The PROCESS Experiment: Exposure of Amino Acids in the EXPOSE-E Experiment on the International Space Station and in Laboratory Simulations

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Abstract

To understand the chemical behavior of organic molecules in the space environment, amino acids and a dipeptide in pure form and embedded in meteorite powder were exposed in the PROCESS experiment in the EXPOSE-E facility mounted on the European Technology Exposure Facility (EuTEF) platform on board the International Space Station (ISS). After exposure to space conditions for 18 months, the samples were returned to Earth and analyzed in the laboratory for reactions caused by solar UV and cosmic radiation. Chemical degradation and possible racemization and oligomerization, the main reactions caused by photochemistry in the vacuum ultraviolet domain (VUV, wavelength range 100–200 nm for photon energy from 6.2 to 12.4 eV) were examined in particular. The molecules were extracted and derivatized by silylation and analyzed by gas chromatograph coupled to a mass spectrometer (GC-MS) to quantify the rate of the degradation of the compounds. Laboratory exposure in several wavelength ranges from UV to VUV was carried out in parallel in the Cologne Deutsches Zentrum für Luft- und Raumfahrt (DLR) Center and Centre de biophysique moléculaire (CBM) laboratories. The results show that resistance to irradiation is a function of the chemical nature of the exposed molecules and the wavelengths of the UV light. The most altered compounds were the dipeptide, aspartic acid, and aminobutyric acid. The most resistant were alanine, valine, glycine, and aminoisobutyric acid. Our results also demonstrate the protective effect of meteorite powder, which reemphasizes the importance of exogenic contribution to the inventory of prebiotic organics on early Earth. Key Words: Irradiation—Photochemistry—VUV—Amino acid—International Space Station—GC-MS analysis—low-Earth orbit. Astrobiology 12, 426–435.

1. Introduction

IN THE CONTEXT OF the emergence of life on Earth more than 4 billion years ago, we are particularly interested in the formation and fate of organic molecules synthesized in space and their delivery to primitive Earth via meteorites, micrometeorites, and comets. We have studied prebiotic molecules formed in interstellar ice analogues (Munoz Caro et al., 2002), the origin of chirality (Meierhenrich et al., 2005), meteorite entry into the atmosphere (Foucher et al., 2010), the effects of the impacts on prebiotic molecules (Bertrand et al., 2009), and the effects of space conditions on organic compounds (Cottin et al., 2008). Since 1994, we have been investigating the chemical processes relevant to the physical conditions encountered in the interstellar medium via several space experiments in which prebiotic molecules in vented cells were exposed to

solar UV. Two 2-week experiments were performed on Foton capsules, Biopan I (Barbier et al., 1998), and Biopan II (Barbier et al., 2001, 2002). Another experiment, Perseus, was exposed for two years on the Mir station (Boillot et al., 2002). Other experiments designed to investigate the protective effect of mineral surfaces on amino acid exposure to space have focused on cometary and meteoritic aspects or were related to Mars or Titan (Guan et al., 2010; Stalport et al., 2010). In collaboration with the LISA laboratory in Créteil (Cottin et al., 2012), we participated in the EXPOSE-E experiment (Chabin et al., 2009; Rabbow et al., 2009) from February 2008 to September 2009. Similar exposure of the same molecules was carried out in parallel in the Cologne Deutsches Zentrum für Luft- und Raumfahrt (DLR) Center and the Centre de biophysique moléculaire (CBM) laboratories. For the CBM experiment, we set up an irradiation chamber in order to

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perform the vacuum ultraviolet (VUV) irradiations. Although it is not possible to accurately reproduce space conditions in the laboratory, especially with respect to the whole range of cosmic radiation, ground experiments are very important with regard to preparation and support of space experiments. The results obtained in laboratories are complementary to those obtained in space and aid in interpretation and discussion of investigations in space.

We are especially interested in amino acids and dipeptides because of their common occurrence in carbonaceous meteorites (Cronin and Pizzarello, 1983; Martins *et al.,* 2007; Martins and Sephton, 2009) and micrometeorites (Brinton *et al.,* 1998; Matrajt *et al.,* 2004) and because of the diversity of their functional groups, an important factor for the formation of macromolecules such as proteins. We used amino acids that had already been detected in carbonaceous meteorites, that is, the proteic amino acids glycine, alanine, valine, aspartic acid, and the nonproteic amino acids aminoisobutyric acid and 2-aminobutyric acid. Glycine, alanine, and 2-aminobutyric acid were chosen to examine the effect of the VUV light on the alkyl chain length. The aminoisobutyric acid, glycine, and alanine were chosen to study the effect of substitution on the α-carbon. Thus glycine, which has no alkyl chain on its α-carbon, could be compared with alanine, which has one methyl on its α-carbon, and with aminoisobutyric acid with two methyls on its α-carbon (Fig. 1). VUV exposure effects on β-carbon substitution can be studied by comparing alanine, 2-aminobutyric acid, and valine. A dipeptide was also added to study the stability of the amide bond. The molecules were exposed both in the pure form and embedded in meteorite powder to study the effect of mineral surfaces as protection against photolysis in space. They also serve as a comparison to similar experiments in which clays and martian soil analogues are used (Barbier *et al.,* 1998; Boillot *et al.,* 2002; Stalport *et al.,* 2010).

The molecules associated with or without minerals were deposited as dry films behind MgF$_2$ windows, which are transparent to UV and VUV. The molecules were exposed in triplicate when they were mixed and in duplicate when only aspartic acid was exposed for a total of 10 samples. Seven batches of samples were prepared: two batches for

the PROCESS experiment on EXPOSE-EuTEF exposed on board the International Space Station (ISS) (one exposed to the solar light behind MgF$_2$ windows, *i.e.,* to photons above 115 nm, one in the dark), three batches in the DLR laboratory (one exposed to the UV lamp from 200 to 450 nm and two in the dark, one with temperature cycling, the other with constant temperature and pressure), and finally two batches in the CBM laboratory (one exposed to a VUV lamp with a wavelength range from 110 to 200 nm, one in the same temperature and pressure conditions in the dark). Only compounds in the free form without meteorite powder in four copies were exposed in the CBM irradiation chamber.

After irradiation in space or in the laboratory, the molecules were extracted, derivatized following chiral (Bertrand *et al.,* 2008) and nonchiral procedures, and analyzed by gas chromatography–mass spectrometry (GC-MS) and high-resolution mass spectrometry.

Here, the results of the different experiments are compared and discussed with regard to understanding the effects of the photochemistry on the organic molecules and the availability of molecules synthesized in space for the aqueous processes on Earth that produced the macromolecules essential for life.

2. Materials and Methods

2.1. PROCESS experiment, EXPOSE-E facility on EuTEF platform on board the International Space Station

EXPOSE-E was launched 7 February 2008 to the ISS together with its external European Technology Exposure Facility (EuTEF) platform during the STS-122 space shuttle mission. On 20 February 2008 the samples were exposed to solar light via telemetry. A set of the samples was exposed to solar radiation, while a second set was kept in the dark. The experiment ended on 2 September 2009, and the EuTEF platform was returned to Earth on 21 September 2009 after 1.5 years of exposure in space (see Cottin *et al.,* 2012 for more details).

The position where our samples were emplaced on the ISS prevented them from receiving continuous sunlight. This was due to the changing position of the Sun and the shadows cast by a nearby structure onto the EuTEF. For our samples, the integrated photolysis time during the experiment in orbit was estimated to be from 1397 h to 1958 h (58–81 days), depending on their position [estimation calculated from ISS orbital parameters by RedShift company (St. Niklaas, Belgium)].

The average duration of irradiation received by the 10 irradiated samples on which this paper is focused was 1696 h (12% standard error).

Table 1 provides the average dose according to the different bandwidths of interest associated with their standard errors: the total dose of solar light (100–1 mm), the photosynthetically active radiation (PAR) band (300–700 nm), the UVA band (315–400 nm), the UVB band (280–315 nm), and finally the UVC band (100–280 nm). In calculating exposure time, all variables were taken into account, including the geometrical position of the samples, filtering effects by the optical windows, and shadowing effects from the lids and the EuTEF structure.
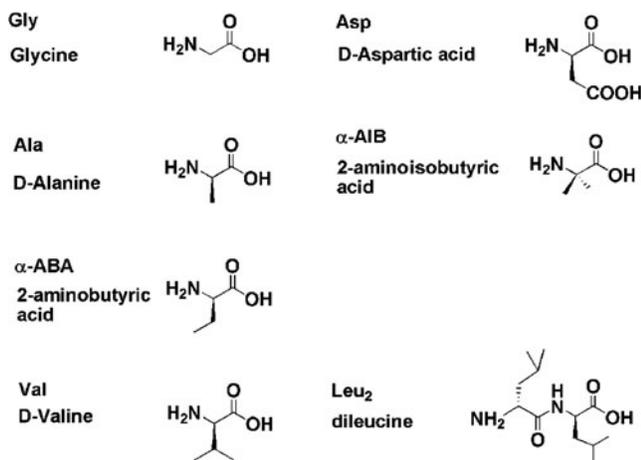

FIG. 1. Chemical name and formula of amino acids.

TABLE 1. AVERAGE DOSE IN THE DIFFERENT WAVELENGTH
RANGES RECEIVED BY THE SAMPLES EXPOSED ON THE ISS

	FULL 100 to 10^6 nm	PAR 300– 700 nm	UVA 315– 400 nm	UVB 280– 315 nm	UVC 100– 280 nm
Energy (kJ·m^{-2})	7415183 ± 14%	3413604 ± 16%	408399 ± 10%	79503 ± 11%	30262 ± 20%

2.2. The DLR experimental setup

Three batches of samples were prepared for exposure in the DLR facility. Two batches were exposed to the same temperature cycles, according to the flight data received by telemetry from EXPOSE-E during the mission. One batch was exposed for 162.9 h to UV radiation with a UV lamp (range 200–400 nm, with irradiance of 1069 W·m^{-2}), while the second batch was kept in the dark. The sample batch exposed to the UV radiation received a dose of 5.81×10^5 kJ·m^{-2}, which corresponds to that received by the samples during the EXPOSE-E mission for the UV range 200–400 nm. The pressure was maintained at 1.7×10^{-3} Pa. The third set was kept at constant temperature and pressure (5°C and 1.7×10^{-3} Pa). The experiments were performed between September 2008 and April 2010.

2.3. The CBM experimental setup

Only samples in the free form were prepared for this experiment at the CBM facility. One batch was exposed to UV radiation with a UV lamp (range 110–370 nm, with irradiance of 53.66 W·m^{-2}) for 17 days, which corresponds to a dose of 7.95×10^4 kJ·m^{-2}. The second batch was exposed to the same temperature and pressure conditions as those on the ISS but was maintained in the dark (for details of the irradiation chamber see Cottin *et al.,* 2008).

2.4. Energy received by the samples

The irradiation ranges used in the DLR laboratory correspond to those received by the samples on the ISS in the 200–400 nm range (112% for our samples) but not to irradiation below 200 nm.

Irradiation in the CBM laboratory corresponds to only 15% of the 100–400 nm energy received by the samples on board the ISS but was 133 times higher in the range 100–200 nm (see Table 2) and under 1% in the range 200–400 nm.

Comparison of the results of irradiations performed at different bandwidths helps to better understand the photochemistry of the compounds.

TABLE 2. DOSE RECEIVED BY THE SAMPLES
IN DIFFERENT WAVELENGTH RANGES ON THE ISS
AND IN THE CBM AND DLR LABORATORIES

Dose (MJ·m^{-2})	100–400 nm	100–200 nm	200–400 nm
ISS	519	1	518
DLR	581	0	581
CBM	80	75	5

2.5. Sample preparation

The amino acids glycine, D-alanine, D-valine, D-aspartic acid, aminoisobutyric acid, 2-aminobutyric acid, and norvaline (used as internal standard) were obtained from Sigma and Aldrich, and the dipeptide dileucine was acquired from Bachem. Before use, the Allende meteorite powder was carefully rinsed by successive sedimentation steps in distilled water. The absence of organic molecules from the meteorite was verified by analysis of extracts from a single meteorite sample (see the analysis of the blank in Fig. 2). To exclude any amino acid contamination, the amino acids used were in the D-form. The methanol used was of "Plus HPLC" quality purchased from Carlo Erba. The water was of milliQ quality from Millipore.

2.5.1. Preparation of the samples with aspartic acid. Samples in pure form: 37.57 μL (50 μg) of a stock solution of D-aspartic acid of 1.331 mg·mL^{-1} in water were deposited on the MgF$_2$ windows with a pipette and then slowly dried.

Samples with meteorite powder: 50 mg of the meteorite powder were mixed with 37.57 μL of the stock solution of aspartic acid and deposited on the MgF$_2$ windows with a pipette and then slowly dried.

2.5.2. Preparation of the samples with glycine, alanine, valine, aspartic acid, aminoisobutyric acid and 2-aminobutyric acid and dileucine. A stock solution at 5 mg/mL of the amino acids and the dipeptide in water was prepared.

Samples in pure form: 20 μL (100 μg) of the stock solution were deposited on the MgF$_2$ windows then slowly dried.

Samples with meteorite powder: 50 mg of the meteorite were mixed with 20 μL of the stock solution and deposited on the MgF$_2$ windows then slowly dried.

2.6. Extraction, sample preparation

After flight, the samples that were shielded against light and kept in an inert atmosphere (under N$_2$ or vacuum) were recovered by washing the windows three times with 100 μL of a methanol/water (50/50 v/v) solution. For the samples in pure form, the solvent was evaporated under vacuum and then taken up in 200 μL of water. The samples with meteorite powder were centrifuged and the supernatant collected. The meteorite powder was washed three times with a methanol/water solution. The supernatants were evaporated under vacuum and then taken up by 200 μL of water. Three analyses of each sample were run. The data given in Table 3 were the medians of the values obtained for each batch of three (in the ISS and DLR) or four (in the CBM) similar samples.

2.7. Derivatization methods

2.7.1. Silylation. Ten microliters of the internal standard (norvaline) at 0.0125 mg·mL^{-1} were added to 50 μ L of each sample and dried by speed vacuum. After total solvent evaporation, the compounds were derivatized by silylation with 20 μL of N-*tert*-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) containing 1% of *tert*-butyldimethylchlorosilane (TBDMSCl) (Fluka) and 40 μL of acetonitrile (Merck, 99.8% purity), shaken by vortex and
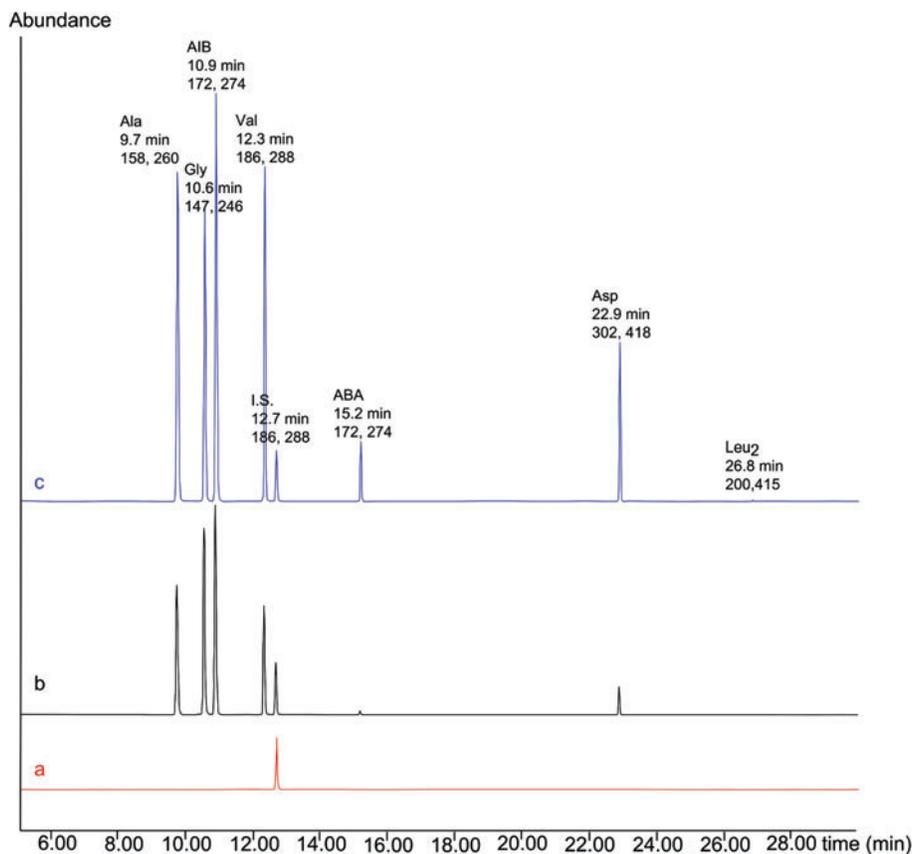
FIG. 2. Chromatograms in SIM mode of silylated extracts analyzed on the CP-Sil 19 CB column of (**a**) a blank of a meteorite powder extract, (**b**) a sample exposed on the ISS, and (**c**) a flight dark control of the ISS. The retention times (in minutes) and the two characteristic ion fragments of the molecules are given. I.S., internal standard (norvaline in these analyses). Color images available online at www.liebertonline.com/ast

sonication for 15 min, and then placed at 60°C for 1 h (see Fig. 3 for derivatization reaction).

2.7.2. Chloroformate alkyl method. This method was developed in order to quantify the racemization of compounds by the formation of diastereoisomer derivatives (see Bertrand *et al* 2008, for details). The racemization of D-alanine and D-valine was examined. The derivatization reactions led to acylation of the amino group and esterification of the carboxylic group of the amino acids. The N(O,S)-ethoxycarbonyl ethyl ester derivatives were analyzed on a chiral column (see Fig. 4).

The compounds were derivatized by 23 μL of ethanol and 13 μL of pyridine. Fifteen microliters of ethyl chloroformate were added to this solution. The vial was vigorously shaken for 2 min, and the derivatives were extracted in the organic layer. Finally, 1 μL of the organic layer was injected into the gas chromatograph.

2.8. GC-MS analysis

After derivatization, 1 μL of each solution was injected into an Agilent 6890 gas chromatograph equipped with a nonchiral CP-Sil 19 CB fused-silica capillary column from

TABLE 3. QUANTITIES OF AMINO ACIDS CALCULATED FOR EACH BATCH OF SAMPLES
IN THE ISS AND IN THE CBM AND DLR LABORATORIES

	Without meteorite powder			With meteorite powder	
	ISS	*DLR*	*CBM*	*ISS*	*DLR*
Ala	43 μg ± 14	59 μg ± 15	97 μg ± 4	80 μg ± 13	68 μg ± 12
Gly	61 μg ± 5	64 μg ± 11	87 μg ± 6	80 μg ± 19	63 μg ± 24
AIB	57 μg ± 12	47 μg ± 10	86 μg ± 10	91 μg ± 11	72 μg ± 14
Val	35 μg ± 18	53 μg ± 12	98 μg ± 6	83 μg ± 12	89 μg ± 8
ABA	6 μg ± 18	11 μg ± 29	49 μg ± 33	52 μg ± 26	40 μg ± 8
Asp	20 μg ± 20	32 μg ± 18	40 μg ± 28	61 μg ± 28	46 μg ± 6
Leu$_2$	0 μg	13 μg ± 18	0 μg	61 μg ± 26	30 μg ± 15

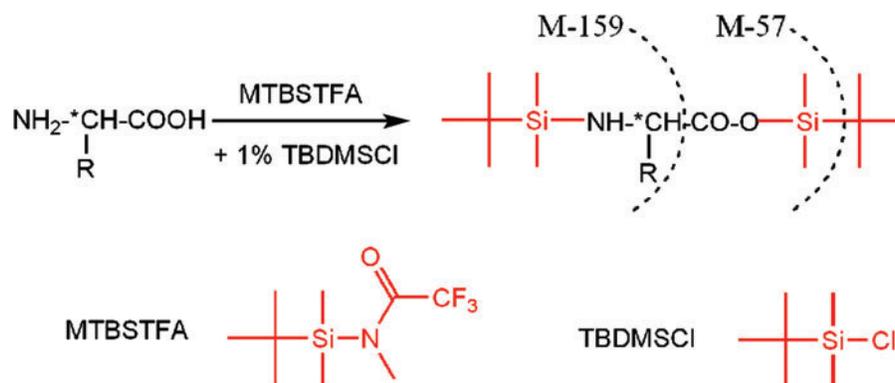**FIG. 3.** Silylation reaction of amino acid with MTBSTFA (with 1% TBDMSCl). Color images available online at www.liebertonline.com/ast

Varian (length 30 m, i.d. 0.25 mm, film thickness 0.2 μm) or with a chiral Chirasil-L-Val column from Macherey-Nagel (length 25 m, i.d. 0.25 mm, film thickness 0.12 μm) coupled with an Agilent 5973 mass spectrometer as the detector (electronic ionization at 70 eV). GC-MS chromatogram acquisition and data processing were performed with the Agilent MSD ChemStation software. Helium was used as the carrier gas (inlet pressure 178 kPa), and splitless injection mode was used. A constant flow mode of 1.5 mL·min^{-1} was selected. The injector temperature was set to 250°C, the mass

spectrometer source to 150°C, and the mass spectrometer quadrupole to 230°C. With the CP-Sil 19 CB column, the oven temperature was set to 100°C or 125°C for 5 min and then programmed to reach 250°C at a rate of 5°C·min^{-1}. With the Chirasil-L-Val column, the oven temperature was set to 80°C for 5 min and then programmed to reach 160°C at a rate of 2°C·min^{-1}.

Identification and quantification of the compounds were performed by comparing the retention times and integrations of peaks in the sample chromatograms and their mass spectra with those of standards (see chromatograms on Figs. 2 and 4).

The amino acid tert-butyldimethylsilyl derivatives are characterized by a mass spectrum in which the most intense spectral peak is the [M-57]$^+$ fragments, corresponding to the molecular ions that have lost a tert-butyl group (57 amu) (Casal *et al.*, 2004; Schummer *et al.*, 2009), and the [M-159]$^+$ fragments (see Fig. 3). Each sample was analyzed by mass spectrometry in both the total ion chromatogram (TIC) and selected ion monitoring (SIM) acquisition modes. In a TIC, the y axis corresponds to the sum of all detected ion currents for each scan, while the SIM mode is a data acquisition technique in which only the currents of a small range of selected ion fragments are monitored in order to maximize the sensitivity. The SIM mode with the [M-57]$^+$ and [M-159]$^+$ fragments was chosen to quantify the amino acids. The dipeptide is represented by a small peak in the chromatogram but is not visible at the scale shown in Fig. 2.

The $N(O,S)$-ethoxycarbonyl ethyl ester derivatives are characterized by a mass spectrum in which the most intense spectral peak is the [M-73]$^+$ fragments, corresponding to the molecular ions that have lost an acylium group [CO$_2$CH$_2$-CH$_3$] (73 amu). The main mass peak is the ion fragment $m/z = 116$ for alanine and $m/z = 144$ for valine.

3. Results

The irradiated samples with and without meteorite powder were compared to flight dark controls (samples maintained in the dark in the same conditions of temperature and pressure as the exposed samples) in the experiment on board the ISS (see Section 3.1) and in the DLR experiment (see Section 3.2). For the experiment in the CBM, only samples in the free form were irradiated (see Section 3.3). All quantification results are shown in Table 3. To compare with
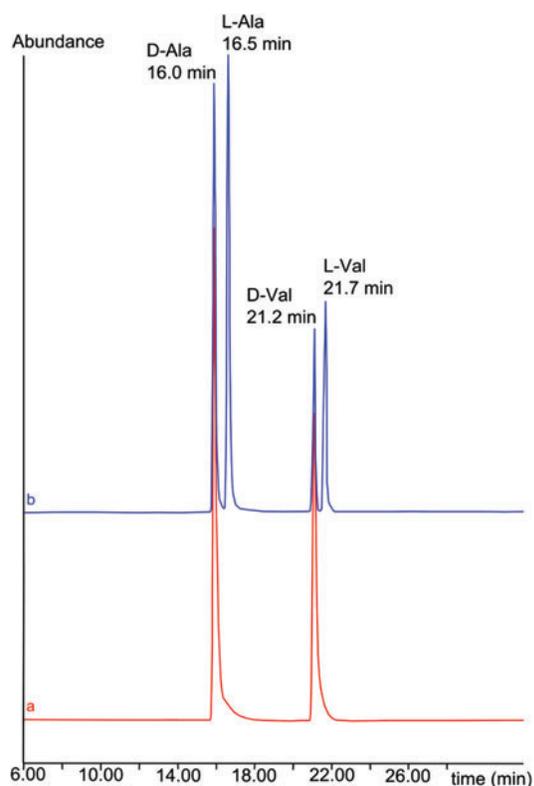

FIG. 4. Chromatograms in SIM mode of the $N(O,S)$-ethoxycarbonyl ethyl ester derivatives of (**a**) a sample exposed on the ISS compared with (**b**) a control solution of L- and D-alanine and L- and D-valine (analysis on the Chirasil-L-Val column). Color images available online at www.liebertonline.com/ast

previous studies, the $t_{1/2}$ (half-life time) of the compounds was calculated for each experiment with a 0th order kinetics assumption (see Section 3.4).

3.1. Racemization.   The compounds were derivatized by the chloroformate alkyl method with ethanol in pyridine and analyzed by GC-MS on the Chirasil L-Val column. No racemization of D-alanine and D-valine was detected in any sample. Figure 4 shows the chromatograms in SIM mode of the N(O,S)-ethoxycarbonyl ethyl ester derivatives of a sample exposed on the ISS compared with a control solution of L- and D-alanine and L- and D-valine.

3.2. Degradation.   In the same batch of samples, some compounds were more resistant to radiation than others. These differences were calculated and appear as error bars in the figures below. The disparity was often even more noticeable for the most damaged molecules (ABA, Asp, and Leu$_2$) and for the compounds associated with meteorite powder (Table 3).
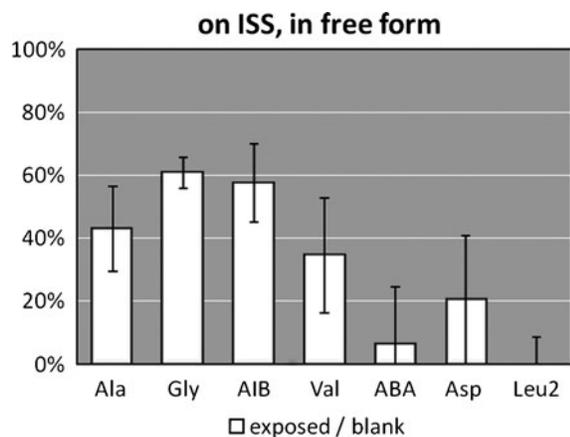
For the dipeptide, reproduction of the extraction, derivatization, and analysis was more difficult than for the other molecules. The results obtained for this compound are therefore less reliable than the results for others.

Figure 2 shows the chromatograms of silylated extracts of (a) a blank of a meteorite powder extract, (b) an ISS exposed sample, and (c) an ISS control sample.
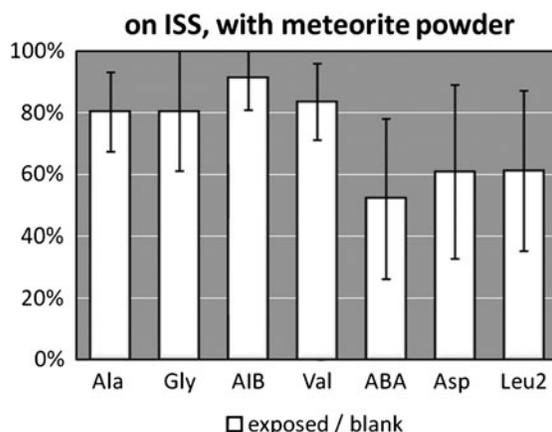
3.1. Results of the PROCESS experiment on board the ISS

Figures 5 and 6 show the range of degradation of the amino acids measured in samples exposed on the ISS in the free form and with meteorite powder. Each batch of samples was compared to the same batches of flight dark controls.

On board the ISS, the amino acids exposed in the free form were degraded by more than 40% (see Fig. 5). The quantity of the dipeptide Leu$_2$ in the samples was too low to be quantified by GC-MS, but the molecule was still present. More than 80% of the compounds associated with meteorite powder were preserved, except for the aspartic and amino butyric acids and the dipeptide, which were altered from

FIG. 6.   Range of degradation of amino acids with meteorite powder in samples exposed on the ISS compared to the flight dark controls (not exposed to sunlight).
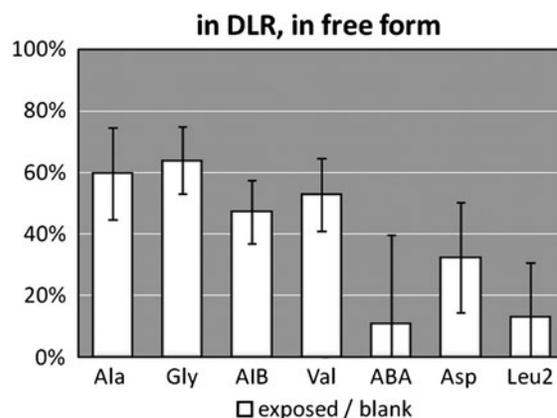
between 39% and 48% (see Fig. 6). The protective effect of the meteorite powder, however, is important, in particular for those compounds that showed the most degradation when exposed in the free form.

In these two forms, free or embedded in meteorite powder, the most resistant compounds were the amino acids alanine, glycine, aminoisobutyric acid, and valine; the most degraded were the dipeptides and the aspartic and aminobutyric acids.

3.2. Results of the DLR experiment

Figures 7 and 8 show the range of degradation of the amino acids measured in samples irradiated in the free form or embedded in meteorite powder with a UV range of 200–400 nm. Each set of samples was compared to the same batches of controls (samples in dark with temperature cycling).

Amino acids exposed in the free form were more degraded than those exposed with meteorite powder. In this experiment, the most resistant compounds were the amino

FIG. 5.   Range of degradation of amino acids in samples exposed on the ISS without meteorite powder compared to the flight dark controls (not exposed to sunlight).

FIG. 7.   Range of degradation of the amino acids in samples exposed in the DLR without meteorite powder compared to controls (samples not irradiated but exposed to the same conditions of temperature and pressure).
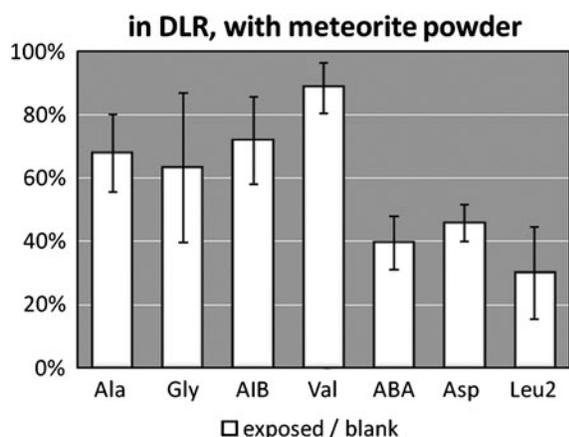
in DLR, with meteorite powder

FIG. 8. Range of degradation of the amino acids with meteorite powder in samples exposed in the DLR compared to controls (samples not irradiated but exposed to the same conditions of temperature and pressure).

acids alanine, glycine, aminoisobutyric acid, and valine (degradation less than 53%), and the most altered were the dipeptide and aspartic and aminobutyric acids (degradation more than 68%).

3.3. Results of the CBM experiment

Figure 9 shows the range of degradation of the amino acids in samples irradiated in the free form with VUV mainly between 110 and 200 nm and with a total energy 6.7 times lower than in the ISS and DLR experiments. As always, each set of samples was compared to the same batches of controls (samples in the dark in the CBM chamber).

The alanine and valine amino acids were the best preserved (only 3% loss for alanine and 2% for the valine) in contrast to the aspartic and aminobutyric acids, which showed 60% and 51% degradation, respectively. The dipeptide Leu$_2$ was not detected by GC-MS in any samples and had probably been completely degraded. Although glycine and aminoisobutyric acid were only weakly degraded (13%
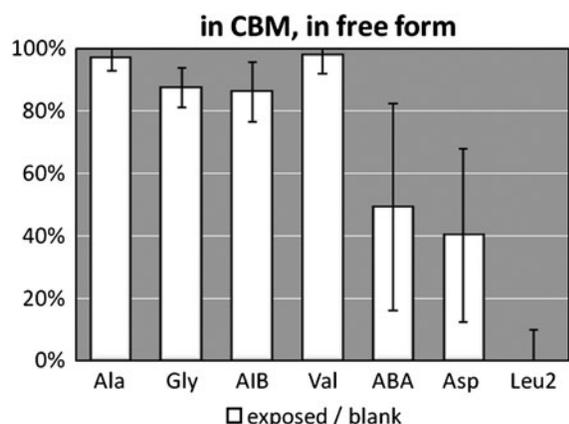
and 14%, respectively), the degradation was significant given the total energy received by the samples.

If the degradation of the amino acids exposed in the CBM laboratory is considered to be linear and degradation obtained with only 15% energy is extrapolated to 100%, 79% alanine and 85% valine could be preserved, but only 16% for glycine and 7% for aminoisobutyric acid. The other compounds, aminobutyric acid, aspartic acid, and dileucine, would be completely degraded.

3.4. Calculation of the half-life time, $t_{1/2}$

Since our samples are rather thick, a 0$^{\text{th}}$ order kinetics assumption was used to calculate the half-life time $t_{1/2}$ of each compound for each experiment by using their degradation rates.

For better comparison between the different irradiations, the half-life times $t_{1/2}$ were calculated for the laboratory experiments (DLR and CBM) as scaled to the 100–400 nm wavelength received by the samples on the ISS (519 MJ·m^{-2} as shown in Table 2).

Table 4 shows the half-life time $t_{1/2}$ calculated for each compound in each experiment with and without meteorite powder.

4. Discussion

The three experiments in the DLR and CBM laboratories and on the ISS gave results that are very interesting to compare.

In the three experiments with or without meteorite powder, the most resistant amino acids were alanine, glycine, aminoisobutyric acid, and the valine, while the most altered ones were aminobutyric acid, aspartic acid, and the dipeptide. The amino acids with a functional group (*e.g.,* aspartic acid), a linear chain (*e.g.,* aminobutyric acid), or with an amide bond (*e.g.,* dipeptide Leu$_2$) were more sensitive to UV radiation than those with hydrocarbon side chains. In addition, the compounds with a ramified chain (*e.g.,* valine) were more stable than those with a linear chain (*e.g.,* aminobutyric acid). This corresponds to the chemical stability of the compounds that were previously observed during simulations of meteorite impacts (Bertrand *et al.,* 2009).

in CBM, in free form

FIG. 9. Range of degradation of the amino acids in samples exposed in the CBM laboratory without meteorite powder compared to controls (samples not irradiated but exposed to the same conditions of temperature and pressure).

TABLE 4. $T_{1/2}$ OF THE COMPOUNDS IN THE DIFFERENT EXPERIMENTAL CONDITIONS (IN SPACE OR IN LABORATORIES, WITH AND WITHOUT METEORITE POWDER) CALCULATED AS THE FUNCTION OF THE DOSE (100–400 nm) RECEIVED BY THE SAMPLES ON THE ISS (519 MJ·m^{-2} AS SHOWN IN TABLE 2)

$t_{1/2}$ (days)	Without meteorite powder			With meteorite powder	
	ISS	DLR	CBM	ISS	DLR
Ala	62±8	98±21	175±15	178±23	110±37
Gly	90±4	109±15	43±7	179±35	96±58
AIB	83±10	75±17	39±14	404±43	118±59
Val	54±10	84±19	244±24	213±26	309±51
ABA	38±7	44±18	11±10	74±19	58±24
Asp	44±9	58±18	9±11	90±25	65±29
Leu$_2$	35±3	45±10	5±4	91±23	50±30

The most obvious difference in free form between both groups was observed in the CBM experiment in which alanine, glycine, aminoisobutyric acid, and valine were far better preserved than the other compounds. Both alanine and valine are very stable, having $t_{1/2}$ of over 175 days.

In both experiments in the DLR and on the ISS, meteorite powder had a notable protective effect on the compounds. The most noteworthy result is shown for the dipeptide. Leu$_2$ in the free form was completely degraded in space, but more than 60% of it was preserved when associated with meteorite powder: the $t_{1/2}$ of dileucine is only 35 days when exposed in free form but more than twice as long (91 days) when associated with meteorite powder. However, the protective effect of the meteorite powder appears to be more important for the compounds exposed in space than for those exposed in the DLR laboratory. This reaction may have been due to the wavelengths at which the compounds were exposed. This hypothesis is corroborated by comparison of the $t_{1/2}$ of the compounds in free form and with meteorite powder in the DLR experiment and on the ISS; the $t_{1/2}$ for the samples with meteorite powder on the ISS were higher except for valine. We can thus conclude that the protective effect of meteorite powder seems more important when the UV energy is high. This finding could be confirmed by future irradiation of molecules with meteorite powder in the CBM laboratory.

The experiment in the CBM laboratory showed that degradation in the VUV range from 110 to 200 nm caused more specific damage to certain amino acids than the less energetic UV ranges above 200 nm. In the alanine–glycine–aminoisobutyric acid–valine group, alanine and valine were far more resistant to degradation (with $t_{1/2}$ over 175 days) than glycine and aminoisobutyric acid (with $t_{1/2}$ under 43 days). In contrast, in the DLR laboratory and on the space station, such a large difference was not measured. Measurements of the absorption spectra of the molecules in the 110–200 nm range would allow an interpretation of these data. Such spectra are currently missing in the literature.

Comparison of glycine, alanine, and aminoisobutyric acid shows no relationship between degradation and substitution of the α-carbon, since glycine, in the free form, was the most stable of the free form samples in the ISS and the DLR experiments, whereas aminoisobutyric acid was the most resistant when associated with meteorite powder in the ISS experiment. Moreover, alanine was the most stable of this group in the CBM experiment. Similarly, comparison of glycine, alanine, and aminobutyric acid shows no relationship between degradation and length of the hydrocarbon chain. The situation is different with respect to substitution of the β-carbon, valine being more stable than aminobutyric acid in all experiments, with or without meteorite powder. We conclude that an amino acid is more stable to photodegradation if its alkyl hydrocarbon chain is branched. This could be verified in the future by the exposure of other compounds, for example, n-butane and isobutane.

Our analyses showed that neither racemization nor oligomerization was identified in any of the three experiments. The effects of photodegradation as the decarbonylation and the decarboxylation of the compounds analyzed by electrospray high-resolution mass spectrometry will be described in a future publication.

Comparison of the results obtained here with those obtained previously shows both similarities and differences.

Our experiments confirmed that the dicarboxylic acids, such as aspartic acid (Barbier et al., 1998, 2001, 2002; Boillot et al., 2002) or mellitic acid (Stalport et al., 2010), are less resistant to exposure than amino acids with a hydrocarbon chain, such as alanine, glycine, or valine. They also confirmed the protective effect of mineral surfaces as previously described for clays by Barbier et al. (1998, 2001, 2002) and Boillot et al. (2002). Our compounds were less damaged when they were associated with meteorite powder than when they were in free form. This is in contrast to the results of Stalport et al. (2010), who used a martian soil simulant, whereas we used Allende meteorite powder. When comparing the molecules glycine and aminoisobutyric acid to previous results, the molecules in our experiments are much more stable than those presented in experiments of Guan et al. (2010) and Stalport et al. (2010), since their $t_{1/2}$ were 90 and 83 days, respectively, in free form and 179 and 404 days when associated with meteorite powder. These differences could perhaps be explained by the different deposition methods, which cause different crystalline forms (and result in different absorption spectra) and different thicknesses of the deposits. Guan et al. (2010) and Stalport et al. (2010) used the sublimation/re-condensation method of deposition, whereas we used the solvent evaporation method. The methods cause different crystallizations of the molecules. Our deposition method by pipette produces a deposit that is significantly less homogeneous and thicker.

Therefore, we used a 0th order kinetics assumption to calculate the half life-time of our samples, while they used a 1st order kinetics assumption with their thin films. Furthermore, Guan et al. (2010) and Stalport et al. (2010) used Fourier transform infrared spectroscopy to analyze their materials, whereas GC-MS analysis was used in the present study.

5. Conclusions

The chemical behavior of amino acids and a dipeptide, in pure form and embedded in meteorite powder to irradiation, was studied in space and in the laboratory (DLR-Cologne, CBM-Orléans). All molecules, with or without meteorite powder, were more or less affected when exposed to solar radiation. The rate of compound degradation was quantified. The results show that resistance to irradiation depends on

(1) the chemical nature (structure and composition) of the exposed molecules,
(2) the emission spectrum of the UV source,
(3) the presence of protective meteorite powder.

In the ISS and DLR experiments, meteorite powder had a significant protective effect on the compounds.

The amino acid with a diacid group, aspartic acid, was more sensitive to UV radiation than amino acids with alkyl chains. The dipeptide with an amide bond was almost completely degraded when not associated with a mineral surface. In contrast, the amino acids with a substituted chain, such as valine, were more stable than those with a linear chain, as in the case of aminobutyric acid.

In the three experiments, neither racemization nor oligomerization was identified for any of the compounds.

Further analyses are underway to understand in more detail the products synthesized by photochemistry.

From the astrobiological viewpoint, some of the exposed compounds could be sufficiently stable in space conditions to survive transport in interstellar space, especially if they are embedded in appropriate mineral matter and if they are in a suitable crystalline form. However, some of the compounds initially present in meteorites, micrometeorites, and comets as molecules with a diacidic group, an amide bond, or a linear hydrocarbon chain could be quickly altered, especially during a long journey in space and if they are not protected sufficiently by mineral surfaces.

All these data suggest that photochemistry may act as a selective filter to the delivery of extraterrestrial amino acids to Earth via meteorites, micrometeorites, or comets.

Other experiments have shown major differences between the results obtained in laboratory experiments and those obtained in Earth orbit. This demonstrates that new experiments with other compounds in low-Earth orbit will be needed to fully understand the effects of photochemistry in space and the fate of organic matter synthesized in space and imported to Earth via meteorites and micrometeorites.

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Author Disclosure Statement

No competing financial interests exist.

Abbreviations

CBM, Centre de biophysique moléculaire; DLR, Deutsches Zentrum für Luft- und Raumfahrt; EuTEF, European Technology Exposure Facility; GC-MS, gas chromatography–mass spectrometry; ISS, International Space Station; MTBSTFA, *N-tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide; PAR, photosynthetically active radiation; SIM, selected ion monitoring; TBDMSCl, *tert*-butyldimethylchlorosilane; TIC, total ion chromatogram.

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