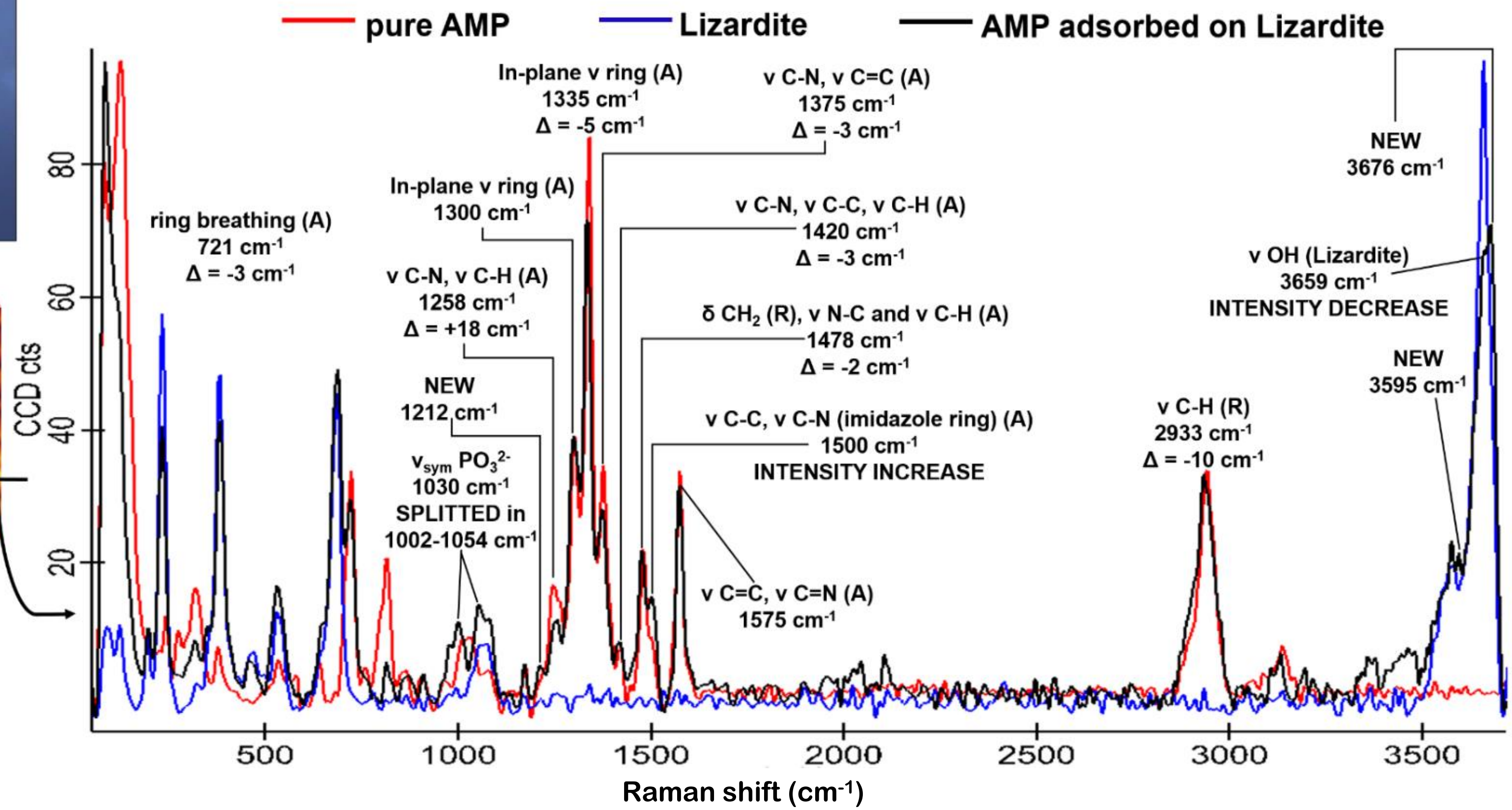


AMP peak 1335 cm^{-1}







Splitting of phosphate stretching vibration, decrease of intensity for stretching of lizardite hydroxyl group, and appearance of new bands in the phosphate and hydroxyl stretching regions, indicate that AMP molecules interact mainly through the phosphate group, presumably forming covalent bonds with metal-hydroxyls of lizardite

2. Characterization of Mars Soil Analogues

Confocal micro-Raman Imaging Spectroscopy (CRIS)

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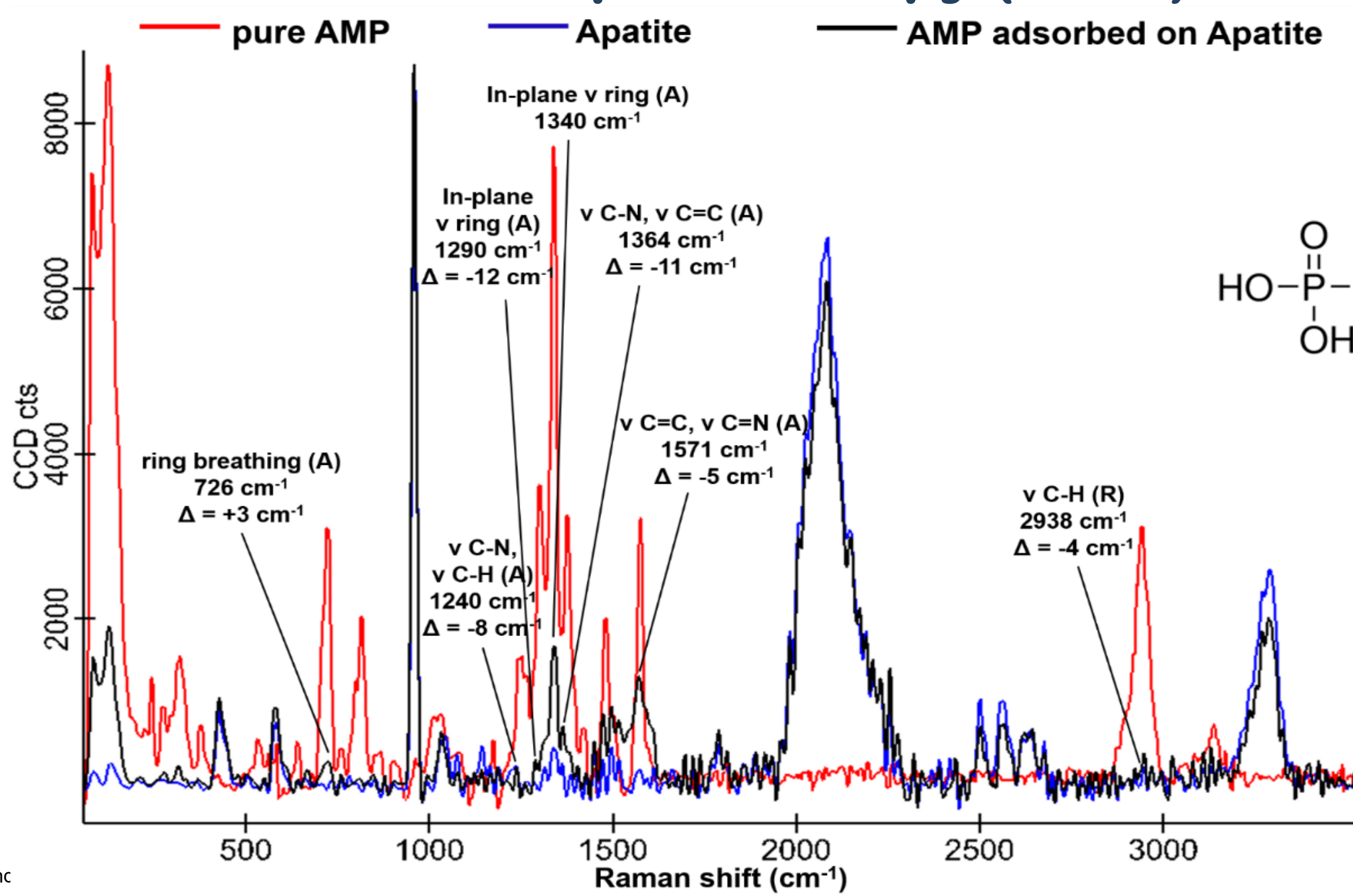

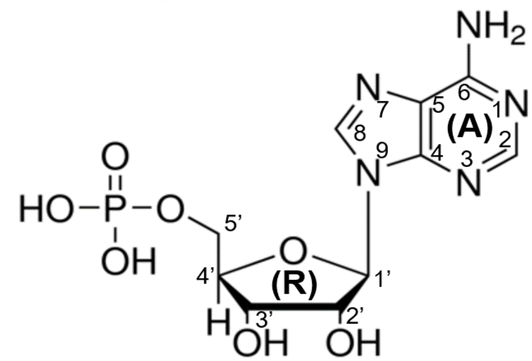

Δ inc

- ➢ Red-shifts of the nucleobase vibrational modes indicate the involvement of the adenine moiety in the interaction with the mineral surface
- ➢ No significant Raman bands for the stretching motion of the phosphate group (maybe only electrostatically-mediated interaction)

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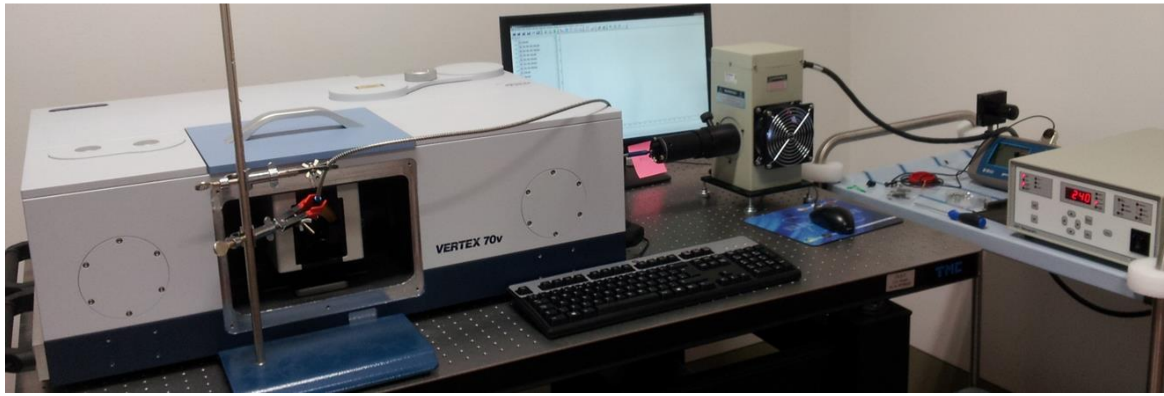
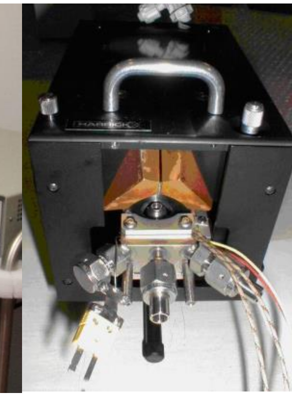
3. *In situ* UV Irradiation under Terrestrial ambient T and P

UV source
Xenon lamp (200-930 nm), flux 2.75*10[17] photons s^{-1} cm^{-2} in 200-400 nm spectral range





DRIFTS analysis *in situ* during UV irradiation

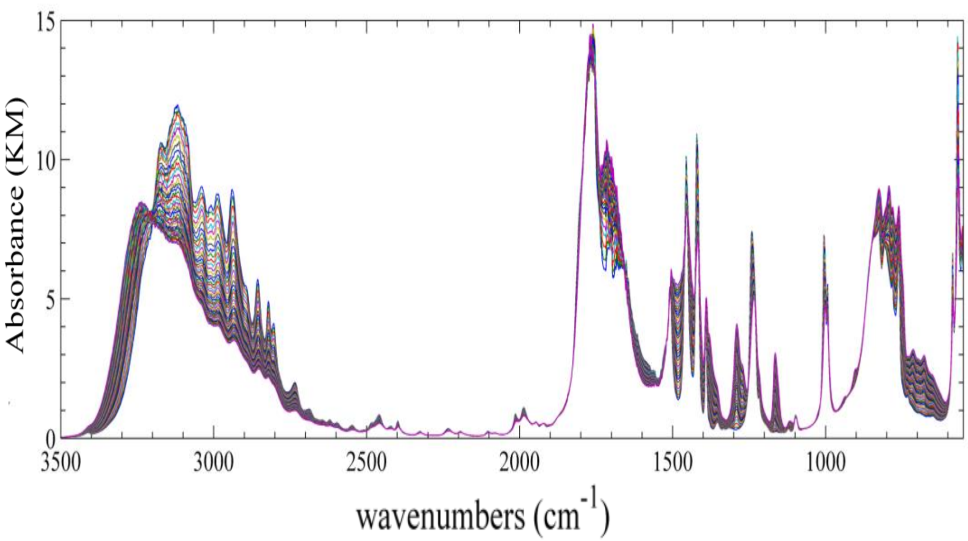
Degradation Kinetics

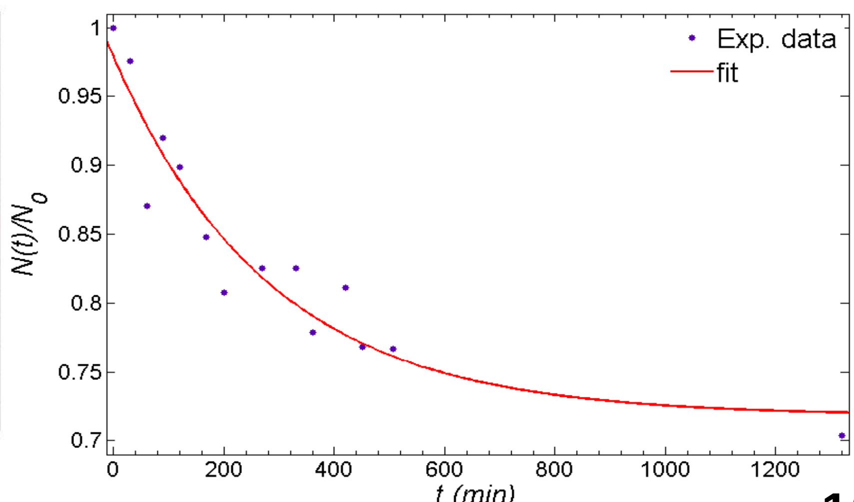
$$N(t)/N_0 = Be^{-\beta t} + c$$

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

$$\beta = \sigma \Phi / A_0$$

- β degradation rate
- $t_{1/2}$ half-lifetime
- σ cross section
- Φ_{tot} UV flux
- A_0 sample irradiated area





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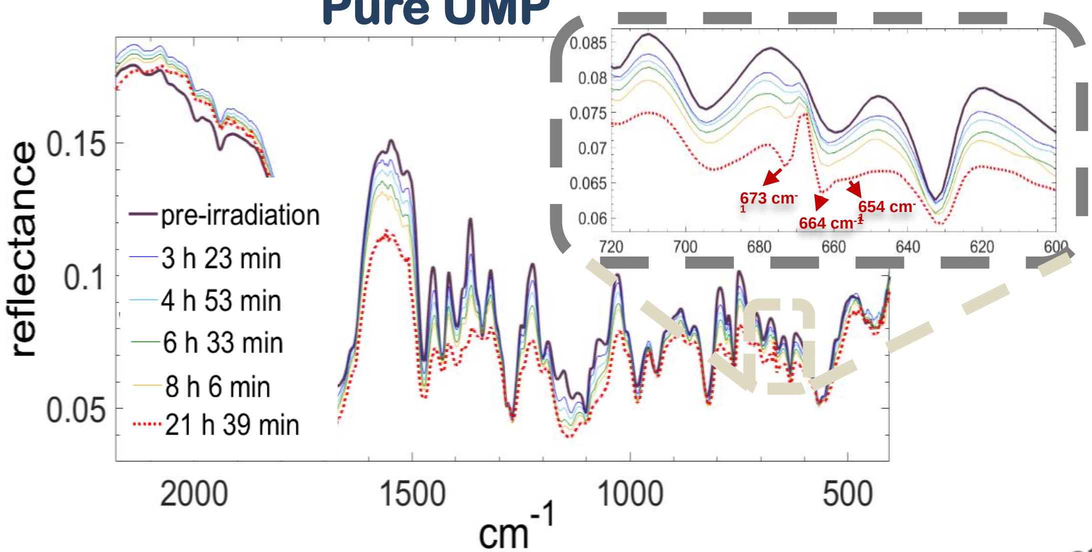
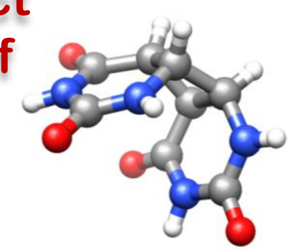
3. *In situ* UV Irradiation under Terrestrial ambient T and P

- **No remarkable changes for pure AMP**
- **Significant changes and appearance of new peaks for pure UMP, likely formation of cis-syn cyclobutane dimer (CBD)**
- **$\sigma_{\text{pure AMP / UMP}} \approx 10^{-22}$ cm^2 and $t_{1/2} \approx$ 30 Martian days**

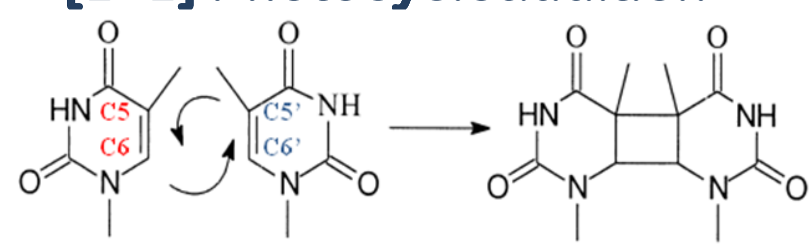
Pure UMP



Marker bands of the possible photoproduct (CBD) in the region of N3-H out-of-plane bending



[2+2] Photocycloaddition



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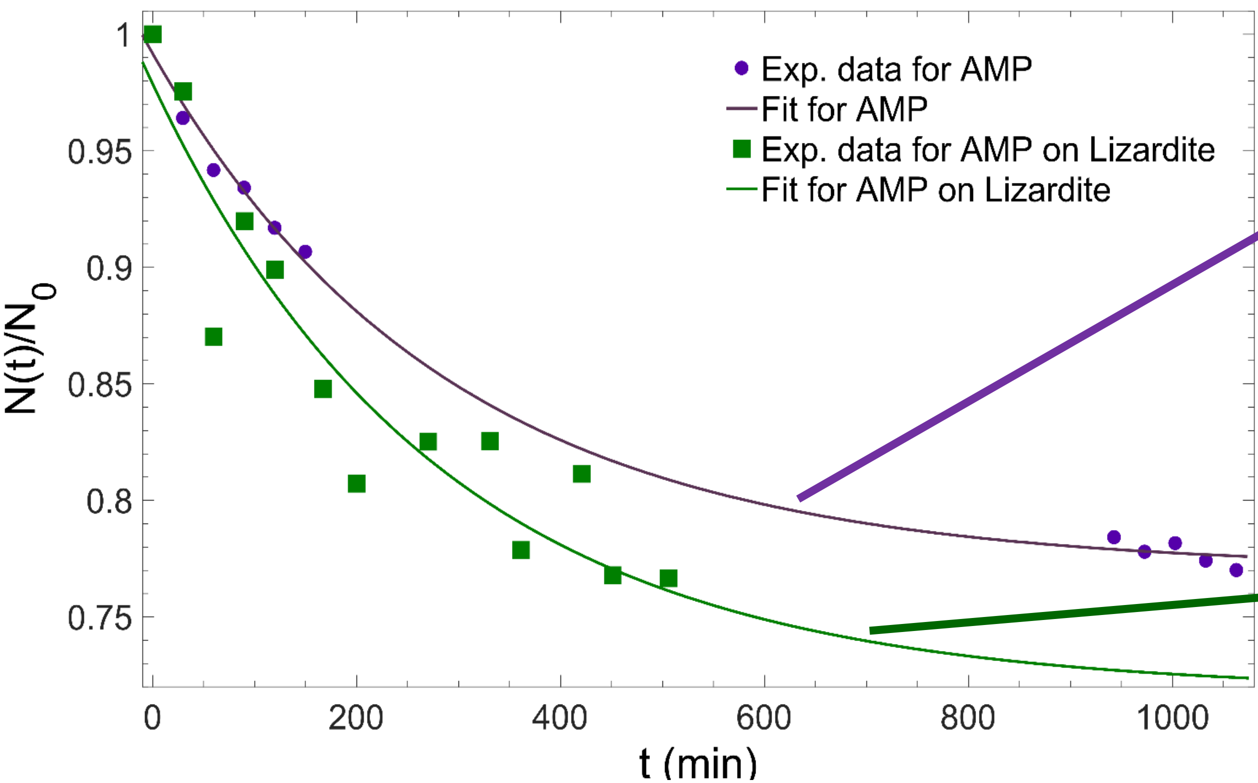
3. *In situ* UV Irradiation under Terrestrial ambient T and P

AMP peak at 1600 cm^{-1} (δ_{sciss} NH_2, ν C=N, ν C=C)



Pure AMP:

$\sigma = (2.1 \pm 0.2) \times 10^{-22}$ cm^2

$t_{1/2}$ = 27±3 Martian days

AMP adsorbed on Lizardite:

$\sigma = (2.2 \pm 0.6) \times 10^{-22}$ cm^2

$t_{1/2}$ = 26±8 Martian days

Similar degradation kinetics => lizardite does NOT behave as a catalyst

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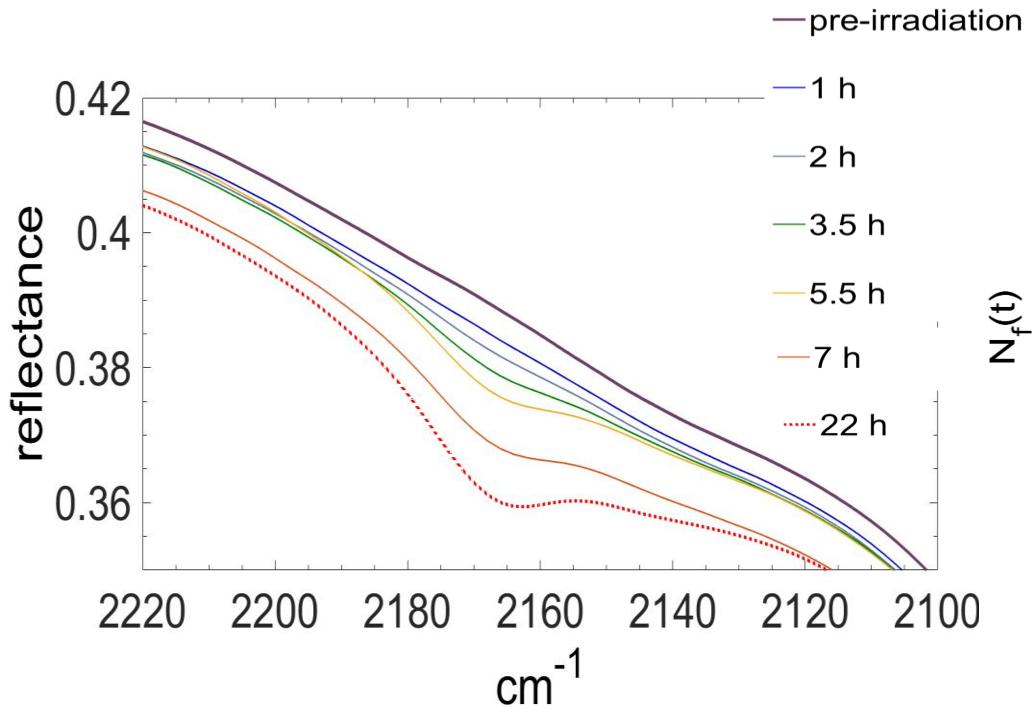
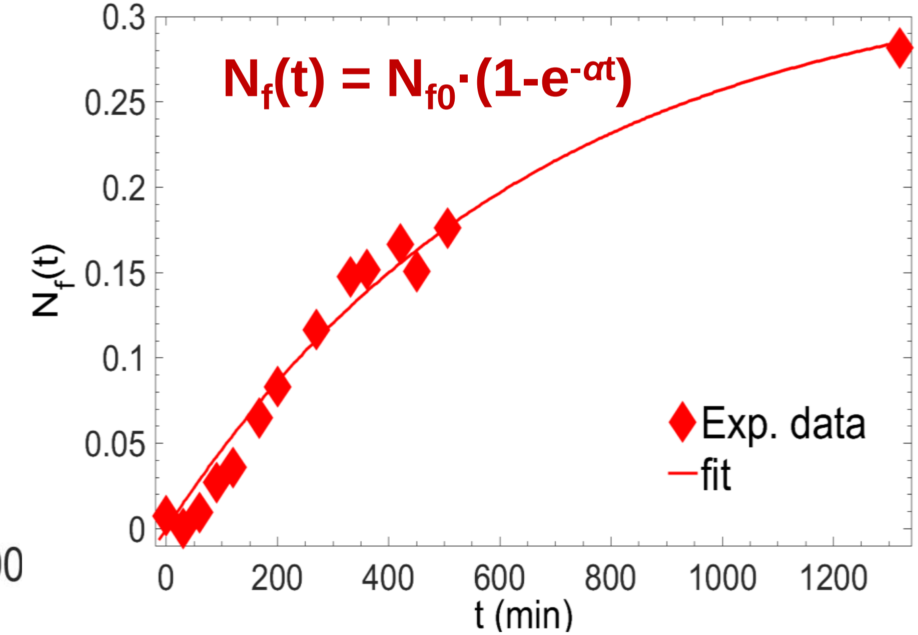
3. *In situ* UV Irradiation under Terrestrial ambient T and P

Appearance of the peak at 2164 cm^{-1} for AMP on Lizardite





Formation of a new peak at 2164 cm^{-1}, likely corresponding to a cyanate OCN- fragment ($\sigma_f \approx 10^{-22}$ cm^2)

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3. *Ex situ* UV Irradiation inside Martian Chamber (T≈-20°C, 6 mbar CO2)

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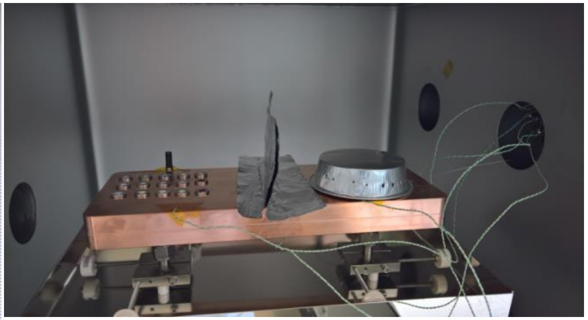

UV source Xenon lamp (180-900 nm), flux $5.42*10^{18}$ photons s^{-1} cm^{-2} in 200-400 nm spectral range

DRIFTS analysis *ex situ* pre- and post- 40 h irradiation

- **Slower degradation** than terrestrial ambient conditions: $\sigma_{pure\ AMP\ /\ UMP} \approx 10^{-25}\ cm^2$, $t_{1/2} \approx 50000$ Martian days
- **NO** formation of **new peaks for AMP**
- **Likely formation of CBD for UMP**
- **NO appearance of the peak at 2160 cm^{-1} for AMP and UMP adsorbed on Lizardite**
- **Current Martian conditions favour preservation** of "building block of life" such as nucleotides

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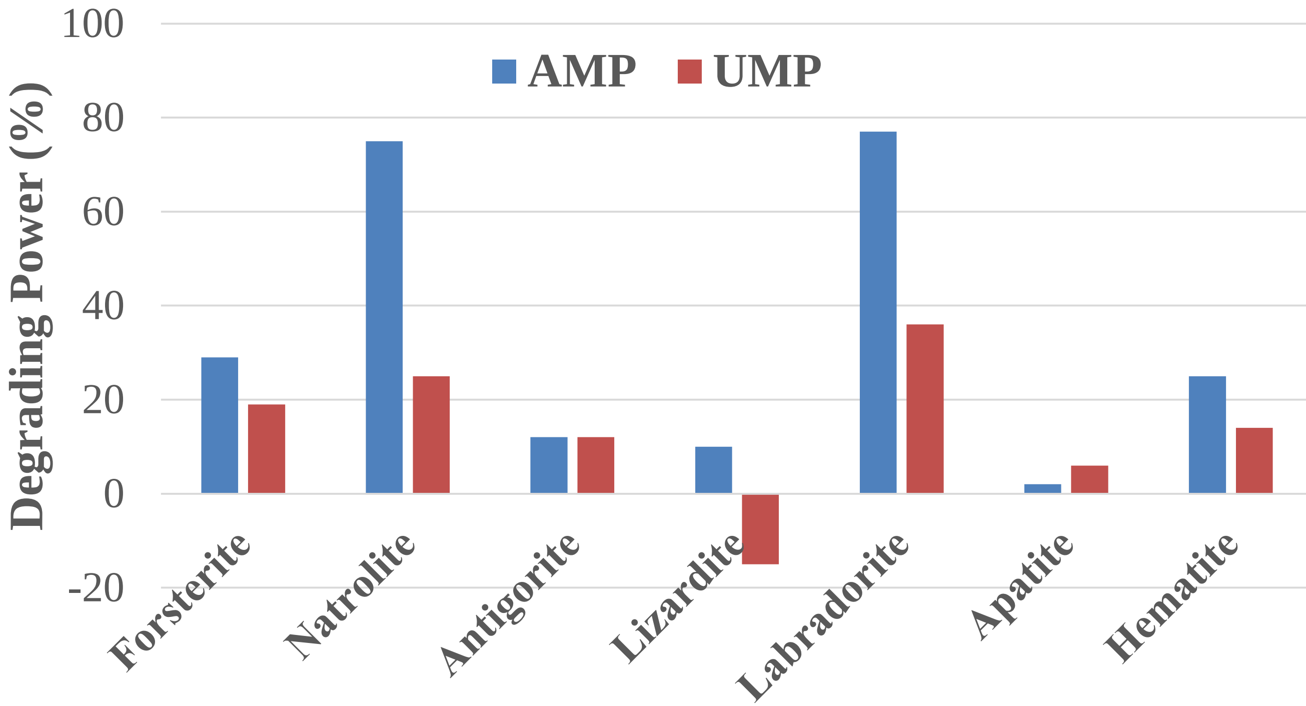
Comparison of different minerals



- **Labradorite** and **natrolite** minerals feature the **greatest catalytic activity**
- **Forsterite** and **Hematite** have an **intermediate behavior**
- **Apatite**, **lizardite** and **antigorite do not show any significant catalytic effect**

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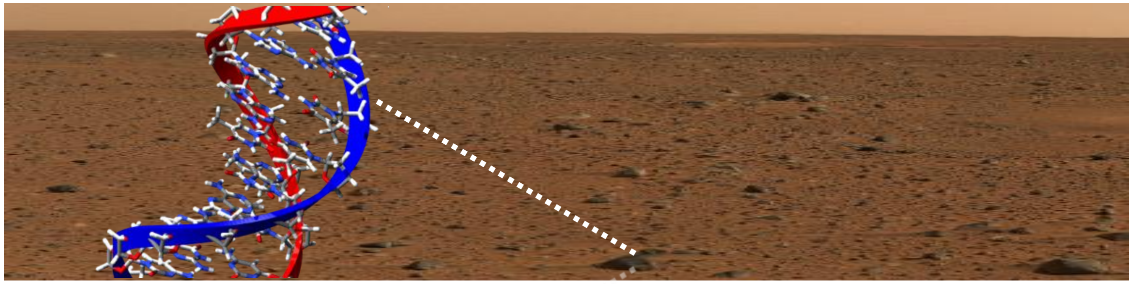
SUMMARY OF THE RESULTS

- Raman and IR spectroscopies are sensitive complementary techniques to investigate molecule-mineral interactions and for detection of biomarkers features
- Martian conditions are more favorable for preservation than terrestrial conditions
- Minerals can act as photocatalysts or photoprotectors. Thus, in high-UV irradiation environments like Mars and early Earth, minerals are primarily involved in the processes of preservation/transformation of organic matter
- The capability of apatite and serpentines to protect important molecular biomarkers of extant life such as nucleotides against damaging UV radiations is encouraging for detecting biomarkers, while feldspars and zeolites should not be targeted for the detection of biomarkers in future life detection missions to Mars



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- Geophysical Laboratory of the Carnegie Institution for Science (Washington DC, USA).