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Chemical evolution of organic molecules under Mars-like UV radiation conditions simulated in the laboratory with the MOMIE setup

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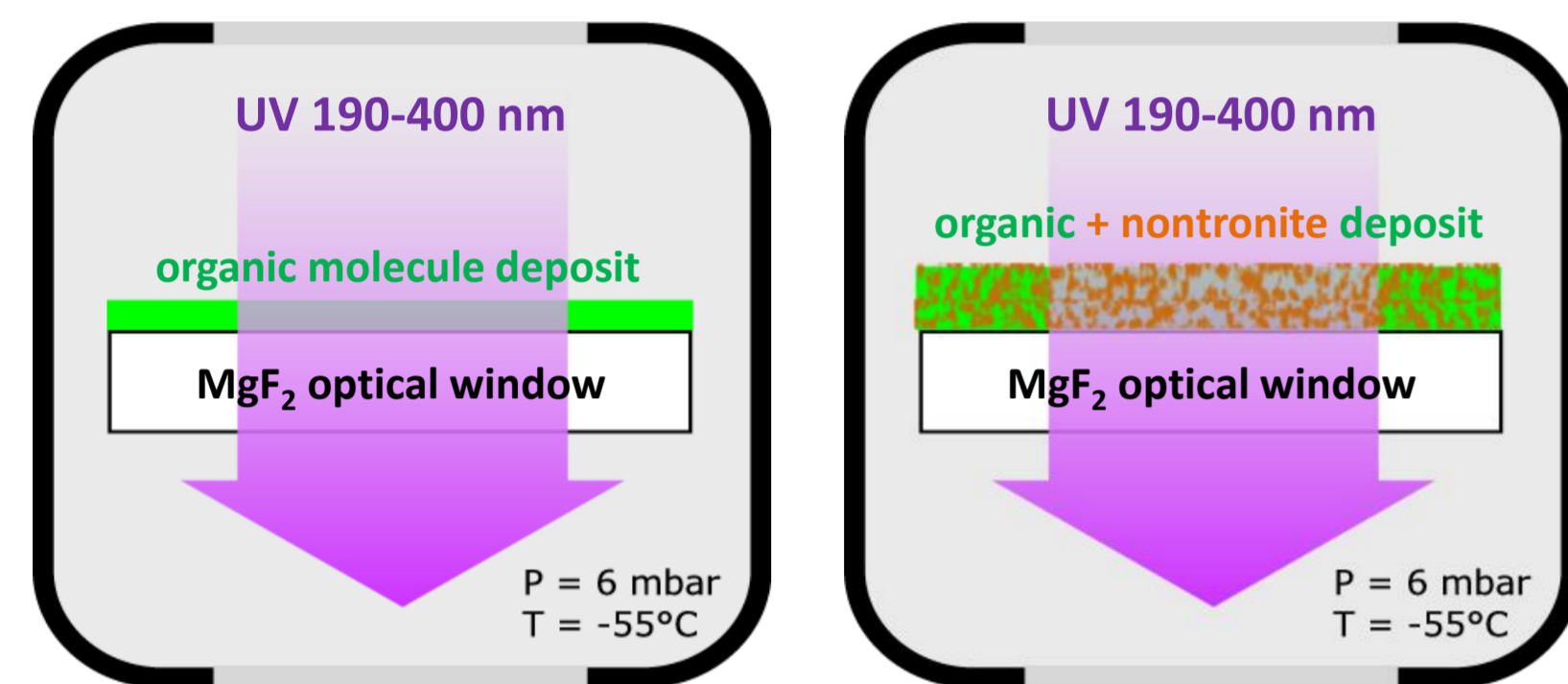
Introduction - The search for organic carbon at the surface of Mars, as clues of past habitability or remnants of life, is a major science goal of Mars' exploration. Understanding the chemical evolution of organic molecules under current Martian environmental conditions is essential to support the past, present and future analyses performed *in situ*. What molecule can be preserved? What is the timescale of organic evolution at the surface? Here we present laboratory work addressing these questions.

Laboratory simulations and samples:

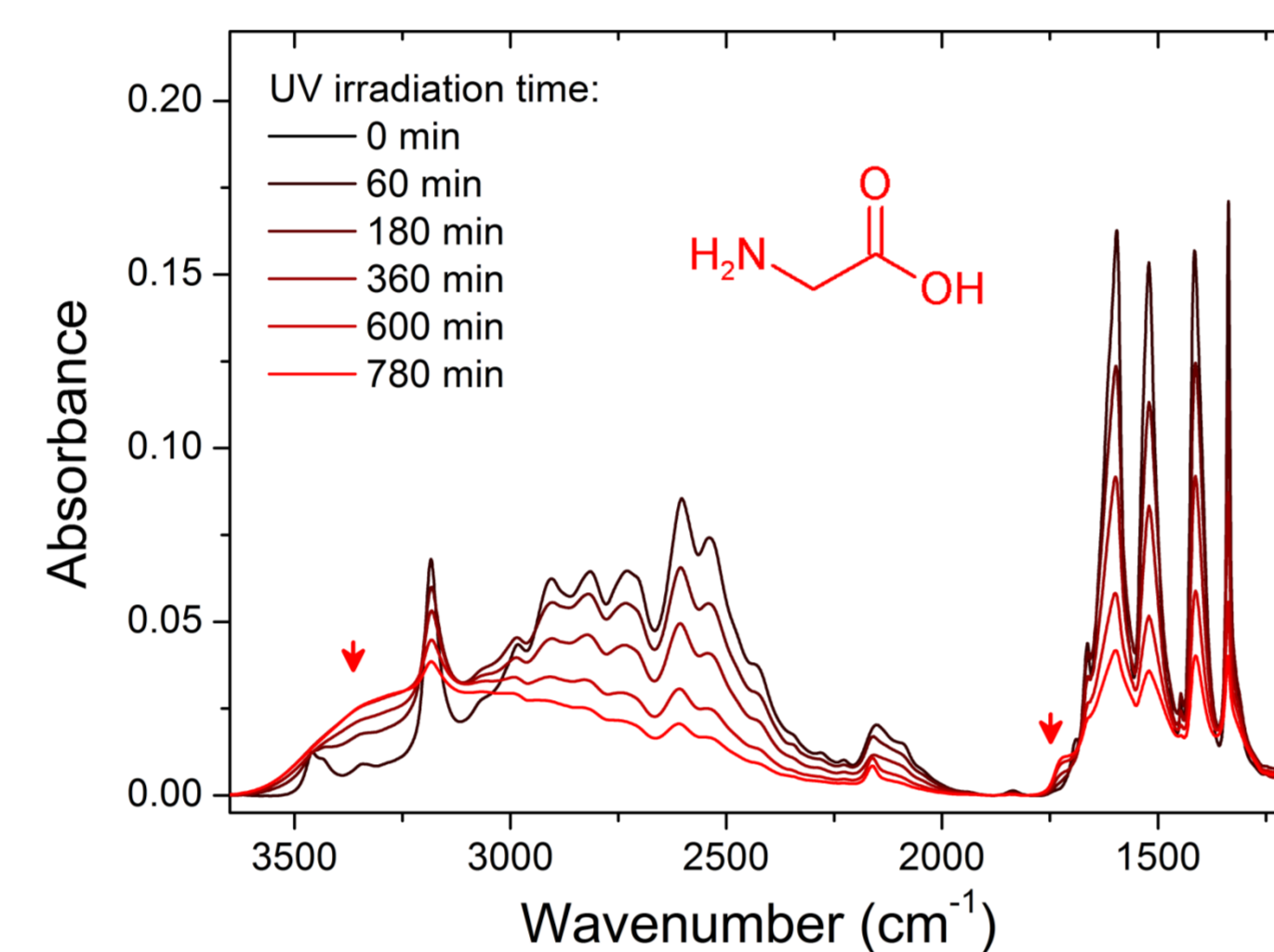
We have performed laboratory investigations dedicated to monitor qualitative and quantitative evolutions of several organic molecules under **simulated Martian surface ultraviolet light (190-400 nm), mean temperature (218±2 K) and pressure (6±1 mbar)**, using the Mars Organic Molecules Irradiation and Evolution (MOMIE) setup (right and [1]).

We have studied **organic molecules representative of endogenous and exogenous sources at Mars**, and spanning a wide range of chemical functions: an amino acid (glycine), a PAH (chrysene), a nucleobase (adenine), a carboxylic acid (mellitic acid) and urea.

To match closely their mineral environment at Mars, some of **these molecules were put in interaction with nontronite**, one of the most abundant clay mineral detected on Mars [2], especially in Gale crater [3]. Both pure organic deposits and deposits of organics mixed with nontronite (below) were submitted to the simulated Mars surface conditions in the MOMIE setup (right). This experimental protocol enables to assess the effect of the clay mineral on the chemical evolution of the organic molecules.



Scheme of two possible configurations of the sample inside the MOMIE reactor.

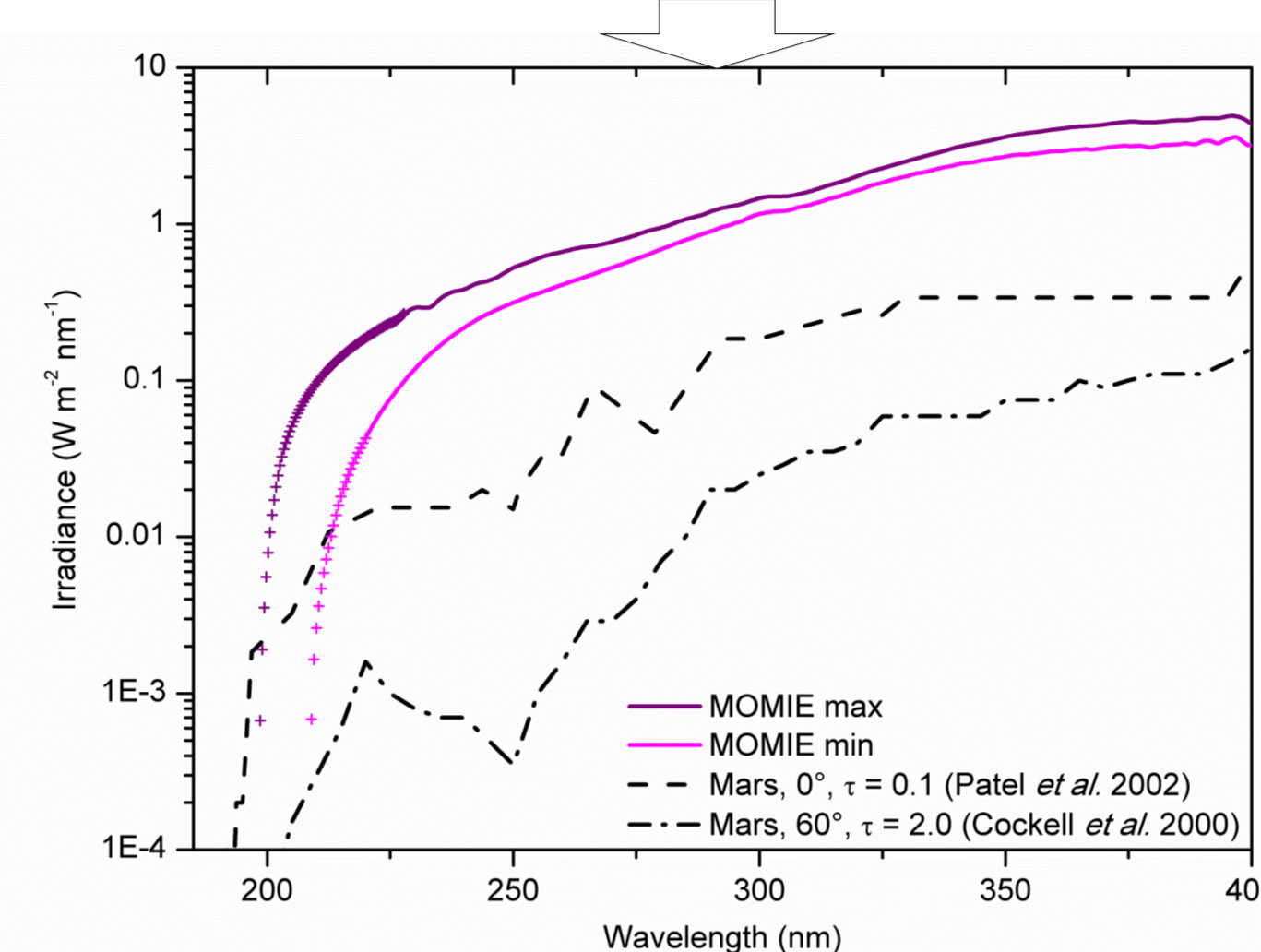


In-situ FTIR spectra of a sample of pure glycine during a simulation [1].

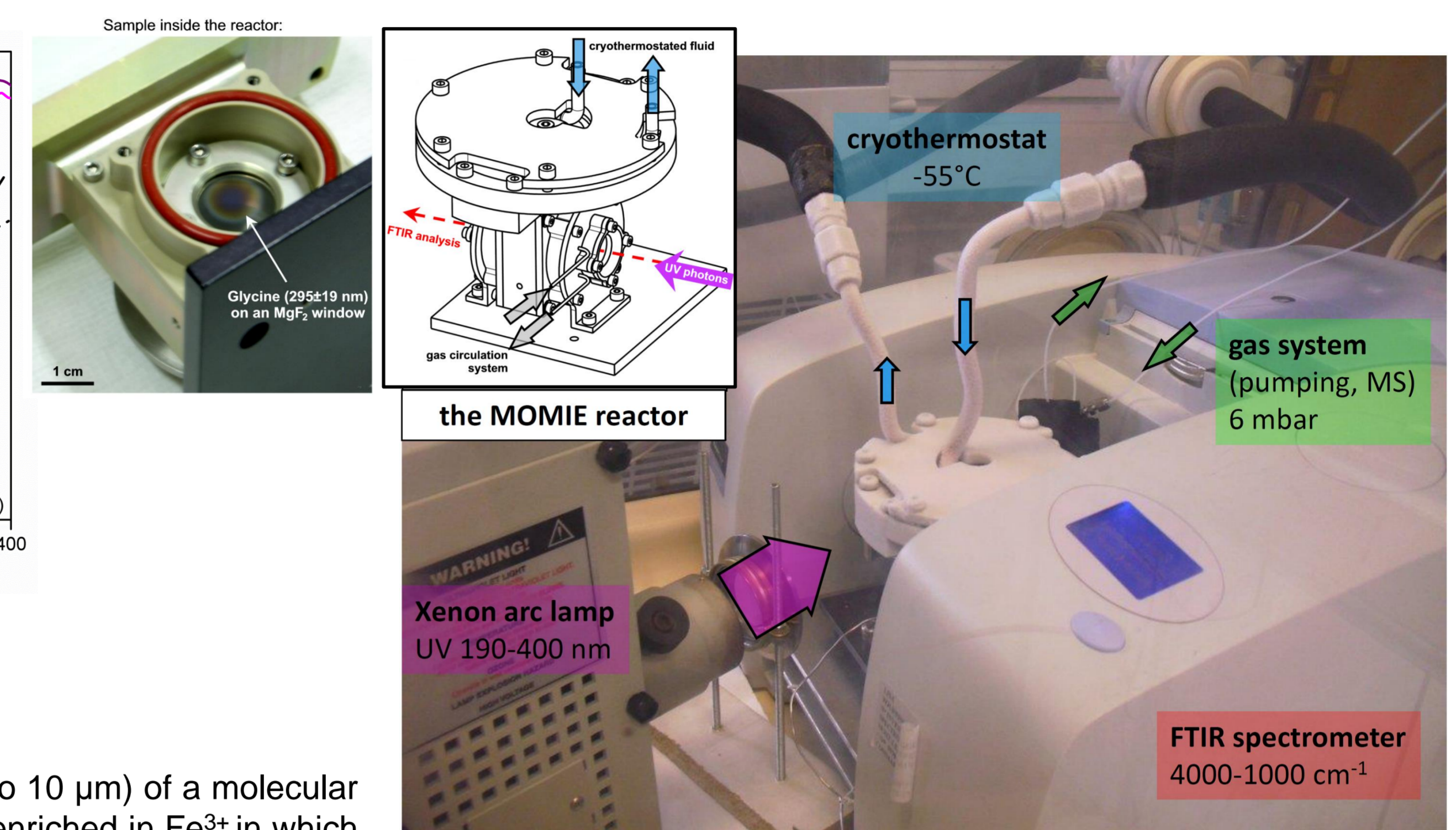
Samples consisted of thin deposits (from 10 nm to 10 μm) of a molecular compound or of synthetic smectite clay nontronite enriched in Fe³⁺ in which the organic compound has been embedded (left).

During the simulations, qualitative and quantitative changes were monitored, mainly using *in situ* transmission infrared spectroscopy (left), and also UV spectroscopy and GC-MS analyzes. These data allow the determination of kinetic parameters controlling the evolution of organic molecules directly exposed to the solar UV flux reaching the Mars surface, or in interaction with Fe³⁺-nontronite clay (see results below).

UV irradiance reaching the samples

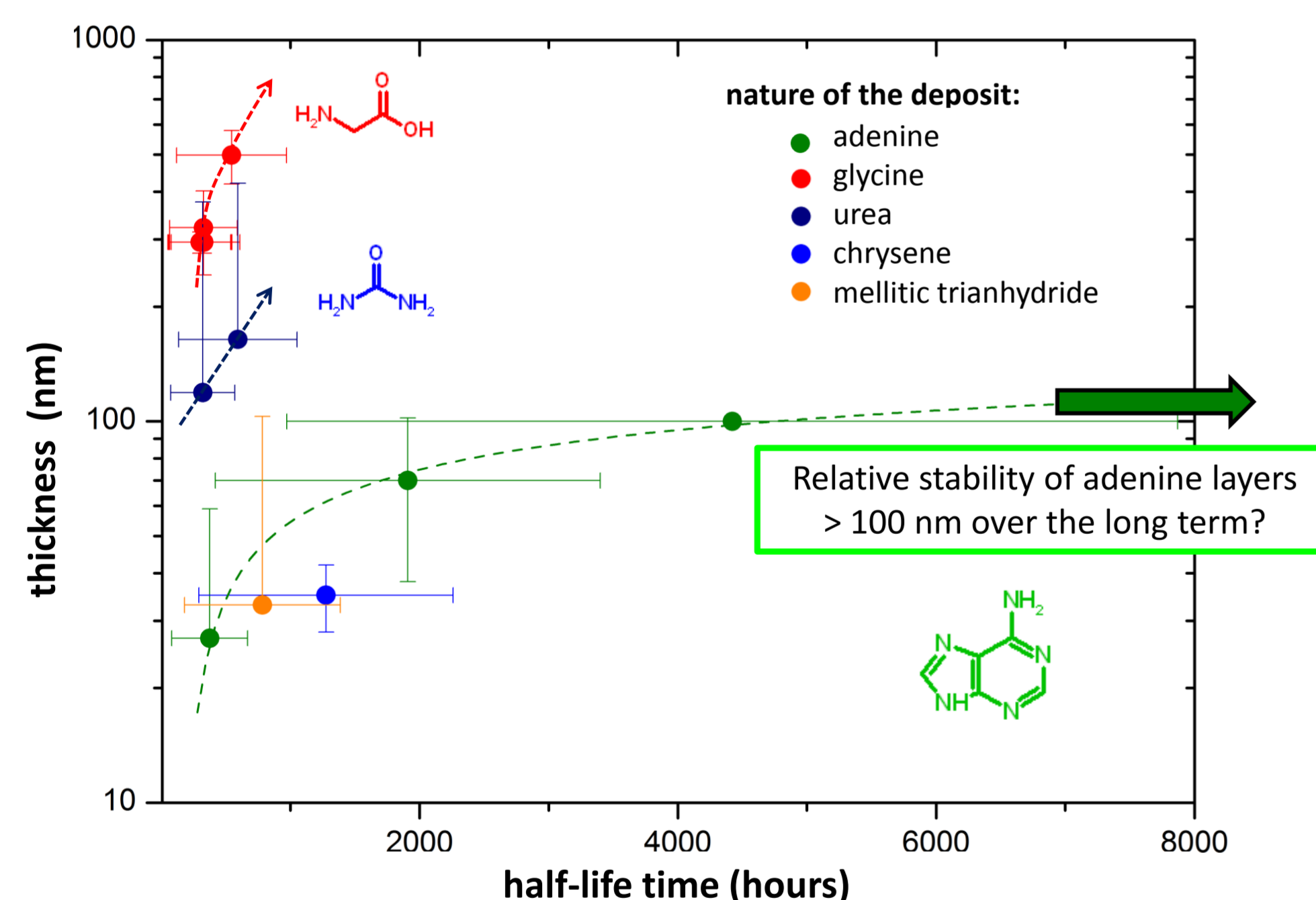


The Mars Organic Molecules Irradiation and Evolution (MOMIE) setup:



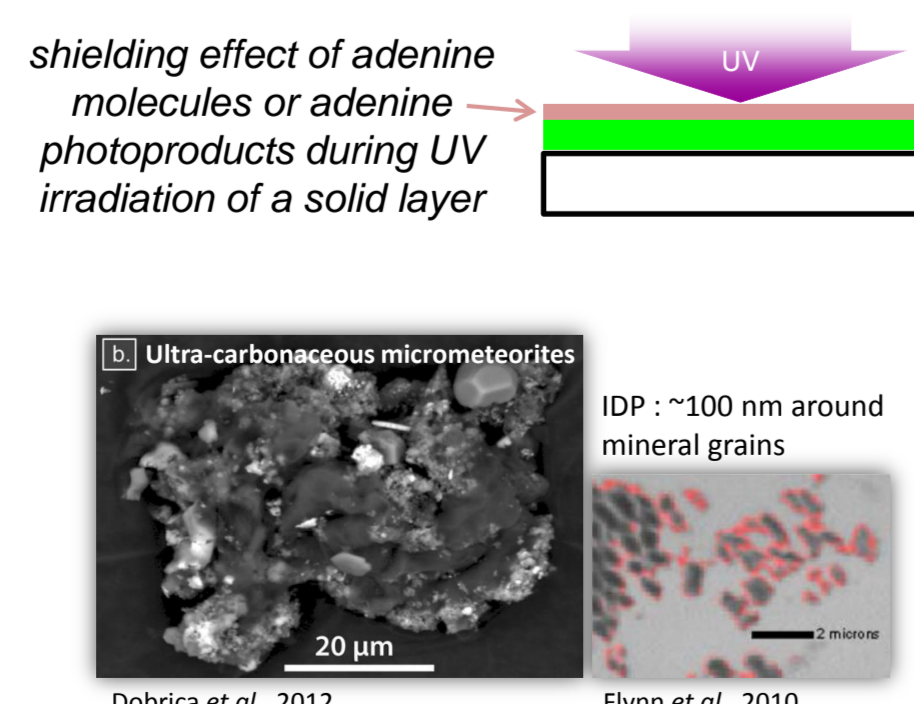
Results and implications for the search of organics on Mars:

Photostability of organic layers on Mars

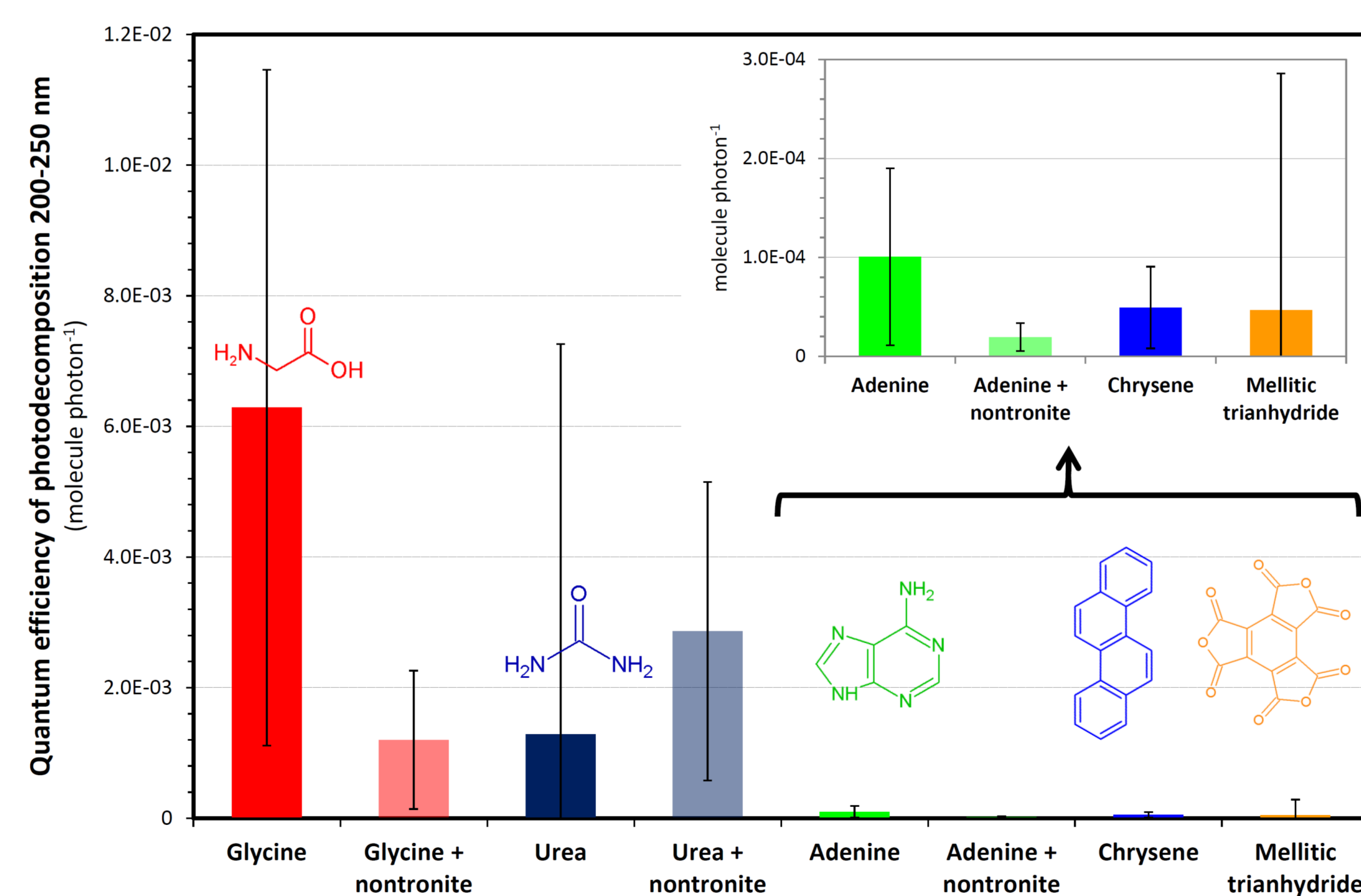


By studying the evolution of several mono-molecular layers of different thicknesses, we have found that the determined half-life times (i.e. the time after which 50% of the initial amount of molecules is transformed) are strongly affected by the initial thickness of the deposit. Solid layers of the studied molecules have **half-lives of 10 to 10³ hours at the surface of Mars**, when exposed directly to Martian UV radiation [4].

The trend observed for adenine layers suggests a relative photostability of this molecule for layers thicker than 100 nm, compared to glycine and urea. Solid organic layers are found in micrometeorites (see pictures on the right) or could have been formed endogenously on Mars.



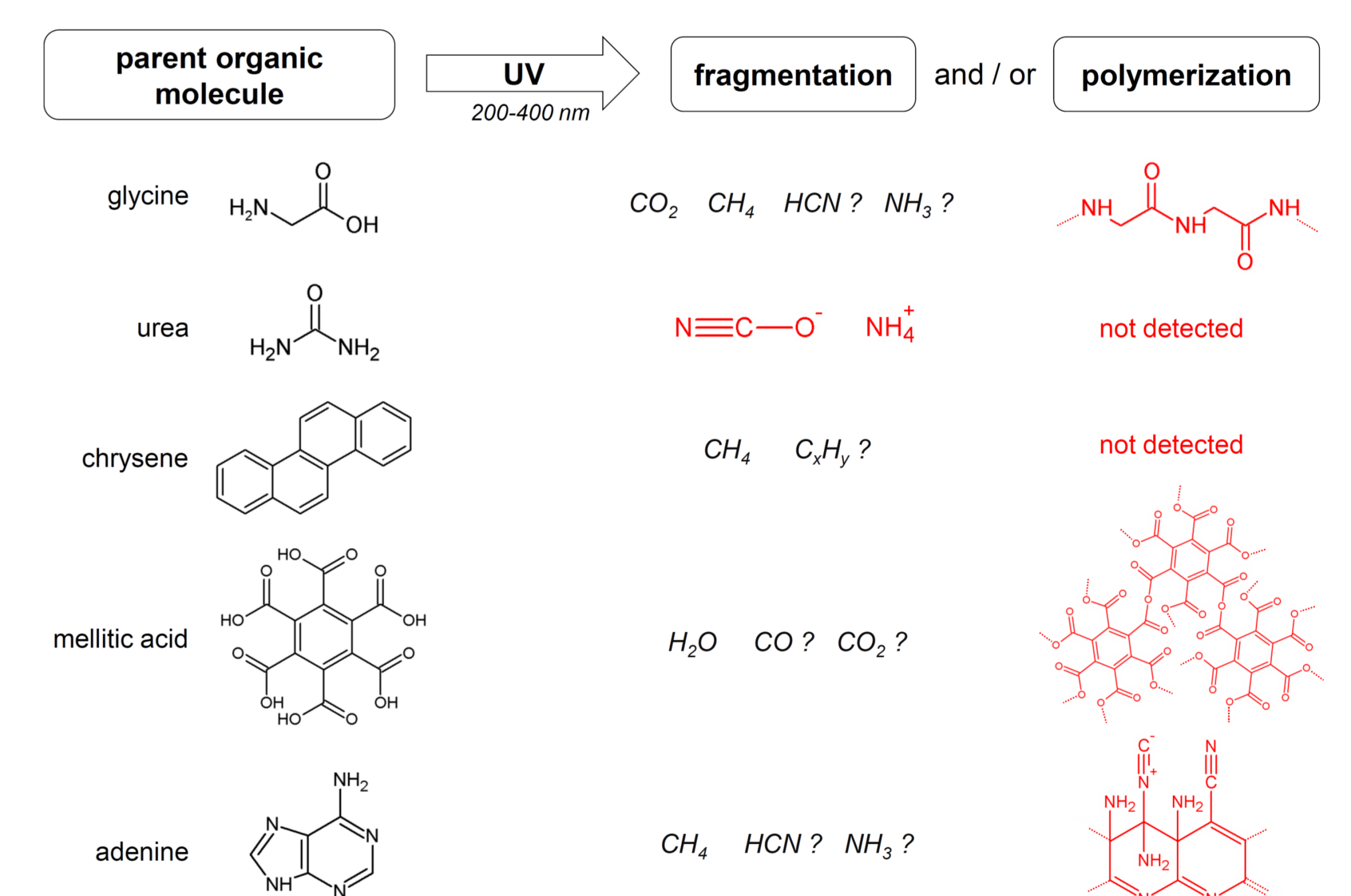
Photodissociation quantum yields, effect of clay



The quantum efficiencies of photodecomposition from 200 to 250 nm range from 10⁻² to 10⁻⁶ molecule.photon⁻¹ and apply for isolated molecules exposed at the surface of Mars [4]. These experimental values are independent on the thickness of the deposits. Consequently, these molecular values enable us to assess the relative strength of the studied molecular structures towards Mars surface UV radiation. The results indicate that aromatic molecules are at least ten times more resistant to Martian UV compared to non-aromatic molecules. These data provide essential inputs for numerical modeling of the evolution of organic molecules at the surface of Mars, and could enrich existing numerical models [5], [6].

Moreover, these results reveal a **pronounced photoprotective effect of Fe³⁺-nontronite on the evolution of glycine and adenine** [7]. Consequently, iron rich smectite clay could be a good target to search for these molecules. Alternatively, the possible catalytic effect observed for urea could indicate a selective protection of organic molecules by Fe³⁺-nontronite under Mars surface conditions. But because of the high error bars, further experiments are needed to confirm and enrich this latter result.

Products of chemical evolution



Qualitatively, we observed that **Mars-like UV irradiation induces fragmentation and/or polymerization of the exposed molecules** [4]. Adenine and mellitic acid lead to the formation of photoresistant solid residues having probably intricate macromolecular structures containing aromatic moieties and extended conjugated systems. These kinds of end-products could be targeted by current and future *in situ* analyses of the Martian soil: MSL Curiosity, MSL 2020, ExoMars etc.

Molecular targets to search for *in-situ*



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References: [1] Poch O. *et al.* (2013) *Planetary and Space Science* 85, 188-197. [2] Ehlmann B. *et al.* (2013) *Space Science Reviews* 174, 329-364. [3] Grotzinger J. *et al.* (2012) *Space Science Reviews* 170, 5-56. [4] Poch O. *et al.* *Icarus*, **accepted**. [5] Moores J. *et al.* (2007) *Icarus* 192, 417-433. [6] Moores & Schuerger (2012) *JGR* 117, E08008. [7] Poch O. *et al.* **in preparation for Astrobiology**.