Chirality in prebiotic molecules and the phenomenon of photo- and radioracemization

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Abstract. The abiotic origin of some biologically active molecules and macromolecules have been reviewed. Particular emphasis has been dedicated to the formation of aminoacids and about the possible mechanisms for their asymmetric synthesis and accumulation. The phenomenon of racemization has been explained in detail and then applied in the context of the photo- and radioracemization. Apparent and true photo- and radioracemization have been distinguished. These phenomena play against the preservation of chirality of asymmetric molecules in meteorites and in space. This fact may explain why low enantiomeric excess have been found in meteorites and limited only to certain aminoacids quite uncommon in terrestrial environments.

It can be hypothesized that chiral molecules are formed in space for instance under the CPL photolysis and then they are slowly and unselectively degraded and radioracemized by cosmic rays and other high energy radiations. However, the experiment on the radioracemization of certain terpenes has shown that the radioracemization rate is not so dramatically high to cause the complete racemization of the mixture even at very high radiation doses. The radioracemization reaction appears not selective at all, therefore the enantiomeric excess observed only in α-methyl amino acids in meteorites must be attributed to water-thermally driven methamorphism which is instead able to cause selective racemization on α-H amino acids but not on α-methyl amino acids.

1. Introduction
It is commonly accepted in the theories of the origin of life that chirality of prebiotic molecules has preceded the emergence of life [1,2]. Without chiral molecules life is impossible because all key biologically active molecules and macromolecules like amino acids, peptides, enzymes, proteins as well as DNA, RNA and sugars, polysugars, terpenes and biologically active heterocyclic molecules cannot display their biological activity. In a simplified view, life is the result of millions of high stereoselective asymmetric reactions.

With the word “asymmetric” we mean that all the mentioned molecules and macromolecules exist and are biologically active under only one of the two possible mirror images, if they posses only one chiral center in the molecule. For instance essentially only the L-amino acids and only the D-sugars like ribose and deoxyribose (the key constituents of RNA and DNA macromolecules and the chiral sites of their monomeric units) are biologically active (however, vide infra). The situation becomes even more complex when we are dealing with molecules having two or more chiral centers. In such cases several couples of enantiomers are possible and, again, only one among them shows biological activity. For example, there are two α-H-amino acids which posses and additional chiral center other than the usual one at the α-carbon, they are isoleucine and threonine.

However, in nature also D-aminoacids play important biological roles which were quite unknown. Although the D-aminoacids are not at all used to build common proteins and enzymes, they are
present in peptidoglycans, crosslinked polysaccharide-peptide macromolecules, the main constituents of cell walls of bacteria.

In the next sections we will introduce briefly into the problem of the origin of chirality in prebiotic molecules and then we will discuss about racemization, a reaction which converts an enantiomer into its optical counterpart until an equimolar mixture of the two optical antipodes is achieved and then permanently preserved. The key purpose of this paper is to review the present knowledge about the emergence of chiral molecules under abiotic conditions and to discuss how it is possible that mixture of aminoacids showing an enantiomeric excess have been found in carbonaceous chondrites extracts although these molecules have been exposed for millions of years to the action of corpuscular and electromagnetic radiation which may have destroyed all the enantiomeric excess originally present. Furthermore, pre-meteoritic material can experience a very harsh ambient conditions in the very early stages of the solar nebula [3] but notwithstanding this, primitive materials like meteorites and presumably comets contain chiral molecules in scalemic mixtures [2].

2. Hypotheses and experimental facts on the origin of amino acids and chirality

The formation of key biological molecules such as amino acids starting from simple mixtures of elemental molecules is a well consolidated experimental fact since the fifties of the last century [4,5]. Sparking a mixture of ammonia, water, nitrogen, carbon monoxide, hydrogen and methane, known as the Miller-Urey synthesis produces a complex mixture of products which includes amino acids. However any energy source other than sparking, is able to produce abiotically a mixture of molecules relevant to sustain life or molecules which are the building blocks of biological macromolecules. In fact, amino acids are formed by proton bombardment of simple gas mixtures such as CH₄, CO, NH₃ and H₂ [6]; proton bombardment simulates the action of cosmic rays on these gases. UV photolysis, known as Sagan-Khare synthesis [7] or catalytic chemistry for instance under the Fischer-Tropsch conditions [8] are both able to produce key biological molecules starting from simple molecules which are available in the Universe for instance in the molecular clouds, in the planetary nebulae in certain circumstellar environments and even in the atmospheres of certain planets and satellites. Even more exotic conditions, like sparking directly into a water solution of carboxylic acids under N₂ [9] or the passage of high intensity ultrasound [10] into a suitable water solution are sufficient to produce a mixture of amino acids.

Amino acids are everywhere in the Earth [11]. Thus, their search especially in extraterrestrial environments can be one of the simplest ways for searching signs of bacterial life. Although their detection is not a definitive indication of the presence of bacterial life. Amino acids have been found in meteorites even in non-racemic mixtures [11,12] but their origin is thought to be abiotic by the majority of the scientists although a minimum margin of uncertainty remains. Furthermore amino acids have also been found in the deep-sea hydrothermal subvents at very high temperatures [13] and are widespread on the earth surface and underground [12]. Particularly interesting is the interpretation of the nature of the amino acids found in the deep-sea vents. The L-enantiomeric excess detected has been interpreted as a proof of the existence of microorganisms and elemental life even at very high and warm depths of the earth crust in agreement with the Gold’s theory [14]. However amino acids can form also abiotically in Strecker-type synthesis under supercritical hydrothermal water flow conditions simulating submarine hydrothermal systems [15]. In any case the abiotically formed amino acids are always a racemic mixture in neat contrast with amino acids having biotic origin. Furthermore, abiotic amino acids are composed by peculiar ω-amino acids like β-alanine or γ-aminobutyric acid and δ-aminovaleric acid which are taken as markers of the hydrothermal abiotic synthesis [13]. These kind of ω-amino acids are quite unusual in the living systems and instead are the result of the decomposition of α-amino acids via specific decarboxylation at the α chiral center (see Scheme 1). For instance, aspartic acid yields β-alanine which is no more optically active and glutamic acids produces via decarboxylation at the α-carbon, γ-aminobutyric acid, a neurotransmitter.
These reactions already imply a racemization since we pass from precursors having an asymmetric carbon atoms to products which are free from chiral centers. However, as we will discuss deeper in the next section a true pure racemization reaction involves exclusively the inversion of the configuration of the chiral center i.e. the $\alpha$-carbon in the amino acids having only one chiral center.

The present situation on the abiotic synthesis of biological molecules and macromolecules has been reviewed recently [16,17] including also the chemistry of the simplest molecules which are the sources of C,N, H and O needed to build the amino acids. From the reviews [16,17] it is possible to appreciate both the successful experimental results and bright theories together with the still overwhelming unsolved problems of the emergence of life, demonstrating how fascinating, challenging and intriguing is the "mystery" of the origin and evolution of the biological word starting from simple organic molecules.

Concerning the formation of chiral prebiotic molecules, a summary of the main hypothesis are reported in Table 1.

| TABLE 1 - HYPOTHESIS ON CHIRAL MOLECULES FORMATION |
|-----------------------------------------------------|
| LINEARLY POLARIZED LIGHT FROM NEUTRON STARS          |
| CIRCULARLY POLARIZED LIGHT FROM FAINT STARS          |
| CIRCULARLY POLARIZED LIGHT ON PLANET SURFACE         |
| INCLUSION POLYMERIZATION IN CHIRAL CLAYS             |
| VESTER-ULBRICH HYPOTHESIS (Parity violation in weak interactions) |
| ACTION OF VERY HIGH PRESSURE ON RACEMIC MIXTURES     |
| ASYMMETRIC INORGANIC SURFACES (acting as catalysts)  |

It is thought (see ref.[1,18] for a complete review) that they are formed inside the molecular clouds lying in proximity of neutron stars which emit photons of all wavelengths which are linearly polarized because derived from the emission of circularly accelerating electrons. Alternatively, chiral prebiotic molecules are formed in solar nebulae where the faint sun irradiate the substrate with circularly polarized light (CPL) generated by multiple aerosol and dust scattering of sunlight. Polarized light causes asymmetric photolysis destroying more selectively one of the two enantiomers, thus creating an enantiomeric excess [1,18]. The resulting prebiotic molecules once formed by the mentioned mechanism (CPL) or by any other unspecified interstellar force field are incorporated into the mantle of interstellar grains and then can be accumulated into comets and asteroids, ready to be delivered to Earth or any other place suitable for the development of life. It has even been hypothesized that chiral molecules can be formed on the earth surface by the action of circularly polarized sunlight which in fact is circularly polarized as a result of multiple reflections and scattering through particles and surfaces [1,18].

The Vester-Ulbricht hypothesis which is connected with the concept of “parity violation” in certain weak interactions such as those involved in the $\beta$ decay of radioactive nuclei with emission of polarized particles has never produced convincing experimental facts that this phenomenon can be the source of the abiotic synthesis of achiral molecules [1,18].

As discussed in a recent review [19] chiral polymer can be formed by the radio- or photopolymerization of appropriate monomers included in clays or in solids having a chiral cavity inside. The shape of the cavity acts as an asymmetric template causing the formation of only one enantiomeric macromolecular chain. In this context it is of extreme importance to mention that are known polymers which do not have *any* asymmetric carbon atoms in their main chain backbone or as pending group but they show optical activity because they have a helix structure. In other words, it is not needed to start from chiral monomers (as it happens for instance for proteins) to get an optical active macromolecule. It is possible to start from any achiral monomer that is able to give a rigid helix structure to the resulting polymer. The optical activity will be observed only if the synthesis will lead
to an excess of right-handed screw rather than a left-handed screw. In such cases no asymmetric carbon atoms are needed. Such an asymmetric synthesis can be done by the so-called inclusion radio- or photopolymerization (in this case no CPL light is needed) of an achiral monomer inside an inorganic solid (e.g. a clay, a natural zeolite) which present a naturally chiral cavity which can act as template [19]. Examples of such chiral polymers whose optical activity derive exclusively from their helical structure are for instance the polysiocyanates [20] but numerous others have been reviewed quite widely recently [21].

Another extremely important point is the fact that the helically chiral polymers can act as chiral auxiliaries in new asymmetric syntheses or may “transmit” their asymmetry to other molecules produced in their presence [22], in line with the concept of “chirality amplification” (see Table 2). Thus, starting from a chiral polymer without asymmetric carbon atoms, it is possible to pass to macromolecules displaying optical activity because of their secondary helical structure.

| TABLE 2 - PROTECTION AND AMPLIFICATION OF CHIRALITY |
|-----------------------------------------------------|
| ADSORPTION AND INCLUSION                           |
| SELECTIVE ADSORPTION ON CHIRAL SURFACES            |
| SPONTANEOUS SYMMETRY BREAKING OF RACEMIC MIXTURES   |
| FAR-FROM EQUILIBRIUM THERMODYNAMICS (PRIGOGINE et al.) |
| POLYMER CHAINS WITH PREFERENTIAL HELICITY          |
| SMALL MOLECULES WITH ASYMMETRIC CARBON ATOMS       |

These macromolecules may act as chiral auxiliaries and act as an aid in the asymmetric synthesis of simple molecules having asymmetric carbon atoms in their structures. In any case the concept of chiral transmission and amplification (Table 2) has also solid mathematical basis on the far-from equilibrium thermodynamics [23]. Other known mechanisms of amplification of the enantiomeric excess [1,18] which may lead to the final accumulation of certain optical antipode involve the phenomena of spontaneous resolution on crystallization (spontaneous symmetry breaking) while other possibilities advocate the selective absorption of one enantiomer on a chiral surface causing the accumulation of the opposite optical antipode in the former racemic solution.

For the sake of completeness, it should be mentioned also another theoretical proposal about the abiotic source of chirality: the action of very high pressure on a racemic mixture. It has been shown both by purely thermodynamic arguments and by Montecarlo simulations that the transition from a racemic to a scalemic mixture (a mixture containing an enatiomeric excess) is thermodynamically possible at pressures of the order of >10^5 bar [24]. This last hypothesis is connected to the explanation of the optical activity of petroleum, if petroleum is produced abiotically [14].

3. Amino acids photo- and radioracemization: a phenomenon against the preservation of chirality in primitive materials in space

Although it is not certain what mechanism has created the prebiotic chiral molecules, it is today a consolidated experimental fact the presence of enantiomeric excess (ee) of certain aminoacids and other biological molecules in the organic substrate of Murchinson and other meteorites [11,12]. It is particularly remarkable that the aminoacids found in ee in meteorites belong all to a class of aminoacids which are rare or unknown in our biosphere: the $\alpha$-methyl amino acids [25] (see Scheme 1). Conversely, the common $\alpha$-H amino acids are found in almost racemic mixtures in meteorites [25]. The point is that $\alpha$-H amino acids are easily racemizable in water solution through the action of heat or by the catalysis of metal ions thanks to a well known mechanism which involves the keto-enol tautomerism as shown in Scheme 2. All the molecules which posses the moiety $-(\text{R})C^*H-(\text{C}=\text{O})$ with $C^*$ the asymmetric carbon atom are subjected to the racemization reaction with the inversion of the asymmetric carbon atom [26] (see also Table 3). On the other hand $\alpha$-methyl amino acids are found
in 15% ee in meteorites because they cannot undergo such kind of racemization reaction thanks to the absence of an H atom attached to the C* atom. The α-methyl amino acids are normally formed in the abiotic laboratory synthesis simulations together with normal amino acids and they are able to form polypeptides with stable α-helices secondary structures and in such a way are able to amplify the modest ee found in meteorites playing a role in pre-RNA world [25]. Thus, the racemization reaction (see Table 3 for a summary), consists in the spontaneous process which converts one enantiomer into an equimolecular mixture of both enantiomers or, more in general, the conversion of a scalemic mixture into a racemic one.

Table 3 - Main Phenomena Causing Racemization

| Phenomenon                          |
|------------------------------------|
| Action of Heat on Scalemic Mixtures|
| Action of Metal Ions on Scalemic Mixtures|
| Action of Light (Photoracemization) |
| Action of High Energy Radiation (Radioracemization) |

Schematically this can be represented by the following reactions:

\[ 2 \text{A}(+) \rightarrow \text{A}(+) + \text{A}(-) \]

Where \( \text{A}(+)^{+} \) is a destrotroratory enantiomer which by the action of heat or other chemical or physical phenomena is transformed into an equimolar mixture of the two optical antipodes in equilibrium each other.

The half life of amino acids racemization is estimated to be of the order of \( >5 \times 10^{5} \) years and occurs mainly by the action of heat or the catalysis of metal ions. It is possible to estimate the age (dating) of fossil skull and bones by checking the D/L ratio of the amino acids still present there [11]. However the racemization rate is greatly retarded if the analytical substrate is protected as it happens in amber insect inclusions. In such cases the amino acid racemization rate is retarded by a factor of \( > 10^{6} \) [27]. However, the chiral molecules in the space (either embedded in grains or in comets and meteorites) are also subjected to the action of high energy ionizing electromagnetic radiation under the form of cosmic rays and X and γ rays of stellar origin as well as UV radiation. The high energy electromagnetic radiation causes the radiolysis (decomposition) or the photolysis of these molecules and also the radioracemization of the substrate destroying the enantiomeric excess.

During the radiolysis a complete molecular fragmentation occurs so that the molecule is degraded into smaller radicals and usually also the chiral center(s) present in the molecule loose its asymmetry in such a degradation process so that a drop in the optical activity of the substrate can be observed as function of the irradiation time.

\[ \text{A}(+) \rightarrow \text{P}_{1} + \text{P}_{2} + \ldots + \text{P}_{3} \]

Where \( \text{P}_{i} \) are the products derived from the decomposition of \( \text{A}(+) \). They are achiral since the asymmetric carbon was lost by the decomposition of the starting chiral molecule \( \text{A}(+) \). This explains the drop in the optical activity of the mixture. Furthermore, during radiolysis or even photolysis certain α-aminoacids like aspartic and glutamic acid undergo a decarboxylation reaction at their asymmetric carbon atom and are converted into the ω-aminoacids respectively β-alanine and γ-aminobutyric acid (see Scheme 1). In general the ω-aminoacids do not posses any chiral center and therefore do not display anymore the optical activity, contributing to the drop of this property as function of the irradiation time. The drop in the optical activity due to degradation, although also called radioracemization or photoracemization does not corresponds to a true racemization. The true
radioracemization occurs in parallel with the radiolysis reaction and involves the formation, in the case of amino acids in solution, of a radical anion which is detectable spectroscopically [28] (see Scheme 1) or a radical center on the asymmetric carbon atom in the solid state.

These intermediates are responsible for the inversion of the configuration of the asymmetric carbon atom in the molecule with the conversion of the given enantiomer into its optical antipode as reported in Scheme 2.
Therefore, starting from a scalemic mixture, the prolonged radiolysis (or the prolonged photolysis) causes an extensive degradation into achiral products. The survived starting substrate at the end of the process will consist of an equimolar mixture of enantiomers without any residual optical activity. Preservation from photoracemization can be ensured if the amino acids are embedded into ices, because the limited capability of UV photons to penetrate into the ices [29] or when they are embedded in complex matrices containing humic-like materials (melanoidins) [30]; in any case radiolysis and radioracemization is granted under the same conditions.

The radiolysis of α-methyl amino acids, which are known to be resistant to thermally-initiated and pH-guided racemization reactions, causes instead extensive radioracemization. For example isovaline suffers significant radioracemization during partial γ radiolysis both in solution and in the solid state [31].

One of the main products of the prolonged radiolysis of amino acids is glycine which is an achiral constituent of proteins [32]. The radiolysis and the photolysis of the free amino acids causes their extensive degradation so that Takano and colleagues [32] have suggested that in any extraterrestrial environment only bound, i.e. polymerized amino acids (for instance in peptides or pseudopeptides) can be searched and found. In fact the polypeptides and the proteins show a significantly higher stability (one order of magnitude) toward radiolysis and photolysis. These results are in perfect agreement with earlier results of Bonner [33] who has shown that (L-Leu)₁₀ and (L-Leu)₇₈ polypeptides are more stable to radiolysis than the free leucine amino acid. However, also in polypeptide form the extent of radioracemization was found comparable to that of leucine monomer [33].

The extent of radioracemization of α-amino acids was found in the range of 2-5% when 55-68% of the aminoacid has been radiolyzed in the solid state and is in the range of 5-11% when the radiolysis has been conducted in NaOH solution. Instead, no radioracemization has been detected in acidic aqueous solutions [34]. The radiation dose used was in the range of 1-30 MGy.

The radiolysis and radioracemization of L-leucine deposited on quartz powder was found comparable to a control sample while the radiolytic decomposition and the radioracemization was enhanced when L-leucine was absorbed on precipitated amorphous silica having a very high surface area [35]. Absorption of L-leucine on clay minerals like kaolin and bentonite enhances the radiolysis and the radioracemization of the amino acid. In any case the maximum radiolytic and radioracemization effect has been observed on L-leucine solutions in water [36].

4. On the racemization of terpenes (isoprenoids)

Terpenes represent an important class of organic molecules formally considered as polymerization products of the hydrocarbon isoprene. Molecules belonging to this class have been detected in meteorites [8] and are thought to be formed under Fischer-Tropsch conditions in the solar nebula [8]. In a recent study [37] the γ radioracemization was focused on tree isomeric chiral terpenes, R(+)-limonene, S(-)-limonene and R(-)-α-phellandrene instead of aminoacids. The three terpenes were γ radiolyzed in sealed vials at room temperature with a total radiation dose of 317 KGy. Despite a relatively high radiation dose used, all the chiral molecules selected for the present study have shown a low radioracemization rate suggesting that also complex chiral molecules may survive with limited damage a relatively high level of high energy electromagnetic radiation dose in the hostile prebiotic environment. The specific optical rotation is defined by the Biot relationship:

\[ \alpha = \left[ \alpha \right]_D \cdot L \cdot c \]

The specific rotation \( \left[ \alpha \right]_D \) represents the proportionality coefficient, (characteristic for each kind of asymmetric molecule under consideration) linking the observed rotation \( \alpha \) with the length \( L \) of the measurement tube and the concentration \( c \) of the solution in g/ml. The value of \( \left[ \alpha \right]_D \) for R(+)-limonene is reduced by 2.6% of its original value after 317 KGY irradiation; consequently, the optical purity defined as the ratio of the \( \left[ \alpha \right]_D \) of the real sample over the \( \left[ \alpha \right]_D \) of the chemically 100% pure enantiomer decreases accordingly. The changes are even more pronounced for S(-)-limonene whose specific optical activity changes from the starting value of -89.9° to -84.2°. This represents 6.3% in change for the optical activity which implies a proportional reduction in the enantiomeric purity of the
sample from 88.7% to 83.1%. For R(-)-\(\alpha\)-phellandrene the changes due to radiolysis involve a reduction of the optical purity from 62.4% to 57.5% [37]. Furthermore it was found that the presence of impurities may have played a role in the selective preservation of one of the two possible optical antipodes under prebiotic conditions [37].

Conclusions
The abiotic synthesis of biological molecules and macromolecules has been studied extensively in the last 60 years. The enormous amount of experimental and theoretical work has given many answers but synthetic theory of the origin of life needs a lot of further and deeper research work. Life is a so complex and intriguing phenomenon that cannot be explained with and reduced to a few chemical reactions [38].

The molecular chirality is of capital importance in the life phenomenon. It is possible to affirm that life and molecular chirality are strongly interconnected each other. There are now reasonable theories and a reasonable number of experimental facts which allow us to affirm that we are starting to understand how chirality emerged in the early stages of the molecular evolution. Circularly polarized photolysis, selective absorption phenomena and the mechanism of chiral amplification are quite convincing although not perfect. In this context, the racemization tendency of chiral molecules can be considered a calamity [1]. Racemization occurs spontaneously and can be activated thermally or by metal ions and is favoured by the presence of water. Photo- and radioracemization are instead activated by photons or corpuscular radiation and occur in parallel with the degradation reactions of the substrate. In this context it is useful to distinguish between apparent and true photo- and radioracemization.

The enantiomeric excess found in meteorites usually involves unusual aminoacids which are not common in terrestrial environment and which are much less prone to racemization than the corresponding terrestrial \(\alpha\)-aminoacids which instead are usually found as chiral mixtures. It appears that the racemization phenomena in meteorites are a combination of radioracemization and water-thermally driven methamorphism which has permitted the selective accumulation of scalemic mixtures of \(\alpha\)-methyl amino acids.

It can be hypothesized that chiral molecules are formed in space for instance under the CPL photolysis and then they are slowly and unselectively degraded and radioracemized by cosmic rays and other high energy radiations. As the experiment on the radioracemization of terpenes has shown [37], the radioracemization rate is not so dramatically high to cause the complete racemization of the mixture even at very high radiation doses. In any case the radioracemization reaction appears not selective at all, therefore the enantiomeric excess observed only in \(\alpha\)-methyl amino acids in meteorites must be attributed to water-thermally driven methamorphism which is instead able to cause selective racemization on \(\alpha\)-H amino acids but not on \(\alpha\)-methyl amino acids.

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