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Review

New trends in the research on biological chirality - Part II: Did life arrive to earth by meteorites?

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ABSTRACT

The present review summarizes concentrated discussions regarding the most important new results of research aimed at understanding the origins of biological chirality. After discussing the key model reaction named as asymmetric autocatalysis (Soai reaction) in Part I, here the most important aspects of possible extraterrestrial origin of biological chirality are summarized. The most decisive results in this direction have been achieved by chemical analyses of meteorite samples as well as by photochemical model reactions.

KEYWORDS: biological chirality, organic matter from space to earth, cosmic dust, meteorites, photochirogenesis.

INTRODUCTION

There is no doubt that *biological* chirality [1-3] is a phenomenon connected with *life* (i.e. with *living* organisms). There is however a serious doubt about whether Natural Sciences, today in the 2019th year of the 3rd Millennium, are able to say in all details *what life is* (i.e. to give a precise definition of life) [4]. The fact that in all living organisms, studied until now, chiral molecules could be found either exclusively or in high excess in favour of one of the enantiomers, is a fundamental fact in biochemistry [5] and one of the best-documented common features of all material systems, which are classified as "living". From the viewpoint of chemistry this is fairly understandable: none of the highly selective chemical reactions observed in "living" beings could have displayed *without* the selectivity in reactions of asymmetric biomolecules. On the other hand, from the viewpoint of biology this phenomenon is observed as selectivity in favour of the *same enantiomers* in the whole "living nature". This observation represents one of the best experimentally documented arguments for the hypothesis that all living beings are somehow related, that is: for the existence of the Tree of Life [6]. If these considerations are true, one can conclude that the enantioselectivity provided by biological chirality, should have operated since the beginning of life on Earth [7] – or *even earlier* [8].

Mosaics of these studies led to a fairly new scenario of the origin of biological chirality, changing also the traditional picture [9] of the orign of life itself. This picture was based mainly on chains of hypotheses (e.g. variants of the "warm little pond"

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This review has been presented at a Mini-Symposium recording the 50th anniversary of the fall of the Murchison meteorite, Accademia Nazionale di Scienze, Lettere e Arti, Modena (Italy), September 26, 2019. The paper is dedicated to Prof. Sandra Pizzarello for her extraordinary contribution to cosmochemical research, particularly on samples from the Murchison meteorite.

hypothesis [10] or interpretations of Stainly Miller's experiment [11]) which were (are) based on the supposition that the "starting" biomolecules (amino acids, carbohydrates, nucleobases, etc.) have been formed from very simlple 2-5 atomic molecules (H_2, CO, CO_2, NH_3, CH_4, etc.) under *conditions of the* "*early Earth*" [12] and then took their misterious journey towards the formation of living organisms, surpassing the threshold of non-living/living matter. This picture appears to change in the last years in the sense that convincing experimental evidence supports the view, that these elementary biomolecules travelled "ready made" by interplanetary/interspacial objects to Earth [13]; moreover the chiral species from these molecules did arrive with more or less enantiomeric excess [14]. The present review makes an attempt to summarize some characteristic facts and observations being in contact with this change of paradigms.

Carriers of organic matter in space

Organic molecules are suspected to "levitate" piece-by-piece in space [15], but their arrival to larger space objects, like Earth is most probably mainly linked to objects which are much larger. The size and mass range of such objects is, however very broad. They are generally classified as powder-like bodys, *cosmic dust* [16] and *chondrites* [17] (together with several more detailed classification systems which will not be discussed in the present review), etc. The generally accepted size range of cosmic dust particles is regarded as from aggregate of a few molecules to 0.1 μm [18], or in terms of mass from 100 fg to 100 mg, while objects heavier than 100 mg are regarded as micrometeorites or meteorites, if larger than a few metric tons, then "planetesimals" or even smaller planets. There is no sharp border between these "classes". It seems unlikely, but the mass of cosmic dust falling to Earth in one year, is a considerable quantity, ranging from 5 to 270 t/day, that is 1825-98550 t/yr, and it is much more, approximately 10-fold of the mass flux of the "larger" objects. The composition of these space-born objects is highly variable, but it can be genearally said that a huge majority of these contain more-less organic phase [19]. This phase is approximately 80% composed of insoluble polymeric material, with structural features which are in course of exploration in several laboratories of the World. That organic fraction which can be mobilized by solvents, pyrolysis + solvents, hydropyrolysis, etc. is composed of a great variety of organic compounds [20]. Some approximate calculations found [21] that the quantity of organic matter falling to Earth each year is ~0.04 t/day, which is 14.6 t/yr corresponding to 28.62 mg/yr × km^2.

The study of the cosmic material is still in its initial stage, which is exeplified very impressively by the title of a report in one of the leading Journals in Natural Sciences, saying that "evidence for the interstellar origin of *seven* dust particles" was studied [22], by a team of 70 scientists! It appears, however, that it would be very important to speed-up these studies since a broad range of information about the origin of the Solar System [19, 23], the origin(s) of terrestrial life [24] and other fundamental questions can be expected (and, in part, already obtained).

Summarizing these studies one could say that at least a considerable fraction of molecules indispensable for start and/or an early function of life has been "imported" by space-born objects (cosmic dust, meteorites, etc.). Moreover, chiral representatives of these "imported" biomolecules arrived in non-racemic form, that is, containing more-less enantiomeric excess from one of their enantiomers. This fact is a fundamentally new result of Natural Sciences and it is getting even more interesting in the light of the fact that the enantiomeric excesses are formed generally by *that* enantiomers which show identical or similar stereochemistry to that of the preferential isomers of biomolecules. Some representative examples of these molecules, which arrived to Earth in non-racemic form are shown in Table 1.

"Importation" of non-racemic biomolecules, however, resulted in the problem of the origin of the extraterrestrial symmetry breaking – that is – the core problem was "exported". This challenge will be discussed in the following part of the present review.

Symmetry breaking in the Universe

The really surprizing fact, that non-racemic chiral compounds arrive to Earth from *somewhere* in the

Table 1. Chiral organic compounds found in non-racemic form in meteorites [14e,f].

Compound name	**Enantiomeric excess, *ee* [%]**
(S)-2-aminobutane (*sec*-butylamine)	8-18
L-2-amino-2-methylbutanoic acid (i-Val)	2.5-19.6
L-2-amino-3-methylpentanoic acid (Ile)	4-50
D-2-amino-3-methylpentanoic acid (*allo*-Ile)	2-60
L-2-amino-2,3-dimethylpentanoic acid	2.2-10.4
L-lactic acid	3-12.3

ee = (L/D +L)x100 or (D/D+L)x100 [%], where L and D are molar quantities of the two enaniomers.

Universe generated many speculations and laboratory attempts by model experiments. These can be classified into two main approaches, *stochastic* or *deterministic* laws that are responsible for the enantio-preference observed in extraterrestrial samples. The possibility of stochastic phenomena as responsible for the generation of (pre)-biological extraterrestrial enantiomeric excesses will be discussed later in this series. Here we shall briefly discuss two possibilities which are plausible candidates for acting as deterministic natural laws responsible for the generation of more-less enantiomeric excess of organic molecules arriving to Earth from “outward”.

One of these possibilities is derived from the *asymmetry of weak nuclear forces*, which was one of the major discoveries of theoretical physics in the second half of the 20th century [25]. This phenomenon could lead to a faint energy difference between enantiomers of chiral molecules [26]. However, while this effect could be demonstrated experimentally with heavier atomic nuclei [27] its observation at molecules could not yet been realized beyond doubt [28]. Theoretical calculations let open the possibility of experimental observation with chiral molecules [29], but apparently still a substantial development in the sensitivity of observation methods is required [30].

The energy difference caused by the asymmetry of weak nuclear forces in enantiomers would be a very plausible deterministic route to enantiomeric excesses observed in space-born organic molecules, first of all because of its general validity overall in the known Universe. However, the very low calculated energy differences make doubtful its role as a general source of non-racemic chiral organic molecules found in extraterrestrial samples. The fact that it could not yet(?) been experimentally demonstrated at molecular systems makes this correlation possibility still more uncertain. If the challenge of the experimental observation of this interesting natural law could ever be met it would open ways for evaluating its real role in prebiotic/ biotic chemistry.

The way of chiral molecules or achiral-to-chiral reactions in the extraterrestrial space also meets another principle, which has the advantage of possessing general validity in the Universe: This is the interaction of circularly polarized electromagnetic radiation (mainly light) with these “traveling” molecular systems. This aspect of the genesis of enantiomeric excesses in the extraterrestrial space became the target of intense research activity in the last few years. This tendency has two bases. One of these is the almost century-old observation that left and right polarized light interacts differently with enantiomers [31]. This opens destructive or synthetic photochemical ways for obtaining enantiomer ratios different from the racemic 1:1. In spite of the several sophisticated attempts this way for obtaining higher enantiomeric excesses no significant results were obtained until the dawn of the 3rd Millennium, when the combination of asymmetric photochemistry with asymmetric autocatalysis provided a real breakthrough, leading to almost quantitative enantioselectivity [2, 32]. These results (together with some other related observations) gave a solid theoretical basis for the supposition that *if there were* circularly polarized light in the interplanetary/intergalactic space, there would be "available" a generally valid preparative tool for the formation of enantiomeric excesses in the extraterrestrial space.

The lacking brickstone of this approach was found approximately 20 years ago [33]: It turned out that in the Universe there are sevaral sources of circularly polarized light. This observation became cornerstone of additional astronomic and model-experiment studies.

The fundamental approach in these efforts *disregarded* the eventual contribution of weak nuclear forces to the production of non-racemic mixtures of chiral molecules in space from racemates or from achiral starting compounds, but *regarded* the possibilities provided by circular polarization. These studies led to the new research direction, named *photochirogenesis* [34].

Photochemical reactions in space are taking place under conditions, which are radically different from terrestrial "open air" or usual laboratory conditions. This difference, obviously, has to be taken into account in *in situ* or model experiments. In both cases the chemical reacions proceed under very low pressure and very low temperature. *In situ* observations need spacialized spacecraft instrumentation while laboratory model experiments require specific equipments. In the last 20 years several succesful attempts have been made in these directions. On-the-spot observations are in course and also a few sample-return missions could be realized, while a number of sample-return plans are in course of realization [35]. Succesful laboratory model experiments have also been reported [34c-e, g-j; 36]. The main message of these experiments is that under controlled paramaters the preperative and mechanistic results are convergent to those which are *supposed* to occur under space conditions (low temperature [37], very low concentrations [38], broad scale of high-energy electromagnetic and corpuscular radiations [12c, 39]).

These efforts are putting together a new and apparently consistent picture of cosmochemical processes, which is (or more exactly: appears to be) the basis of finding the extent and mechanisms of contribution of extraterrestrial physical and chemical factors to the emergence of that class of material processes which we call as *life* (even if its accurate definition is not yet elaborated in all details). This panorama of new observations leads to the paradigm change, as already mentioned, in the sense that the most important early steps of the origin of life had not necessarily been of *terrestrial* (endogenic) character, but also *extraterrestrial* (exogenic) factors could have been of a certain importance. The *extent* and *ratio* of these factors is not yet known, but it represents an attractive research goal and it can be reasonably hoped that additional important advances will be reached in a relatively near future.

CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest associated with the contents of this article.

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