The Search for a Deterministic Origin for the Presence of Nonracemic Amino-Acids in Meteorites: A Computational Approach

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ABSTRACT   Amino-acid enantiomeric excesses (ee's) have been detected in different types of carbonaceous chondrites, all in favor of the L enantiomer. In this article, we discuss possible deterministic causes to the presence of these amino-acid ee's in meteorites and evaluate in particular enantioselective photolysis by circularly polarized light (CPL). The electronic circular dichroism spectra of a set of amino- and hydroxy-acids, all detected in chondritic matter but some with ee's and others without ee's, were calculated and compared. The spectra were calculated for the most stable conformation(s) of the considered molecules using quantum mechanical methods (density functional theory). Our results suggest that CPL photolysis in the gas phase was perhaps not at the origin of the presence of ee's in meteorites and that the search for another, but still unknown, deterministic cause must be seriously undertaken. *Chirality 00:000–000, 2011.*   © 2011 Wiley-Liss, Inc.

KEY WORDS: enantiomeric excesses; homochirality; symmetry breaking; electronic circular dichroism; circularly polarized light

INTRODUCTION

Since the first report nearly 15 years ago by Cronin and Pizzarello of amino-acid enantiomeric excesses (ee's) on carbonaceous chondrites,[1] a considerable amount of research has been devoted to these ee's. Amino-acid ee's have since then been detected on different CM-, CI- and CR2-type chondrites.[1–7] The research undertaken has often been motivated by the fact that it is thought that ee's brought to the young Earth by meteorites could have played a role in the origin of homochirality of life on Earth today, i.e., to the fact that the components of the biological macromolecules of life on Earth are only present under one of their enantiomeric forms.[8–12] Whether or not there is a link between homochirality on Earth today and these meteoritic ee's, their existence is a fascinating fact and the study of scenarios that could have lead to their origin under relevant abiotic conditions are without doubt worth investigating.

Carbonaceous chondrites are fragments of nondifferentiated asteroids or comets i.e., small bodies which during their accretion never reached temperatures higher than 500 K. The constitutive matter of nondifferentiated asteroids should consequently not have been significantly modified with respect to its previous state in the protosolar nebula. Chondritic matter is for this reason sometimes described as "pristine matter." This expression must however not be taken literally as some physical and chemical changes will certainly have occurred during accretion, as illustrated by the fact that aqueous metamorphism can be observed in the mineral matrix of carbonaceous chondrites.[13] It can nevertheless safely be concluded that these chemical changes were certainly not as important as those that occurred during the accretion of the parent bodies of differentiated chondrites.

It is not known when, where and even how the chondritic amino-acids were formed. To date amino-acids have not been detected in interstellar clouds but their presence cannot be excluded with certainty due to limitations of the spectroscopic methods used when trying to detect them. Regardless of this issue, the presence of amino-acids presenting an ee on chondritic matter is a consolidated experimental fact and the origin of the detected ee's remains a question of fundamental interest. The measured ee's range, depending on the amino-acid and the carbonaceous chondrite under investigation, between 3 and 18.5% and is always in favour of the L form.[1–7] Measurements were in all cases performed with great care and the ee's reported for α-dialkyl amino-acids, which are not copiously present in the terrestrial biosphere (some of them have recently been detected in peptide antibiotic produced by certain species of microfungus,[14]) and which are not prone to racemization provide evidence against terrestrial contamination.

It is known to all chemists that the synthesis of a chiral molecule will always yield a racemic mixture, i.e., a 50/50 mixture of the two enantiomers, if the reactants are achiral and if the reaction is performed in the absence of any chiralizing agent such as a chiral solvent or a chiral catalyst in a nonracemic form. Since the experiments undertaken in the 1950s by Miller[15] it is known that amino-acids can be synthesized under abiotic conditions via the electric sparking of a mixture of simple molecules like H_2O, CH_4, CO and NH_3. This type of synthesis under relatively high pressure plasma conditions would however not be able be to lead to a nonracemic mixture of amino-acids. Another plausible reaction

which can lead to the synthesis of amino-acids under abiotic conditions is the Strecker reaction, i.e., the addition of HCN on an aldehyde in the presence of ammonia (or ammonium chloride) and water.[16–19] The Strecker reaction can yield non racemic mixtures of amino-acids when performed in the laboratory in the presence of a chiral organic catalyst.[20] This observation is however of no help when trying to explain the origin of ee's in chondritic matter as the presence of a non-racemic chiral organic catalyst in an extraterrestrial environment raises essentially the same question regarding the creation of an enantiomeric excess. The synthesis of amino-acids via the UV irradiation of interstellar ice analogs, which will be discussed later, would also not be able to yield a non racemic mixture of amino-acids.

Hypotheses based on spontaneous symmetry breaking can be put forward to explain how imbalances in the amounts of the amino-acid enantiomers detected on carbonaceous chondrites might have appeared.[21] Symmetry breaking could simply arise from statistical fluctuations relative to the equimolar racemic state.[22–24] When small populations are considered, such as those likely to be present in interstellar environments, these fluctuations can be large relative to the total number of molecules; for a racemate composed of N molecules the Gaussian distribution is centred at N/2 and has a width at half height equal to $\sqrt{N}$. The spontaneous separation of a racemic mixture during crystallization with the formation of conglomerates (crystals composed of only one of the enantiomers) can also be suggested to explain symmetry breaking. Total conversion of the mixture to one enantiomorphic crystal state can even be achieved through secondary crystallization caused by stirring.[25,26] The conditions required for this to occur are however tightly constrained and they would not likely have been met in the protosolar nebula from which the parent bodies of carbonaceous chondrites would have accreted.[21]

When considering scenarios based on spontaneous symmetry breaking, it is important to remember that the probability of formation of an ee for one or the other of the enantiomers is exactly the same. Consequently whichever enantiomer becomes predominant is purely a matter of chance. The fact that only L amino-acid excesses have been observed in the different carbonaceous chondrites analyzed to date clearly argues in favour of a deterministic origin for the initial enantiomeric imbalance at the level of the proto or presolar nebula. One deterministic origin could be related to the non conservation of parity of the electroweak forces. Parity violation has as consequence that an energy difference exists between the two enantiomeric forms of a molecule.[27] To date it has not been possible to experimentally measure a parity violation energy difference (PVED) at the molecular level but *ab initio* quantum mechanical calculations give PVED values which suggest ee's of around $10^{-15}\%$ for amino-acids.[28–30] These ee are well below the ee's that would be due to statistical fluctuations and the "signal" would be smaller than the noise.

A deterministic scenario which could have lead to the amino-acid ee's detected on carbonaceous chondrites, and which we wish to further investigate in this article, is one in which circularly polarized light (CPL) was responsible for the initial breaking of symmetry in the protosolar cloud or even before, in the interstellar medium. The preferential photolysis by CPL of one enantiomer in a racemic mixture was first successfully demonstrated by Kuhn in 1929.[31] Since then the results of several experiments on the interaction between UV-CPL and chiral compounds have been reported. An enantiomeric excess of a few percent has for example, been obtained for leucine, both in solution[32–34] and in the solid state.[35] CPL can also be used as a chiralizing agent leading to an enantioselective synthesis starting from achiral reactants. Kagan et al. were the first to report in 1971 the asymmetric synthesis of organic compounds in the presence of CPL.[36] Experimental simulations have shown that it is possible to obtain complex organic molecules, including amino-acids, by subjecting interstellar ice analogs, which contain simple molecules like H_2O, NH_3, and CH_3OH, to vacuum UV irradiation.[37–42] Results regarding ee's have however to date been inconclusive when the ice analogs were irradiated with CPL.[43] As no photochemical step which involves a chiralizable polyatomic electronically excited state can be suggested in this type of synthesis, it is unlikely that it would be able to lead to amino-acid ee's.[44] A hypothetical enantioselective synthesis inside the protosolar nebula and in presence of CPL is consequently difficult to propose to explain the presence of non racemic mixtures of amino-acids in chondritic matter.

The possible role of CPL in the creation of the ee's observed in chondritic matter via asymmetric photolysis by UV-CPL deserves more consideration and has been evaluated and discussed in the literature since the late 1970s.[45–53] Possible sources of CPL in space are (i) synchroton radiation by electrons trapped in the magnetic field of neutron stars, (ii) the dichroic extinction of light by nonspherical grains aligned by a magnetic field and (iii) the Mie scattering of light by nonspherical dust particles aligned in a high-mass-star-formation region.[46,54] UV-CPL has to date not been observed in space but this is simply a consequence of high extinction due to the presence of interstellar dust which makes its observation much harder. Of course, for CPL to have had a deterministic effect on the creation of ee's in favour of the same enantiomer in different carbonaceous chondrites, the location of the source of CPL must have been such that the protosolar nebula from which the parent bodies of these carbonaceous chondrites accreted could not have been subjected to light presenting circular polarizations of both helicities.

As the destructive asymmetric photochemistry of amino-acids only yields small ee's, it would be difficult to obtain by this mechanism ee's of the order of those observed for meteoritic amino-acids.[9] This means that amplification of an initial ee created by CPL would have had to have taken place, for example, on the parent body of the carbonaceous chondrites where the amino-acids would have furthermore been protected from total photolysis.[55] Several different simple mechanisms have been proposed in the literature for asymmetric amplification of small initial imbalances. Asymmetric autocatalysis, in which one enantiomer catalyzes its own production while inhibiting that of its enantiomer, can technically turn a small imbalance between two enantiomers into a near-total preference. The concept, first proposed nearly 50 years ago by Frank,[56] has since been extensively studied.[57–61] Physical processes involving phase changes, such as crystallization and sublimation, have also been shown to be able to amplify small enantiomeric excesses.[62–64] It is highly improbable that autocatalytic reactions could have taken place on asteroids and amplification through physical processes is, perhaps, more plausible.

In this article, we are interested by the investigation of a possible deterministic mechanism for the creation of an ini-
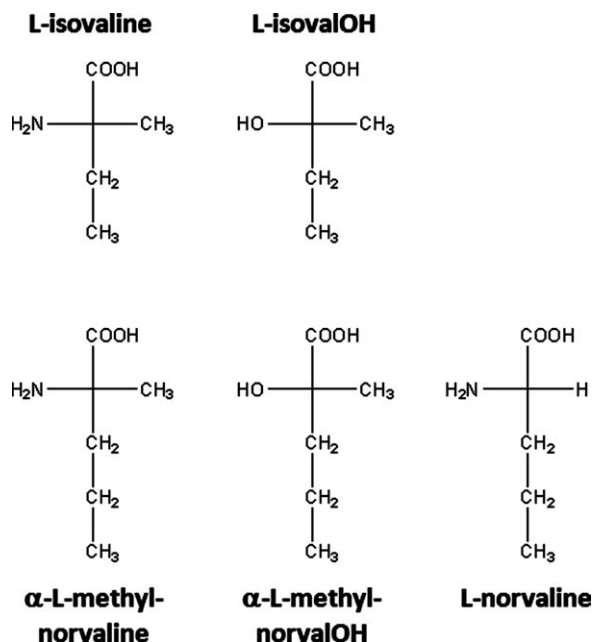
Fig. 1. Fisher projection of the L- configuration of the five molecules for which the ECD spectra were calculated.

tial ee for meterotic amino-acids. In this context, we present a theoretical study of the interaction between CPL and chiral amino-acids and hydroxy-acids (Fig. 1). Two α-methylated amino-acids, isovaline and α-methyl-norvaline, for which ee have been detected in chondritic matter were studied as were their corresponding hydroxy-acids which have also been detected on carbonaceous chondrites[16] but for which no ee's has been reported. Norvaline, a nonmethylated α-amino-acid which is racemic in chondritic matter was also considered in this study. UV-CPL mediated asymmetric photolysis will depend on the difference in the molar absorption coefficients of enantiomers for left and right CPL (Δε) and the electronic circular dichroism (ECD) spectra of compounds of interest were calculated using DFT. No experimental data under relevant conditions are, to the best of our knowledge, available for these compounds which justifies our quantum mechanical approach.[65] It also seems that the ECD spectra of these compounds have never been calculated. The aim of our approach is to see if it is possible to explain the differences observed in the ee's of these compounds by differences in their spectra.

MATERIALS AND METHODS

All calculations were undertaken using the Gaussian03 software,[66] with the DFT theory using the B3LYP functional[67,68] and different basis sets: 6-31G*,[69,70] 6-31+G**[69–71] or 6-311++G**,[71,72] without any particular options. The ECD spectra were calculated using the TDDFT theory, with the B3LYP functional and the 6-311++G** basis set.

All calculations were performed on the high performance HP XC Cluster at the Computing Center of the Université Libre de Bruxelles (ULB) and the Vrije Universiteit Brussel.

RESULTS AND DISCUSSION

Even if it not known with certainty when and where chondritic amino- and hydroxy-acids were formed, it is highly unlikely that their synthesis occurred in the gas phase as the density of the interstellar medium is too low. Synthesis

would have occurred on astronomical bodies or at the surface of interstellar dust grains in the dense clouds on which precursor molecules would have been adsorbed.[73] As mentioned earlier, the Strecker reaction is a plausible route for the abiotic synthesis of amino- and hydroxy-acids.

To evaluate if CPL could have played a role in breaking the enantiomeric symmetry of α-methylated amino-acids detected in carbonaceous chondrites we calculated the ECD spectra of amino- and hydroxy-acids considering that they were in their most stable conformation in the gas phase at temperatures of around 10–20 K, temperatures which are characteristic of dense clouds.[74,75] These conditions were chosen based on the working hypothesis that the molecules could have desorbed from the grains on which they were synthesized, and that during this process they would have been able to rearrange towards their most stable conformation(s) in the interstellar gas phase. The molecules could have later returned to the grains where they would have been shielded from total destruction by further UV radiation.[55]

The most stable conformation(s) of the different molecules were obtained by optimizing different initial conformations chosen because they present stabilizing intramolecular hydrogen bonds. Two possible intramolecular bonding patterns were considered for the amino-acids and three for the hydroxy-acids, as schematically represented in Figure 2. Staggered conformations were considered around the Cα-Cβ bonds leading to a set of six different initial conformations for the amino-acids and nine for the hydroxy-acids.

The geometry optimization of the different initial conformations was undertaken using the 6-31G* basis set. For each molecule the potential energy of the three optimized conformations presenting the lowest potential energy minimum were also calculated using the more complete 6-31+G** and 6-311++G** basis sets. As convergence was observed, the further geometry optimizations using successively the 6-31+G** and the 6-311++G** basis sets, were only performed for the most stable conformation of each molecule, except for norvaline where the two most stable conformations were retained as the difference in their potential energy minimum was less than 0.5 kJ/mol (for the other systems the energy difference between the two most stable conformations was larger than 2.5 kJ/mol). This small energy difference means that 10% of the second most stable popula-
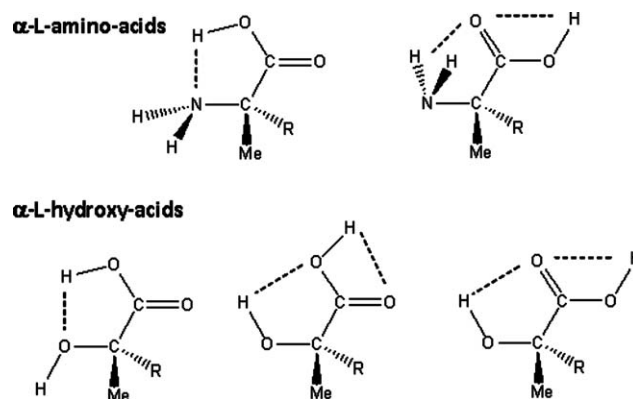

Fig. 2. Schematic representation of the hydrogen bonding patterns in the initial conformations chosen for the calculations of the most stable conformations of the different molecules. R represents the side chain of the molecule.
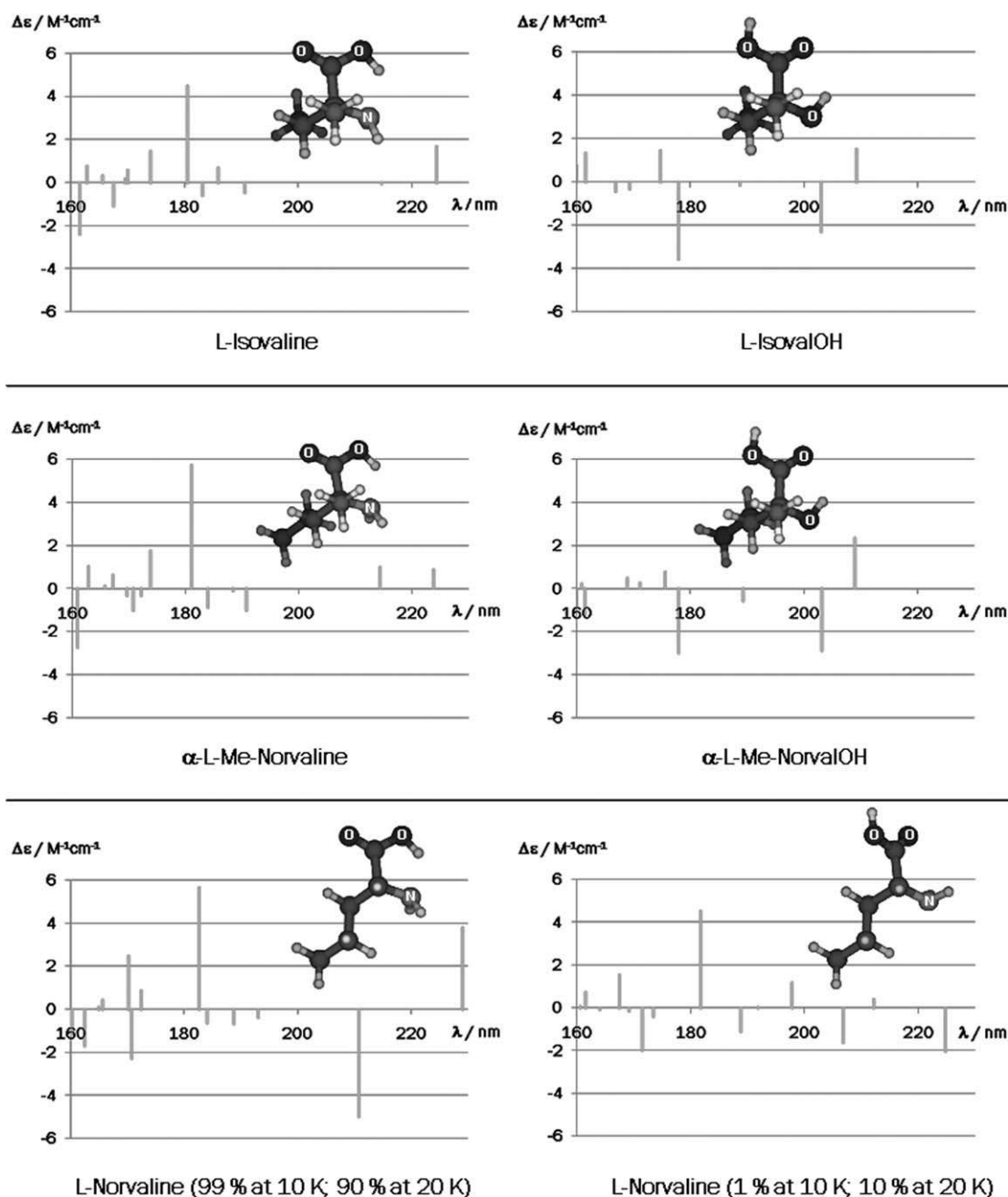
Fig. 3. Calculated ECD spectra of the five molecules investigated in this study.

tion would be present at 20 K. The root mean square deviations between the conformations optimized using the 6-31G* and 6-31+G** basis sets and using 6-31+G** and 6-311++G** basis sets were at most 0.07 Å and 0.01 Å, respectively, confirming convergence.

To evaluate the plausibility of our working hypothesis that the molecules were able to gain enough energy to rearrange towards their most stable conformation(s) in the gas phase, we undertook calculations to estimate the energy barriers between the three most stable conformations of isovaline obtained using the 6-31G* basis set (see Supporting Information for details). The highest calculated barrier is 60 kJ/mol. This energy corresponds to the energy of IR radiations of 2 μm wavelength and it is therefore plausible that the molecules were able to rearrange following the absorption of IR radiation.

The ECD spectra of the selected conformations of the five different molecules were calculated by TDDFT and the 6-311++G** basis set (see Supporting Information for the atom coordinates of these conformations). The calculated quantity which characterizes the intensity of a CD transition from the ground state to the exited state i is the rotatory (or rotational) strength (cgs units: 10^{-40} esu erg cm/G) given by eq. 1

$$R_{0i} = Im\{\langle\psi_0|\bar{\mu}|\psi_i\rangle.\langle\psi_i|\bar{m}|\psi_0\rangle\} \tag{1}$$

where $\bar{\mu}$ and $\bar{m}$ are respectively the electric and magnetic dipole moments of the molecule. The rotatory strength is linked to the chiroptical properties of the molecule via eq. 2

$$R_{0i} = 22.97 \int_{CD\ band} \frac{\Delta\varepsilon(E)}{E} dE \qquad (2)$$

where $\Delta\varepsilon$ is the difference in the absorption coefficients for left- and right- CPL (units: $M^{-1}\ cm^{-1}$) and E is the energy of the transition from the ground state to the exited state i (units: eV). As the temperature is considered to be 20 K, the molecules can be thought to be in their rovibrational ground state and consequently only lines will be observed in the spectra and eq. 2 can be reduced to eq. 3

$$R_{0i} = 22.97 \frac{\Delta\varepsilon}{E}. \qquad (3)$$

The rotatory strengths associated to the electronic transitions corresponding to wavelengths between 160 and 240 nm were calculated and the ECD spectra for the most stable conformations of the five molecules are shown in Figure 3. The upper limit was chosen because for photolysis to occur, the radiation must be sufficiently energetic so as to be able to break molecular bonds. A rapid evaluation of this energy may be obtained from the energy necessary to break a C—C or C—N bond. This energy is 500 kJ/mol at most which corresponds to a light with a wavelength of around 240 nm. None of the molecules exhibited a transition at a wavelength above 230 nm.

Asymmetric photolysis of two enantiomers can occur following absorption of CPL of a specific photochemically relevant wavelength where the CD of the molecule is different from zero. In the case of broad band CPL, asymmetric photolysis is also possible if the integral of the CD over all the photochemically relevant wavelengths is different from zero as it is unlikely that the rotational strengths of the alternating CD of the photochemically active absorption bands will sum exactly to zero.

Racemization, the process by which enantiomers are converted from one handedness to the other, is a very important issue to discuss. Indeed, if racemization occurred on the parent body after accretion of the grains, it could have erased any enantiomeric excess previously created in the interstellar clouds. The nonmethylated amino-acids are known to undergo racemization even under mild conditions, such as those that they would have been exposed to during aqueous phase of the asteroidal parent body, owing to their weakly acidic Cα hydrogen.[76] α-methylated amino-acids and hydroxy-acids lack the acidic H and are therefore not subject to racemization under mild conditions.

When comparing the different spectra in Figure 3, it can be observed that both α-methylated amino-acids and the non-methylated amino-acid, norvaline, exhibit a relatively strong ECD line around 225–230 nm, whereas the hydroxy-acids have no transitions at wavelengths above 210 nm. The lines around 225–230 nm are of the same sign in the different spectra except in the spectrum of the second most stable conformation of norvaline. If only CPL of wavelengths above 210 nm was present in space, an enantiomeric excess, of the same handedness, would be expected for both α-methylated amino-acids and no photolysis would be expected for the hydroxy-acids. As far as norvaline is concerned, the fact that the transition around 225–230 nm is not of the same sign in the two most stable conformations of the molecule could lead to the creation of a less pronounced enantiomeric excess for this molecule compared to the α-methylated

TABLE 1. Sum of the $\Delta\varepsilon$ in the *ECD* spectra of our set of molecules

Molecule	Sum of the $\Delta\varepsilon$ 1/(Mol cm)
L-Isovaline	5.4 (13 lines)
L-IsovalOH	−2.5 (8 lines)
α-L-methyl-norvaline	4.8 (14 lines)
α-L-methyl-norvalOH	−3.6 (9 lines)
L-Norvaline (90% at 20K)	1.5 (13 lines)
L-Norvaline (10% at 20K)	1 (4 lines)

amino-acids, excess which would have furthermore probably been completed erased due to racemization. It is however difficult to imagine that only CPL at wavelengths above 210 nm were present in space. The creation of the initial enantiomeric imbalance via this scenario can for this reason be considered as highly improbable.

If scenarios based on the presence of broad band CPL are to be evaluated, it is necessary to look at the sum of the rotatory strengths of the different molecules. Table 1 presents, for each of the spectra represented in Figure 3, the sum of the $\Delta\varepsilon$ of the calculated ECD lines in the frequency zone previously defined. According to the data in Table 1, all the studied compounds could be subject to asymmetric photolysis in the presence of a flat distribution of CPL. The signs of the sum of the rotatory strengths suggest that ee's of opposite chiralities would however be created for the methylated amino-acids compared to the methylated hydroxy-acids. The sums of the rotatory strengths for the two conformations of norvaline are the smallest. Less efficient asymmetric photolysis could consequently be expected for this compound which furthermore, as mentioned earlier, can undergo racemization. As no enantiomeric excesses are reported for the methylated hydroxy-acids detected in carbonaceous chondrites and as they should not be prone to racemization, it is difficult to rationalize our results in the light of reported experimental data. Our work clearly shows that it is possible that CPL in the range 160–240 nm was not at the origin of the ee's observed for amino-acids on carbonaceous chondrites.

CONCLUSIONS

Amino-acids exhibiting ee's of up to 18.5% have been detected in carbonaceous meteorites which fell to earth during the 20th century. The number of samples studied is not very large but as the samples come from different parent bodies and all show an ee in favor of the same enantiomer, it is tempting to conclude that these ee's have a deterministic origin. In this article, we tested the plausibility of one specific deterministic origin for the presence of non racemic amino-acids in carbonaceous chondrites: the enantioselective photolysis of racemic mixtures of amino-acids. On the basis of our work, we are lead to conclude that enantioselective photolysis by UV-CPL radiation in the interstellar gas phase is perhaps not the deterministic cause that we are looking for. This conclusion obviously leads to the following question: what could then have been the deterministic cause? As mentioned in the introduction, one possibility could be parity violation but as the enantiomeric excess expected from a PVED is evanescent and well below statistical fluctuations, this possibility can also be excluded. Two other possibilities remain. The most obvious one is the existence of another but still

unknown deterministic cause. The second one is less challenging but cannot be totally excluded; it consists in accepting, even if it is of low probability, the fact that all the recorded ee are of the same sign is simply the result of a "happy coincidence". Of course, science has nothing to say about "happy coincidences" except that they cannot be totally excluded!

We do not wish to conclude by saying that the origin of chondritic ee's might forever remain outside the field of scientific research and continue to be shrouded in mystery. We prefer to suggest that the search for another but still unknown deterministic cause must be seriously undertaken.

ACKNOWLEDGMENTS

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