NON-RACEMIC AMINO ACID PRODUCTION BY ULTRAVIOLET IRRADIATION OF ACHIRAL INTERSTELLAR ICE ANALOGS WITH CIRCULARLY POLARIZED LIGHT

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ABSTRACT

The delivery of organic matter to the primitive Earth via comets and meteorites has long been hypothesized to be an important source for prebiotic compounds such as amino acids or their chemical precursors that contributed to the development of prebiotic chemistry leading, on Earth, to the emergence of life. Photochemistry of inter/circumstellar ices around protostellar objects is a potential process leading to complex organic species, although difficult to establish from limited infrared observations only. Here we report the first abiotic cosmic ice simulation experiments that produce species with enantiomeric excesses (e.e.'s). Circularly polarized ultraviolet light (UV-CPL) from a synchrotron source induces asymmetric photochemistry on initially achiral inter/circumstellar ice analogs. Enantioselective multidimensional gas chromatography measurements show significant e.e.'s of up to 1.34% for (^{13}C)-alanine, for which the signs and absolute values are related to the helicity and number of CPL photons per deposited molecule. This result, directly comparable with some L excesses measured in meteorites, supports a scenario in which exogenous delivery of organics displaying a slight L excess, produced in an extraterrestrial environment by an asymmetric astrophysical process, is at the origin of biomolecular asymmetry on Earth. As a consequence, a fraction of the meteoritic organic material consisting of non-racemic compounds may well have been formed outside the solar system. Finally, following this hypothesis, we support the idea that the protosolar nebula has indeed been formed in a region of massive star formation, regions where UV-CPL of the same helicity is actually observed over large spatial areas.

Key words: astrobiology – astrochemistry – comets: general – ISM: molecules – meteorites, meteors, meteoroids

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1. INTRODUCTION

Ices are widely observed in many astrophysical environments (Gibb et al. 2004; Dartois 2005), particularly in dense molecular protostellar clouds from which stars, disks, debris such as asteroids and comets, and eventually planetary systems form. Direct comparison between laboratory and astronomical infrared (IR) spectra allows the determination of the composition and structure of such cosmic ices. These observations have shown that the chemical composition of interstellar and cometary ices appears to be very similar (Gibb et al. 2000; Neslusan 2002; Crovisier 2007), because cold and non-evolved cometary ices are believed to be, at least in part, leftovers from the initial interstellar solid-state molecular matter present in dense clouds.

Extraterrestrial ices are subjected to various energetic processes. Among them, UV photochemistry leads to the formation of new chemical species due to highly reactive radicals produced by energetic photons within the ice matrix (d'Hendecourt et al. 1982). Such a phenomenon most probably occurs in space, since species that are formed in experiments from UV irradiation of ice analogs such as carbon dioxide, formaldehyde, ammonium cyanate, formamide, and tentatively urea have been detected in both astrophysical ice environments and laboratory simulations (d'Hendecourt & Jourdain de Muizon 1989; Schutte et al. 1996; Schutte & Khanna 2003; Raunier et al. 2004; Oberg et al. 2009). Although difficult to detect through conventional astronomical

spectroscopy, essentially because of strong spectral confusion and masking that arise from major ice constituents, experiments on laboratory analogs and their UV-driven chemical evolution to organic residues may serve as a useful template to understand the fate of ices in astrophysical environments.

In the laboratory, simulations of photo- and thermochemistry lead to the formation of complex semi-refractory organic residues, known to contain a large variety of organic compounds (Bernstein et al. 1995; Muñoz Caro & Schutte 2003; Nuevo et al. 2010). Most of these organics are chiral because photochemistry, radical chemistry and subsequent reactant diffusion will statistically produce racemic chiral species (i.e., they have equal numbers of the left and right enantiomers), even from achiral simple ice molecules, if no asymmetry factor is involved in the process. Among these organics, the detection of up to 16 different amino acids has been reported in one experiment including achiral (glycine, sarcosine, β-alanine) and chiral amino acids (alanine, serine, aspartic acid, etc.; Muñoz Caro et al. 2002), and confirmed in several other similar experiments (Bernstein et al. 2002; Nuevo et al. 2008). Note that this detection is obtained after acid hydrolysis treatment of the macromolecule which forms these residues.

In parallel, chiral organics including amino acids have been found in meteorites such as Murchison and Murray, some of them displaying small but measurable enantiomeric excesses (e.e.'s) of the L form only, after a similar acid hydrolysis treatment (Engel & Macko 1997; Cronin & Pizzarello 1997,

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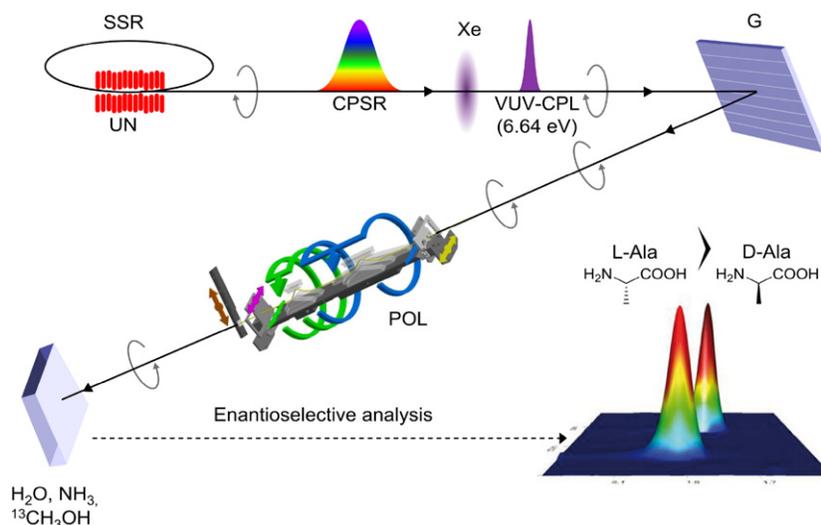
Figure 1. Full schematic of the experimental setup for the asymmetric photochemical synthesis of amino acids from achiral interstellar precursor molecules. This setup consists of different elements for the production, filtering, and calibration of circularly polarized electromagnetic radiation, the simultaneous deposition and irradiation of interstellar ice analogs, and the enantioselective analysis of amino acids via multidimensional GC. VUV circularly polarized synchrotron radiation (CPSR) is produced by the HU640 undulator (UN) on the SOLEIL storage ring (SSR) and collected by the DESIRS beamline. High-energy harmonics of the undulator are then cut off by passing through a gas filter filled with xenon (Xe). The CPSR, with a 7% bandwidth Gaussian-like spectrum centred at 6.64 eV, is then simply reflected by the monochromator's grating (G) placed at the zeroth order. At this point, the CPSR circular polarization rate (94% $\pm$ 2%) was calibrated and measured by an insertable in-vacuum VUV polarimeter (POL). The pulse then irradiates the condensed H_2O, NH_3, and $^{13}CH_3OH$ mixture at $T = 80$ K.
(A color version of this figure is available in the online journal.)

1999). Thus, it is reasonable to ask whether any sort of asymmetric process leading to an enantioselective enrichment is at work in astrophysical environments, and under which conditions these excesses are generated. Furthermore, if such an asymmetric process is a valid phenomenon in common astrophysical environments, it has implications for the formation of our solar nebula and obviously for the prebiotic conditions on the primitive Earth.

Among the mechanisms thought to generate significant e.e.'s in astrophysical environments, UV-circularly polarized light (UV-CPL) is one of the most commonly described and debated (see Bailey 2001 and references therein) if only as it is a historically suggested phenomenon proposed by van't Hoff as early as 1897. However, it has never been experimentally proven to be relevant in a coherent astrophysical scenario. Since UV-CPL is expected to induce photochemistry just as unpolarized UV photons do, we tested such a scenario in a laboratory simulation using UV-CPL to drive the photochemistry of cosmic ice analogs under plausible astrophysical conditions and search for the generation of chiral species with significant e.e.'s, such as proposed by Greenberg et al. (1994). Previously attempted experiments provided inconclusive results, either due to intrinsic limitations in the photon flux and/or to the detection limits of the analytical methods used (Nuevo et al. 2006; Takano et al. 2007), or because they were not readily applicable to a realistic astrophysical situation (Takano et al. 2007).

2. LABORATORY EXPERIMENTS

The experimental setup, which has been largely discussed elsewhere (Nuevo et al. 2007), was adapted to be mounted on the vacuum UV (VUV) DESIRS beamline[8] at the SOLEIL synchrotron facility (France). The undulator feeding the DESIRS beamline provides a very high quality VUV light beam with fully adjustable polarizations (Marcouille et al. 2007) which,

by polarimetry (Nahon & Alcaraz 2004), can be calibrated and tuned to generate quasi-perfect circular VUV-CPL of any chosen helicity, i.e., right (R) and left (L), as well as linearly polarized light (LPL; Figure 1). This radiation, filtered from its high-energy harmonics by a gas filter and transmitted by the zeroth order of the monochromator's grating, has a typical 7% bandwidth and an integrated flux of about 1×10^{15} photons cm^{-2} s^{-1} at the sample position. For this set of experiments, we selected an irradiation photon energy of 6.64 eV (Figure 2), which is close to the maximum intensity of the circular dichroism (CD) spectrum (n–$\pi*$ transition) of most α-hydrogenated amino acids measured in the amorphous solid state (Meierhenrich 2008; Meierhenrich et al. 2010).

Empirically, our goal was to search for enantioselective synthesis of chiral organic materials triggered by UV-CPL under simulated inter/circumstellar conditions. For this, ice mixtures of composition of H_2O:CH_3OH:NH_3 (2:1:1), assumed to be a good representative model for interstellar ices, were deposited onto a cold ($T = 80$ K) IR-transparent window in order to monitor the evolution of the composition and thickness of the ice, and to correlate these parameters with the number of synchrotron radiation (SR) photons irradiating the ice samples during the experiments. The use of a higher temperature (80 K), rather than observed temperatures for interstellar ices (10–20 K), was decided to enhance diffusivity and recombination of photoproducts within the ices, since a lower temperature simulation is truly impossible given the incompatibility with beam time and flux constraints at the SOLEIL synchrotron facility. However, since the complete cycle of inter and circumstellar grain evolution comprises cycles through warmer regions (hot cores) in which grain temperatures rise significantly (200 K), astronomical organic residues should be produced via pathways similar to those in our laboratory simulations. Indeed, previous experimental studies showed that the irradiation temperature (10 or 80 K) has very little influence on the final composition of the organic residues (Muñoz Caro & Schutte 2003; Nuevo et al. 2008). Finally, we used
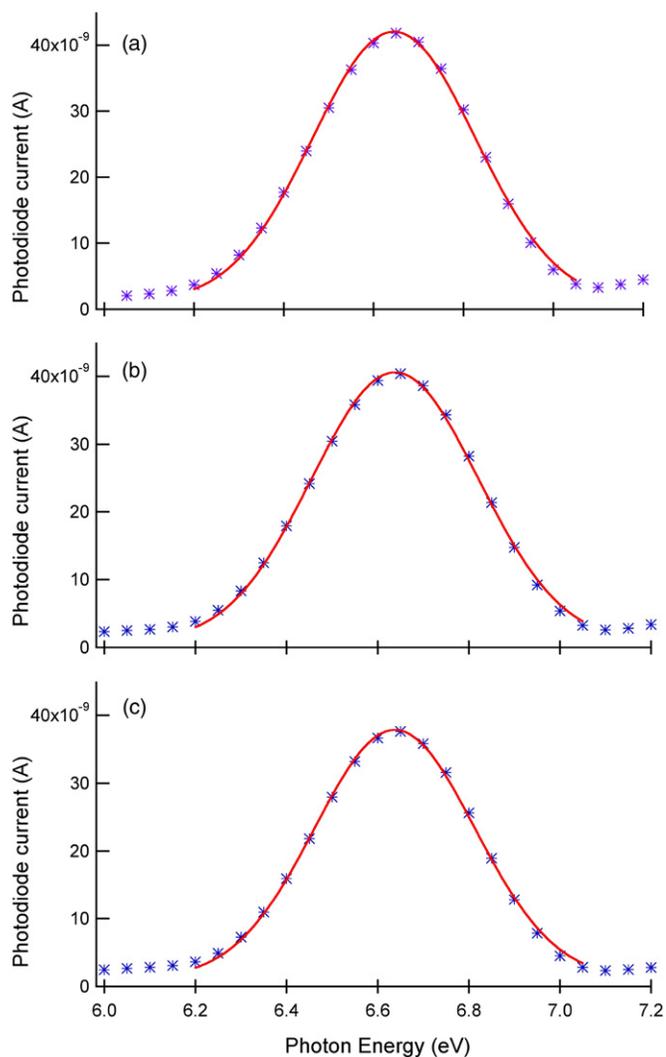
Figure 2. Spectrum of the SR used for the irradiation. The spectra were measured by a photodiode for the three polarization states: (a) right-handed circular polarization, (b) left-handed circular polarization, and (c) linear polarization. As shown by the gaussian fits (solid lines), the central photon energy is 6.641 ± 0.003 eV, and the FWHM 0.418 ± 0.010 eV. The relative integrated photon fluxes in the two CPL modes are similar within 2% and correspond to an absolute value of about 5×10^{14} photons s^{-1}.

(A color version of this figure is available in the online journal.)

isotopically labeled ^{13}C-methanol as the only source of carbon in the starting mixture, to prevent any confusion due to potential biological contamination of our samples. The measurements presented in this work are thus only related to the ^{13}C-labeled compounds formed in our residues.

In order to provide an interpretable and consistent set of data, four experiments were performed: one using R-CPL, one L-CPL, one LPL, and finally a blank experiment run in the same vacuum system with no ice deposition, and in which the substrate was irradiated with a regular H_2 UV lamp, to trace any in situ contamination. The two CPL helicities (R and L) are expected to induce e.e.'s of opposite signs, whereas LPL is expected to induce no e.e. at all. At the end of simultaneous deposition and irradiation for ~36 hr, the samples were allowed to warm up to room temperature (1 K minute^{-1}). During this procedure, the various photochemically produced radical species diffuse and combine. At this point, the first stereogenic centers form, and enantiomeric enrichments may be induced from the interaction with CPL. Therefore, L- and R-

CPL samples were additionally irradiated for about 10 hr at room temperature, to potentially favor enantioselective photoreactions based on a photon–molecule asymmetry transfer, a process suspected by Curie (1894). This protocol was chosen because the precise moment when the asymmetry due to the CPL interaction appears in the experimental process is so far unknown. However, this simulation remains astrophysically relevant, particularly in hot molecular core environments, where grains are heated and complex gas-phase molecules, thermally desorbed from the ices, are observed (Bottinelli et al. 2007).

The samples were then analyzed by enantioselective gas chromatography (GC). Due to the very small quantities of material produced and the necessity to measure statistically significant e.e.'s, a two-dimensional gas chromatography/time-of-flight mass spectrometry (GC×GC-TOFMS) technique was employed. This technique was shown to provide superior separation and enhanced sensitivity compared to conventional one-dimensional GC. The water-soluble and acid-soluble components of the samples were then extracted and separated using standard separation techniques employed for residue analysis. The extraction procedures are described in the Appendix.

As known from previous simulations, the abundance of amino acids decreases rapidly with increasing number of atoms in the molecule (Nuevo et al. 2008). Not surprisingly, glycine is the most abundant amino acid in our samples, followed by alanine with an abundance smaller by a factor of ~14. Chiral amino acids of higher molecular weight (aminobutyric and diaminopropanoic acids) were not abundant enough to allow any significant measurement. We thus focused our analysis on D- and L-enantiomers of ^{13}C-alanine, present at the nanomole level.

3. RESULTS

The ability to cleanly separate both left and right enantiomers and also separate them from overlapping peaks by applying two-dimensional GC techniques is illustrated in Figure 3. The measured L e.e.'s of alanine for each of the three different UV-light polarization states explored, given in Table 1, are e.e.$_L$ = -1.34% ($\pm 0.40\%$) and $+ 0.71\%$ ($\pm 0.30\%$) for the R- and L-CPL samples, respectively. The LPL sample provides, as expected, an e.e. very close to zero ($-0.04\% \pm 0.42\%$), confirming that the excesses are due to the UV polarization state. Note that these error bars are 3σ, giving a confidence level larger than 99.7% for these measurements. The blank sample chromatogram (not shown) has no measurable peak of alanine.

Although the photon-induced e.e. values switch sign with the photon helicity as expected, the absolute e.e. for the R-CPL sample is ~2 times larger than for L-CPL. This may be explained by the applied experimental protocol. Based on the IR spectroscopy monitoring of the first sample (R-CPL), we decided, for the second case (L-CPL) to decrease the photon-to-deposited-molecule ratio by increasing the molecule deposition flux to obtain a larger quantity of residue. Therefore, the R-CPL sample was built up with roughly twice as many photons per deposited molecule (N_{phot} molec^{-1}) as the L-CPL sample. To first order, this ratio turns out to be comparable to the ratio of the measured absolute e.e.'s, so that the absolute excesses appear to be proportional, in our experiments, to the number of "chiral" photons per deposited molecule. The enantioenriched formation of stereogenic centers in the organic matter is clearly favored by a higher ratio of CP photons over deposited achiral ices.

The net result of this experiment is that the UV-CPL irradiation of a plausible cosmic ice mixture consisting initially
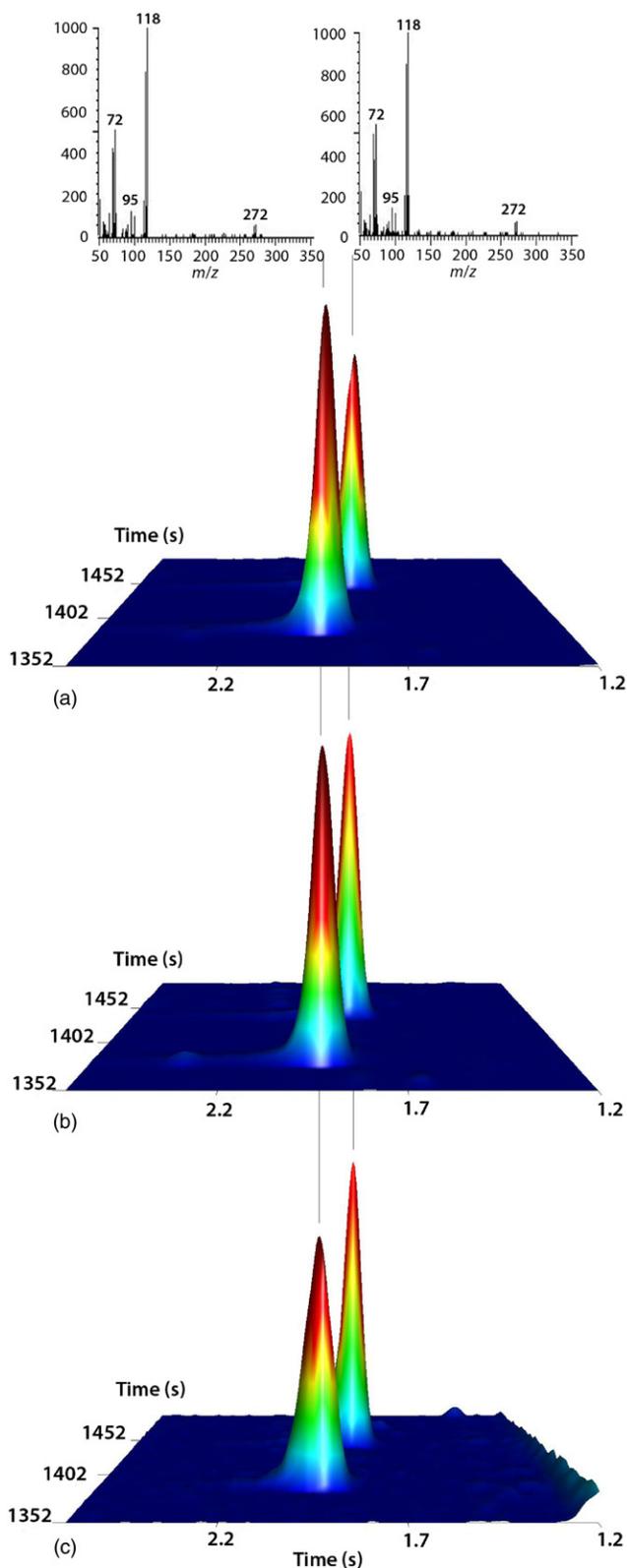
Figure 3. Multidimensional gas chromatograms of ^{13}C-alanine enantiomers for the three polarization regimes. Amino acids L-alanine (left signals) and D-alanine (right signals) were produced by the 6.64 eV UV photoirradiation with (a) left-handed circularly polarized light (L-CPL), (b) linearly polarized light (LPL), and (c) right-handed circularly polarized light (R-CPL). The alanine produced by irradiation with L-CPL shows an enantiomeric excess for the first eluting enantiomer, i.e., L-alanine, whereas the irradiation with R-CPL results in an enantiomeric excess of the second eluting enantiomer, i.e., D-alanine. Mass spectra for both enantiomers, given on the top of the figure, are identical.

(A color version of this figure is available in the online journal.)

Table 1
Measured Enantiomeric Excesses for ^{13}C-alanine

UV Polarization	N_{phot} molec^{-1}	e.e.$_L$ (%)	3σ Error Bars (%)
R-CPL	$\sim$5	-1.34	0.40
LPL	$\sim$2.5	-0.04	0.42
L-CPL	$\sim$2.5	$+0.71$	0.30

of only achiral molecules induces the production of significant e.e.'s of photon helicity-dependent signs for alanine, the simplest chiral proteic amino acid, depending on the helicity of the CPL. Contamination issues are resolved by the use of only ^{13}C-labeled molecules initially and the measurements on ^{13}C alanine only. Note that the absolute value of the maximum excess (1.34%) is compatible with the e.e.$_L$ measured for alanine in the Murchison meteorite (1.2%), as well as for some other meteoritic α-hydrogenated amino acids (Cronin & Pizzarello 1999). Higher enantiomeric excesses, such as those measured for isovaline in Murchison (up to 18.5%, see Pizzarello et al. 2003 and Glavin & Dworkin 2009), cannot be explained solely by the asymmetric effect of UV-CPL. Amplification of a small initial enantiomeric excess, such as those obtained in our experiment, by aqueous alteration on the parent body has been proposed (Glavin & Dworkin 2009) but for which no precise explanation does exist yet. These excesses can later be amplified by catalytic processes to reach a nearly homochiral state (Bonner 1991), a phenomenon that is beyond the scope of this Letter.

4. ASTROPHYSICAL IMPLICATIONS

In order for this experiment to be astrophysically relevant depends of course on the presence of astronomical sources of CPL. The first objects suspected to produce UV-CPL were neutron stars, but it has been shown that they actually do not (Bailey 2001 and references therein). Magnetic white dwarfs may generate substantial rates of UV-CPL, but they too are not good candidates due to their variability in polarization signs (Bailey 2001). Astronomical UV-CPL of the same helicity on large spatial scales is most probably produced by dichroic scattering (Lucas et al. 2005) on aligned grains by a magnetic field in reflection nebulae close to regions containing massive stars. The hypothesis that the material from which the Sun was formed and was at some stage processed in such regions is supported by the presence of short-lived isotope products in meteorites coming from a nearby very massive star (Duprat & Tatischeff 2007; Tatischeff et al. 2010; Dauphas et al. 2010), a possibility that has been considered for more than 30 years.

CPL has indeed been observed in reflection nebulae, for example, in the massive star formation region Orion OMC-1, in the infrared range (Bailey et al. 1998; Fukue et al. 2010) at levels of up to 17% and, according to these studies, the levels of polarization should well be similar in the UV. Importantly, the spatial distribution and scale of *one constant polarization helicity* (R or L) are much larger than the sizes of forming planetary systems. Thus, the L-only e.e.'s found in meteorites are probably not "universal," but valid only at the scale of a "solar nebula." A complementary test for this hypothesis would be the detection of L-only enantioenriched molecules in cometary materials. The in situ measurements of comet Churyumov–Gerasimenko by the COSAC instrument onboard the European space mission *ROSETTA* may yield conclusive results on this matter. In our experiments, we recall that the detection of e.e's in the amino acid alanine reported here, and

not in other potential chiral species produced, results simply from our methodology where GC×GC-MS is used only for the detection of amino acids. Chiral asymmetry should in fact be embedded in the macromolecular semi-refractory residue that remains on the sample holder at room temperature, a residue that most probably also remains on interstellar grains when heated to such temperatures as it is the case in molecular hot cores. Significantly, recent experiments reported by Kawasaki et al. (2006) have shown that the non-racemic primitive meteoritic materials are observed to be located within the organic fraction, and more importantly, that the mineral phases did not engender this asymmetry, a result which stands in favor of our scenario.

5. CONCLUSIONS

In this Letter, the UV-CPL irradiation of an astrophysically relevant achiral ices mixture has been shown to lead to the formation of chiral organics containing a slight but statistically significant asymmetry. The amino acid alanine displays e.e.'s (up to 1.34%) that were shown to depend on the helicity of the CPL used and are proportional to the number of photons per deposited ice molecule. This experimental result strongly supports a scenario in which the Sun was born in a massive star-forming region where molecular symmetry breaking took place, leading ultimately to the exogenous delivery of non-racemic prebiotic seeds to the surface of the primitive Earth (Oró 1961; Brack 2009). Besides, the link between the e.e's measured in this non-directed and thus "natural" experiment, such as in the Urey–Miller experiment (Miller 1953), and the L excesses measured for some meteoritic amino acids reinforces the idea that a fraction of the soluble organic materials in primitive meteorites finds its origin in the photochemistry of inter/circumstellar ices, a process which has been widely debated since the mid 1980s.

APPENDIX

Water-soluble compounds of the samples and blanks were extracted from their MgF_2 windows with $4 \times 50 \, \mu L$ of H_2O (Fluka, for organic trace analysis) and transferred into reaction vials. The remaining residues on the windows were extracted with $2 \times 50 \, \mu L$ of 0.1 M HCl. After evaporation of H_2O and HCl, the extracted samples were hydrolyzed in $300 \, \mu L$ of 6 M HCl at 110°C for 24 hr. Following hydrolysis, the samples were evaporated to dryness, and pure water was repeatedly added and evaporated ($3 \times 300 \, \mu L$) until a pH of 6.0 was obtained. They were then dissolved in $50 \, \mu L$ of 0.1 M HCl, and $25 \, \mu L$ of a 2,2,3,3,4,4,4-heptafluoro-1-butanol/pyridine mixture (3:1, v/v) were added. To this solution, $5 \, \mu L$ of ethyl chloroformate were added. Vials were capped tightly and shaken vigorously for 10 s to form N-ethoxycarbonyl

heptafluorobutyl ester (ECHFBE) derivatives. Finally, $20 \, \mu L$ of chloroform were added, and the vials were shaken again for extraction of the amino acid ECHFBE derivatives into the organic phase. Such organic phases were withdrawn and transferred into 1 mL GC vials equipped with $100 \, \mu L$ inserts for analyses.

The GC×GC-TOFMS Pegasus IV D system is a time-of-flight mass spectrometer operated at a storage rate of 200 Hz, with a 35–350 amu mass range and a detector voltage of 1.6 kV. Data were processed using the LECO Corp ChromaTOF™ software. The column set consists of a Varian-Chrompack Chirasil-D-Val primary column (25 m × 0.25 mm ID, 0.08 μm) modulator-coupled to a DB Wax secondary column (1.4 m × 0.1 mm ID, 0.1 μm). Helium was used as carrier gas at a constant flow of 1 mL minute^{-1}. Sample volumes of 1 μL were injected in the splitless mode at an injector temperature of 230°C. The primary oven was operated as follows: 40°C (1 minute), warm up to 80°C at 10°C minute^{-1}, 80°C (3 minutes), warm up to 180°C at 2°C minute^{-1}, 180°C (15 minutes). The secondary oven was offset by 30°C more than the primary oven, and a modulation period of 4 s was applied.

The samples were alternately injected five times in order to accurately determine any e.e. with reliable statistical error bars. Intrinsic effects due to the enantioselective device were investigated by analyzing the LPL sample, which was expected to provide, by definition, a racemic material with an e.e. of 0. The measured e.e.'s in the R- and L-CPL samples could therefore be corrected from the small systematic column-related effects. Volume peak integration for both enantiomers was performed using software-based calculations and taking into account recent evaluations of possible modulation-induced errors (Harynuk et al. 2008).

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