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Symmetry Breaking

Molecular Chirality in Meteorites and Interstellar Ices, and the Chirality Experiment on Board the ESA Cometary Rosetta Mission

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chirality · circularly polarized light · mirror-symmetry breaking · origin of life · Rosetta mission

Dedicated to Professor Volker Schurig on the occasion of his 75th birthday

Life, as it is known to us, uses exclusively L-amino acid and D-sugar enantiomers for the molecular architecture of proteins and nucleic acids. This Minireview explores current models of the original symmetry-breaking influence that led to the exogenic delivery to Earth of prebiotic molecules with a slight enantiomeric excess. We provide a short overview of enantiomeric enhancements detected in bodies of extraterrestrial origin, such as meteorites, and interstellar ices simulated in the laboratory. Data are interpreted from different points of view, namely, photochirogenesis, parity violation in the weak nuclear interaction, and enantioenrichment through phase transitions. Photochemically induced enantiomeric imbalances are discussed more specifically in the topical context of the "chirality module" on board the cometary Rosetta spacecraft of the ESA. This device will perform the first enantioselective in situ analyses of samples taken from a cometary nucleus.

1. Introduction

The ESA Rosetta mission,[1] successfully launched in March 2004, has now completed its 10 year journey to comet 67P/Churyumov-Gerasimenko (67P/C-G). Contrary to its predecessor missions Giotto and Vega to comet 1P/Halley,[2] Deep-Space 1 to comet 19P/Borrelly,[3] Stardust to comet 81P/Wild 2,[4] and Deep Impact to comet 9P/Tempel 1,[5] Rosetta is the first space mission designed and constructed to follow a cometary nucleus through perihelion passage and to deposit a landing unit on the cometary nucleus. The Philae lander detached from the Rosetta spacecraft on November 12, 2014 and soft-landed on the surface of the cometary nucleus, the morphology and chemical composition of which is largely unknown. Philae contains the "Cometary Sampling and Composition" (COSAC) instrument, which is equipped with a chirality module for the in situ identification, separation, and quantification of organic molecules, including enantiomers, expected to be present in cometary ices. The planned analyses will provide essential information on the formation of the solar system and possibly on the origin of molecular asymmetry in biological systems.[6]

Nature's selectivity in the discrimination between left and right enantiomers has fascinated scientists since Louis Pasteur's first investigations on chiral molecules. The origin of this distinctive and essential feature of homochirality, however, remains elusive. A multitude of hypotheses and speculations have been put forward during the last few decades. One possible scenario involves the photochirogenesis of small enantiomeric excesses (*ee*) in extraterrestrial matter, followed

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by the exogenous delivery of organic molecules to Earth and the amplification of the generated asymmetry to a near-homochiral state. Three distinct approaches are commonly in use for the validation of this hypothesis: 1) meteorite analysis to provide information on enantiomeric enhancements of extraterrestrial origin, 2) laboratory simulations of interstellar ices to advance our understanding of asymmetric photochemical mechanisms involved in the generation of an enantiomeric excess, and 3) the ultimate step, in situ analysis of pristine cometary matter by the COSAC instrument of the Rosetta mission. Data obtained by research in these fields is expected to provide valuable insight into the origins of biomolecular homochirality.

This Minireview links the experimental simulation of interstellar ices with information obtained from the stereochemical elucidation of extraterrestrial organic matter. It will serve as a basis for the interpretation of upcoming data from the Rosetta lander and for understanding the enantiomeric enhancements detected in extraterrestrial samples and in cometary ices in particular. We give an overview of current studies on the homochirality of life as a result of the asymmetric evolution of cosmic matter and highlight existing scientific hypotheses on the source of the chiral bias in biomolecules.

2. Enantiomeric Enhancements in Meteoritic Samples

Meteorites, in particular carbonaceous chondrites, are some of the oldest and most primitive solid materials. They display unique physical and chemical records of the formation of the solar system approximately 4.56 billion years ago, long before homochiral life originated on Earth. The enantiomeric enhancements observed in some meteoritic organic compounds are to date the only reference for molecular asymmetry that is not influenced by the terrestrial biosphere. Therefore, understanding of the origin of this phenomenon is crucial for solving the puzzle of biomolecular homochirality.

2.1. The Stereochemistry of Organic Molecules in Meteorites

It became apparent through the epochal experiments of Harold C. Urey and Stanley L. Miller that specific biological building blocks can be formed from a primitive reducing gas mixture of water, methane, and ammonia.[7] However, our vision of the atmosphere on early Earth has evolved since 1953, and it is now believed to have consisted mostly of carbon dioxide, nitrogen, and water. Under such conditions,

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Cornelia Meinert studied chemistry at the Universities of Rostock and Leipzig. After receiving her PhD at the Helmholtz Centre for Environmental Research by Dr. Werner Brack, she became a postdoctoral research fellow at the University Nice Sophia Antipolis, where she studied the asymmetric photolysis of amino acids and used GC×GC techniques for the enantioselective analysis of cometary and meteoritic matter. In 2013, she became a Chargé de Recherche of the CNRS. Her current research focuses on the origin of the homochirality of biomolecules.

Iuliia Myrgorodska obtained her Masters degree in chemistry at the University of Nice Sophia Antipolis, where she has been a PhD student funded by the French Ministry of Science and Education since 2013; her supervisors are Prof. Meierhenrich and Prof. Nahon. Her thesis is dedicated to studies of the asymmetrical photolysis of biological building blocks by circularly polarized light and the origin of enantiomeric enhancement in extraterrestrial samples.

Zita Martins graduated in chemistry at the Instituto Superior Técnico in Portugal in 2002. She received her PhD in astrobiology on the chemical analysis of organic molecules in carbonaceous chondrites at Leiden University by Professor Pascale Ehrenfreund. In 2009, she became a Royal Society University Research Fellow at Imperial College London. Her research focuses on the detection and identification of organic molecules of prebiotic relevance in interplanetary samples, such as meteorites.

Louis Le Sergeant d'Hendecourt completed his PhD in the research group of Prof. J. Mayo Greenberg at Leiden University. He is now Directeur de Recherche at the Institut d'Astrophysique Spatiale (IAS) in Paris-Orsay, where he initiated and runs the group "Astrochimie et Origines". He mimics interstellar conditions in his laboratory that enable the making-up of tiny quantities of analogues of insterstellar ices in which organic residues can be produced by ultraviolet photochemistry. He was awarded the silver medal of the CNRS in 2003.

prebiotic molecules are produced only in trace amounts.[8] As an alternative source of prebiotic molecules, outer-space chemistry has been suggested.[9] In space, chemical reactions can take place both in the gas phase and on ice and mineral grain surfaces during the accretion phase of protoplanetary bodies. Many of the reaction products are thus incorporated into asteroids, interplanetary dust particles (IDPs), cometary ices, and other interplanetary objects. The structure of this diverse range of organic molecules depends on the environment in which they have formed.

Meteorites are asteroid remnants that survived impact on the surface of the Earth. Primitive meteorites, such as carbonaceous chondrites, are important reservoirs of a wide variety of organic compounds. Their material can be broadly described in terms of solubility in aqueous and organic solvent systems. Insoluble and soluble components make up 70 and 30% of the total carbon content, respectively. Insoluble organic matter (IOM) has a complex kerogen-like macromolecular network. Regardless of its high abundance, little is known about the molecular composition of IOM. Spectroscopic[10] and decomposition[11] studies suggest a general structure composed of aromatic-ring clusters bridged by aliphatic chains containing S, N, and O atoms, with peripheral branching and functional groups. However, this refractory material is not soluble in water, and its influence on prebiotic chemistry is disputable.

The complex distribution of soluble organic matter has been studied extensively in carbonaceous meteorites, including the Murchison and Murray meteorites. These studies revealed a series of alkyl-substituted bicyclic and tricyclic aromatic compounds,[13] aliphatic compounds ranging from C_1 to C_7, including both saturated and unsaturated hydrocarbons,[14] more than 80 amino acids (Figure 1), including diamino acids,[15] *N*-alkylated amino acids[16] and iminodiacids,[17] small amounts of aldehydes and ketones up to C_5,[18] a wide spectrum of carboxylic acids and hydroxycarboxylic acids,[19] several nucleobases,[20] and sugar acids.[21] A comprehensive overview of the organic composition of carbonaceous chondrites is provided by theme-specific review articles.[22]

From the diverse array of meteoritic organic molecules, amino acids, hydroxycarboxylic acids, monocarboxylic acids, and amines have been investigated in terms of their stereochemical composition. The chirality of meteoritic amino acids is discussed in detail in Section 2.2. Amino acids exhibit the widest range of reported *ee* values: from 60% D-*ee* for *allo*-isoleucine[23] to 18% L-*ee* for isovaline.[24] The *ee* value varies significantly for different amino acids, as well as for the same amino acid in different meteorite samples, even within the same chondrite.[25] Surprisingly, meteoritic aliphatic amines and carboxylic acids that might share a common chemical origin with amino acids were recently detected as racemates.[26] Studies of enantiomeric distribution within hydroxycarboxylic acids gave another unexpected result: Lactic acid turned out to be the only hydroxy acid species to display an excess of one enantiomer.[27] The lack of consistency in the observed enantiomeric distribution may speak against a universal explanation of their origin. Such explanations take into account the possible role of ultraviolet circularly polarized light (UV-CPL),[28] deracemization during aqueous alterations,[29] and possible asymmetric effects of inorganic matrices within the meteorite,[30] or, alternatively, the complex interplay between compound-specific physicochemical properties, synthetic pathways, and/or so-far unknown symmetry-breaking effects.[25]

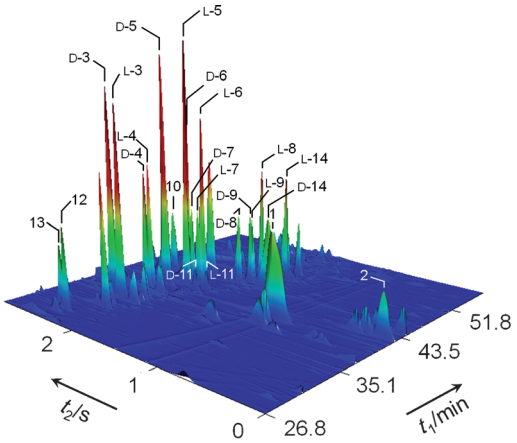

Figure 1. Section of a two-dimensional enantioselective gas chromatogram showing amino acids detected in the Murchison meteorite. Many of the detected amino acids are chiral. 1: glycine; 2: β-alanine; 3: alanine; 4: isovaline; 5: α-aminobutyric acid; 6: valine; 7: α-methylvaline; 8: isoleucine; 9: *allo*-isoleucine; 10: proline; 11: *tert*-leucine; 12: *N*-ethylglycine; 13: *N*-methylalanine; 14: leucine. Single-ion monitoring (SIM) at 102, 116, 130, 144, and 158 amu; chromatographic conditions are provided in Ref. [12].

2.2. Enantiomeric Enhancement in Meteorites: Up to 18% ee in L-Isovaline

After the first discovery by Engel and Nagy,[31] enantiomeric enrichment in meteoritic amino acids attracted much attention in the scientific community. In an extract of the Murchison meteorite, an *ee* value of 30% in the L enantiomer was found for alanine, which is assumed to be one of the first molecular building blocks. Even though it was later concluded that the presented *ee* value was not entirely indigenous,[32] this study deserves special mention as pioneering research on extraterrestrial enantiomeric enrichment.

Subsequent studies focused on α-dialkylated amino acids as species with rare occurrence in the biosphere and a low rate of racemization. In contrast to proteinogenic amino acids, which can lose and reacquire their α-hydrogen atom through the attainment of equilibrium during aqueous alteration, α-dialkylated amino acids are believed to preserve pristine *ee* values. An investigation on the terrestrially rare C_5–C_7 amino acids in the Murchison meteorite demonstrated non-zero *ee* values in favor of the L configuration for α-amino-α,β-dimethylpentanoic acid, isovaline, norvaline, and α-methylnorvaline,[24,25,33] whereas β-aminobutyric acid was found to be racemic.[34] Table 1 presents an overview of reported *ee* values of amino acids in carbonaceous meteorites.

Isovaline, the most abundant of the α-dialkylated chiral amino acids, shows one of the highest reported *ee* values (see

Table 1: Detected *ee* values of amino acids in carbonaceous meteorites.

Amino acid	L-*ee* (%)	Meteorite[a]
isovaline	−1.0 to +18.5[24]	EET, LEW, LON, MN, MY, OR, QUE
norvaline	−0.7 to +3.7[24b]	EET, LON, MN, OR, QUE
α-methylnorvaline	2.8, 1.4[33]	MN, MY
valine	−0.4 to +43.6[24b, 34]	EET, LEW, LON, MN, MY, OR, QUE
α-methylvaline	2.8, 1.0[33]	MN, MY
α-methylnorleucine	4.4, 1.8[33]	MN, MY
isoleucine	3.6 to 50[23]	EET, GRA LAP, ME, MIL, PCA, QUE
allo-isoleucine	−60 to −2.2[23]	EET, GRA LAP, ME, MIL, PCA, QUE
α-amino-α-methylheptanoic acid	7.0[25]	MN
α-amino-α,β-dimethylpentanoic acid	1.4 to 5.2[25]	MN, MY
allo-α-amino-α,β-dimethylpentanoic acid	2.2 to 10.4[25]	MN, MY
α-methylglutamic acid	2 to 3[23]	MN

[a] EET: EET 92042; GRA: GRA 95229; LAP: LAP 02342; LEW: LEW 90500; LON: LON 94102; MN: Murchison; MY: Murray; OR: Orgueil; ME: MET 00426; MIL: MIL 07525; PCA: PCA 91082; QUE: QUE 99177.

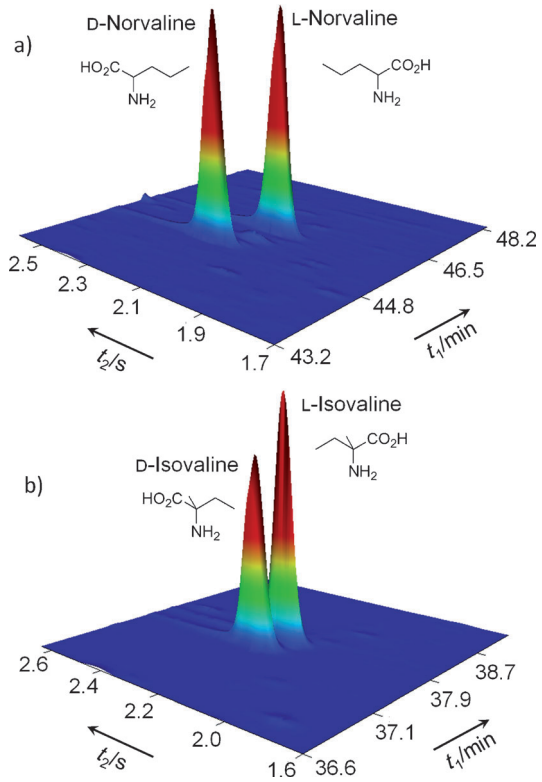

Figure 2. Sections of a two-dimensional enantioselective GC×GC-TOFMS gas chromatogram showing a) racemic D- and L-norvaline enantiomers ((−0.04 ± 0.39) %ee_L) and b) enantiomerically enriched D- and L-isovaline enantiomers ((4.61 ± 0.83) %ee_L) identified in a sample of the Murchison meteorite. SIM at 144 amu; for analytical conditions, see Ref. [12].

Table 1 and Figure 2).[24] Pizzarello et al.[24a] interpreted the high enrichment of isovaline in the L form as a result of its distinct synthetic pathway. It is generally thought that amino acids in meteorites are formed through Strecker cyanohydrin synthesis from aldehydes and ketones. In this case, the enantiomeric enhancement of isovaline was proposed to be derived from its aldehyde precursor. Later, Glavin and Dworkin[24b] demonstrated a direct relationship between the degree of aqueous alteration and the amplification of meteoritic L-isovaline. Although the indigenousness of the *ee* values of α-dialkylated amino acids leaves no doubt, the question of the origin of this enantiomeric enrichment remains open.

3. Chirality Investigations in Simulated Comets

Taking into consideration the evolutionary relationship between meteorites and IDPs with their icy mantles,[35] one would expect to find similar molecular and chiral signatures (e.g. amino acids and their *ee* values) within comets. So far, however, only small volatile molecules have been detected with confidence in cometary atmospheres. The failure to detect such signatures can be explained by the insufficient sensitivity of telescopes for the analysis of refractory compounds or the absence of liquid water essential for prebiotic chemical processing.[36] The achiral amino acid glycine was identified in a sample of the comet Wild 2.[37] For better insight into the molecular and stereochemical composition of pristine cometary matter and thus an understanding of the original symmetry-breaking influence, laboratory interstellar-simulation experiments and the in situ analysis of cometary ices are necessary.

3.1. Organic Molecules in Simulated Cometary Ices

Knowledge on cometary ices has been obtained by remote observations of comets and by the identification of volatile and refractory components adsorbed on interstellar dust. The results have led to the development of experimental methods that enable the production of both refractory materials and frozen volatiles with chemical, structural, and morphological characteristics that are assumed to reproduce those observed and/or expected in comets.[38] According to the comet core–mantle grain model developed by Greenberg,[39] small molecules condense from the gas phase on the cold surface of interstellar dust grains, thereby forming an icy mantle. During the deposition, the grain and mantle are subjected to energy in the form of UV photons and cosmic-ray particles. This processing is assumed to result in the formation of free radicals and creates a highly conducive environment for the transformation of ice-trapped radicals and molecules into prebiotically relevant organic compounds, such as amino acids, nucleobases, and sugars[40] (Figure 3). Further aggregation of interstellar dust particles results in the formation of larger bodies, such as comets.

Such processes are generally simulated in the laboratory by the deposition of a gaseous mixture of key interstellar species under high vacuum on a cold surface and irradiation with UV light or charged particles. The organic residue formed in such experiments provides valuable information on

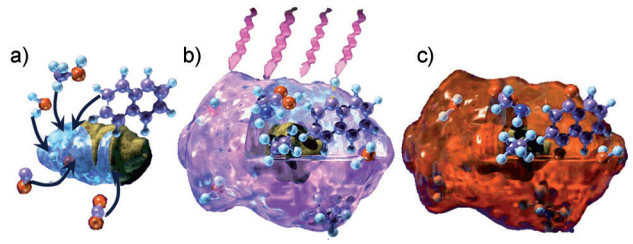

Figure 3. Development phases of interstellar dust particles: a) Silicate grains accrete ice layers from volatile molecules present in the surrounding gas phase (H_2O, CO_2, CO, CH_3OH, and NH_3). b) During the growth process, the icy mantle is irradiated with UV photons, which create radicals and initiate photochemical reactions. c) The radical-induced reactions produce a complex network of organic molecules, including amino acids. Adapted from reference [28a].

the possible composition of the cometary nucleus: information that is inaccessible by remote observations.

A remarkable diversity of organic compounds has been synthesized within interstellar-ice analogues by both UV and charged-particle irradiation.[41] Bernstein et al.[42] detected glycine, alanine, and serine as products after acid hydrolysis of a residue originating from a 20:2:1:1 $H_2O/CH_3OH/NH_3/CH_3CN$ gas mixture. Independently, Muñoz Caro et al.[43] identified 16 amino acids in the hydrolyzed and derivatized organic residue obtained by UV irradiation of $H_2O/CH_3OH/NH_3/CO/CO_2$ (2:1:1:1:1). Muñoz Caro et al. used ^{13}C-labeled precursors to exclude contamination as a possible source of organic molecules. Further experiments of Meinert et al.[44] provided an up-to-date list of 26 amino acids, including proteinogenic and nonproteinogenic amino acids, diamino acids, and *N*-(2-aminoethyl)glycine. All amino acids were detected as racemates, as no chiral influence was introduced into the system. The analysis of a nonhydrolyzed residue by Briggs et al.[45] resulted in the detection of only glycine, the simplest amino acid (see also Ref. [46]). It was therefore proposed that the products of the photochemical reactions are incorporated into some macromolecular structure, and then released upon acid hydrolysis. Apart from amino acids, different mixtures of simulated interstellar ices produced purine and pyrimidine compounds, urea, and polyols, along with other prebiotic molecular structures.[47]

The majority of the detected compounds were identified in meteorites as well. Thus, a logical question arises: "Do pristine cometary chiral molecules, like the further-altered meteoritic molecules, exhibit any enantiomeric preference?" To answer this question, we introduce in Sections 3.2 and 4.1 a set of experiments in which prebiotic chiral molecules and/or their precursors have been subjected to truly chiral entities, such as CPL.

3.2. Enantiomeric Enhancements in Simulated Cometary Ices

The interaction of matter with UV-CPL has been proposed as one of the possible sources of biomolecular asymmetry (see Section 4). This notion implies a scenario in which the first symmetry-breaking event occurred when the giant molecular cloud from which our solar system formed was exposed to asymmetric CPL of a given helicity.[48] This hypothesis was tested by systematically simulating interstellar ices by irradiation with right- and left-handed UV-CPL.

The first attempts to perform absolute asymmetric synthesis from an ice mixture of H_2O, CH_3OH, and NH_3 by irradiation with CPL at a wavelength of $\lambda = 167$ nm resulted in a small *ee* value of 1%, which lay within the limits of detection of the instruments and methods.[49] Further improvement of the experimental procedure by changing the CPL wavelength to $\lambda = 187$ nm and using multidimensional gas chromatography for advanced analysis yielded in ee_L values of up to -1.34%.[50] In recent investigations by Modica et al.,[51] statistically relevant *ee* values were induced in five enantiomeric pairs of amino acids, with a maximum value of -2.54% ee_L for 2-aminobutyric acid. The sign of the induced *ee* values depends on the helicity as well as the energy of the CPL and was identical for all five amino acids at $\lambda = 121$ nm for each given helicity. Similar *ee* values to those induced photochemically in laboratory ices can be expected for cometary amino acids.

These studies, however, do not provide information on the mechanism for the asymmetric formation of amino acids. It remains difficult to distinguish between the two relevant mechanisms of absolute asymmetric photosynthesis and absolute asymmetric photolysis.

4. Stereochemical Mechanisms for Enantiomeric Enrichment

Many theories exist to explain the original instance of enantiomeric enrichment. These theories can be broadly classified according to Jacques Monod's famous phrase into "chance and necessity" or alternately "probabilistic versus deterministic".[52] The "chance" school hypothesizes that homochirality arose from a random symmetry-breaking event and assumes an equal probability of generating a world with an opposite handedness. The supporters of the "necessity" model assume a selection process between enantiomers and a unique definitive solution to the origin of biological asymmetry. In this section, we group the main theories for the generation of an enantiomeric excess according to the nature of the chiral influence involved.

4.1. Enantiomeric Enhancement Induced by Asymmetric Photochemistry

Among photochemical effects, only circularly polarized light and a static magnetic field collinear with a light beam are truly chiral systems and thus can potentially produce an enantiomeric enhancement within initially racemic mixtures.[53] Both of these mechanisms were proposed to be responsible for the symmetry breaking in biomolecules.[48,54]

With CPL, the electric-field vector *E* and the magnetic-field vector *B* remain constant in magnitude but proceed in the form of left or right helices around the axis of the direction of propagation. Therefore, CPL can distinguish between two

enantiomers owing to the difference in absorption of left-handed and right-handed CPL, an effect that is wavelength-dependent and known as circular dichroism (CD). This chiroptical property leads to the preferential destruction of one of the enantiomers, as demonstrated in numerous experiments.[55] A detailed mechanistic understanding of the photochemical nature of the mirror-symmetry-breaking event upon CPL irradiation is provided in the literature[28,56] and illustrated in Figure 4.

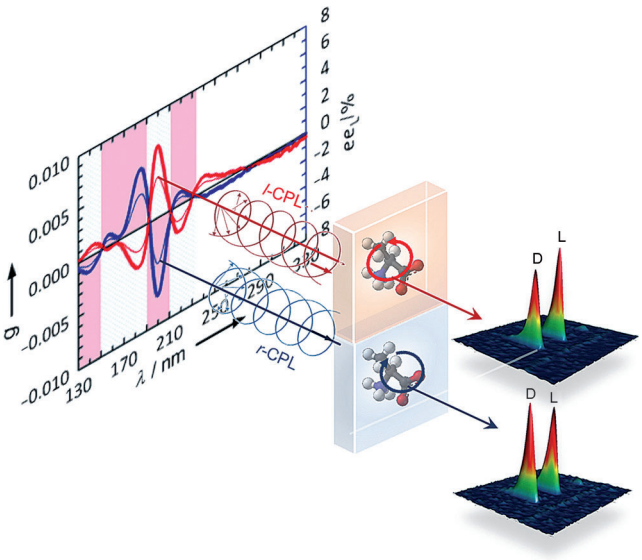

Figure 4. Photolytic induction of enantiomeric enrichment in racemic alanine. Interaction with CPL of sufficient energy imparts a slight bias for the less photoabsorbent enantiomer as the more photoabsorbent enantiomer undergoes faster photolysis. The degree and sign of the induced asymmetry depend on the helicity of the CPL, the energy of the driving electromagnetic radiation, the photolysis rate, and the ratio between the differential extinction ($\Delta\varepsilon$) and the extinction coefficient (ε) of the enantiomers. This ratio is also known as anisotropy, $g = \Delta\varepsilon/\varepsilon$, which itself depends on the wavelength of the incident CPL. Anisotropy spectra include crucial information about enantioselective photolysis. These data enable the selection of a CPL wavelength for induction of greater enantiomeric enrichment, prediction of the sign of the induced enantiomeric enrichment, and the calculation of expected *ee* values.

It is hypothesized that extraterrestrial organic material, prior to its delivery to Earth by IDPs, meteorites, and/or comets, has been exposed to interstellar UV-CPL and thus become enriched in one of the enantiomeric forms; its symmetry has been broken. Autocatalytic processes could have amplified small *ee* values to produce a state close to homochirality. The detection of circularly polarized electromagnetic radiation in the infrared wavelength domain from several star-forming regions[48d,57] provided additional support for this proposed scenario. Calculations show that ultraviolet CPL capable of inducing enantiomeric enhancement is also present[58] but cannot be observed owing to the high degree of dust obscuration of UV light in such environments.

An oriented beam of unpolarized light passing through a static magnetic field is another example of a truly chiral influence. Similarly to the CPL model, enantiomers absorb the radiation traveling parallel or antiparallel to the applied magnetic field to different extents. This effect is referred to as magnetochiral dichroism (MD). It was demonstrated to induce very small *ee* values (10^{-5} %) in specific chiral ferromagnetic molecules.[59] The ubiquity of magnetic fields and unpolarized light in the cosmos led Barron[54] to propose this effect as a candidate for the abiotic generation of an enantiomeric excess. However, given the fact that MD depends upon very high magnetic fields of up to 15 T and results in such small asymmetry, it is now thought by adherents of this assumption that meteoritic enantiomeric enhancement has been caused either by UV-CPL generated from a directed magnetic field (Faraday effect) or by direct asymmetrical magnetooptical effects distinct from Faraday rotation.[60]

Both chiral influences cause enantiomeric enhancement in either the L or the D form, depending on the local nebular region, but not when averaged over the entire cosmos. Given the data from astronomical observations[48d,57] and the most recent experiments,[49,50,55] we can conclude that the origin of biomolecular asymmetry is probably a consequence of photochemical effects based on CPL.

4.2. Enantiomeric Enhancement upon Crystallization, Phase Transition, and Viedma Ripening

Chiral-symmetry breaking upon spontaneous crystallization has long been known for sodium chlorate solution.[61] Achiral sodium and chlorate ions are known to crystallize as two separate chiral solid phases in the form of a racemic mixture,[62] but under specific stirring conditions, the sodium chlorate can precipitate randomly as a single chiral phase. Later, this phenomenon was determined to be a result of secondary nucleation enhanced by agitation under far-from-equilibrium conditions.[63]

In 2005, a new mechanism of symmetry breaking was demonstrated for sodium chlorate. A single chiral solid state was formed under "near-equilibrium" conditions, under which no new crystals nucleate. This phenomenon is known as "Viedma ripening".[64] Extension of this approach to proteinogenic amino acids under prebiotically plausible conditions resulted in a solid-phase enantiomeric enrichment of up to 99% for aspartic acid.[64b] L-Aspartic acid was thus proposed to be an ancestor of left-handed molecules.[65] The choice of aspartic acid was by no means a coincidence, as it is one of two proteinogenic amino acids that meets all necessary requirements for "Viedma ripening", that is, 1) the formation of conglomerate crystals and 2) fast racemization of the enantiomers in solution.

These restrictions leave little room for chiral-symmetry breaking in the other 17 chiral proteinogenic amino acids, and especially in meteoritic α-dialkylated analogues, which are resistant against racemization. The sublimation protocol recently introduced by Viedma et al.[66] reveals both the conversion of a racemic compound into a racemic conglomerate and subsequent enantioenrichment; it might open new horizons for the enantiomeric purification of previously overlooked amino acids.

Regardless of the significance of chiral-symmetry breaking upon crystallization, current data provide a rather poor explanation for the observed meteoritic *ee* values, and the model has low astrophysical relevance, as chiral molecules in outer space are believed to be incorporated in a macromolecular matrix[25] rather than existing in a solution under constant stirring or grinding. Further investigation of chiral resolution through sublimation and other astrophysically admissible processes may provide new insight on this topic.[67]

4.3. Enantiomeric Enhancement Induced by the Weak Nuclear Interaction

All universal interactions were considered to be entirely symmetrical before the discovery in 1956 of the parity violation in the weak force.[68] Parity violation means that the true mirror image of an object or experiment is energetically not equivalent to the original.[69] It was demonstrated that in the β-decay, mediated by the weak force, radioactive ^{60}Co nuclei emit exclusively left-polarized electrons, which therefore violate parity.[70] As a consequence, we expect a small energy difference between two enantiomers.[71] This energy gap has not yet been measured, but it was calculated to have an order of 10^{-12}–10^{-15} J mol^{-1}[72] with a magnitude and sign that depend on the particular conformer of the studied compound. Owing to this dependence, there is no general answer to the question of which enantiomer is generally favored. Quack[73] pointed out that even if parity violation causes a left or right preference on the molecular level, this preference is not necessarily linked to the evolution of biomolecular homochirality.

Another indirect way that weak nuclear forces could cause enantiomeric enhancement is chirality transfer from spin-polarized electrons to chiral molecules. The enantiomers of a chiral molecule become ionized at different rates upon irradiation with β-electrons, thus resulting in enantioselective degradation. This effect known as "electronic circular dichroism" was first measured for the optical isomers D- and L-camphor, which did not weaken the passing spin-polarized electrons equally.[74] It was applied to induce optical activity in leucine,[75] tryptophan,[76] and alanine;[77] however, the kinetic energy of the investigated spin-polarized electrons was by orders of magnitude too high for efficient enantiomer-discriminating absorption.

In early 1962, Ulbricht and Vester[78] proposed to use bremsstrahlung radiation produced by decelerated spin-polarized electrons to produce enantioselective interactions within organic matter. Each individual step in the Vester–Ulbricht mechanism has received experimental confirmation. First encouraging results were obtained by Garay,[79] who detected small differences in the ultraviolet absorption spectra of D- and L-tyrosine after exposure for 18 months to $^{90}SrCl_2$ β-rays and bremsstrahlen. Subsequent experiments produced either very small[80] or no[81] asymmetrical effects and were considered inconclusive and contradictory.[82] However, they do not preclude the contribution of the Vester–Ulbricht scenario to enantiomeric enrichment in interstellar evolution, during which numerous β-radiators have been present.[28]

4.4. Amplification of Enantiomeric Enhancements by Autocatalytic Processes

A tiny enantiomeric excess produced by one of the above-mentioned mechanisms can be increased by means of autocatalytic processes to homochirality. Models for the amplification of an enantiomeric imbalance were divided by Blackmond[83] into those governed by kinetics in far-from-equilibrium processes and those based on thermodynamics and equilibrium phase behavior.

The first theoretical model of spontaneous asymmetric amplification was proposed by Frank in 1953.[84] In this model, a large enantiomeric excess can be generated in a chemical reaction in which one enantiomer catalyzes its own formation while inhibiting the formation of the other enantiomer. Soai et al.[85] provided the first experimental proof for this model when they reported the formation of 5-pyridyl alcohol with up to 90% *ee* from the same alcohol with a small initial *ee* value upon treatment with diisopropylzinc and pyrimidine-5-carboxaldehyde. This reaction clearly does not occur under prebiotic conditions, but it is an important example of the absolute asymmetric synthesis of enantiomerically enriched products. The Soai reaction was later shown to be extremely sensitive to initial *ee* values as small as those produced upon CPL irradiation.[86] Its kinetic model has been studied in detail by the groups of Blackmond[87] and Buhse.[88]

Another example of the Frank model is the amplification of an initial enantiomeric disproportion through physical processes, such as evaporation, crystallization, or sublimation under "far-from-equilibrium" conditions. This strategy has proven to be effective for threonine,[89] aspartic acid, and glutamic acid,[90] as well as for valine.[91]

The autocatalysis based on equilibrium phase behavior is fully reflected in crystallization under "near-equilibrium" conditions as described by Viedma.[64b,92] Moreover, Klussmann et al.[93] established that the coupling of solid–liquid phase behavior and amino acid catalysis results in an efficient thermodynamically controlled mechanism for asymmetric amplification.

In attempts to link the opposite chirality of nucleotides and amino acids, it was proposed that a small imbalance in the D/L ratio of amino acids might have played a crucial role in the generation and/or amplification of *ee* values in nucleotide precursors. Studies carried out by Mathew et al.[94] showed that proline could influence a reaction by increasing the rate of the formation of one of the two possible optical isomers of the product. Further investigations by the same research group revealed that amino acids with a small initial enantiomeric excess can drive the formation of enantiomerically enriched nucleotide precursors, thus paving the way to homochiral RNA.[95]5. The Chirality Module on Board the Rosetta Lander Philae

For the advancement of our scientific knowledge about the origin and evolution of extraterrestrial molecules and particularly about the origin of the observed asymmetry in

meteoritic matter, the underlying mechanisms of the formation of these molecules have to be understood. This challenge is being taken up, at least partially, by the Rosetta mission.

Approved in 1993 as the "Planetary Cornerstone Mission" of the ESA and launched in 2004, the Rosetta spacecraft has finally reached its target comet 67P/C-G. The Rosetta[1] spacecraft is composed of two principal elements: the lander Philae and the orbiter Rosetta. Each of them is equipped with 10 instruments specifically designed to accomplish the mission objectives. In November 2014, the Philae lander detached from the Rosetta spacecraft to perform the first scientific in situ investigation of a cometary nucleus (Figure 5).

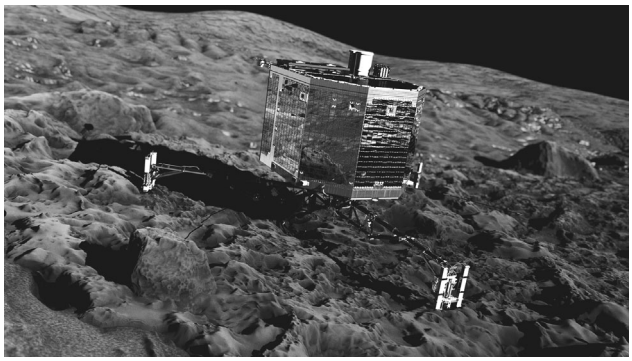

Figure 5. Computer graphic of the Rosetta lander Philae on the surface of the nucleus of comet 67P/Churyumov-Gerasimenko. Philae is equipped with an enantioselective GC–MS instrument with three chiral stationary phases. Image credit: ESA.

A drilling system (SD-2) will obtain samples from a depth of up to 23 cm and distribute them to the other instruments for the investigation of their chemical composition, density, near-surface strength, porosity, texture, ice phase, and thermal properties. Among these instruments, the "Cometary Sampling and Composition" (COSAC)[96] experiment is of high importance for stereochemical investigations. The COSAC instrument is equipped with a multicolumn gas chromatograph (GC) and a time-of-flight mass spectrometer (TOFMS), and is connected to an electronic system that allows remote operation of the suite. The GC system includes a set of eight parallel capillary columns and two types of pyrolysis ovens. The chromatographic columns vary in their stationary phase, film thickness, diameter, and length; three of them can resolve chiral organic molecules. COSAC is the first instrument sent to space for the investigation of chirality.[97]

On the basis of remote observations,[36] previous flyby missions,[2–5] and interstellar ice simulations,[42,43,45,49–51] the cometary nucleus has been imagined as a "dirty snowball" owing to its high content of dust, organic material, and ice. Analysis of the stereochemical and molecular composition of this "dirty snowball" is the objective of the COSAC experiment. Before a cometary sample is subjected to chromatographic separation, it will be derivatized with *N,N*-dimethylformamide dimethyl acetal[98] to transform refractory molecules through methylation into volatile species. After separation on the GC column, these molecules enter the TOFMS, where they become ionized and produce characteristic spectral signals allowing structural elucidation.

The main interest in the COSAC instrument regards the separation and quantification of chiral organic molecules.[99] The list of Rosetta-relevant chiral molecules includes hydrocarbons, amines, alcohols, diols, carboxylic acids, and amino acids.[97–100] The investigators responsible for the COSAC chiral module assume that there is a reasonable chance of finding partial enantiomeric enrichment in chiral molecules as result of the exposure of the cometary ices to extraterrestrial chiral fields.[28] An identical or similar excess of L-configured molecules to those observed in meteorites would support the assumption that chiral organic molecules were indeed delivered to early Earth during the late heavy-bombardment phase by comets and/or other small interplanetary bodies whose organic content may be of interstellar/presolar origin, from the molecular cloud from which our solar system formed. Even though the physicochemical mechanisms for the generation of an enantiomeric excess are not yet fully understood, the results of the COSAC experiment will bring us one step closer to solving the puzzle of how homochiral life could have originated on Earth.

6. Summary and Outlook

The main astrobiologically relevant hypotheses to explain the origin of biomolecular asymmetry assume the induction of a small enantiomeric excess by either photochemical effects, parity violation, or phase changes and its amplification by autocatalytic processes on Earth. The key step, chiral-symmetry breaking, has been puzzling scientists for over 50 years. In view of the results of ice-simulation experiments and analyses of meteoritic samples, UV-CPL can be considered as one favorable candidate for the original asymmetrical influence. Nevertheless, alternative sources of chiral imbalance must not be overlooked. The long-awaited results from Rosetta's chirality module will hopefully provide crucial insight into the stereochemistry of prebiotic molecules within interstellar objects. The detection of prebiotic chiral molecules in comets will be an important step towards understanding the emergence and development of homochiral life.

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