

# The PROCESS Experiment: An Astrochemistry Laboratory for Solid and Gaseous Organic Samples in Low-Earth Orbit

Hervé Cottin,<sup>1</sup> Yuan Yong Guan,<sup>1</sup> Audrey Noblet,<sup>1</sup> Olivier Poch,<sup>1</sup> Kafila Saiagh,<sup>1</sup> Mégane Cloix,<sup>1</sup>  
Frédérique Macari,<sup>1</sup> Murielle Jérôme,<sup>1</sup> Patrice Coll,<sup>1</sup> François Raulin,<sup>1</sup> Fabien Stalport,<sup>1</sup> Cyril Szopa,<sup>2</sup>  
Marylène Bertrand,<sup>3</sup> Annie Chabin,<sup>3</sup> Frances Westall,<sup>3</sup> Didier Chaput,<sup>4</sup> René Demets,<sup>5</sup> and André Brack<sup>3</sup>

## Abstract

The PROCESS (PREbiotic Organic ChEmistry on the Space Station) experiment was part of the EXPOSE-E payload outside the European Columbus module of the International Space Station from February 2008 to August 2009. During this interval, organic samples were exposed to space conditions to simulate their evolution in various astrophysical environments. The samples used represent organic species related to the evolution of organic matter on the small bodies of the Solar System (carbonaceous asteroids and comets), the photolysis of methane in the atmosphere of Titan, and the search for organic matter at the surface of Mars. This paper describes the hardware developed for this experiment as well as the results for the glycine solid-phase samples and the gas-phase samples that were used with regard to the atmosphere of Titan. Lessons learned from this experiment are also presented for future low-Earth orbit astrochemistry investigations. Key Words: Astrochemistry—Astrobiology—Low-Earth orbit—EXPOSE—Photochemistry—Hardware. *Astrobiology* 12, 412–425.

## 1. Introduction

THE EARTH'S ORBIT is subjected to radiation from the Sun and galactic cosmic rays. Cosmic radiation that enters the Solar System consists of protons, electrons,  $\alpha$ -particles, and heavy ions. Solar particle radiation is emitted as solar wind during chromospheric eruptions and is made of up to 95% protons,  $\alpha$ -particles, and heavy ions. Protons and electrons do not reach Earth because they are trapped by the geomagnetic field. The solar electromagnetic radiation above Earth's atmosphere is composed of 46% IR radiation, 46% visible light, and only 8% UV light (Iqbal, 1983; Horneck *et al.*, 2002). These UV photons are, however, the most energetic and occur at sufficient levels to induce photochemical evolution.

Photochemistry plays an important role in the chemical evolution of organic matter in the Solar System and interstellar medium, specifically in the vacuum ultraviolet (VUV) domain ( $\lambda < 200$  nm). As a consequence, studies of the photolysis of molecules related to various astrophysical environments are common in many laboratories;

compounds of interest are in the gas or solid phase. Various UV sources are used in the laboratory, which includes sources that are monochromatic [*e.g.*, H<sub>2</sub>/He (122 nm), Xe (147 nm), or CH<sub>4</sub>/He (193 nm) (Cottin *et al.*, 2000)], sources that simulate a wider UV spectral range [*e.g.*, H<sub>2</sub> (122 and 160 nm) or D<sub>2</sub> discharge lamps (190–400 nm) (Ten Kate *et al.*, 2005), high-pressure Xe lamps (190–400 nm) (Stalport *et al.*, 2009)], and even synchrotron sources that scan the entire spectrum in stepwise fashion (Schwell *et al.*, 2008). Nevertheless, it is not possible to simulate the entire range of wavelengths that correspond to the most energetic parts of the solar UV spectrum below 200 nm (Cottin *et al.*, 2008). The lack of a source of adequate fidelity notwithstanding, such studies are necessary to understand chemical evolution in astrophysical environments, particularly those with astrobiological relevance: environments rich in organic molecules (comets, asteroids, meteorites, Titan, localized regions of the interstellar medium) or those hypothesized to contain organics, such as Mars (Ten Kate, 2010).

<sup>1</sup>Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR CNRS 7583, Université Paris Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, Créteil, France.

<sup>2</sup>UPMC Université Paris 06, Université de Versailles Saint-Quentin, CNRS/INSU, LATMOS-IPSL, Paris, France.

<sup>3</sup>Centre de Biophysique Moléculaire, CNRS, Orléans, France.

<sup>4</sup>Centre National d'Études Spatiales, Toulouse, France.

<sup>5</sup>ESA ESTEC, Noordwijk, the Netherlands.

Typical flux for a laboratory VUV lamp is roughly  $10^{15}$  photons $\cdot$ cm $^{-2}\cdot$ s $^{-1}$  for  $121\text{ nm} < \lambda < 200\text{ nm}$ . For the same wavelength range, the solar flux is of the order of  $2 \times 10^{13}$  photons $\cdot$ cm $^{-2}\cdot$ s $^{-1}$  (Thuillier *et al.*, 2004). Therefore, laboratory experiments might be claimed to be “more efficient” with 50 times higher flux than occurs in space. However, the photon flux advantage is largely negated by the possibility of running simultaneous experiments in space; several hundred samples can be exposed at the same time and under the same conditions in Earth orbit. Due to limitations on sizes and geometries of laboratory radiation sources, however, only a few samples can be photolyzed simultaneously in the laboratory (total areas of a few square centimeters for classical lamps, and only a few square millimeters for synchrotron sources at comparable UV flux).

But the main reason for conducting experiments in space is that it is only there that the UV spectrum inherent to the Solar System exists. In ground laboratories, it is not yet possible to simulate the entire range of wavelengths that correspond to the most energetic parts of the solar spectrum, which is from 100 to 200 nm. These wavelengths are, however, the most efficient at causing chemical change. Because of this, results obtained in the laboratory are extremely difficult to extrapolate to extraterrestrial environments.

For more than two decades, astrobiological experiments have been performed successfully in low-Earth orbit (LEO). The exposure facilities Biopan/Foton (Demets *et al.*, 2005), EXPOSE-E (EXPOSE-EuTEF, on the European module Columbus), and EXPOSE-R (on the Russian module Zvezda) on the International Space Station (ISS) (Rabbow *et al.*, 2009) have provided opportunities to study the evolution of biological, organic, or mineral material and respective chemical processes directly in Earth orbit and, thus, overcome the operational difficulties of laboratory simulations (Ehrenfreund *et al.*, 2007; Cottin *et al.*, 2008; Horneck *et al.*, 2010; Olsson-Francis and Cockell, 2010; Stalport *et al.*, 2010b).

Astrochemistry experiments have previously been implemented in space and were mainly devoted to the exposure of amino acids to space conditions with the intent to measure their stability. These experiments have shown that amino acids are readily destroyed in space unless they are protected in a mineral matrix, which include the DUST experiments on Biopan-1 in 1994 and on Biopan-2 in 1997 (both outside Foton Russian automated capsules) (Barbier *et al.*, 1998, 2002) and the PERSEUS-EXOBILOGIE experiment on the Mir station in 1999 (Boillot *et al.*, 2002). More recently, two astrochemistry experiments were flown and returned safely to Earth: ORGANICS and UVolution. The ORGANICS experiment on Biopan-5 in 2005 was designed to study the reaction of polycyclic aromatic hydrocarbons and fullerene-like material to solar radiation, including vacuum UV (Ehrenfreund *et al.*, 2007). The results of this experiment show that the small fluence collected during the Foton capsule flight was not sufficient to measure any photodestruction, and they confirm that these compounds are very stable compounds in space. The UVolution experiment on Biopan-6 in 2007 compared the kinetics of photolysis in space and in the laboratory for solid state samples related to comets and Mars. The results of this experiment show that current extrapolation procedures of laboratory simulations, which typically only take into account the influence of the Lyman  $\alpha$  line at 122 nm, to space conditions are extremely uncertain

and can lead to errors of a factor of 100 on the kinetics for some molecules (Guan *et al.*, 2010). Laboratory simulations of martian conditions tend to have smaller offsets and are therefore more favorable, which shows that lamps simulating the UV flux that reaches the martian surface ( $\lambda > 190\text{ nm}$ ) are acceptable. However, there still remains a factor of 2 to 13 between space and lab results, depending on the molecule under consideration (Stalport *et al.*, 2010a).

This paper focuses on the PROCESS experiment (PREbiotic Organic ChEmistry on the Space Station), which was the only experiment on EXPOSE-E concerned exclusively with astrochemistry related to astrobiology questions. We describe in detail the experimental hardware and the results of glycine solid-phase samples and gas-phase samples related to the atmosphere of Titan (containing CH<sub>4</sub>). The results related to other samples exposed in PROCESS are detailed in the works of Bertrand *et al.* (2012) and Noblet *et al.* (2012).

## 2. The PROCESS Experiment

The goal of PROCESS, following the heritage of the previous astrochemistry experiments conducted in LEO, was to improve our knowledge of the chemical nature and evolution of organic molecules, in condensed or gas phase, that occur in extraterrestrial environments and are of significance to the study of astrobiology.

PROCESS was designed to study the stability of selected organic compounds in space and, if they are found to be unstable, the space-related effect [*i.e.*, vacuum and temperature (sublimation), energetic particles (radiolysis), and UV photons (photolysis)] responsible for their evolution (and into what they are evolving). To distinguish between those factors, several layers comprised of the same samples were exposed in space and in a ground vacuum facility for 1.5 years under environmental conditions that will be detailed later in this paper.

A specific focus was directed toward the study of the photolysis of organic compounds: photoproducts and kinetics that can then be applied to astrophysical environments. The reaction of a molecule with photons can be written:



If the sample is optically thin, the decrease of the molecule's number ( $N_t$ ) follows a first-order kinetic (Eq. 2).

$$-\frac{d[N]}{dt} = J[N] \quad (2)$$

The integration of Eq. 2 leads to  $\ln(N_t/N_0) = -Jt$  (Eq. 3), where  $J$  ( $\text{s}^{-1}$ ) is the photodestruction constant related to the kinetics of the reaction. By definition,  $J = \int \sigma_{\lambda}^{\text{abs}} \phi_{\lambda} I_{\lambda} d\lambda$ , with  $I_{\lambda}$ , photon flux (photon $\cdot$ cm $^{-2}\cdot$ s $^{-1}$ );  $\sigma_{\lambda}^{\text{abs}}$ , absorption cross section (cm $^2$ );  $\phi_{\lambda}$ , quantum yield of photodissociation. It should be noted that there are few data on these two parameters in the literature. Therefore, the constant  $J$  must be measured experimentally with an appropriate photon source. As discussed in the Introduction, the best photon source for astrochemical studies in the Solar System is the Sun itself.

The PROCESS experiment was submitted to the International Research Announcement for Research in Space Life

Sciences at the International Space Station—ILSRA-2004 ESA Specific Announcement. It was coordinated (principal investigator: H. Cottin) by the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) in partnership with the Centre de Biophysique Moléculaire (CBM) and the Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS). After peer review, it was selected and versed to the research pool of the ESA European Programme for Life and Physical Sciences in Space. The PROCESS experiment was later scheduled to be part of the EXPOSE-E facility payload, outside Columbus, the European module of the ISS.

The surface allocated for PROCESS on the EXPOSE-E facility allowed for selection of 20 kinds of samples to be repeated twice for each layer of the experiment.

All the samples were prepared and conditioned in the participating laboratories in June 2007 and delivered to the German Aerospace Center (DLR) in Cologne for integration into EXPOSE-E trays on 5 July 2007. Then EXPOSE-E was shipped to Florida (Kennedy Space Center) and stored before launch, which was initially scheduled in early December 2007 but then postponed to February 2008.

PROCESS was launched as part of EXPOSE-E and Columbus with the Space Shuttle Atlantis STS-122 mission on 7 February 2008. Lids covering the PROCESS samples were opened on 20 February 2008 and closed on 20 August 2009 (1.5 years of exposure). After termination of the exposure sequence, the whole EXPOSE-E facility was recovered during an extravehicular activity conducted on 2 September 2009. Upon return to Earth on 21 September (by Space Shuttle Discovery STS-128), EXPOSE-E was shipped to Europe, where the PROCESS sample package was removed from EXPOSE-E before distribution to participating laboratories. PROCESS samples were eventually made available for analysis at LISA, CBM, and LATMOS on 3 November 2009. Hence, samples were inaccessible to the science team over the course of 2 years and 4 months. Such delays between preparation and launch, and termination of the experiment and recovery of the samples, are inherent to long-duration exposure in Human Spaceflight programs on the ISS. Yet they create difficulties for the analysis of the samples (*e.g.*, leaks and stability of the IR source of the spectrometer used for the analysis of the sample before and after exposure, as will be discussed later in this paper (see also Noblet *et al.*, 2012).

### 2.1. PROCESS in EXPOSE-E

The EXPOSE-E facility is shown in Fig. 1. Three experiment trays are equipped with four squared sample carriers each. Carriers for the PROCESS experiment (two exposed sample carriers) can contain up to 20 sample cells with quartz windows that allow an irradiation down to 190 nm (for Mars simulations) or MgF<sub>2</sub> windows that allow the transmission of UV photons down to 115 nm. The cells were installed on tray 3 of EXPOSE-E, as shown in Fig. 1, and can be covered with lids before and after the actual exposure sequence.

The European Space Agency has provided sample cells that are open (vented) toward open space through the internal EXPOSE-E venting system. This results in the loss of gaseous compounds produced by the degradation of the exposed refractory molecules. It also makes the irradiation of gaseous mixtures impossible. Since one of our goals was to

also analyze gaseous compounds, the scientific team at LISA and the Centre National d'Études Spatiales (CNES) has been working on the development of closed cells.

### 2.2. PROCESS hardware

**2.2.1. Open cells.** Open cells are shown in Fig. 2. Samples are deposited on the inner side of the window (MgF<sub>2</sub> or quartz). Such cells are used for kinetics studies of solid organic compounds. Gaseous photoproducts cannot be analyzed because they are vented to space. This effect is beneficial for accurate kinetic measurements because the gases cannot interact with the sample as would be the case in a closed cell.

**2.2.2 Closed cells.** Closed cells can be used either to study the photolysis of a gaseous mixture (simulation of an atmosphere) or to collect the photodissociation products of a solid molecule. Such a collection of gaseous photodissociation products of a solid molecule allows for results that complement measurements for the same molecule in open cells. PROCESS is the first LEO experiment embarking such closed cells.

Closed cells are made of two aluminum cylinders that are screwed one into the other (Fig. 3). A window (MgF<sub>2</sub> or quartz) is glued at each end of the cell. Tightness is ensured by a Viton O-ring between the two parts and an additional glue film at the junction of the two parts (design of the cells: COMAT aerospace, Toulouse, France).

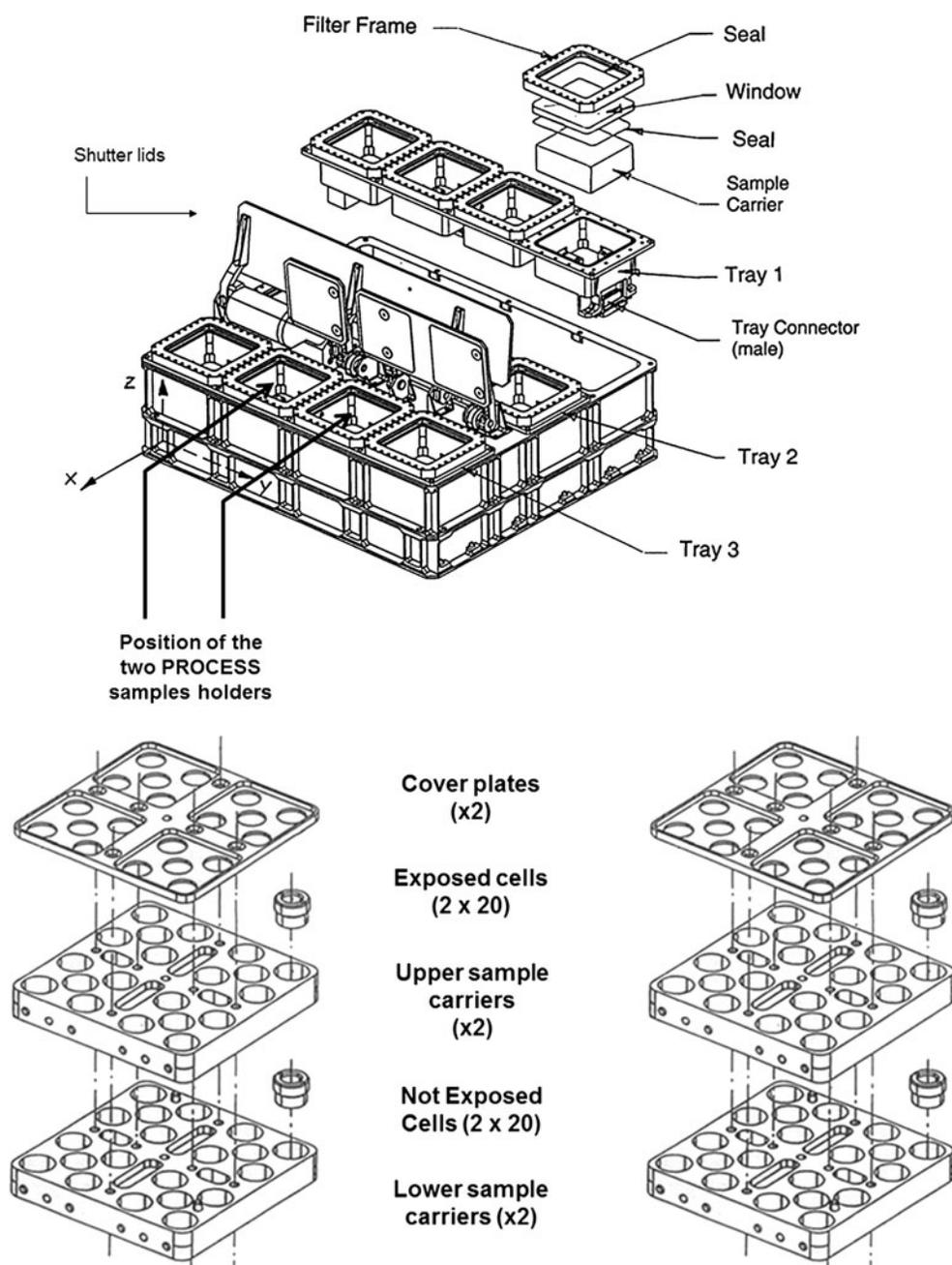
### 2.3. Samples

**2.3.1. Sample preparation.** Solid samples were prepared in a vacuum sublimation system as described in Guan *et al.* (2010). The thickness of the deposit was monitored by interferometry to ensure that the sample would be homogeneously photolyzed in space.

Solid samples that cannot be sublimated were deposited with an evaporative method. The molecule was dispersed as a powder in a solvent to prepare a suspension that was deposited in the cell. Finally, the sample was obtained after the total evaporation (vacuum evaporation) of the solvent. This method was described by Boillot *et al.* (2002).

Gaseous samples were prepared in an "analytical cell" such as the one shown in Fig. 4. Although termed "analytical," this cell was used for both filling and sampling the closed cells with gas and for IR analysis of the gaseous content of the closed cells. It consists of two main stainless steel parts on the inside to which both parts of a closed cell are separately fitted on two different holders. As the two analytical cell parts are tightly adjusted, one opposite the other, the content of the resulting device can be evacuated. The gaseous sample for the experiment (for instance a N<sub>2</sub>/CH<sub>4</sub> mixture) can then be introduced into the analytical cell before the bottom holder is used to screw the bottom part of the closed cell in its top part, which thus encloses the gaseous sample inside a closed cell.

The closed cell can then be removed from the analytical cell, and a glue film is deposited at the junction between the two parts of the cell to improve its tightness. The closed cells can then be placed onto a sample holder for the experiment. After the return of the cells and before analysis, the glue film is removed with a CH<sub>2</sub>Cl<sub>2</sub> bath, and the two parts of the



**FIG. 1.** The EXPOSE facility ( $480 \times 520 \times 327.5$  mm) is made of three experiment trays into which four square sample carriers ( $77 \times 77 \times 26$  mm) are fitted (top). The in-flight component of the PROCESS experiment was made of two sample carriers, the location of which is shown in the top part of the figure. Each of the two sample carriers was designed to receive 20 exposed sample cells and 20 dark controls (bottom). Pictures courtesy of Kayser-Threde GmbH.

closed cell are unscrewed inside the analytical cell, which would have been evacuated beforehand. The gaseous sample to be analyzed is then released inside the analytical cell and can further be injected into a gas chromatograph.

**2.3.2 Sample exposure principle.** For each molecule or mixture type the following pattern was applied (Fig. 5):

- Two cells [top layer in the (A) section of Fig. 5] were exposed to the influence of UV, cosmic rays, temperature fluctuation outside the ISS, vacuum;
- Two cells acted as flight dark controls [bottom layer in the (A) section of Fig. 5], which were exposed to the influence of cosmic rays transmitted through the top layer of samples, temperature, and vacuum;
- Two cells could have been exposed to a solar simulator ( $\lambda > 190$  nm) in a vacuum facility on the ground at DLR Cologne [top layer in the (B) section of Fig. 5] and had a temperature history similar to the samples in space (transmitted via telemetry from the ISS). We chose, however, only to expose some of the PROCESS samples on this layer (Bertrand *et al.*, 2012). Those samples were

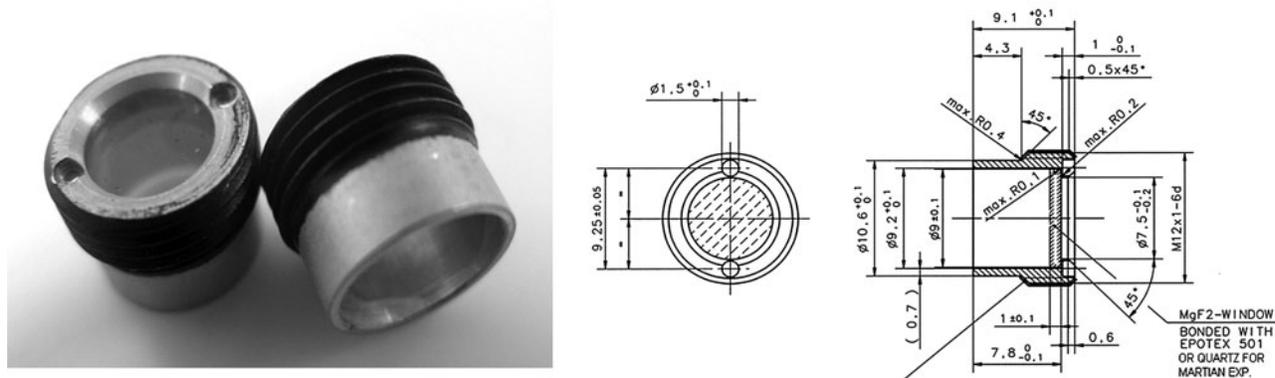


FIG. 2. Design of an open cell made of an aluminum cylinder on top of which a  $\text{MgF}_2$  or quartz window is glued. The organic molecule is deposited onto the inside face of the window. Right diagram courtesy of COMAT aerospace.

exposed to simulated UV photons (Rabow *et al.*, 2012), temperature cycling, and vacuum.

- Two cells were placed right below in the same vacuum chamber in the dark but submitted to the same temperature cycling and to vacuum (bottom layer in the (B) section of Fig. 5).
- Two cells were stored in another vacuum facility, at the DLR, at 5°C to study the influence of vacuum only [single layers in the (C) section of Fig. 5].

Additional laboratory simulations on individual samples were conducted in the participating laboratories, with various UV sources such as commercial VUV lamps at CBM (Cottin *et al.*, 2008; Bertrand *et al.*, 2012) or with a high-pressure Xenon UV lamp at LISA for the MOMIE project that simulated solar UV at the surface of Mars (Stalport *et al.*, 2009) and with laboratory-made microwave discharge VUV sources (Cottin *et al.*, 2000; Guan *et al.*, 2010).

**2.3.3. PROCESS samples.** The list and localization of the samples selected for each layer of PROCESS are shown in Fig. 6. One-fourth of the samples (1–5, 10–15) were exposed in closed cells behind quartz windows that simulated the spectrum of photons transmitted to the surface of Mars.

Results concerning these samples are detailed in Noblet *et al.* (2012). Another fourth of the samples (26–30, 36–40) containing amino acids was prepared and analyzed at CBM and are presented by Bertrand *et al.* (2012). Samples containing polyoxymethylene, hexamethylenetetramine, and polyacrylonitrile (16–17, 19–22) were used to the study the origin of distributed sources in comets (*i.e.*, the reason why the spatial distribution of some molecules detected in the gas phase of comets cannot be explained by a direct sublimation from the nucleus or by the photolysis of another observed gaseous compound) (Cottin and Fray, 2008). Samples containing Titan's tholins (laboratory analogues of the organic solid-phase aerosols synthesized in the atmosphere of Titan) were used to study the cycle of carbon and nitrogen in the atmosphere of Titan, and those with guanine were prepared to measure the photostability of this nucleobase in comets and carbonaceous asteroids. Measurements carried out on those samples are not sufficiently conclusive at the present stage of interpretation to be discussed in an article. They will be presented in future papers, when compared to future LEO experiments and further laboratory studies. Other samples, which were placed in closed cells filled with  $\text{CO}_2$  to act as gaseous actinometers, will not be discussed as well since

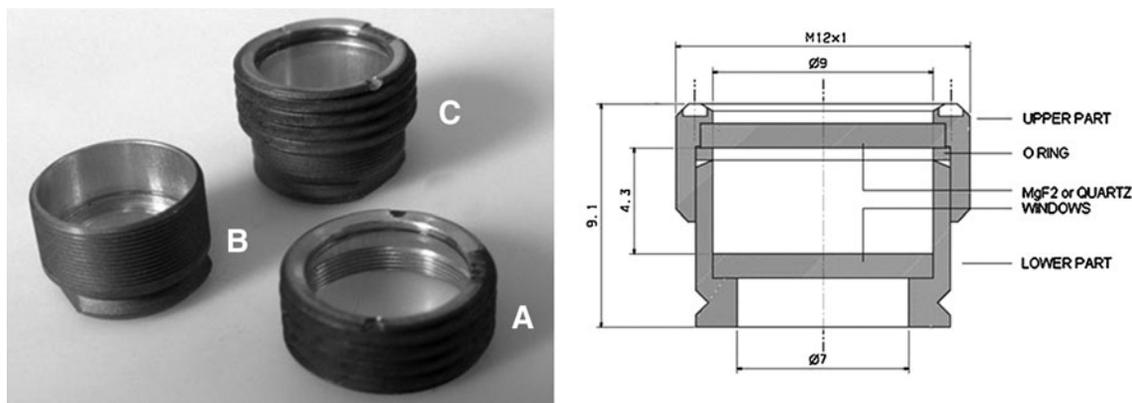


FIG. 3. Design of a closed cell. Two aluminum cylinders are screwed into each other. (A) Top; (B) bottom; (C) complete cell composed of a top (A) and a bottom (B). Two  $\text{MgF}_2$  or quartz windows are glued at both ends to allow the analysis of molecules inside the cell by spectroscopy. Sealing (relative to lab atmosphere or vacuum in space) is ensured by a Viton O-ring. Right picture courtesy of COMAT aerospace.

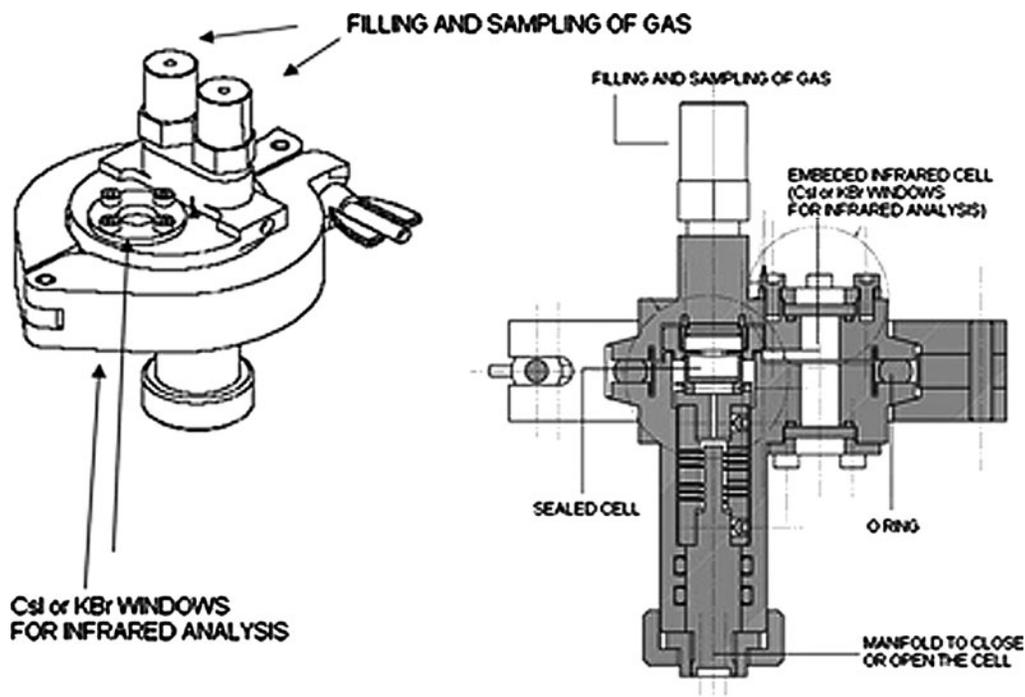


FIG. 4. Design of the analytical cell. This cell allows for the filling or sampling of gases inside a sealed cell that can be fitted inside the holder. An embedded IR cell can be used for analysis of gases in the IR range. Picture courtesy of COMAT aerospace.

leaks from the cells resulted in a loss of most of the gaseous sample during exposure.

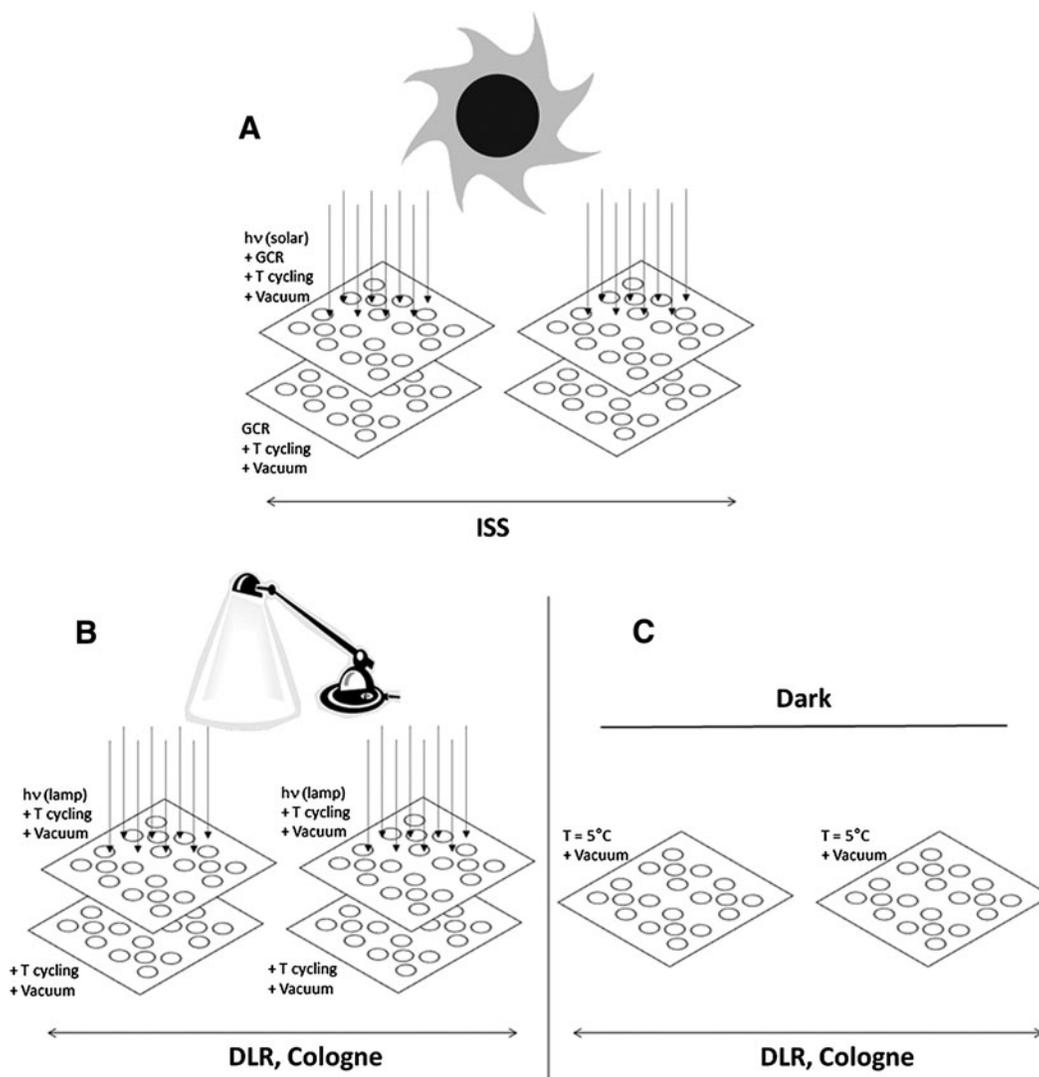
The results for a few samples not listed above will be discussed here with the intent to qualify and improve our procedures and hardware as opposed to addressing the relevant planetary science issues related to them, which would be beyond the scope of this paper. We will present and discuss the measurements for pure glycine on  $\text{MgF}_2$  windows, which were selected so as to study the photostability of this molecule detected in meteorites (see for instance Martins *et al.*, 2007) and cometary dust particles (Elsila *et al.*, 2009). We will also discuss measurements for gaseous mixtures of  $\text{CH}_4/\text{N}_2$  and  $\text{CH}_4/\text{Ar}$ , which were selected to prepare for future experiments in which we plan to analyze Titan-like atmosphere scenarios.

#### 2.4. PROCESS environmental conditions

**2.4.1. Photons.** PROCESS samples were exposed to the space environment between the opening and the closing of the lids covering the experiment for the duration of 1.5 years. During this period, samples were not always exposed to solar photons due to the orbit of the ISS around Earth, the ISS orientation relative to the Sun, and various shadows cast by the solar panels and local environment in the vicinity of EXPOSE-E. The actual duration of the exposure of the samples to UV photons was reconstructed from measurements by sensors embedded in EXPOSE-E, and calculation was provided by the company RedShift (St Niklaas, Belgium) with a 3-D model of the ISS that took into account the orbital parameters of the ISS and the position of its fixed and mobile elements (including solar panels and logs of the docking of spaceships). Results from those simulations indicate that the

total exposure duration of the samples to the Sun was quite heterogeneous from one part of EXPOSE-E to another and even in area between the samples of one specific experiment. For PROCESS, the exposure time ranged from 1190 to 1958 h ( $\pm 15\%$ ) and is known for each sample location.

**2.4.2. Particles.** The energetic particle environment was measured by the R3DE experiment, which was part of the EXPOSE-E payload (Dachev *et al.* 2012). The average dose of particles was calculated to have been  $91.1 \mu\text{Gy}\cdot\text{day}^{-1}$  for galactic cosmic rays (GCR),  $426 \mu\text{Gy}\cdot\text{day}^{-1}$  for South Atlantic Anomaly (SAA) protons, and  $8.6 \mu\text{Gy}\cdot\text{day}^{-1}$  for outer radiation belt (ORB) electrons, which results in a total of  $525.7 \mu\text{Gy}\cdot\text{day}^{-1}$ . The R3DE was only measuring particles that reached the top surface of EXPOSE-E, behind a shielding of  $0.4 \text{ g}\cdot\text{cm}^{-2}$ , which comes very close to the shielding of the flight-exposed samples ( $0.31 \text{ g}\cdot\text{cm}^{-2}$ ). This resulted in a total dose deposited onto our exposed samples that was estimated to have been 53.1 mGy from GCR (583 days of exposure from liftoff to landing, since GCR are sufficiently energetic to get through the lids), 237.7 mGy from SAA protons (558 days of exposure, *i.e.*, 583 days – 25 days during which the lids over the samples were closed), and 4.8 mGy from ORB electrons (also 558 days of exposure), which resulted in a total of 295.6 mGy. For the dark flight controls, the shielding was between 1.11 and  $1.21 \text{ g}\cdot\text{cm}^{-2}$ . No measurements were made by the R3DE at that shielding depth. It can then only be assumed that the dark flight samples were shielded against the ORB electrons, not at all against GCR, and partly against the SAA protons. Therefore, because the largest contribution to the dose was made by the SAA protons, we cannot calculate a value for the dose received by the dark flight samples, not



**FIG. 5.** Scheme showing the experimental breakdown of samples between the ISS and DLR Cologne, and the environmental conditions to which they were exposed. A total of 40 samples were exposed directly in LEO, with 40 dark controls directly below them (A). The same disposition was reproduced in an irradiation chamber at DLR Cologne (B), with an additional series of samples that were kept in vacuum, in the dark, at 5°C (C).

even an estimated number. However, the comparison of results measured on the different layers of samples does not reveal any distinguishable contribution of energetic particles to the evolution of our samples.

**2.4.3. Temperature.** Temperature was measured on EXPOSE-E. Over the 18 months, 10 high-temperature periods (maximum +40°C) were experienced alternating with 10 cold periods (minimum -12°C) caused by changes of the ISS orbital plane with respect to the Sun. Superimposed was a rapid temperature rhythm caused by the 91 min orbital loops of the ISS across the dayside and nightside of Earth. Day/night variations spanned over 10°C during the hot periods and over 5°C during cold periods. On 20 March 2009, an exceptional peak of 55°C was recorded. On that day, the ISS was temporarily placed in position perpendicular to the Sun to facilitate the installation and testing of new solar panels.

The average temperature of the facility over the whole flight was close to 15°C (Rabbow *et al.*, 2012).

## 2.5. Analytical methods

Samples discussed in the present paper were analyzed with IR spectroscopy (solid films) and gas chromatography coupled with mass spectrometry (GC-MS).

**2.5.1. Infrared.** A Fourier transform infrared spectrometer (Perkin Elmer—BXII) was used. Spectra were measured by transmission through the MgF<sub>2</sub> windows, with a resolution of 4 cm<sup>-1</sup> and between 4000 and 1000 cm<sup>-1</sup>. Indeed MgF<sub>2</sub> is not transparent for lower wavenumbers [MgF<sub>2</sub> cut-off in the IR domain is at 1000 cm<sup>-1</sup> (10 μm)].

Infrared spectra were measured in the laboratory before and after the experiment. The spectra of the samples were compared to reference spectra to search for new compounds. Relative quantification is achieved by measurement of the area of a characteristic absorption feature of the studied molecule, which is directly proportional to its abundance. Then *J* is calculated with Eq. 3 using a plot of the logarithm

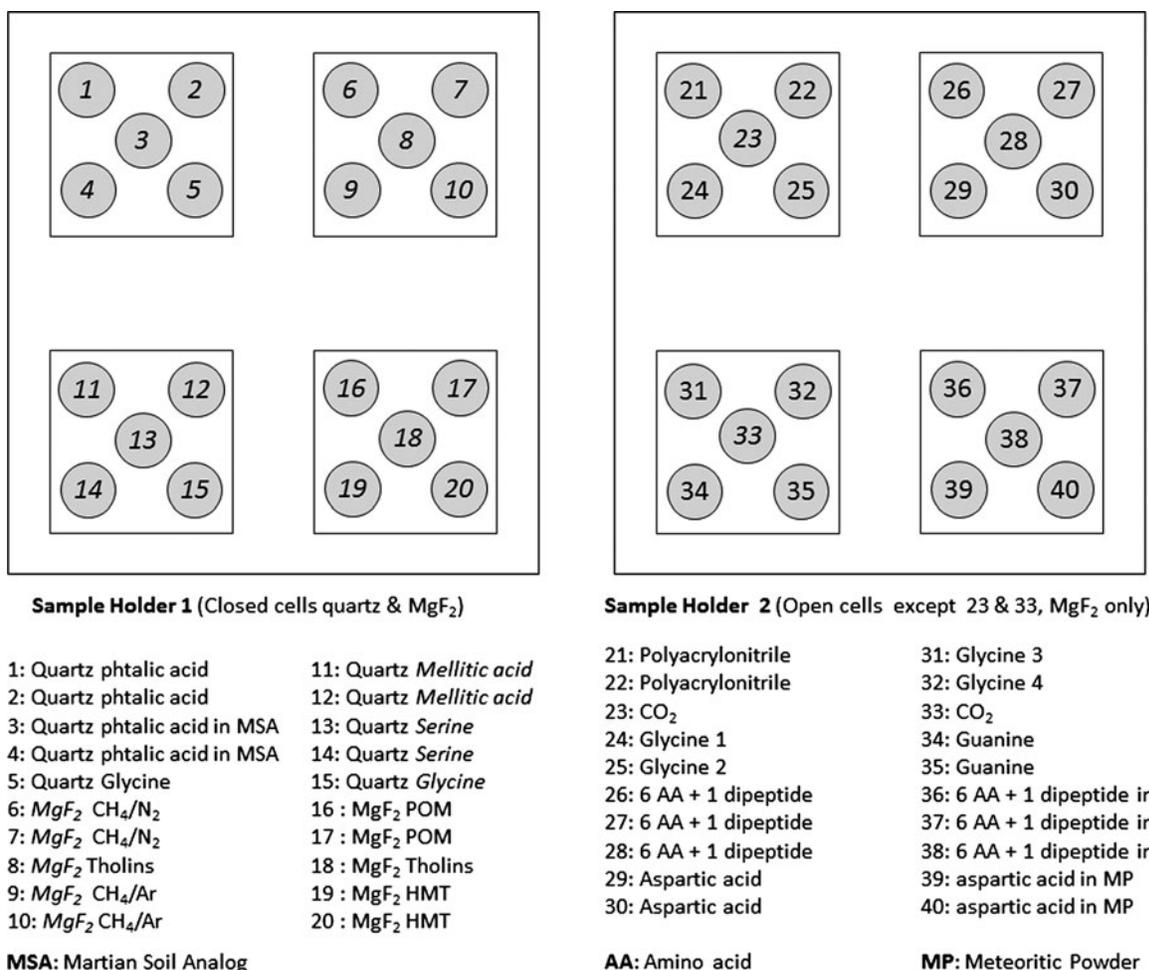


FIG. 6. Nature and location of the PROCESS samples. Italic numbers on the scheme refer to closed cells, while regular numbers refer to open cells. AA is a mixture of glycine, alanine, valine, aminobutyric acid, aminoisobutyric acid, and aspartic acid. Dipeptide is dileucine. Glycine 1, 2, 3, 4 are different thicknesses of glycine samples. HMT, hexamethylenetetramine; POM, polyoxymethylene.

of the relative abundance of the studied compound as a function of time.

Therefore, no absolute measurement is required in the case of the first-order kinetics for photolysis that we are assuming (see for instance in Guan *et al.*, 2010). This allows quantitative analysis of the samples through both open and closed cells.

**2.5.2. Chromatography.** Once released into the analytical cell, gaseous samples were transferred for analysis by gas chromatography (VARIAN CP 3800) coupled to a mass spectrometer (VARIAN Saturn 2200), with a MXT-Q Plot column (length 30 m, internal diameter 0.25 mm, film thickness 10  $\mu\text{m}$ —Restek). Temperature program was 40°C during 4 min then rose at 10°C·min<sup>-1</sup> up to 150°C. Pressure was set from 15 to 25 psi at 1.5 psi·min<sup>-1</sup>. Total time of analysis was 30 min. This method was optimized for the analysis of small hydrocarbons. Compounds were identified in two ways, as follows: (1) by comparing their retention time to that of known standards and (2) by their mass spectrum. Quantification of the compounds was achieved with calibration curves for each molecule.

### 3. Results

#### 3.1. Glycine

The glycine samples were prepared by vacuum sublimation. This method led to the formation of thin films of the molecule in its zwitterion configuration (<sup>-</sup>NH<sub>3</sub>-CH<sub>2</sub>-COO<sup>-</sup>). The samples were a mixture of the  $\alpha$  and  $\gamma$  form of glycine (Takagi *et al.*, 1959; Guan *et al.*, 2010). Such glycine samples were selected for exposure for all our three recent experiments in LEO—UVolution, PROCESS, and AMINO—for comparison and cross calibration between the experiments. In the case of PROCESS, four glycine samples, unlike the other molecules, were prepared for each layer of the experiment, in contrast to the two glycine samples on UVolution and AMINO. Each of the four samples had a different thickness (~ 300, 400, 500, and 600 nm) to test the procedure described by Cottin *et al.* (2008) to calculate the kinetics of photodegradation from samples of increasing thickness and not with an average on two samples with the same thickness. This experiment failed due to a wrong estimate of the total Sun exposure duration at the time of the preparation of the samples (~240 h of Sun on the samples was estimated

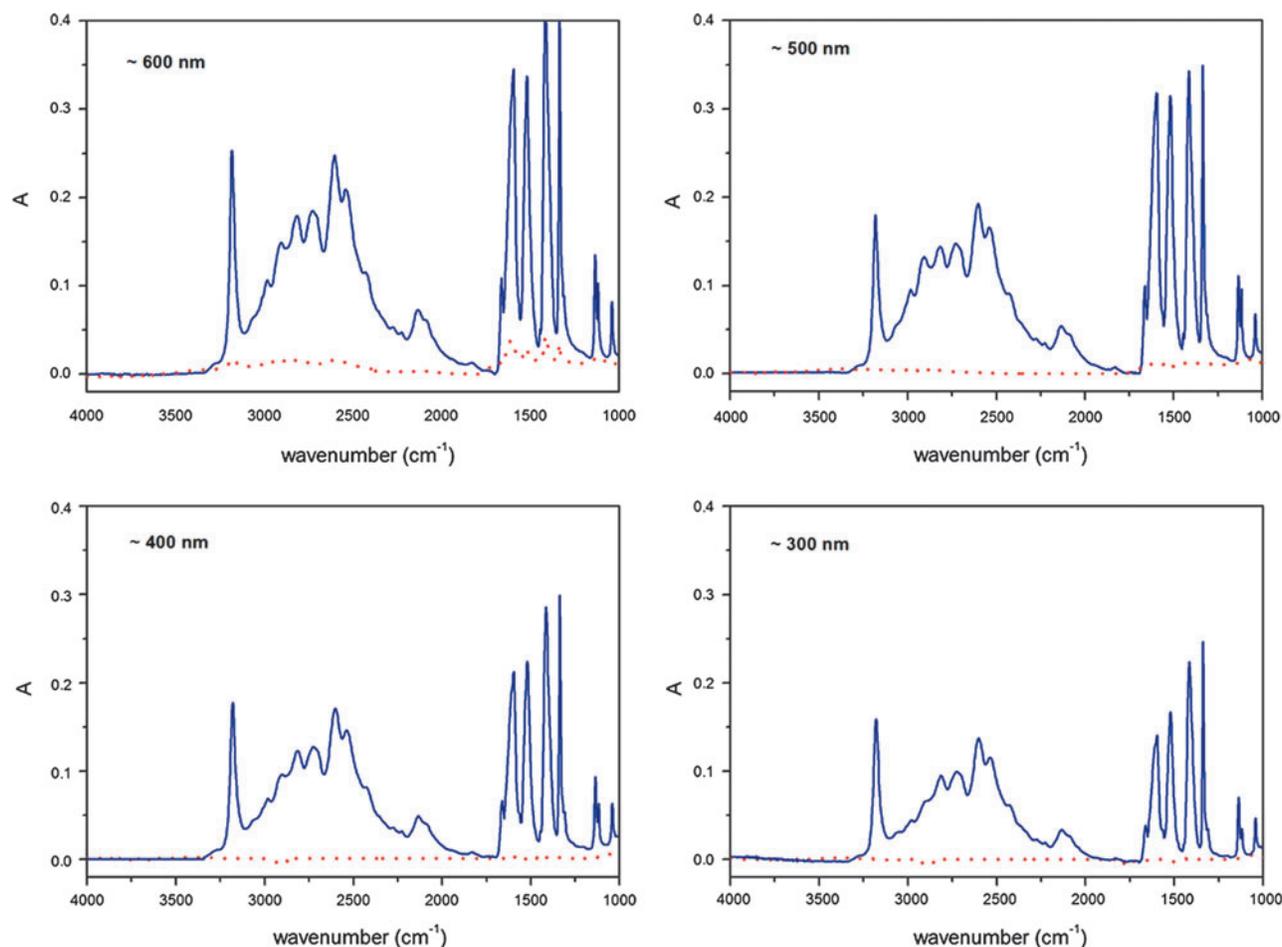


FIG. 7. Spectra of the four flight-exposed samples of glycine before (solid line) and after (dotted line) the flight. The thickness of the initial sample is shown on the spectra. Color images available online at [www.liebertonline.com/ast](http://www.liebertonline.com/ast)

compared to an average of  $\sim 1500$  h calculated with correct flight parameters). Due to this incorrect estimate, we prepared samples that were too thin to have a measurable amount of material remaining after the return to Earth. Results are shown in Fig. 7 for exposed cells and Fig. 8 for flight dark control. The 300, 400, and 500 nm exposed samples were entirely photodegraded. On the thickest exposed sample ( $\sim 600$  nm), 13% of the initial sample remained on the  $\text{MgF}_2$  window. Flight dark control samples do not present any significant variation. Control samples kept on Earth showed a similar behavior to the flight dark controls (results not shown).

### 3.2. $\text{CH}_4/\text{Ar}$ and $\text{CH}_4/\text{N}_2$

Two kinds of gaseous  $\text{CH}_4$ -containing samples were exposed to prepare for future experiments related to the Titan atmosphere. Samples were made of (1) Ar: 1 bar /  $\text{CH}_4$ : 0.5 bar and (2)  $\text{N}_2$ : 1 bar /  $\text{CH}_4$ : 0.5 bar.

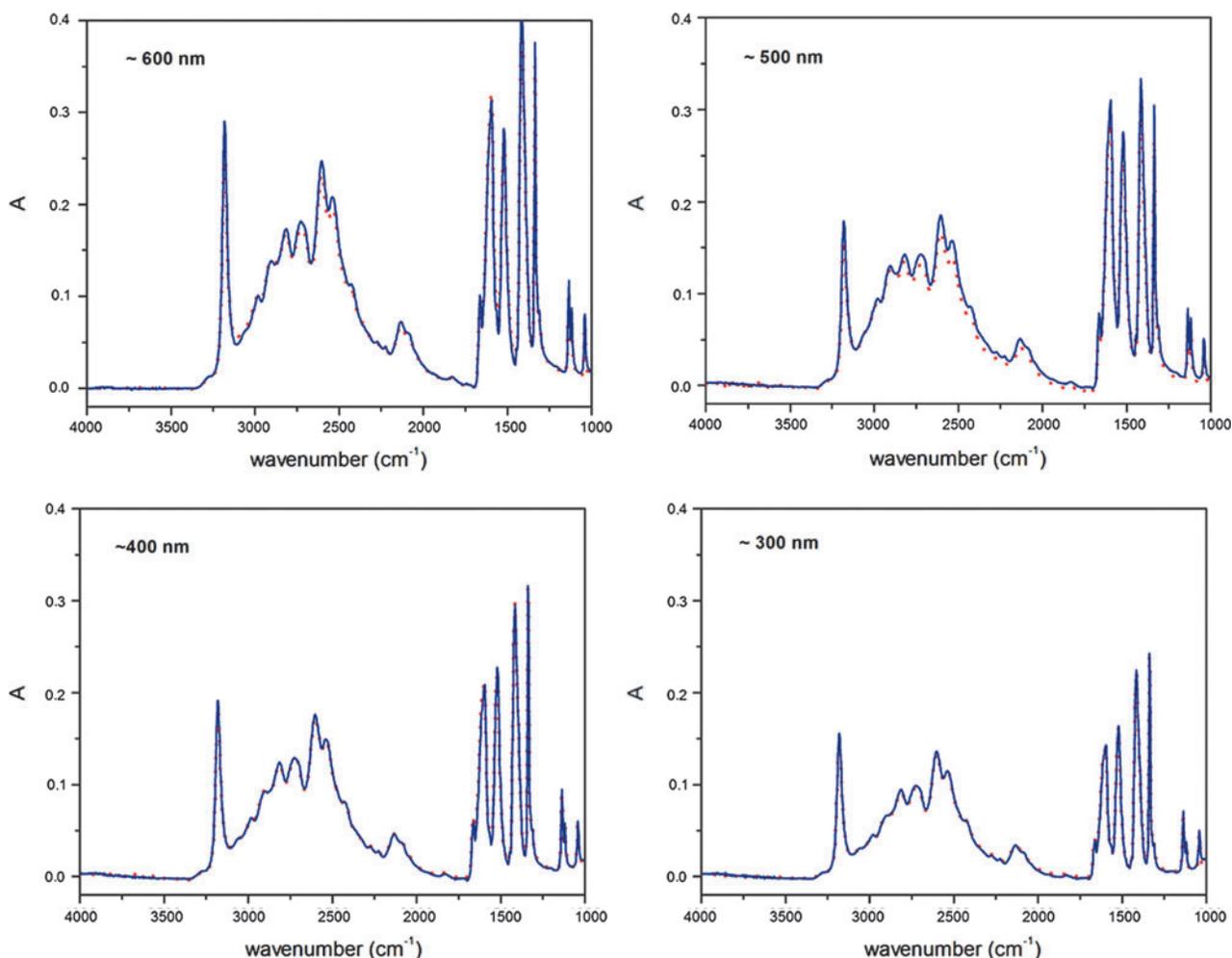
Figure 9 shows chromatograms for a set of  $\text{CH}_4/\text{Ar}$  containing cells, with a flight-exposed cell, a flight not-exposed cell, a cell kept in the dark but submitted to the same temperature cycling as those outside the ISS, and a cell kept in the dark at  $5^\circ\text{C}$  for the duration of the experiment. Small hydrocarbons that resulted from the photolysis of methane,

such as ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), isobutane ( $\text{C}_4\text{H}_{10}$ ), butane ( $\text{C}_4\text{H}_{10}$ ), and pentane ( $\text{C}_5\text{H}_{12}$ ), were detected in the flight-exposed cell. Results for the other  $\text{CH}_4$ -containing samples are similar. The amounts of ethane and propane were measured and are shown in Table 1.

## 4. Discussion

### 4.1. Glycine

The decay of glycine in the exposed cells (Fig. 7) can be attributed to photolysis since no significant change in the IR spectra was measured in the other control layers: flight dark control (Fig. 8), DLR samples kept under vacuum with temperature variations that simulate those experienced on the ISS, and DLR samples kept under vacuum at  $5^\circ\text{C}$ . Comparing behavior between each experimental layer showed that interaction with energetic particles or sublimation could not have been responsible for the evolution of the exposed samples. Indeed, sublimation could not have been responsible for the decay of the exposed samples of glycine (Fig. 7), otherwise samples submitted to the same temperature except UV would also have disappeared. The only difference between samples shown in Fig. 7 and Fig. 8 is photochemistry. From the RedShift simulation, we discerned that the



**FIG. 8.** Spectra of the four flight-exposed samples of glycine before (solid line) and after (dotted line—barely visible since superimposed on the solid line) the flight. The thickness of the initial sample is shown on the spectra. Color images available online at [www.liebertonline.com/ast](http://www.liebertonline.com/ast)

four exposed samples of glycine were exposed to the Sun for 1570 h (300 and 400 nm) and 1740 h (500 and 600 nm). The 300, 400, and 500 nm exposed samples were entirely photo-degraded. As shown in Fig. 10, this is consistent with the photolysis rate derived from our previous LEO experiment Uvolution, for which a value for the photolytic constant  $J$  of glycine was measured ( $J = 1 \times 10^{-6} \pm 0.1 \text{ s}^{-1}$ ) (Guan *et al.*, 2010). However, some glycine was still present after the sample return on the thickest sample ( $\sim 600 \text{ nm}$ ), and 13% of the initial sample could be observed on the  $\text{MgF}_2$  window. This makes sense because this sample was too thick to consider that the photolysis followed a first-order kinetic. When the upper layers of glycine were photolyzed, they absorbed most of the photon flux and hence protected the lower layers and delayed their degradation [see for instance Cottin *et al.* (2003) for the modeling of photolysis in UV optically thick samples]. This observation is also consistent with the measurements presented by Bertrand *et al.* (2012), who reported that only 40% of the glycine in their samples was degraded in rather thick samples ( $\sim 1 \mu\text{m}$ ). No new compound that resulted from the photolysis of glycine was observed in the solid phase.

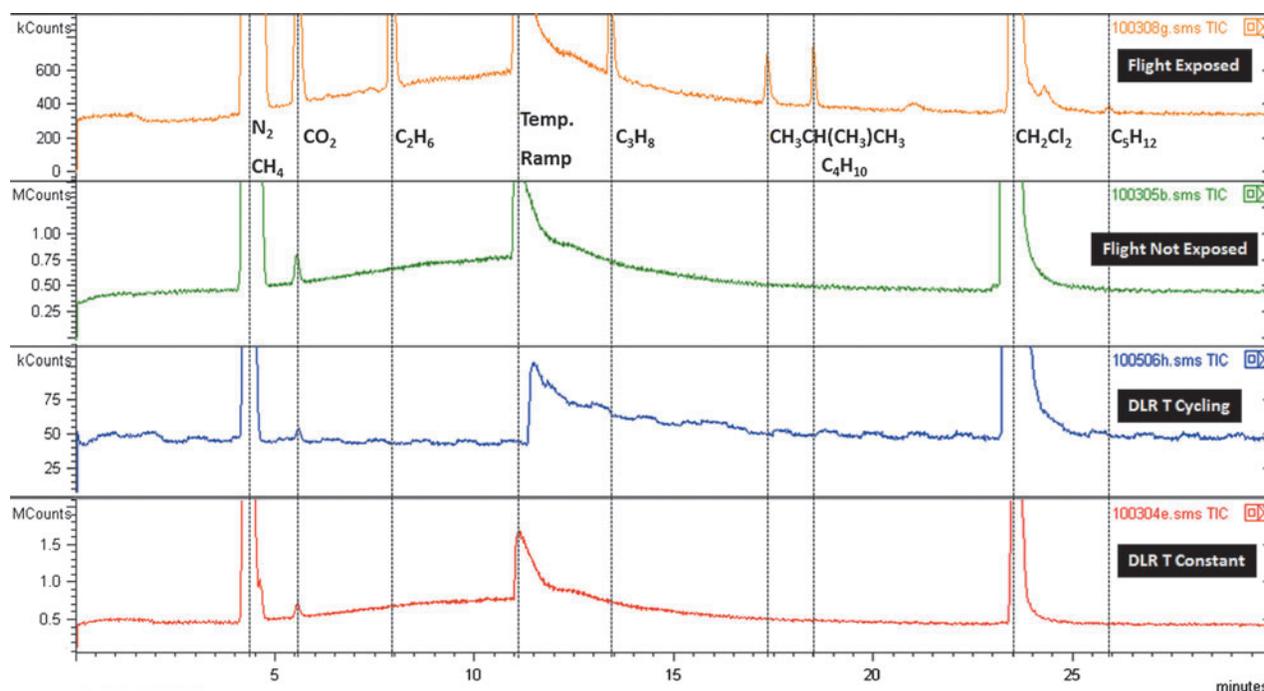
Although they are not conclusive in terms of calculation of a photolysis rate, results observed for glycine are consistent

with what can be expected from previous measurements in LEO. The results strengthen the importance of having an estimation of the total time the samples are exposed to the Sun before preparing the samples. It shows also that some compounds cannot be studied during long-duration exposure programs if there are no *in situ* measurements of the sample during the experiment in LEO.

#### 4.2. $\text{CH}_4/\text{Ar}$ and $\text{CH}_4/\text{N}_2$

The pressures and mixing ratios of gases used in our closed cells are not relevant to the upper layers of the atmosphere of Titan, which are photolyzed in the VUV range of the solar spectrum. The samples in the closed cells, however, must be considered as a validation test for gas-phase experiments in LEO and as a first attempt toward more realistic simulations of gaseous mixtures' photochemistry in the future.

It should be noted, however, that the results with regard to these samples were undermined by two limitations. The first is that the procedural blanks employed in the laboratory (we had chosen not to use such blanks in LEO due to our limited amount of samples) showed the presence of contamination.



**FIG. 9.** Chromatograms measured during the analysis of  $\text{CH}_4/\text{Ar}$  closed cells. In addition to hydrocarbons resulting from the photolysis of methane, additional products were detected:  $\text{CO}_2$  due to leaks during the injection of the sample into the chromatographic column, and  $\text{CH}_2\text{Cl}_2$  due to the procedure to remove the glue film before analysis. The rise of signal at 12 min is due to the temperature programming of the gas chromatography column during analysis. Color images available online at [www.liebertonline.com/ast](http://www.liebertonline.com/ast)

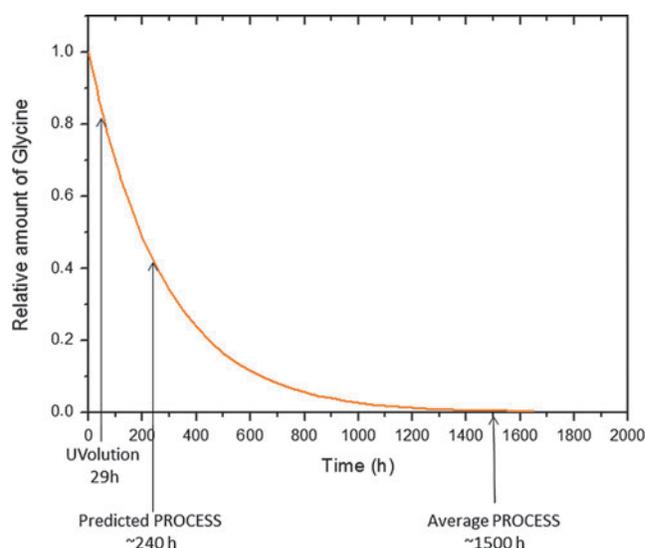
After photolysis of closed cells filled with pure nitrogen with laboratory UV lamps at a photon dose equivalent to that encountered in space, traces of hydrocarbons were detected, including ethane and propane (see also Noblet *et al.*, 2012). It is likely that these compounds were produced by the photo-degradation of the O-rings between the two parts of the closed cells, which may have been exposed to UV to a limited extent. However, the amount of those contaminants produced during these control experiments is negligible compared to the actual amount of photoproducts produced, which will be discussed later in this section, given that they represent less than one percent of the products measured when methane is photolyzed. The second issue is that the gaseous samples were accommodated in our first generation of closed cells, which were not sufficiently tight to ensure a negligible leaking over long-duration experiments. Moreover, the leaking rate was not the same from one cell to another and ranged from 5% to 100% of gas loss between the filling step and the postflight analysis.

**TABLE 1.** MEASURED VALUES FOR  $\text{C}_2\text{H}_6$  AND  $\text{C}_3\text{H}_8$  WITH GC-MS, IN  $\text{CH}_4$ -CONTAINING FLIGHT-EXPOSED CELLS, CORRECTED BY CROSS CALCULATION FOR THE LEAKING

Mixture	Exposure duration	Leak	Measured $\text{C}_2\text{H}_6$ molec·cm <sup>3</sup>	Measured $\text{C}_3\text{H}_8$ molec·cm <sup>3</sup>
$\text{CH}_4/\text{N}_2$	1254 h	60%	$7.9 \times 10^{17}$	$1.58 \times 10^{17}$
$\text{CH}_4/\text{N}_2$	1297 h	5%	$1.4 \times 10^{19}$	$2.80 \times 10^{18}$
$\text{CH}_4/\text{Ar}$	1443 h	100%	—	—
$\text{CH}_4/\text{Ar}$	1486 h	20%	$1.8 \times 10^{19}$	$2.36 \times 10^{18}$

As the evolution of the leaking over time is not known, the amount of photoproducts measured by gas chromatography after sample return was corrected by simple cross multiplication, which resulted in extremely rough approximations.

Our results are consistent with current knowledge of methane photochemistry as presented by Okabe (1978),



**FIG. 10.** Predicted degradation for a thin glycine film in LEO as a function of time assuming a first-order kinetic with  $J = 1 \times 10^{-6} \text{ s}^{-1}$ . Color images available online at [www.liebertonline.com/ast](http://www.liebertonline.com/ast)

Smith and Raulin (1999), and Romanzin *et al.* (2010).  $C_2H_6$  is indeed the major photoproduct, and in the  $C_2$  family, it should be about an order of magnitude more abundant than  $C_2H_2$  and  $C_2H_4$ , which were not detected in our measurements. After more than 1200 h of photolysis,  $C_3H_8$  is expected to be the second most abundant methane photoproduct (E. Arzoumanian, private communication). To date, modeling is not sufficiently advanced to account for the  $C_4$  and  $C_5$  products we detected.

Those results are encouraging from a qualitative point of view. Major photoproducts were detected, and we demonstrated the feasibility of gas-phase studies in LEO. However, at this stage of the study, it is not reasonable to try to derive any quantitative information such as kinetics constants to improve the modeling because our results are significantly biased by the leaks and the rough correction operated, and because modeling did not take into account the production of species such as butane, isobutane, and pentane, which were detected.

The leaking issue will be solved in the future by the use of a new generation of closed cells manufactured for the AMINO experiment, under the supervision of Air Liquide (Grenoble, France). The body of these new cells will be made of stainless steel, the  $MgF_2$  windows will be brazed, and the vacuum tightness between the two parts of the cells will be ensured by laser soldering. This new hardware will experience a leak level below  $10^{-10}$  mbar  $\cdot L \cdot s^{-1}$ , which is suitable for long-duration experiments in orbit (loss < 10% for 2 years in space). The AMINO cells were returned to the laboratory after 2 years on the EXPOSE-R facility and are being analyzed at the time of the writing of this paper. Results with these new cells will be presented in a future publication. With tight cells and improved modeling that takes into account the production of compounds such as butane, isobutane, and pentane, a comparison of LEO results with modeling and additional laboratory experiments will be useful to improve our understanding of methane photochemistry that occurs in the atmosphere of Titan.

## 5. Conclusion

This paper presents the hardware and principle of the PROCESS experiment, which was part of the EXPOSE-E payload outside the European module of the ISS from February 2008 to August 2009. It comes in support of more detailed discussions of the results presented in Bertrand *et al.* (2012) and Noblet *et al.* (2012).

Low-Earth orbit astrochemistry experiments proved to be an extremely useful complement to laboratory experiments, since it is not possible to reproduce the full solar spectrum in the VUV domain in the laboratory. Additionally, these experiments allow the simultaneous exposure of a large number of samples not only to UV photons but also to solar and galactic energetic particles. None of our measurements have yet shown any significant contribution from these kinds of energetic particles, while UV photolysis has been shown to be critical to the evolution of the samples.

PROCESS was the first of a series of three astrochemistry long-duration exposure experiments outside the ISS. After PROCESS, the AMINO experiment was exposed to space conditions from March 2009 to January 2011 on the EXPOSE-

R facility outside the Russian module Zvezda. The last experiment of the series, Photochemistry on the Space Station (PSS), should be flown late in 2013 for a total duration of 18 months.

PROCESS sample preparation and analysis after return to our laboratories has provided important lessons for the following experiments:

- (i) the importance of a good anticipation of the actual dose to which samples will be subjected before their preparation;
- (ii) the need for a conception and production of tightly closed cells that were used in AMINO and will be used in PSS;
- (iii) the need to improve the current exposure setup to enable continuous measurement of samples, for example, with an onboard spectrometer, as it is the case with the recent NASA nanosatellite O/OREOS (onboard UV spectrometer) (Mattioda *et al.*, 2012), or for the VITRINE project, which will be equipped with an onboard IR spectrometer.

In addition to “classical” LEO solid-phase sample exposure and measurements, such as that conducted in the past on the Mir station and on the ESA Biopan facilities (Barbier *et al.*, 1998, 2002; Boillot *et al.*, 2002; Ehrenfreund *et al.*, 2007; Guan *et al.*, 2010; Stalport *et al.*, 2010a), PROCESS has demonstrated the feasibility of gas-phase studies in space. The closed-cell concept will now be used for more realistic studies with regard to simulation of the atmosphere of Titan.

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## Author Disclosure Statement

No competing financial interests exist.

## Abbreviations

CBM, Centre de Biophysique Moléculaire; CNES, Centre National d'Études Spatiales; DLR, German Aerospace Center; GC-MS, gas chromatography coupled with mass spectrometry; GCR, galactic cosmic rays; ISS, International Space Station; LATMOS, Laboratoire Atmosphères, Milieux, Observations Spatiales; LEO, low-Earth orbit; LISA, Laboratoire Interuniversitaire des Systèmes Atmosphériques;

ORB, outer radiation belt; PSS, Photochemistry on the Space Station; SAA, South Atlantic Anomaly; VUV, vacuum ultraviolet.

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Address correspondence to:

*Hervé Cottin*

LISA

*Universités Paris Est Créteil and Paris Diderot*

CNRS

*Institut Pierre Simon Laplace*

UMR 7583

*61 avenue du Général de Gaulle*

*94014 Créteil cedex*

*France*

*E-mail: herve.cottin@lisa.u-pec.fr*

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