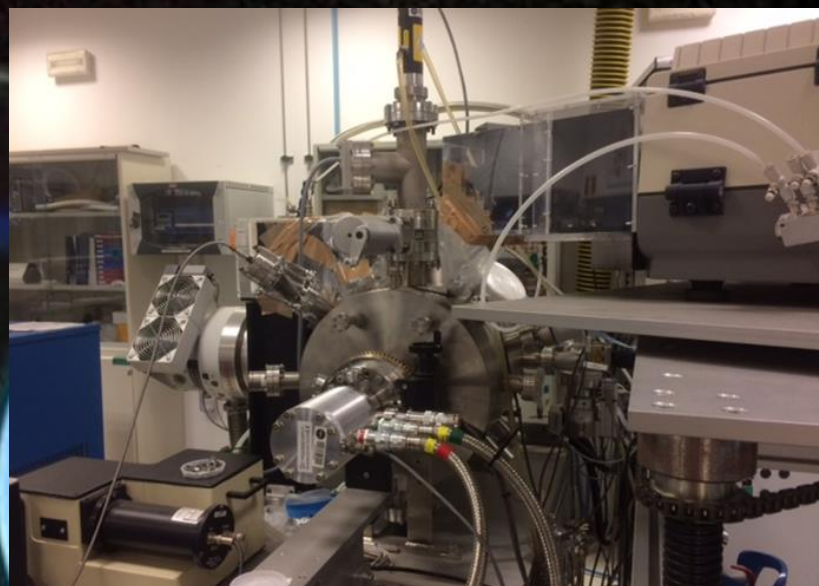
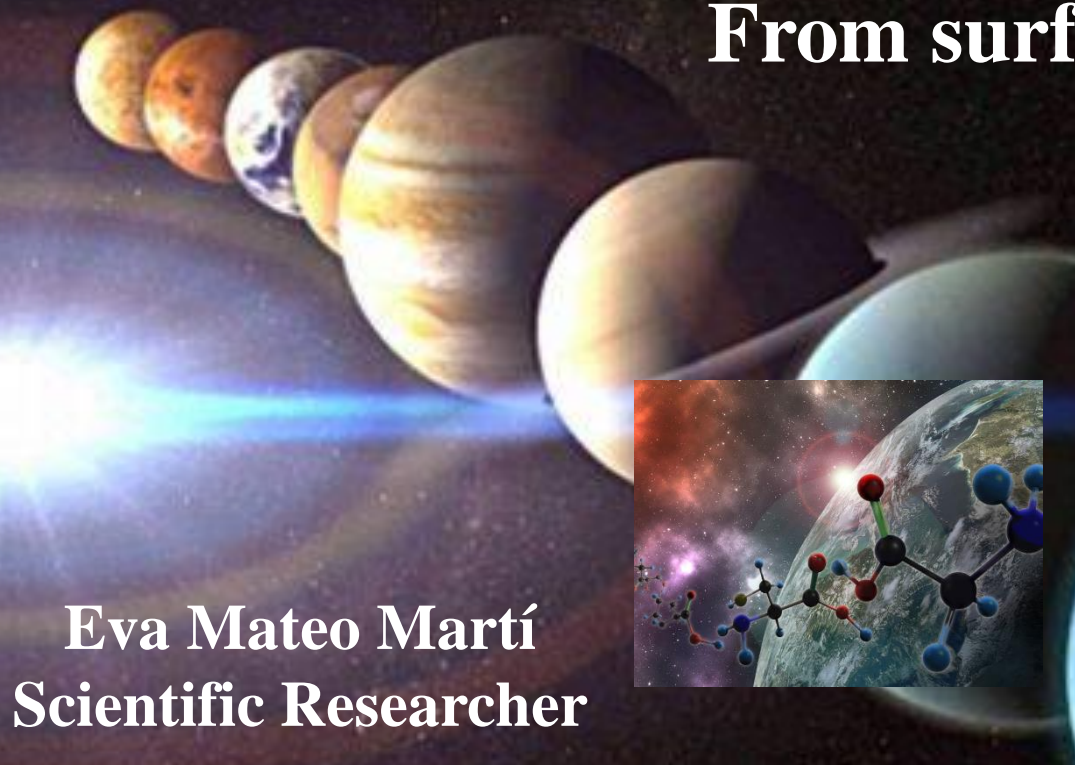


Photochemistry studies on a simulation chamber: From surfaces to biomolecules.

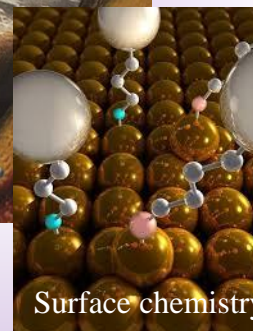
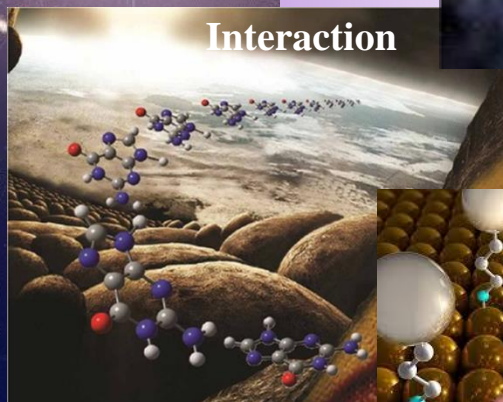
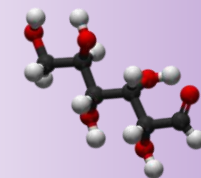


Eva Mateo Martí
Scientific Researcher



The relevance of molecules and minerals surfaces on the path to molecular complexity

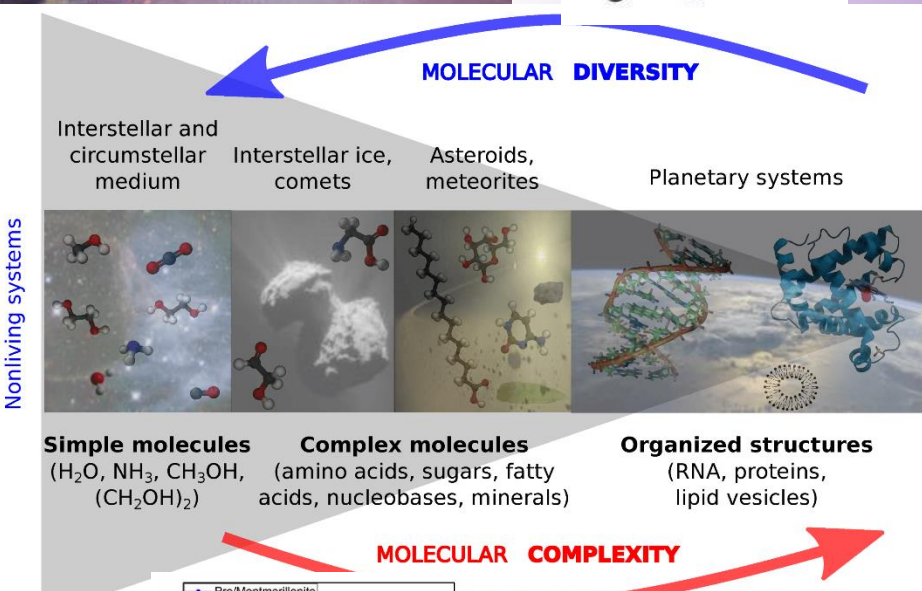
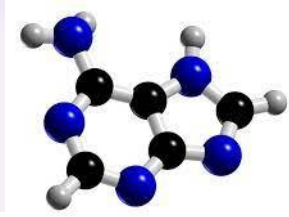
Minerals surface can protect, preserve and concentrate biomolecules, catalyze reactions by providing catalytic sites on the surface and drive molecular chemistry.



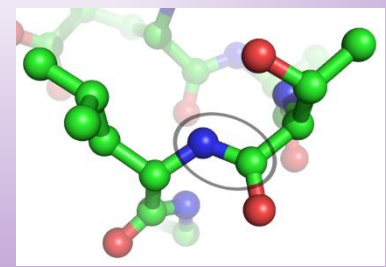
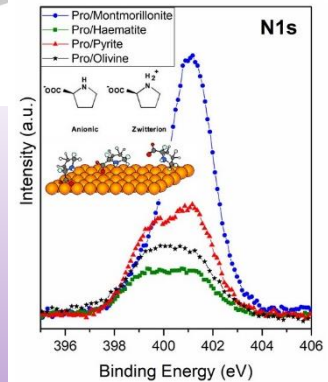
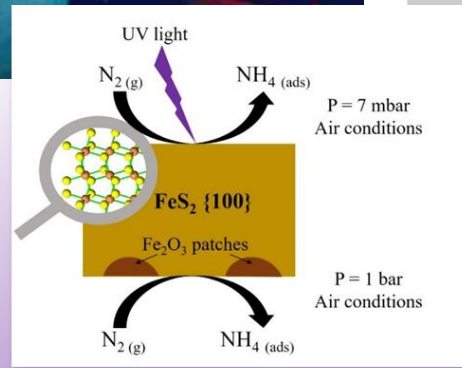
Crucial role in origin of life
Abundant in the primitive earth
Molecular Complexity

Complex geochemical or space environments.

The role of molecules on minerals surfaces on the path to molecular complexity



Spectroscopic molecular signatures



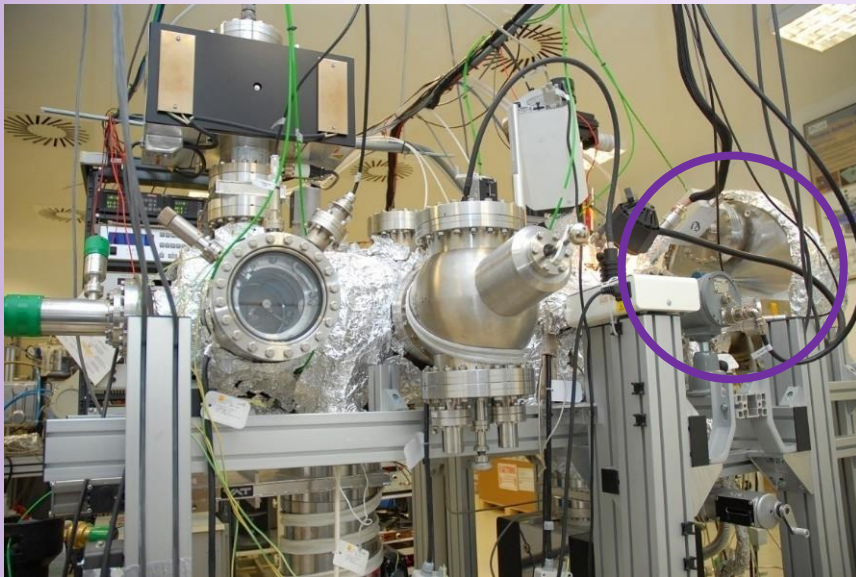


Surface Science Approach

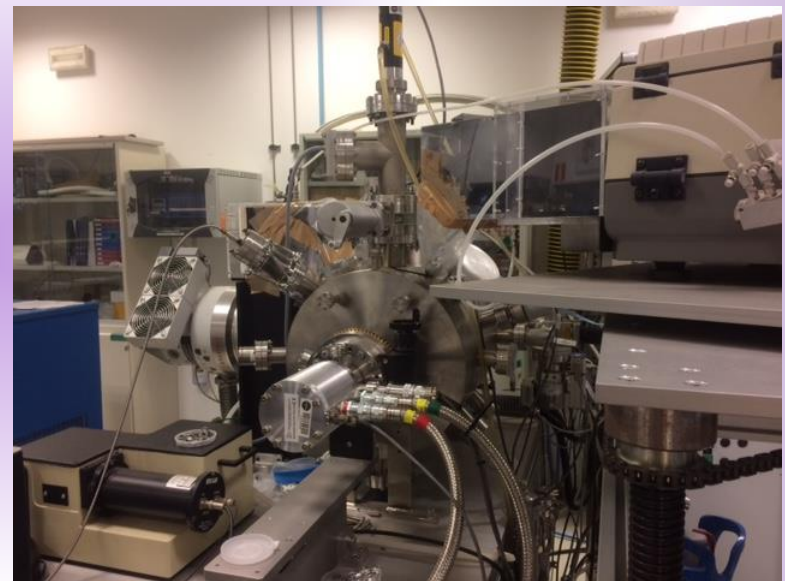
Deeply study the molecule/surface interaction:

Controlled environmental conditions/ Searching for spectroscopic fingerprints

UHV/ Surface Science techniques



Spectroscopy and Microscopy on Surfaces (SMS)

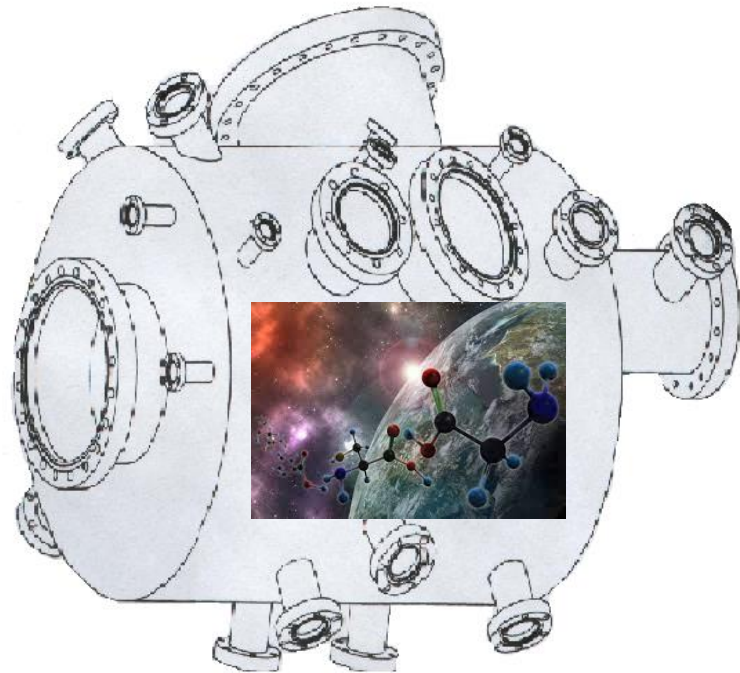


Planetary Atmospheres and Surfaces Chamber (PASC)

PASC and SMS: to have the ability to **reproduce environments in a controlled way** and use **powerful in-situ techniques**.

X-ray photoemission (XPS): the elemental composition and chemical state of these elements.

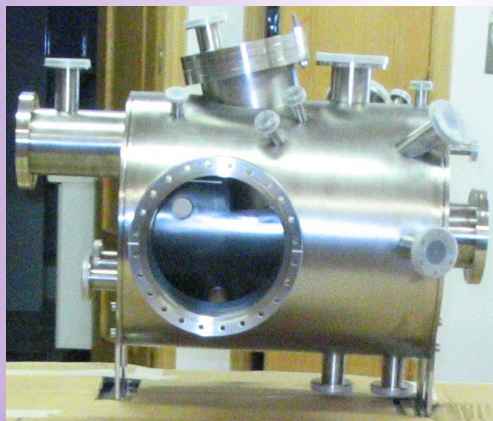
Planetary Atmospheres and Surfaces Chamber



Defined as **infrastructures** developed in the laboratory, consisting of a **stainless steel container**, in which the conditions found in the **atmosphere and surfaces** of most planetary objects can be reproduced or simulated **in a controlled manner**, by controlling physicochemical parameters such as P, atmospheric composition, temperature and irradiation sources.

Advantages:

- Cheaper than space mission
- Control conditions (no possible analogs)
- Repeat experiments



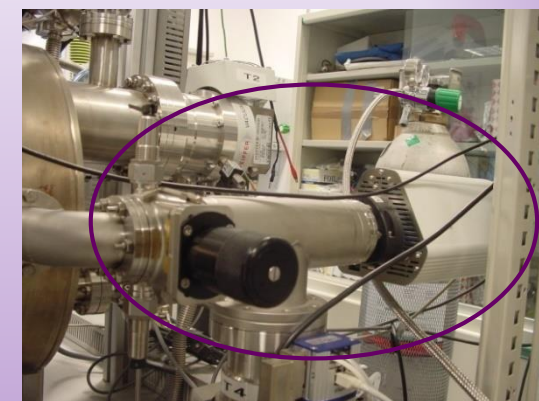
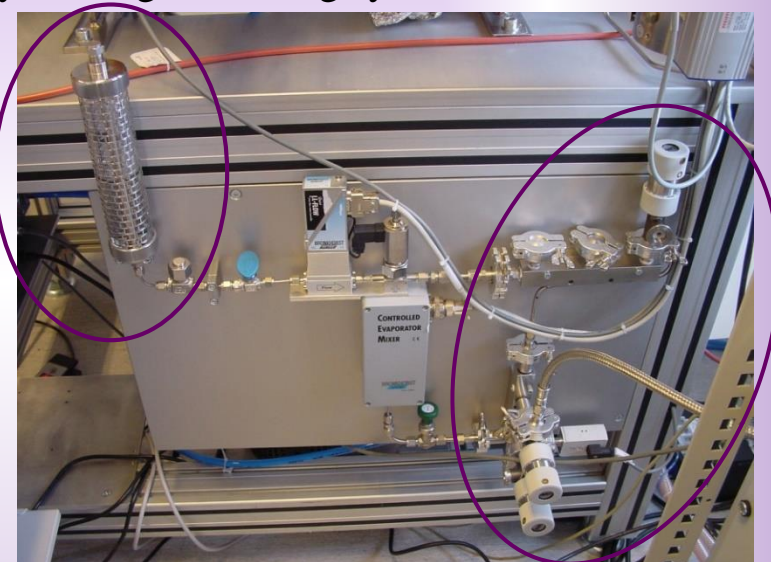
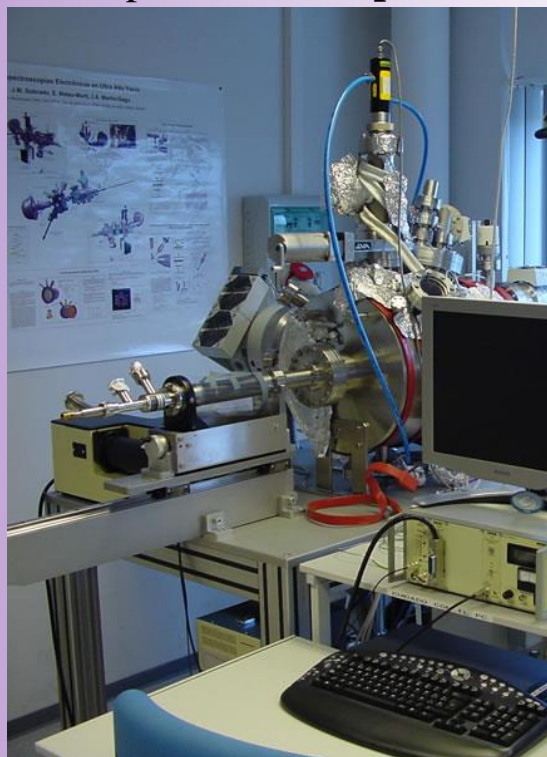
Chamber: 500 mm long by 400 mm diameter.





Planetary Atmospheres and Surfaces Chamber

The planetary simulation chambers are **versatile systems that reproduce the conditions of the desired environment** by **valves** that regulate the set-up of **gases**, a system that monitors on a computer that the composition of the atmosphere is accurate (**MS**), **gauges or sensors** that provide the **pressure** value of the atmosphere and **temperatures** in the sample, being regulated by cooling or heating systems.



Gas composition

Water vapor

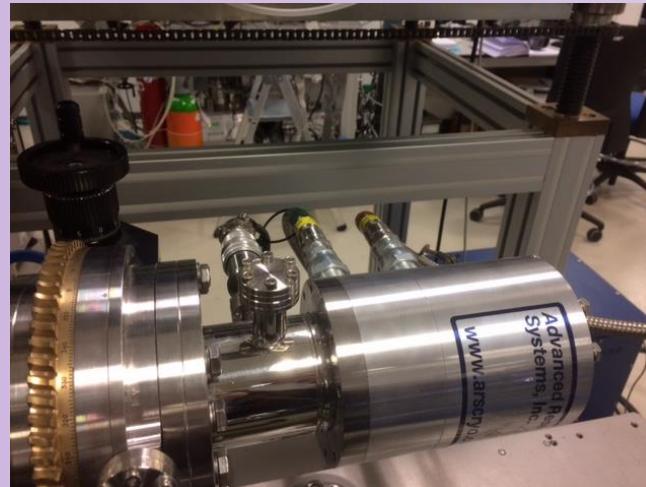
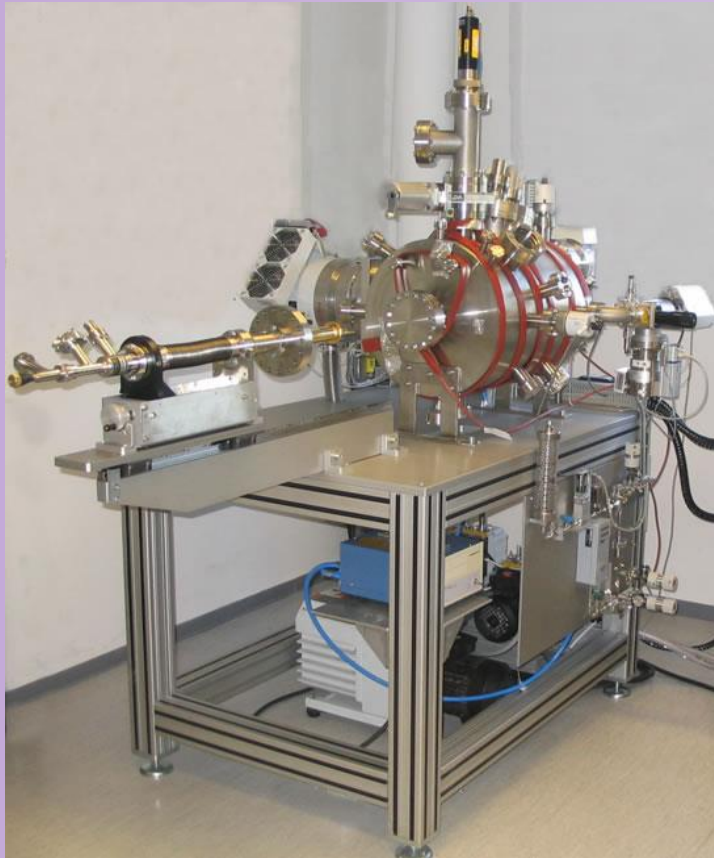
Residual gas analyzer RGA (ppm)

Pressure range: 5 mbar- 5×10^{-9} mbar

Planetary Atmospheres and Surfaces Chamber

Temperature Surface range: 10K-325K

A helium close cooling system connected to the sample holder cools down the sample.



Sample holder size: 5 - 35mm

The sample is placed into a removable sample container, which is made of copper with a gold coverage layer to improve the thermal conductivity.



Planetary Atmospheres and Surfaces Chamber

In-situ analysis techniques:

UV, RAIRS and Raman Spectroscopies.

Characterization of the sample under study

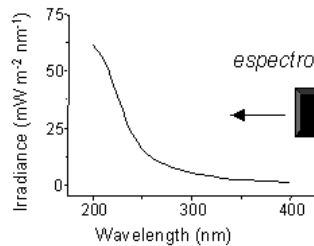


Irradiation by Deuterium lamp

UV (150W, 200-500nm)

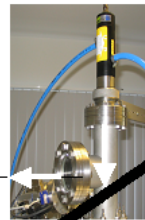
UV

UV spectrum in reflectance



spectroradiometer

Reflectance



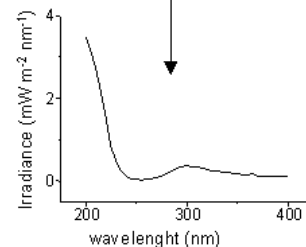
Beam-splitter

Transmittance

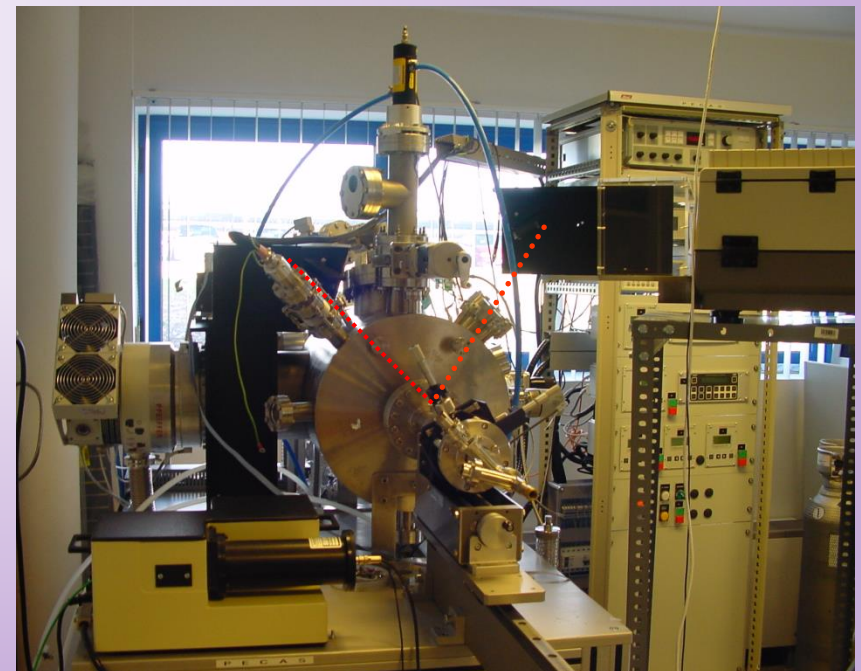
Basalt dust

CaF₂ window

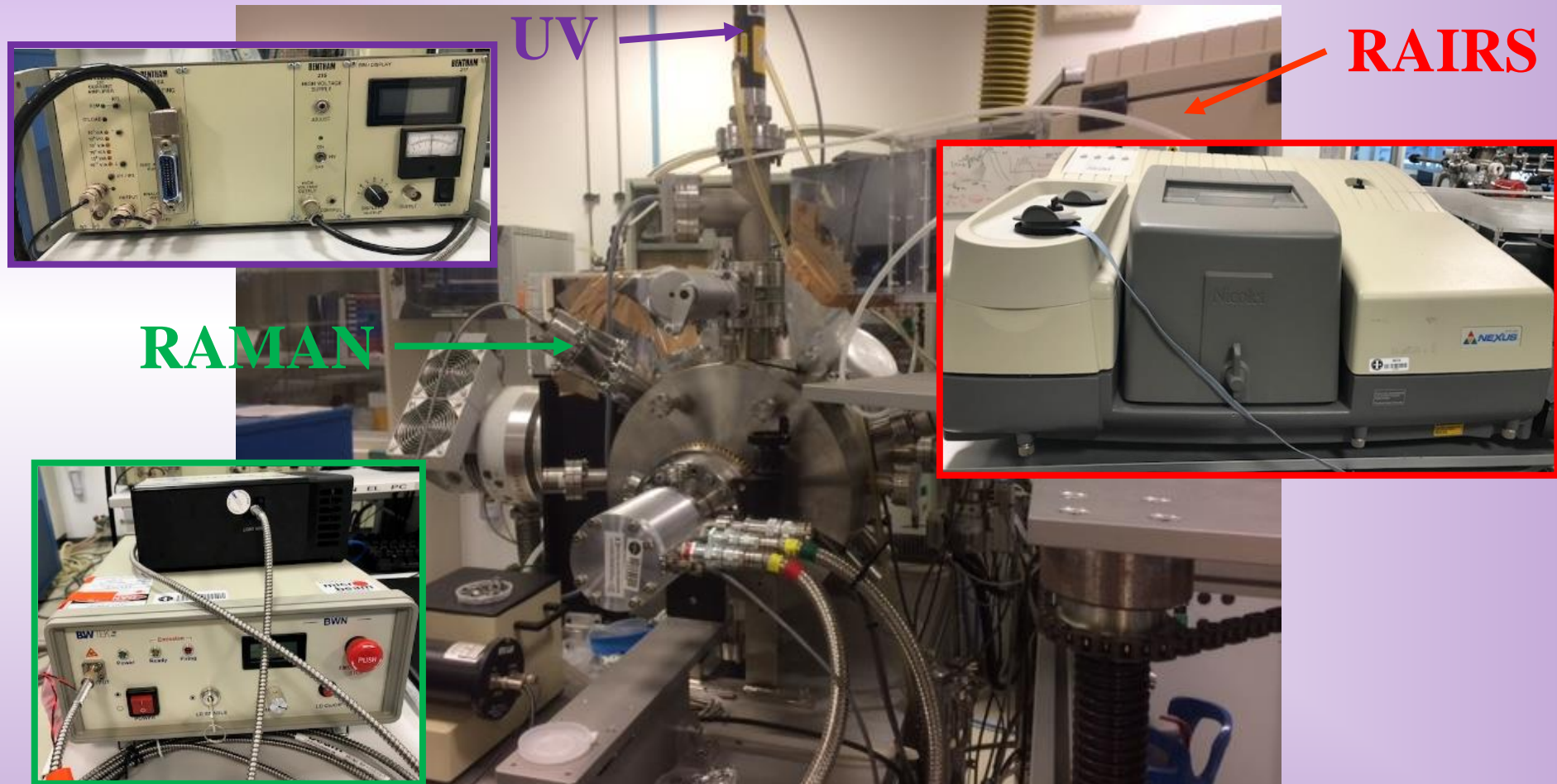
spectroradiometer



UV spectrum in transmittance

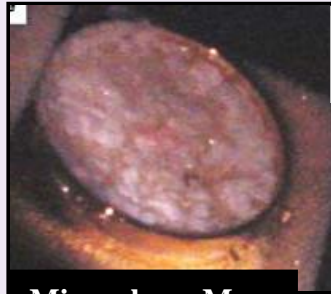
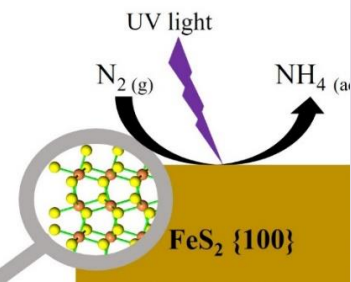


Planetary Atmospheres and Surfaces Chamber



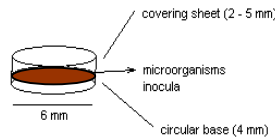
Planetary Atmospheres and Surfaces Chamber

UV-Photocatalysis

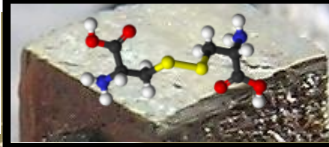


Minerals on Mars

PASC



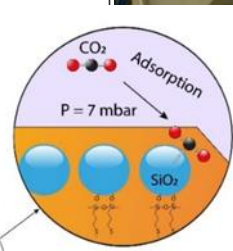
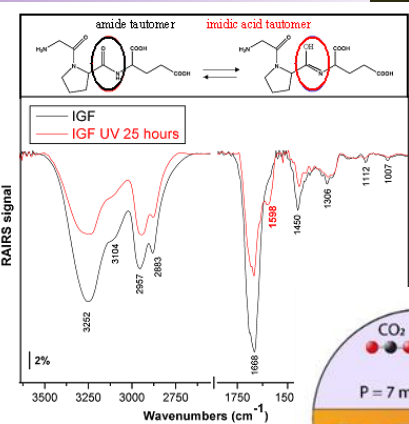
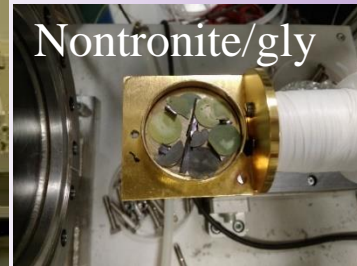
Prebiotic Chemistry



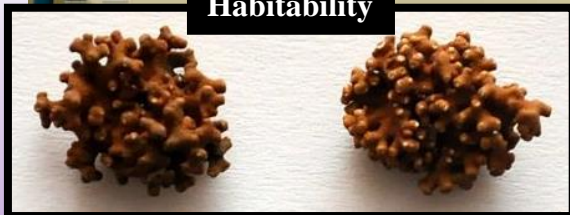
Ceres



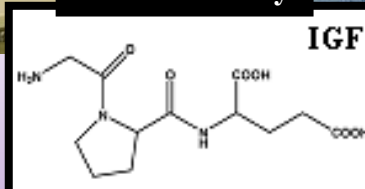
Nontronite/gly



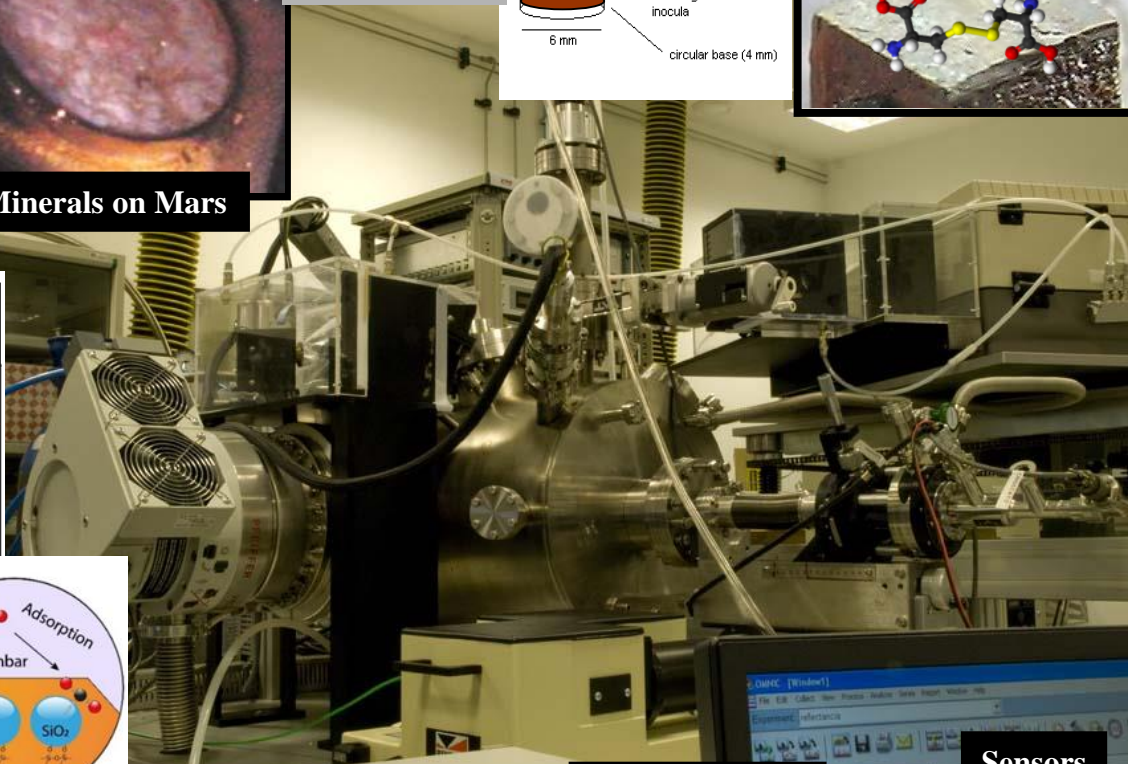
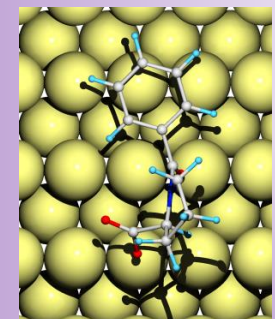
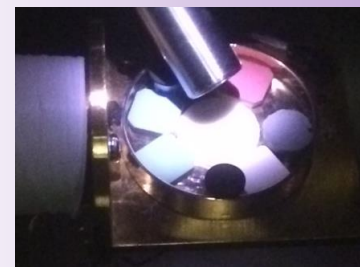
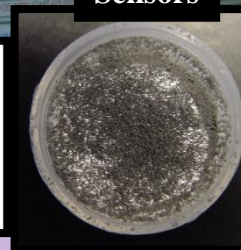
Habitability



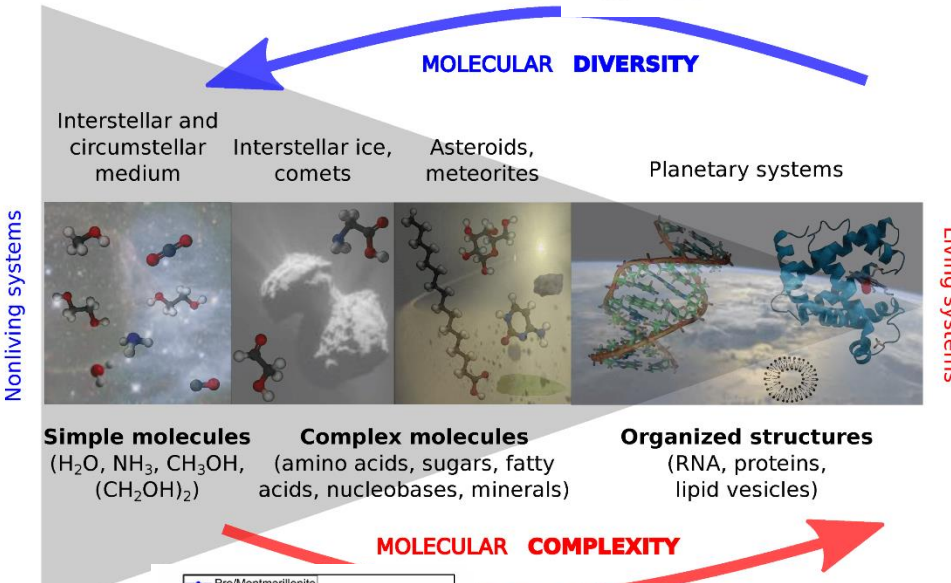
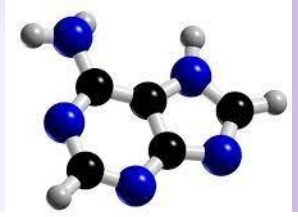
Photochemistry



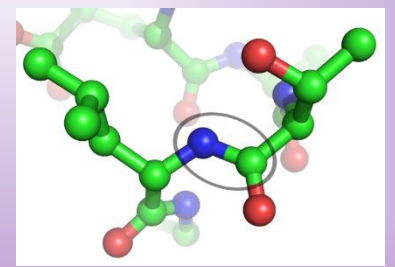
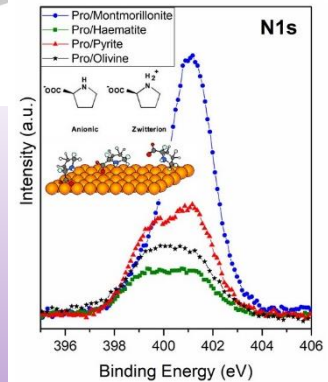
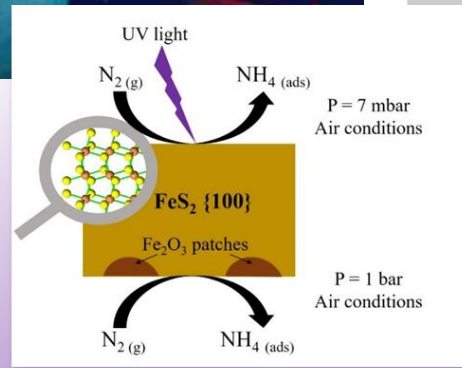
Sensors



The role of molecules on minerals surfaces on the path to molecular complexity



Spectroscopic molecular signatures

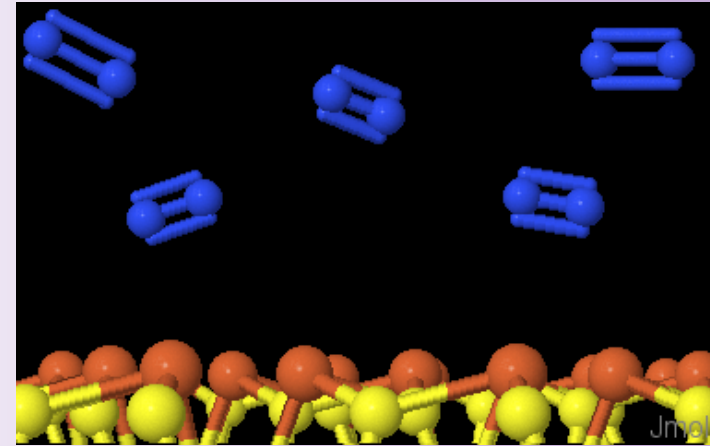




Pyrite-induced uv-photocatalytic abiotic nitrogen fixation: implications for early atmospheres and life

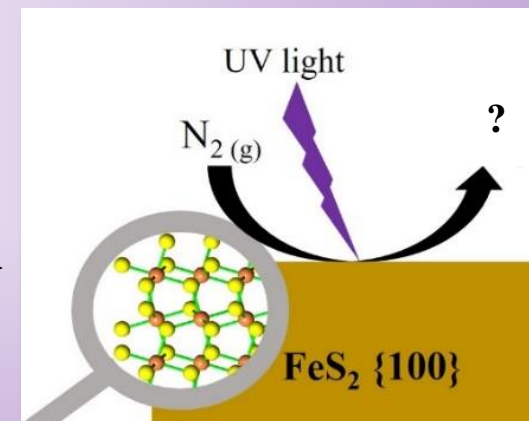
Why do we care about nitrogen?

- **Nitrogen is an essential element for life:** is the building block of many complex organics and prebiotic molecules such as amino acids, nucleic bases, DNA etc...
- Important for the evolution of life, **essential for key metabolic activities** of cells and for the emergence of habitable conditions on Earth



Prior to the emergence of life, there must have been an abiotic process that could fix nitrogen in a biochemically usable form.

Investigate **the role of pyrite on the fixation of molecular nitrogen** and catalysing influence of minerals surfaces with respect to it.



Iron sulphide (FeS_2) is the most abundant sulphide mineral in the Earth's crust. Easily affected by environmental conditions, highly reactive, easily oxidized: **Catalyst**



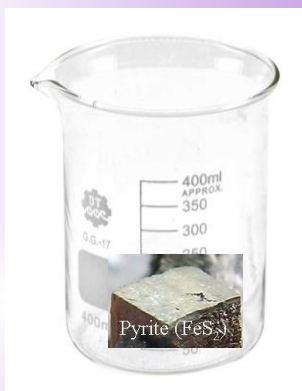
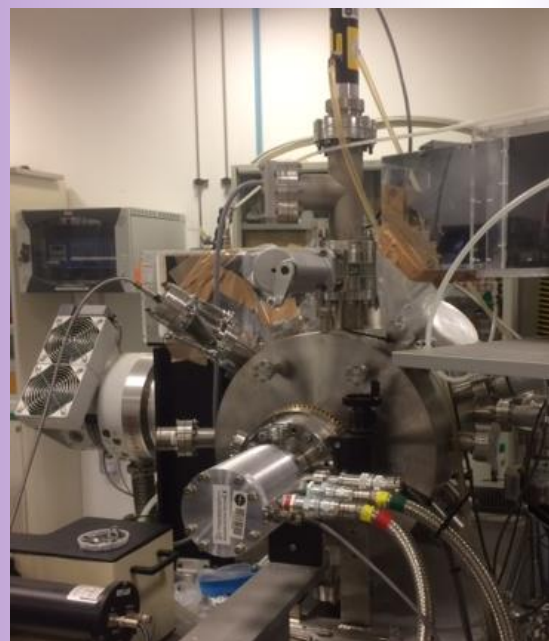
Pyrite-induced uv-photocatalytic abiotic nitrogen fixation

PASC (Planetary Atmospheres and Surfaces Chamber): Experimental

Pyrite surfaces were cleaned in H_2SO_4 solution, water rinsed and dried by blowing compressed air.

P, gas, T^{ra}, UV

Samples were exposed during **two hours** to of ultraviolet irradiance in the **200 nm- 400 nm** range inside **PASC chamber** under these conditions :



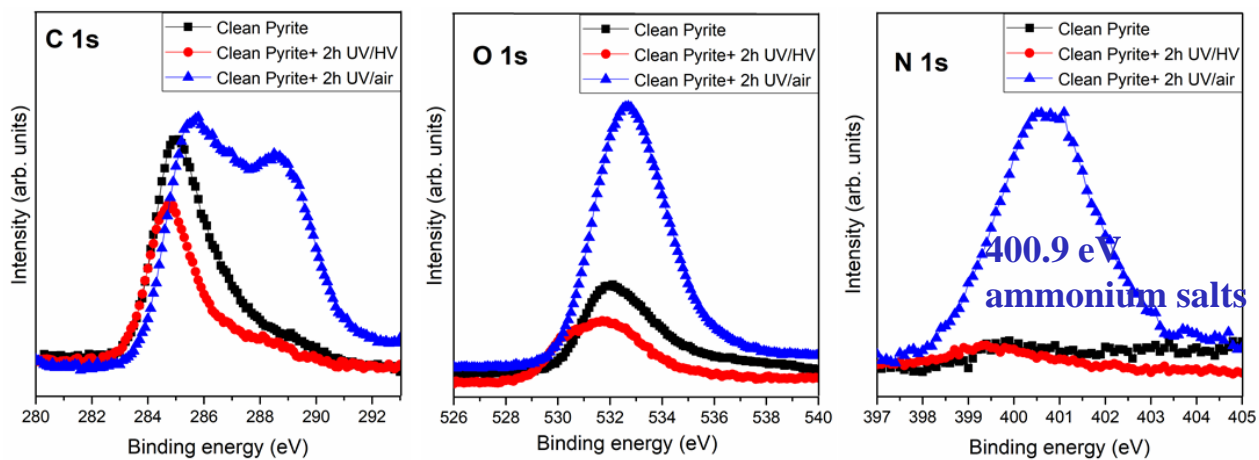
UV	UHV	7 mbar Air	Air
ON	Pyrite	Pyrite	Pyrite
OFF	Pyrite	Pyrite	Pyrite (4 days)

Characterization of pyrite surfaces was performed by XPS and IR spectroscopies before and after the UV exposition.

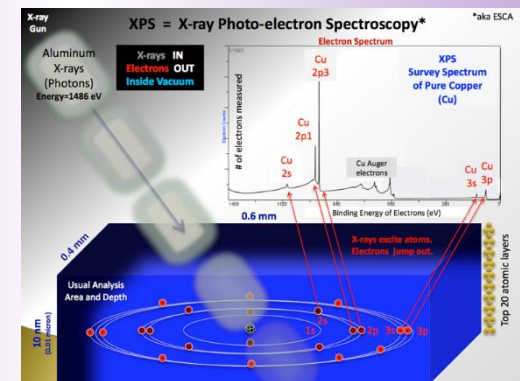
Pyrite-induced uv-photocatalytic abiotic nitrogen fixation

Pyrite surface UV-irradiated under HV and air conditions

XPS photoemission spectra of C 1s, N 1s and O 1s of pyrite surfaces



XPS is a surface-sensitive spectroscopic technique: chemical composition of the surface but it not only shows what elements are present, but also what other elements they are bonded to



Clean pyrite and **HV conditions** shows similar spectral features, no N₂ signature.

Clean pyrite surface exposed to UV/ambient air conditions:

- Appearance of new carbon species as carbonates, C-N and C-S.
- Increased intensity of oxides species.
- Appearance of a strong nitrogen signal after UV irradiation at air conditions.

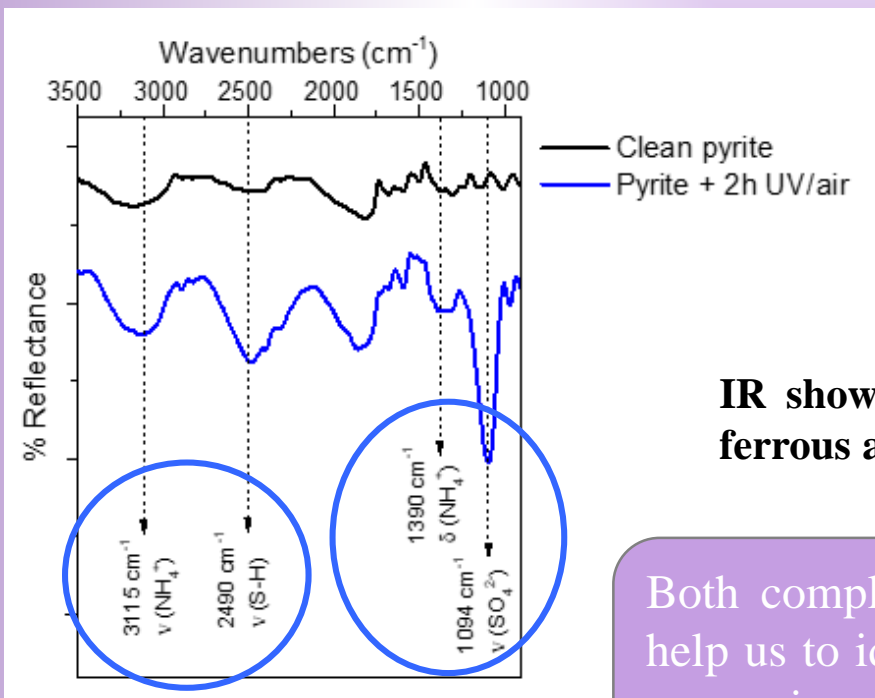
XPS is based on the photoelectric effect, in which a free electron is ejected from an atom after it has absorbed the energy of a photon from a source (X-rays).

$$E_k = h\nu - E_b - \phi$$

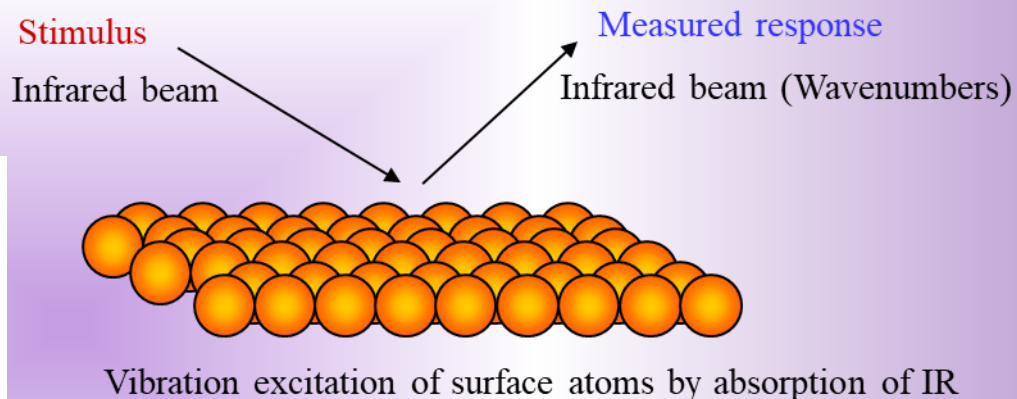
N₂ feature appears only if the UV irradiation process take place in the presence of air. Nitrogen as amonium salt species on the pyrite surface are detected.

Pyrite-induced uv-photocatalytic abiotic nitrogen fixation

Infrared spectrum of clean pyrite surface (black), after 2 hours of UV irradiation at air conditions (blue).



Surface science techniques



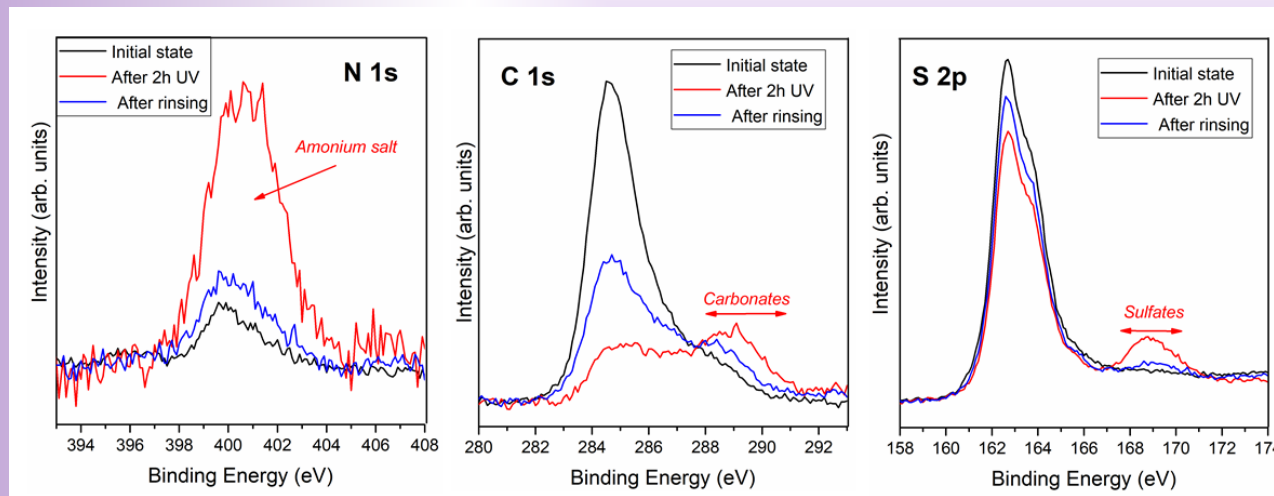
IR shows the appearance of new vibrations frequencies: ferrous ammonium sulfate salt during the UV-photocatalytic.

Both complementary spectroscopies, XPS and infrared, help us to identify the nitrogen signal suggesting ferrous ammonium sulfate as the chemical species formed during the UV-photocatalytic nitrogen fixation process.



Pyrite-induced uv-photocatalytic abiotic nitrogen fixation

XPS photoemission spectra of N 1s, C 1s and S 2p of pyrite surface: **Release of fixed nitrogen.**



Ammonium sulfate salt (an inorganic salt with a high solubility).

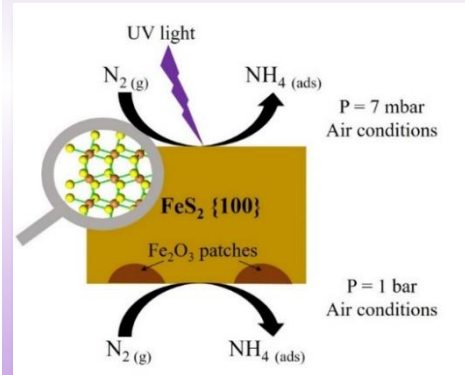
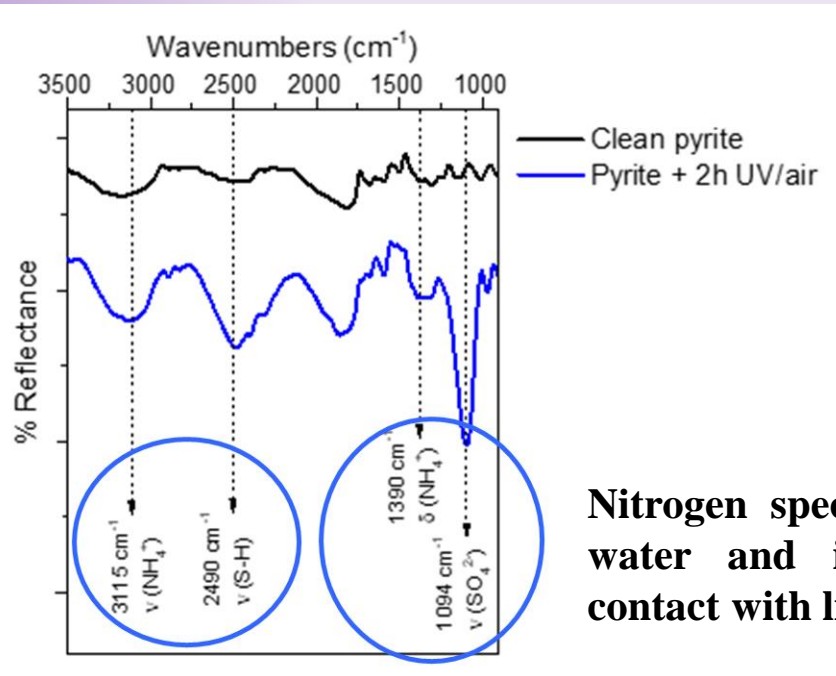
We have rinsed the pyrite surface.

XPS confirms diminution of the nitrogen feature, and decrease of sulfates and carbonates species, which are easily removed from the surface after rinsing with water.

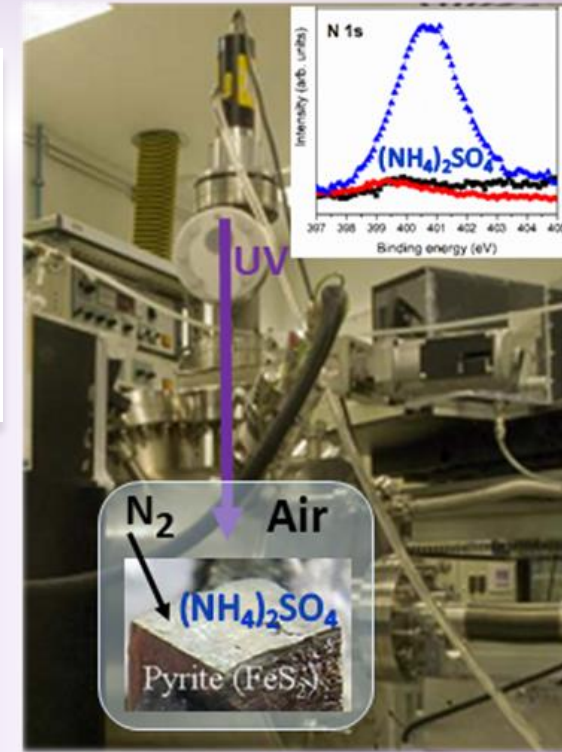
This indicates that the nitrogen species are highly soluble in water, as expected for an ammonium salt, and is easily removed upon contact with liquid water.

Release of fixed nitrogen

ferrous ammonium sulfate

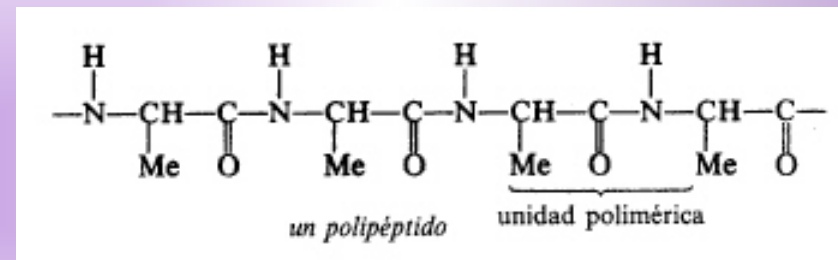
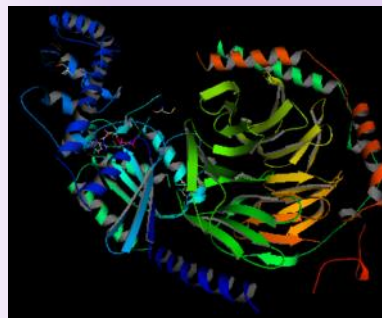
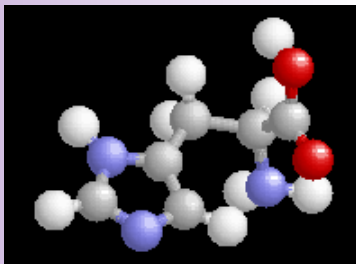
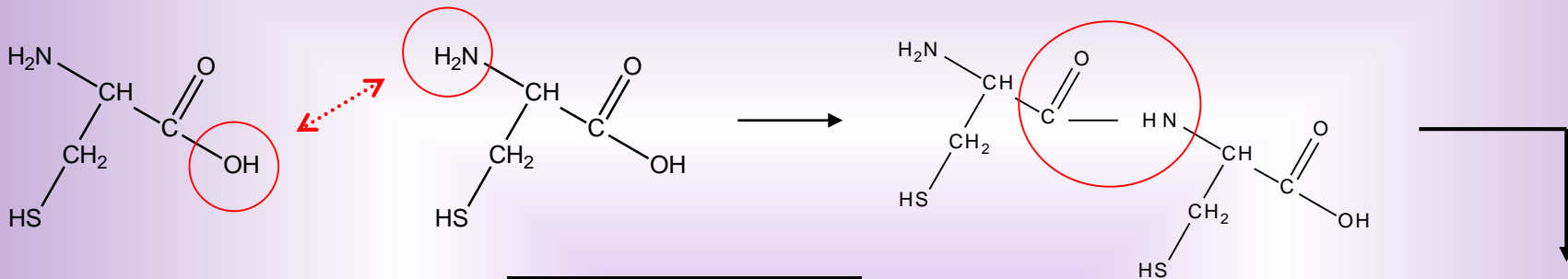


Nitrogen species are highly soluble in water and is easily removed upon contact with liquid water.



A surface of pyrite exposed to a **wet** (liquid water) –**dry** (Solar irradiance) cycle would naturally fix within a few hours of solar exposure atmospheric nitrogen as **ammonium** and then release it when in contact with water. This ammonium is then available for prebiotic chemistry and life, while the pyrite surface is again exposed to the atmosphere and ready for a new catalytic reaction.

Peptides: target molecules



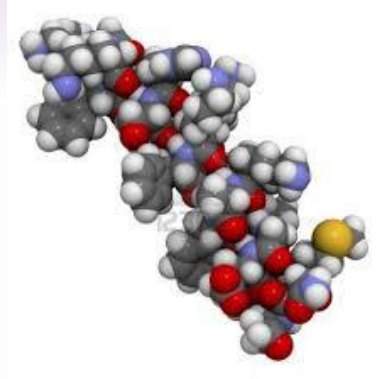
Peptides play a decisive role in many physiological processes.
 Peptidic bonds, at the heart of the majority biomolecules
 Peptides a good model to learn about more complex molecules

To studying **chemical changes induced by UV irradiation**, therefore trapping primary products of **photochemical transformations**.

Matrix isolation technique

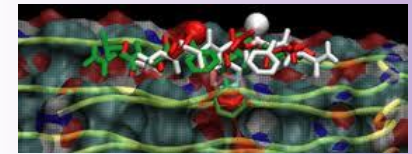
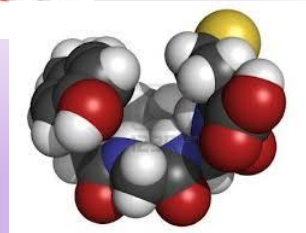
Peptides isolated argon matrix as a way of testing their stability under irradiation process

UV

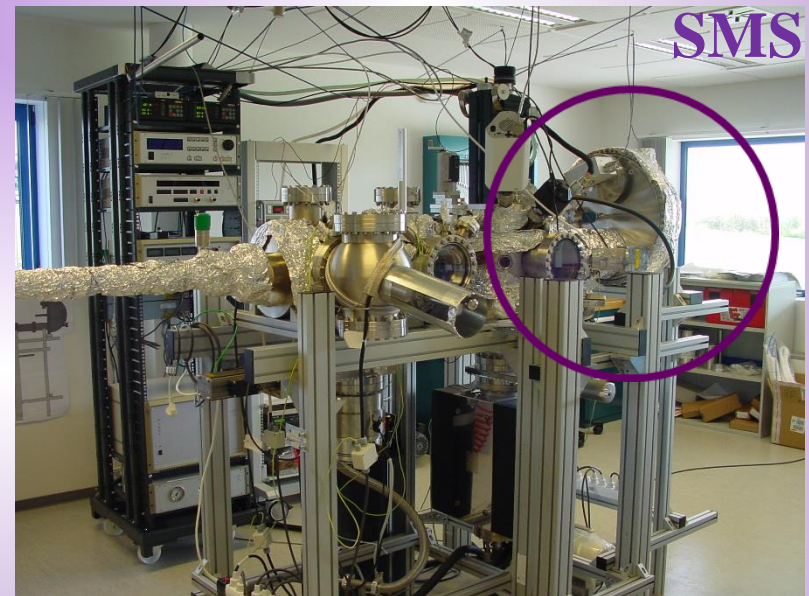


Molecular Detection

Biological Activity



How?



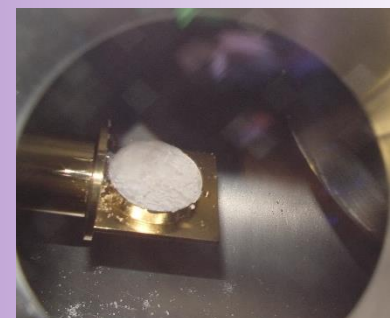
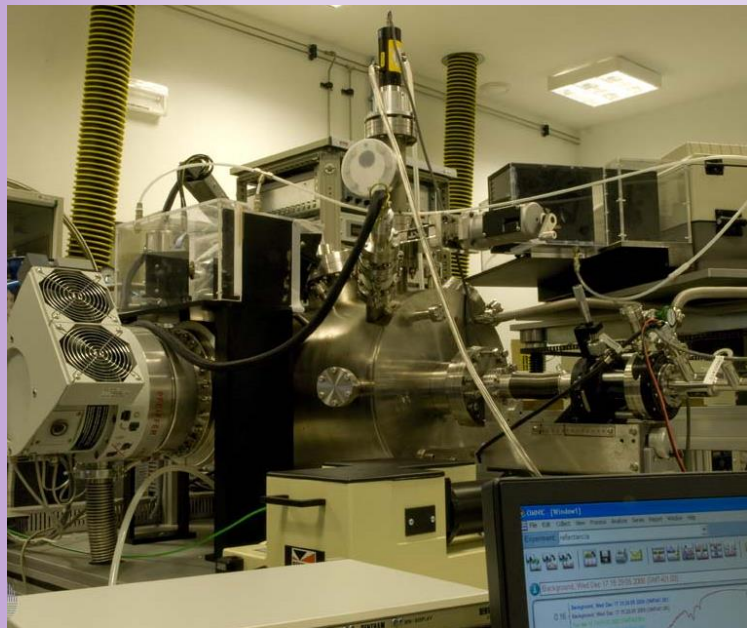
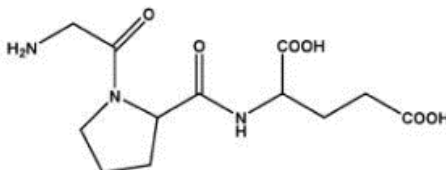
Study of a peptide under UV irradiation by combining RAIRS and XPS expecting considerable changes in the molecule functionality (bioactivity).



Peptides: target molecules

Involved in numerous biological processes

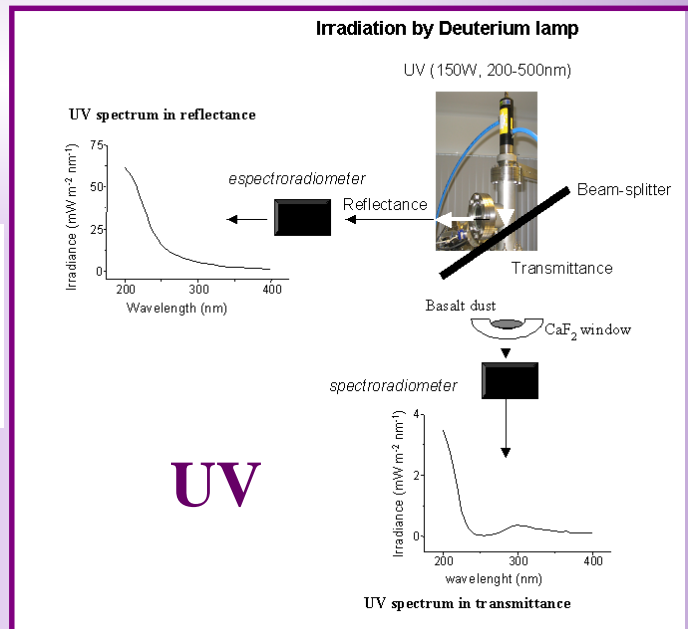
Gly-Pro-Glu



The matrix isolation technique: co-deposition of noble gas together with vapors of a studied compound onto a cold window placed on a cold finger of a cryostat.

IR bands are efficient fingerprints of molecular functional groups. **XPS and IR** characterizing chemical changes of molecules upon UV-irradiation, being **highly sensitive and non-destructive**.

Peptide-argon matrix, under clean vacuum conditions, investigating its stability/reactivity

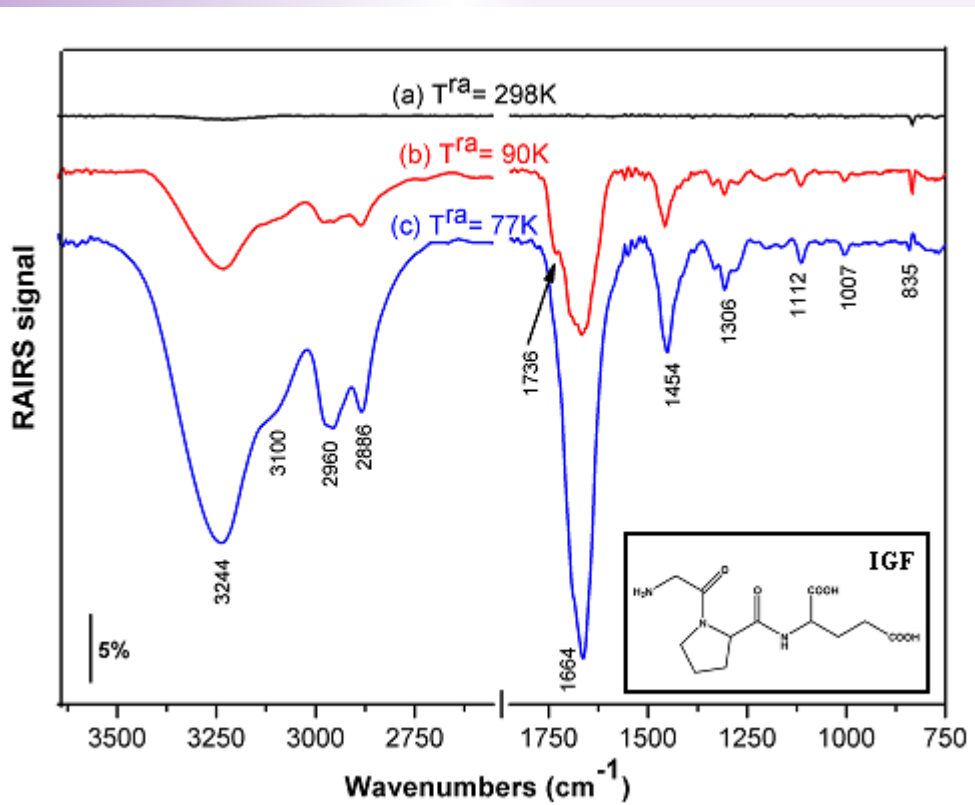


RAIRS



FT-RAIRS characterization of IGF Ar⁺ matrix formation

RAIRS recorded during IGF argon matrix formation under vacuum conditions at different T^{ra}



Ar+ Matrix deposition:

RT no vibration molecular features observed
90 K appear some IR bands related to the IGF
77 K the infrared bands became more intense

Amide I band of the peptide 1664 cm⁻¹ (C=O str).

N-H bonds str 3244 cm⁻¹

The amide III 1220–1300 cm⁻¹ (C-N and C-C stretching /N-H in-plane and C-O bending vib)

Backbone peptide structure (CH₂ 2960, and 2886 cm⁻¹, CH₂ scissor 1454 cm⁻¹)

RAIRS confirm the presence of the intact IGF molecule in this new condensed phase.



FT-RAIRS characterization of IGF Ar⁺ matrix formation

IGF in argon was then UV irradiated 25 h.

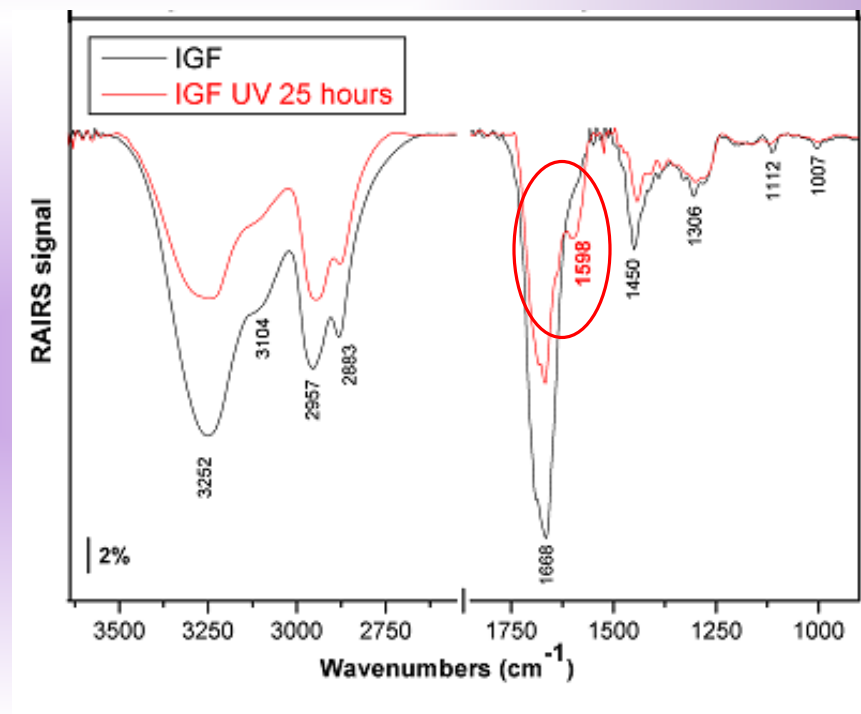
Bands assigned to several chemical groups of IGF

Changes in the intensity and shape after irradiation.

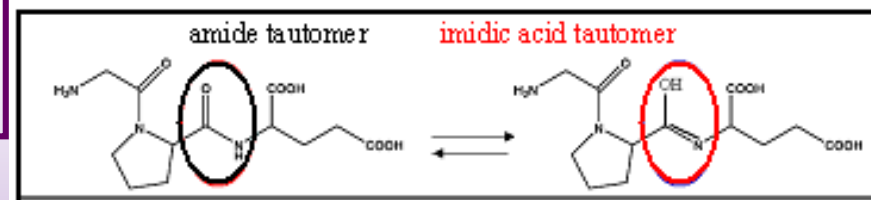
Appearance of a **new infrared band at 1598 cm⁻¹** (COO⁻ /a C-N group; tautomeric amide to imide conversion)

After UV irradiation, peak at 1668 cm⁻¹ (C=O-NH-) amide, partial conversion into the imidic acid at 1598 cm⁻¹ (COH=N-).

RAIRS: IGF argon matrix before and after UV.



A phototautomerism process:
which involves **proton transfer** or H from one functional group to another, and a **switch of a single bond and its adjacent double bond**.

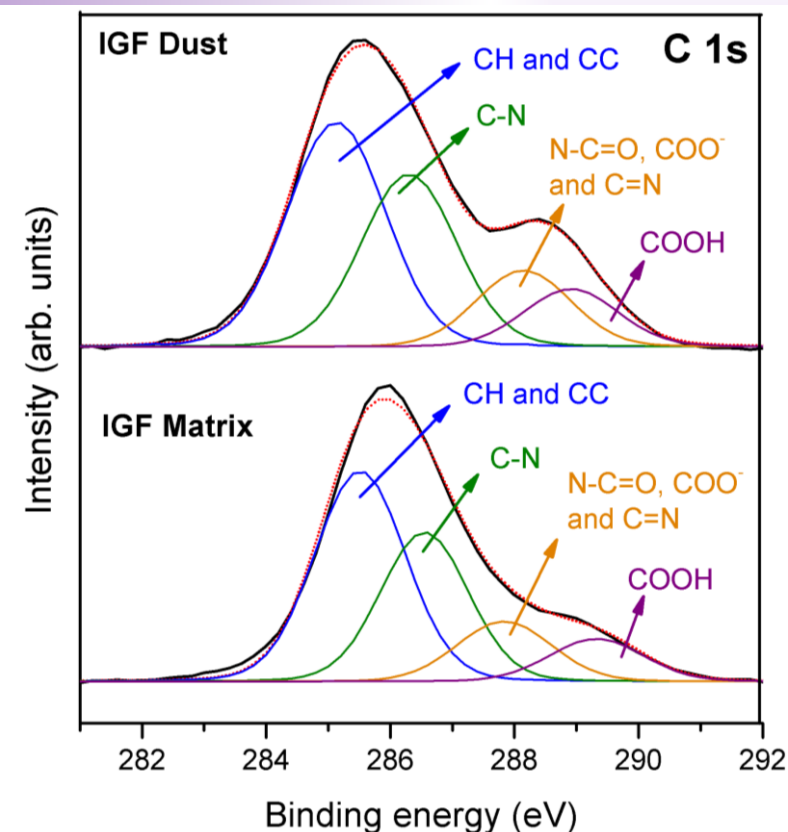


Difficult to undoubtedly confirm tautomerism/assign other bands related to the imidic form due to the overlapping of the infrared frequencies



XPS characterization of the IGF dust and argon matrix

XPS analyses of the IGF samples, dust or in matrix, were expected to **help making clear the chemical changes induced by UV irradiation and suggested by the RAIRS spectra**; hopefully XPS can help discriminating between a deprotonation of the carboxylic groups and a conversion between the amide and imide tautomers.

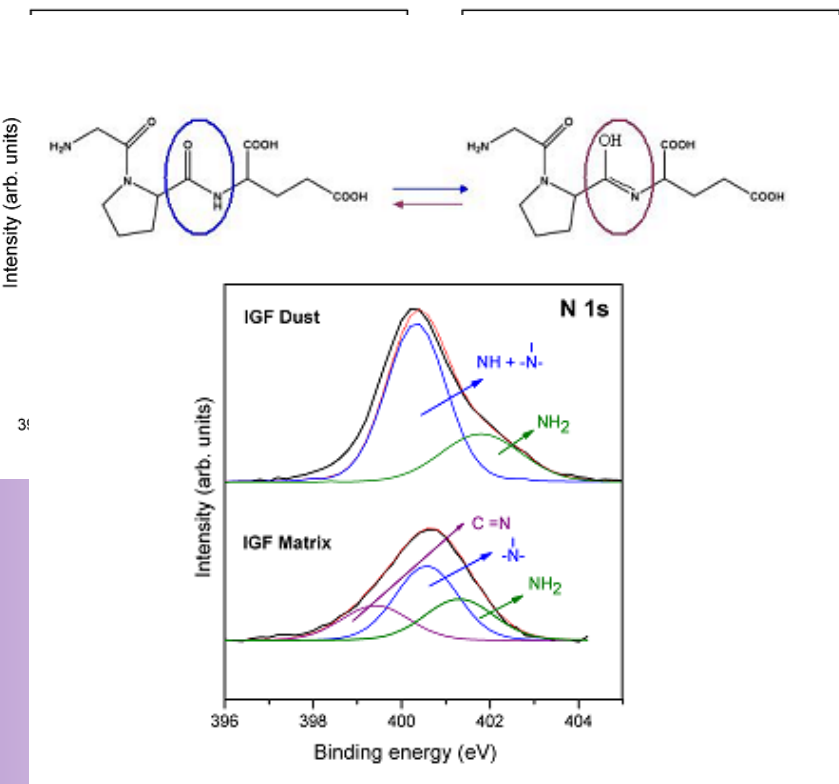


Element	BE	IGF dust Assignment	% (± 2)	BE	IGF-Matrix Assignment	% (± 2)
C	285.1	CH, CC	43	285.5	CH, CC	46
	286.3	C-N	32	286.5	C-N	31
	288.1	N-C=O, COO ⁻ , C=N	14	287.9	N-C=O, COO ⁻ , C=N	13
	289.0	COOH	10	289.3	COOH	10
N				399.4	C=N	23
	400.3		73	400.5		48
	401.7	NH ₂	27	401.3	NH ₂	29
O	531.6	C=O	76	531.6	C=O	58
	533.2	OH	24	533.2	OH	42

Comparison of XPS core-level peak of C(1s) for IGF dust and IGF matrix.

Not any observable changes in the C 1s peak (C=O decreases compensated by new C=N groups).

XPS characterization of the IGF dust and argon matrix



	<u>IGF dust</u>			<u>IGF-Matrix</u>	
BE	Assignment	% (± 2)	BE	Assignment	% (± 2)
			399.4	C=N	23
400.3		73	400.5		48
401.7	NH ₂	27	401.3	NH ₂	29
531.6	C=O	76	531.6	C=O	58
533.2	OH	24	533.2	OH	42

O 1s and N 1s peaks show significant changes in their shapes.
O 1s peak, OH groups, increases, to expend of C=O.
N 1s presents three components, two at similar B.E. as before UV irradiation, ca 400.5 eV and 401.3 eV, and a new one at 399.4 eV

XPS data are in agreement with hypothesis of tautomerism form amide to imide.
XPS can confirm a conversion between the amide and imide tautomers

These O 1s and N 1s peak modifications suggest that **part of the C=O and C-NH bonds have been converted to C-OH and C=N ones respectively**, in other words, that **some of the IGF molecules initially under the amide form, have been converted into the imidic form**; in good agreement with a partial conversion of the IGF peptide into the imidic tautomer

Influence of UV irradiation on peptides isolated argon matrix as a way of testing their stability under irradiation process

Successful formation of the tripeptide (IGF) argon matrix under vacuum conditions.

Spectroscopic characterization of peptide matrix reactivity before/ after UV-irradiation.

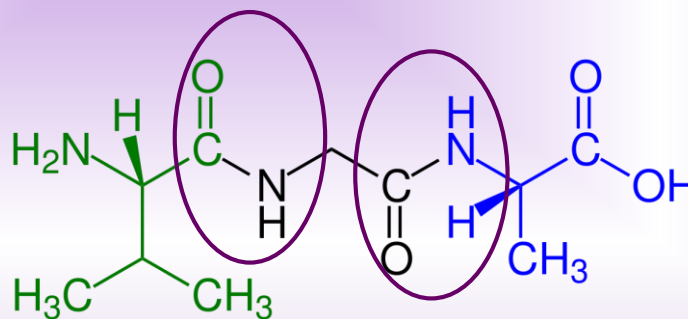
Spectroscopy evidence that UV irradiation of peptides induces tautomeric transformation.

Matrix isolation is a powerful tool for studying photochemical process of peptides.

Peptidic bonds are fragile under UV irradiation part of them undergo into imidic acid form.

Important conclusion is:

Peptidic bonds, at the heart of many biomolecules, are fragile under UV irradiation; part of them rapidly undergo a transformation into the imidic acid form.

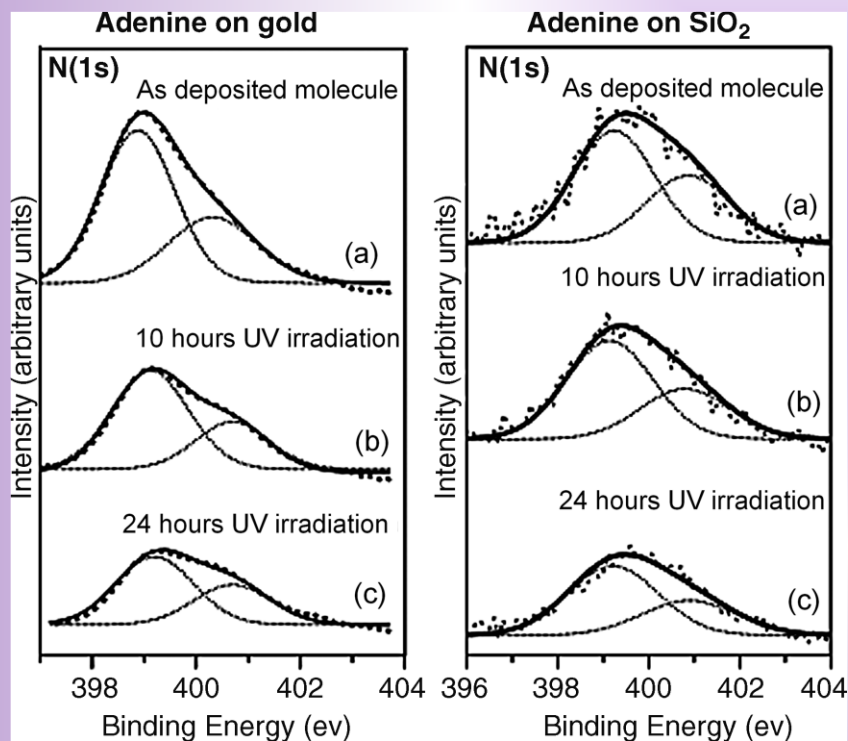
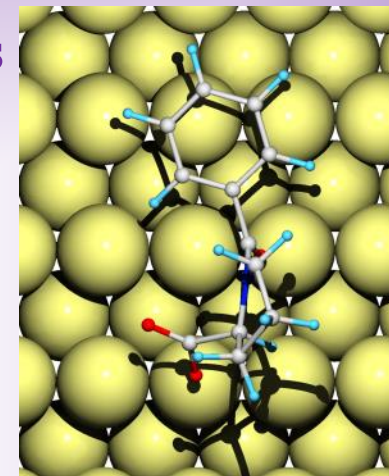


Detection and chemistry of biomolecules in the solar system/Space exploration

Stability of biomolecules on surfaces under planetary environments

We have studied the **photostability and photochemistry of adenine** molecule, and chemical binding on surfaces (gold/silicon), by **XPS** and **RAIRS** techniques.

UV radiation under interplanetary space conditions induces desorption and partial dissociation of the molecule, which is dependent on surface nature.



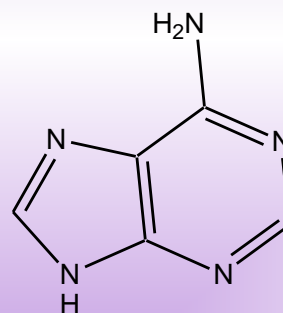
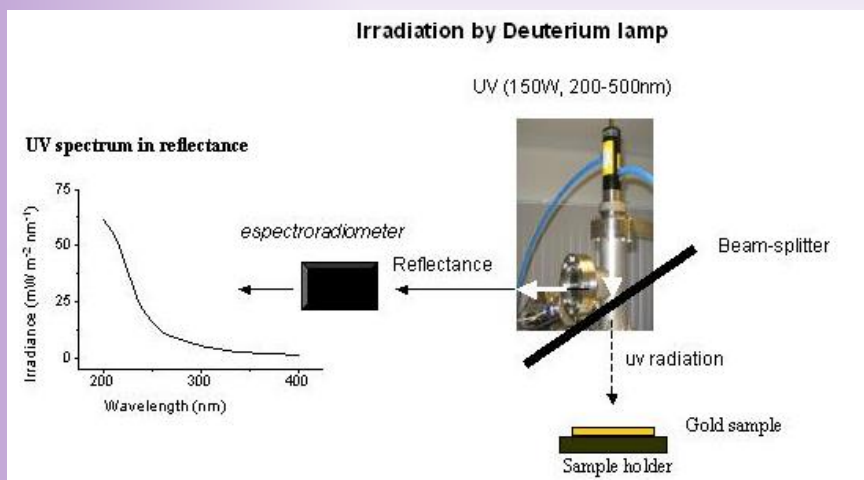
Biomolecular stability and the role play by surface (metallic and mineral):

- **Nucleobases** (similar chemical forms) **fragment easily** when adsorbed **on metallic grains**.
- Chemical reactions that allow for **the assembly** of superior molecular structures could be easily catalyzed **on mineral oxide surfaces (as sand or clays)** rather than on metallic rocks.

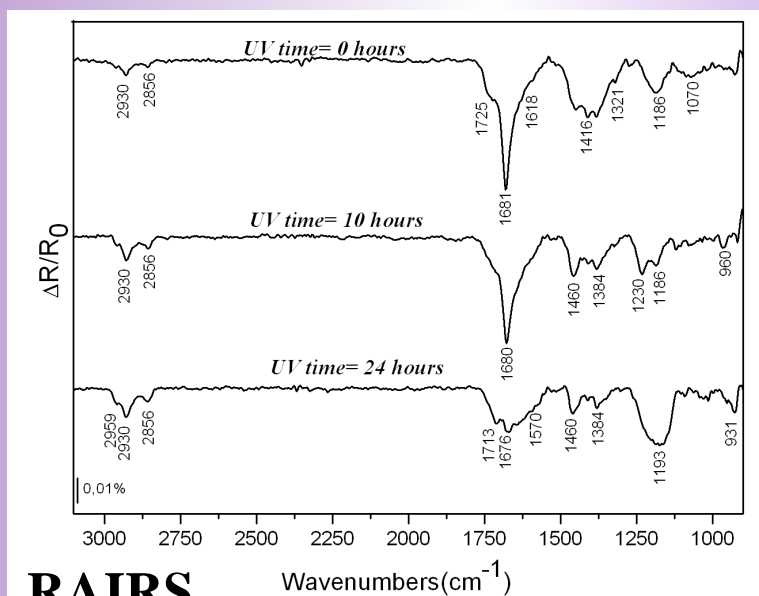
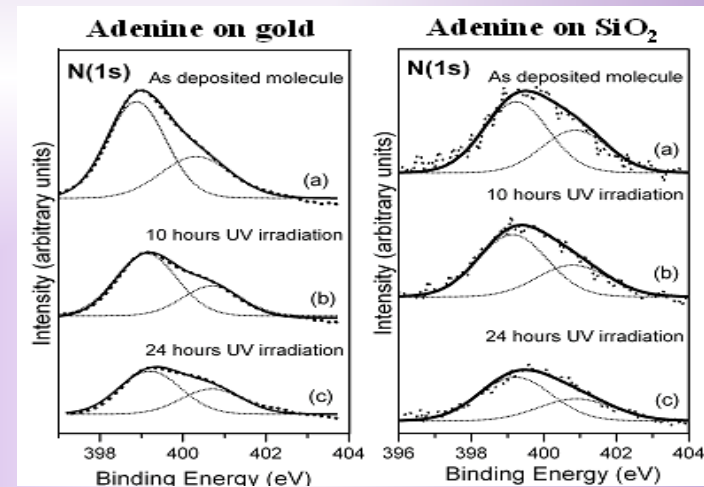
Implications: prebiotic chemistry and relevant to an understanding of lifetime and abundance of these molecules in space

Photostability studies of adenine nucleic base on Au and Si

XPS



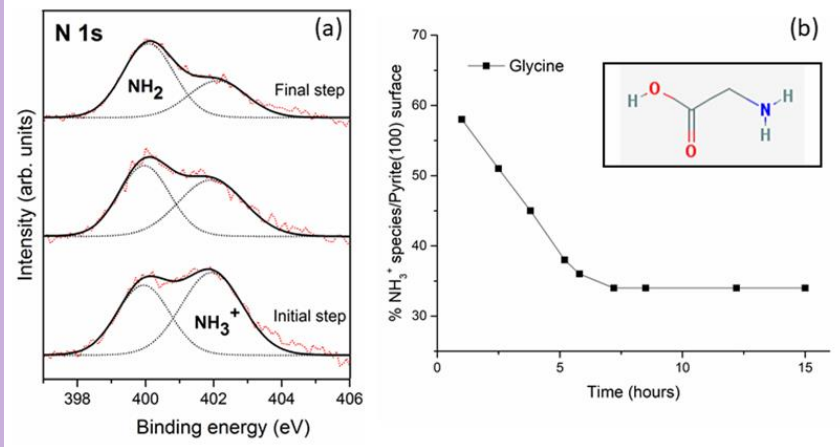
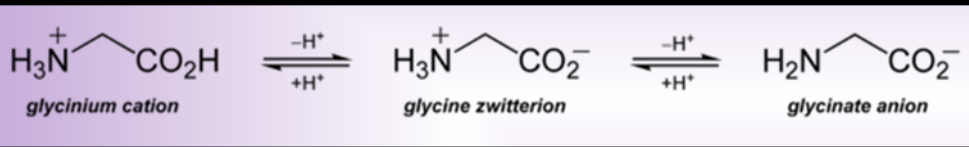
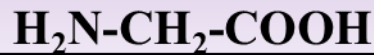
Adenine



An **unambiguous signature** of the presence of the molecule on the surface is N peak. Molecule adsorbs as an **entire entity**

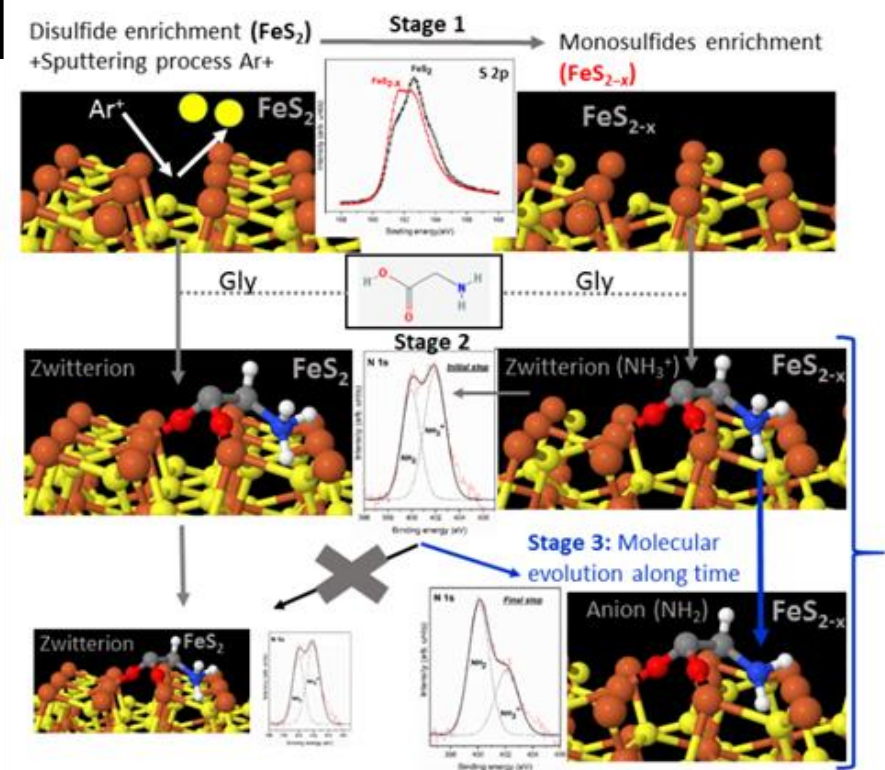
- Surface plays an important role on the photostability of molecules
- Nucleobases could enlarge their resistant against UV radiation when adsorbed on isolating or semiconducting surfaces

Chemical evolution of amino acids on surfaces



Pyrite surfaces favor the adsorption of **zwitterion** species. Chemical species of **glycine molecule on pyrite surface evolve from zwitterion form to anionic form with time.**

Scheme of different stages of the atomic evolution of the mineral and molecular chemistry of pyrite.



***Stage 1:** Disulfide conversion to monosulfides by Ar^+ sputtering, with generation of S vacancies and Fe dangling bonds

***Stage 2:** Molecular adsorption on both surfaces

***Stage 3:** Chemical molecular evolution over time on monosulfide surface (with sulfur vacancies). Disulfide surfaces (without sulfur vacancies) do not show a molecular evolution

Atomic structure of a mineral's surface influences the **chemical form of the adsorbed molecule**, the surface nature (environment conditions) crucially drives the molecular chemistry.

Different mineral compositions modify the molecular/surface interaction

We have performed the first spectroscopic characterization of **L-proline adsorption on different minerals of prebiotic interest, such as montmorillonite, olivine, iron disulfide and haematite**

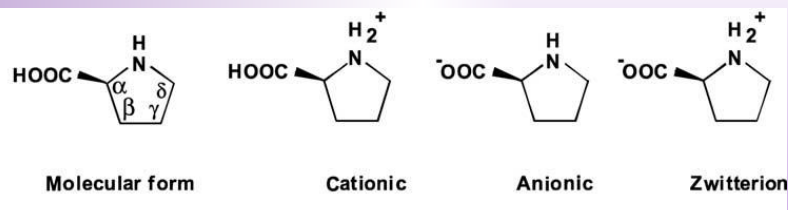
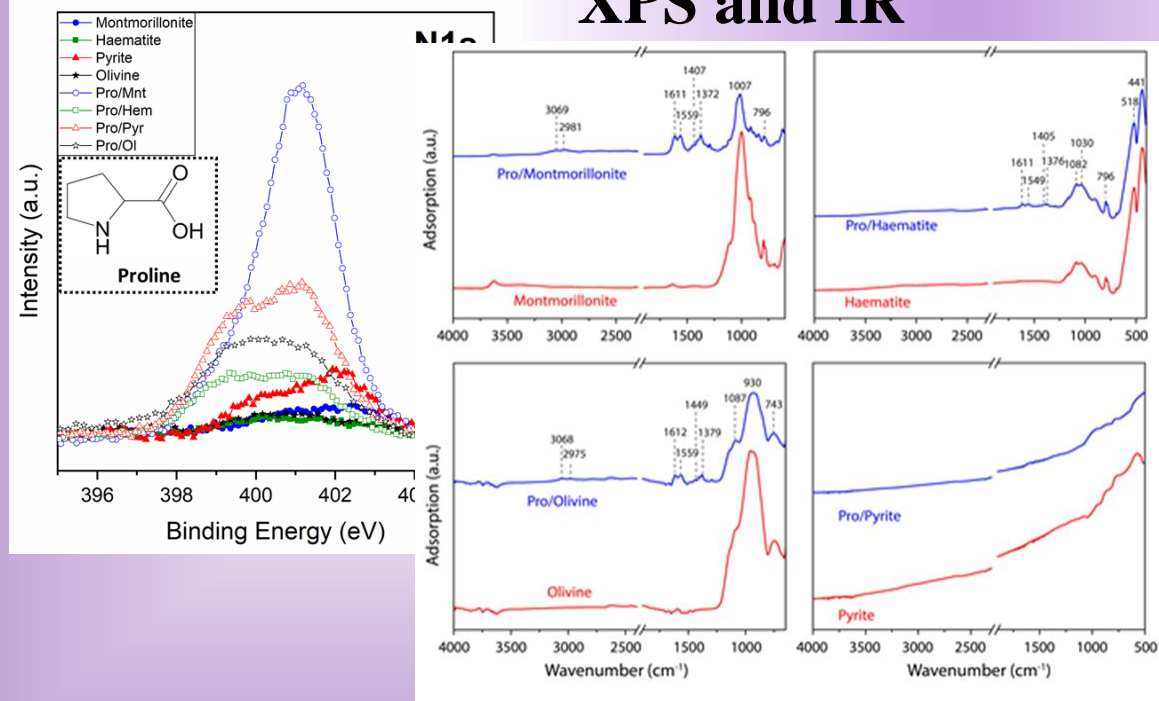


Table 2. Summary of the proline species percentages adsorbed on each molecule/mineral studied system.

System of study	Anion	Zwitterion	Mineral composition
Pro/Mnt	19%	81%	Mg, Ca, Na silicate
Pro/Iron disulfide	65% (+ N-Fe)	35%	Iron sulfide
Pro/Ol	57%	43%	Fe Mg silicate
Pro/Hem	50%	50%	Iron oxide

XPS and IR



Each mineral present affinity towards one of the two preferable molecular forms of L-proline.

Functional groups more kindred to the mineral surface, thus leaving the groups less reactive with the mineral free and available to activate chemical reactions with other molecules, leading to an increase in chemical complexity.

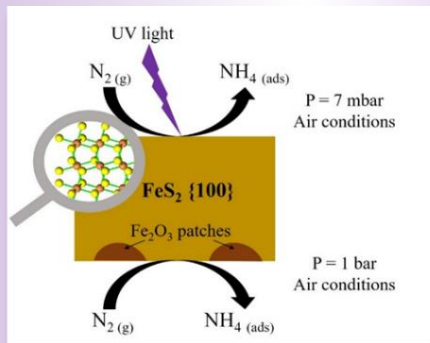
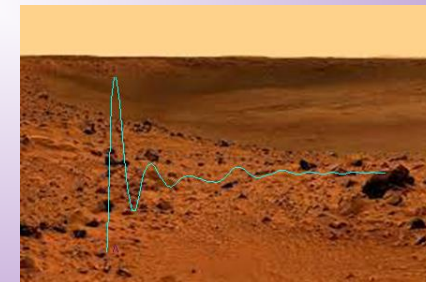
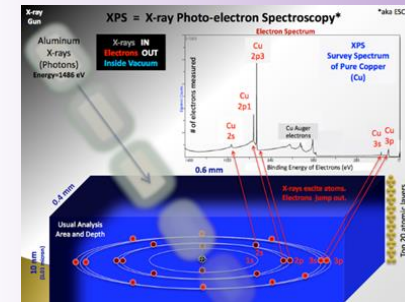
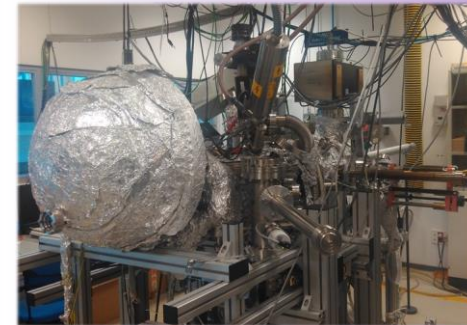
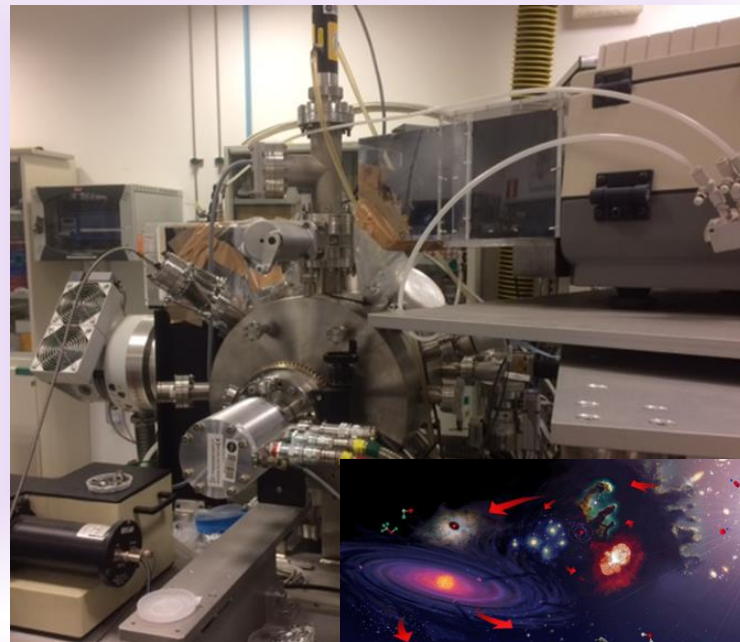
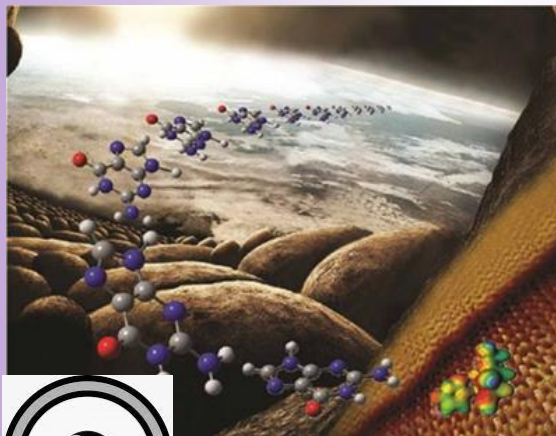
Search for minerals with the highest molecular concentration potential, and capable of protecting the molecules in their structure from UV damage.

Conclusions

UHV Chambers: Planetary Atmospheres and Surfaces Chamber

Interaction processes
Molecules/surfaces

*Surface Science
approach*



Prebiotic Chemistry
Planetary exploration

It is relevant to study these processes at the atomic surface level.



How to deal with “Nuclear Astrochemistry”?

How can we study it?

Several approaches?

Surface science approach to study biomolecules/ mineral surfaces interaction under geochemical or space? constrains

Molecules?

Minerals, surfaces?

Environment Context?

Energy and irradiation?

Tools, techniques and theory?

