

Review

Chance and Necessity in the Evolution of Matter to Life: A Comprehensive Hypothesis

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Abstract: Specialists in several branches of life sciences are trying to solve, piece by piece, the immensely complex puzzle of the origin of life. Some parts of the puzzle seem to appear with a rather high degree of clarity, while others remain totally obscure. We cannot be sure that life emerged only on our Earth, but we believe that the presence of large amounts of water in its liquid state is absolutely essential for the emergence and evolution of living matter. We can also assume that the latter exploits everywhere the same light elements, mainly C, H, O, N, S, and P, and somehow manipulates the same simple monomeric and polymeric organic compounds, such as alpha-amino acids, carbohydrates, nucleic bases, and surface-active carboxylic acids. The author contributes to the field by stating that all fundamental particles of our matter are “homochiral” and predominantly produce in an absolute asymmetric synthesis amino acids of L-configuration and carbohydrates of D-series. Another important point is that free atmospheric oxygen mainly stems from the photolysis of water molecules by cosmic irradiation and is not necessarily bound to living organisms on the planet.

Keywords: origin of life; biological homochirality; deracemization; super-high-velocity impact; absolute asymmetric synthesis; amino acids; origin of oxygen; photolysis of water; escape of hydrogen



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1. What Is Life?

One can find in the literature more than 130 definitions of the term “life”. Most of them relate to *Homo sapiens* and sound like a philosophical exercise. More valuable are those definitions that try to formulate what separates living creatures from non-living matter. The physicist Erwin Schrödinger [1] defined living matter as that which “avoids the decay into equilibrium”. This definition implies that, when alive, organic systems consume energy from their environment and function against the Second Law of Thermodynamics, which says that entropy of any system must steadily increase. In official NASA documents, the ability of living matter to evolve is stressed: “Life—self-sustained chemical system, capable of Darwin’s evolution” [2]. More generally: “Life is self-reproduction with variations” [3]. Though the above definitions seem to be rather logical, they are by no means sufficient from the point of view of life sciences. For instance, they give no answer to the simple question of whether viruses are alive or not. Viruses lack any metabolism, synthetic capacities, and self-reproduction ability, and therefore, they obviously are on the inanimate side of the barrier between life and non-life. On the other hand, in view of the richness and diversity of the viral world and the recent discovery of giant viruses, they clearly were “highly important actors in evolution, in particular, during its early steps, transferring genes from one organism to another” [4].

Carroll emphasizes chirality as an essential feature of life: “Life is that which self-reproduces a homochiral environment” [5]. While operating within information theory, he provided a quantitative framework for understanding the role of chirality in biology. Indeed, it is clear now that the specific chirality of molecular building blocks in polymeric species of living systems is essential for them to function as enantioselective chemical reagents but also that homochirality of starting molecular pool is essential for these polymeric species to emerge. In other words, homochirality of initial organic molecules is the

pre-condition for the living systems to both emerge and further proliferate. This requirement is at least valid for the palette of amino acids in proteins and saccharides in nucleic acids and polymeric carbohydrates. In the living matter on Earth, all amino acids belong to the L-configurational series, and all saccharides relate to D-pentose.

One may ask whether the homochirality of the initial organic molecules is truly crucial for primitive life to emerge. If the answer is yes, then what is the origin of homochirality? Could it not result in a further step of evolution? To answer this question, we have to approach it from the point of view of general laws of chemistry and analyze, step by step, unquestionable conditions for the emergence of the first living matter anywhere in the Universe.

2. Water—Essential Prerequisite of Life

First, we assume that life was born in a solution. Only a good solvent could simultaneously accumulate a whole palette of various organic molecules and provide them with high global mobility. Numerous chemical reactions would thus proceed on various sites of the planet, both simultaneously and in sequence, resulting in the formation of manifold more complex chemical structures. Some of the latter could decay and reassemble again in a different manner. No one solid state (nor any melt) would ever furnish the initial organic building blocks with such combinatorial reaction possibilities.

What type of solvent would be most suitable for serving in the capacity of the cradle of life? No doubt, it is water in its liquid state. Water is the most abundant compound in the universe and it necessarily participated in one way or another in the formation or evolution of life in any planetary system. Fortunately, the Earth acquired, from the very beginning or soon afterwards, huge amounts of water. When the Earth was hot, water resided in the very heavy atmosphere, but some million years later, it condensed and formed oceans, which covered almost the entire surface of the planet.

The ability of water to dissolve both numerous inorganic and organic compounds is unique. This ability is due to several peculiarities of this substance, the most important of which are extremely high dielectric constant, ability to solvate ionic species, enter coordination sphere of transition metal ions, form hydrogen bonds with polar organic compounds, and even include several non-polar compounds into some kind of water clusters.

Evaporation of aqueous solutions would concentrate the dissolved mixtures to a high extent and increase the probability and rate of mutual interactions of the components. Interestingly, the freezing of aqueous solutions also results in the ultimate concentration of dissolved matter. This last unique behavior of water serves as the basis for a special manner of conducting chemical reactions, especially polymerization, called cryochemistry [6]. For these reasons, the presence of liquid water on the surface of young planets can be assumed to be an essential prerequisite of the chemical evolution of organic matter. It must be added here that liquid water can also exist at temperatures much higher than 100 °C, as is the situation deep in the oceans in the vicinity of “black smokers”. Surprisingly, these areas were found to be densely populated with thermophile organisms. However, it is difficult to imagine that life could initially emerge there, because strong convection flows near the local heat sources would rapidly remove all reaction products so that organic compounds could hardly accumulate there in the required high concentrations. Moreover, hot water presents a strong hydrolyzing and racemizing environment for the majority of polymeric biomolecules. This danger does not necessarily apply to higher forms of life. The latter may have adapted to a rather unfriendly environment. Thus, certain organisms proliferate rather successfully in lakes with extremely high salinity levels and even in alkaline waters.

While remaining in the frames of the chemical pathways of matter evolution from the aqueous solutions of numerous inorganic and organic compounds to life, we also must suppose a more probable location for this miraculous event to happen: in the bulk ocean or in smaller lakes and bays.

The majority of researchers hold the view that the formation of complex organic structures requires, according to the chemical law of mass action, a mechanism of concentrating

numerous smaller organic molecules in a rather constrained location. When taking into account that in times of Hadean there was much more water on Earth than there is at present, one must conclude that life could not have emerged in the ocean, not even in the vicinity of hydrothermal vents emitting organics and mineral salts and catalytically active “smoke” microparticles. As early as the 1920’s, Russian biochemist Alexander Oparin [7] suggested that life emerged in a primordial soup—a concentrated rich mix of carbon-based chemicals. Though there were no large continents on the early Earth, certain volcanic islands were nonetheless present. On some elevated parts of land, locations could have existed similar to the hot springs found in Yellowstone National Park. In addition, many water-filled large craters remained after meteoritic impacts. Such closed hot spots could circulate and distill all the waters coming with springs, rains, and rivers, thus producing the required primordial soup [8,9].

However, a group of researchers reasonably argued that “no single environmental setting can offer enough chemical and physical diversity for life to originate. Instead, any plausible model for the origin of life must acknowledge the geological complexity and diversity of the Hadean Earth” [10]. These authors critically analyzed eight broad categories of possible environmental settings of the Hadean Earth (3.8–4.5 Ga) where organic compounds were likely to form. Rather important are the already mentioned hydrothermal vents, lightning in volcanic eruption clouds, pumice and volcanic ash particles in the atmosphere, etc. Each of the sources could have contributed one or more of the required components and/or reaction steps between them, together leading to life. “Global diversity and local scarcity of reactants and products were keys for prebiotic chemistry” [10]. From this point of view, life emerged as a result of the functioning of a global chemical reactor. Of course, the reactor that accomplishes the final self-assembly of all the numerous starting ingredients into any “protocell” must be accessible to the distribution streams functioning in the atmosphere and hydrosphere between the diverse array of production settings. Therefore, life more likely emerged in shell waters near ocean shores [11]. Contrary to isolated lakes and hot springs, oceanic waters could have contributed there to the primordial soup through regular tides and probably frequent tsunamis. Indeed, beaches would have allowed a huge variety of reactants to be concentrated and processed. “Furthermore, beaches have four characteristics advantageous for prebiotic organic synthesis: accumulation of heavy detrital minerals, evaporation-concentration cycles, a gradient in water activity, and high porosity” of the supporting bed [10].

Recently, Marshall pointed out the paradoxical role of water in the process of the creation of life. On the one hand, water is essential for all the processes of matter’s evolution to life, but, on the other hand, it breaks down proteins, nucleic acids, and other key molecules [12]. In this way, water promotes some kind of selection of more stable structures and clusters and the destruction of the more vulnerable ones at their links. Similarly, many basic chemicals of life require ultraviolet radiation from sunlight to form. They cannot be synthesized deep in the oceans, but only in their surface layers or after complete drying of the solution and forming a film on the surface of shore minerals. Adsorption and the presence of transition metal ions in minerals also exert a strong catalytic effect in both the synthesis and the destruction of compounds. Meanwhile, general support is growing for the idea that life started through numerous cycles of synthesis and destruction through hydrolysis and irradiation in wet–dry cycles in small bodies of water having at times a connection to the ocean. The primordial soup pool had to become highly concentrated or even dry out completely from time to time.

Finally, at the end of this section on the role of water in the evolution of matter into life, it is worth mentioning that other liquid media are existing on the surface of certain planets, such as very hot sulfuric acid on Venus or very cold methane–ammonia mixtures on Jupiter [2]. Though both media are able to dissolve special groups of organic compounds and permit them to interact with each other, no complex chemistry can be conceived to occur in such solutions.

3. Chemical Composition of Living Matter

Within less than 20 min after the mysterious Big Bang, the major mass of matter was established. It consisted of hydrogen, helium, and small amounts of lithium. Occasional fluctuations in the density of matter distribution in space resulted in the formation of galaxies and stars. In the fission reactors in stars, a series of elements—up to iron ^{56}Fe —were formed from ^1H , ^4He , and ^6Li . Specifically, the fission of three He nuclei resulted in the formation of carbon ^{12}C , that of four produced oxygen ^{16}O , and that of five produced neon ^{20}Ne . (In reality, the chain of nuclear transformations is much more complicated.) Heavier elements are believed to have formed in neutron stars and supernova blasts. At present times, about 100 elements can be found in the universe, with the amount of each rapidly dropping with their atomic numbers. Even now, the number of hydrogen atoms exceeds the number of other elements by a factor of many thousands to millions. The most abundant (stable isotopes of) elements are: H, He, O, C, N, Ne, Mg, Si, Fe, S, Ar, Ca, Ni, Zn, etc. [13–15]. The accumulation of a sufficient amount of the above set of elements necessarily required several billions of years, so life could not have emerged very soon after the Big Bang.

With the dominating role of hydrogen, elements tend to form chemical compounds precisely with this particular element. Thus, a major form of existence of oxygen is water, H_2O ; that of carbon is methane, CH_4 ; that of nitrogen is ammonia, NH_3 (and N_2); and that of sulfur is hydrogen sulfide, H_2S . Some elements have a high affinity to oxygen and form oxides such as SiO_2 , FeO , CO , and CaO . Finally, iron, nickel, and many heavier metals remain in their free state. No doubt, the initial nebula that gave birth to the Solar system some 4.5 billion years ago had a similar composition of basic elements and compounds.

Condensation of certain parts of the nebula into planets such as Venus, Earth, and Mars, and the following accretion of them is mostly due to solid matter, planetesimal, asteroidal, and smaller debris, dust, and gas particles. Indeed, Earth's outer veneer amounts to up to 20 km in thickness. Gaseous components such as noble gases, hydrogen, methane, nitrogen and ammonia, hydrogen sulfide, and even water were concentrated during the planet formation to a smaller extent. As our star Sun was lit up at that moment, an intensive burst of radiation and particle waves swept the light components out of the primary atmospheres of the above planets into the more distant area of the Solar system, where gaseous giants such as Jupiter and Sirius were formed. For these reasons, relative contents of such elements as H, C, O, S, N, and especially He, Ne, Ar, on Earth are smaller than generally in the universe.

The initial differentiation of the melted earth's mass resulted in the formation of basically metallic Fe–Ni kern, metal-silicate and metal-oxide-containing mantel, while the Earth's crust and hydro- and atmospheres accumulated major amounts of compounds composed of the above “organogenic” elements H, C, O, S, N, P. We expect other planets in the habitable zones around their stars to follow similar steps of formation. For the emergence of living matter, the above light and reactive elements are essential, of which carbon is the most important one. Its outstanding property is the ability to form long linear or cyclic chains that can include any of the above heteroatoms and bear versatile substituents in many positions. Many of the compounds thus formed are water-soluble and can react with each other in solutions or in a dry state. We can suppose that the emergence of life is only possible on planets with plenty of water and a rich carbon-based world. We can note here that another element capable of forming chains and incorporating some heteroatoms is silica, but no living matter could emerge in a silicon world, since such compounds are not water-compatible, and no rich silicon chemistry is possible in any non-polar solvent.

Interestingly, modern organisms, with extremely sophisticated metabolism cycles, make use of a whole series of metalloenzymes and cofactors containing many metal ions such as Cd, Ca, Co, Cu, Fe, Fe-S, Mn, Mg, Mo, Ni, Zn, K, Se, and W. Obviously, some transition metal ions also contributed to the formation of the first living systems by catalyzing numerous organic reactions.

At some stage of accretion, the melted mass of planet's matter was sterile and entirely "mineral". Initially, Earth's hot and heavy atmosphere was mainly composed of hydrogen, water, methane, nitrogen, carbon monoxide, and some smaller amounts of NH_3 and H_2S . Their nature was clearly reducing. The heavy bombardment with meteorites only increased its reduced character. "There is enough iron in the late veneer to reduce 1.8×10^{23} moles of H_2O to H_2 and FeO , which corresponds to reducing of 2.3 oceans of water to hydrogen" [16]. Organic compounds thus had to be synthesized anew on our Earth, which was favored by the established reducing conditions on the planet. (Of course, some additional organics was also delivered by chondritic meteorites.)

4. Prebiotic Organic Chemistry on Earth

Self-assembling of any protocell required the availability of a vast variety of starting organic compounds. In the literature, hundreds of experiments have been described dealing with the formation of more or less complicated organic structures from what was available in the early Earth's atmosphere, namely H_2 , H_2O , CH_4 , NH_3 , CO , H_2S , HCN , and H_2CO . Surprisingly, many alpha-amino acids were found to form rather easily just on the action of electric spark discharge on gaseous mixtures of H_2 , CO , N_2 , H_2O , CH_4 , and NH_3 , which could imitate the early planet's atmosphere [17–19]. Similar synthetic results are caused by the action of other physical fields such as heat, radioactivity, cold plasma, UV light, pressure shock, etc. [20–23]. Surprisingly, simple amino acids are formed even at extremely low temperatures on collisions of icy bodies containing deeply frozen mixtures of methanol, NH_4OH , and CO_2 [24,25]. On the contrary, Managadze observed the formation of simple amino acids, in addition to many other unidentified compounds, in a hot plasma torch, which results from super-high-velocity collisions of solid bodies [26,27]. Matter exists within plasma in a totally atomized and ionized form, but dissipation and cooling of plasma creates many opportunities for recombination and condensation processes. In all the above events, a wide array of other compounds simultaneously form, amines, amino alcohols, hydroxy acids, aliphatic acids, etc. [28,29]. A rather endemic amino acid, tryptophan, was unexpectedly found in a hydrothermal vent on the ocean floor, called a black-smoker chimney [30]. The vent emitted acidic fluids with high concentrations of gases and metal ions in a chemically reduced form. Additionally, indol was detected, but, surprisingly, no simpler amino acids. Additionally unexpected was the ease of formation of pyruvate, formate, acetate, and methanol from CO_2 and H_2 in mineral-rich environments of a hydrothermal vent [31,32].

Sutherland's group intensively investigated reactions occurring in concentrated solutions of phosphate, some simple organic compounds, and cyanamide under wet-dry cycles and UV irradiation. (Pumice and volcanic ash can serve as a source of phosphorus, one of the important elements required for life.) As early as 2009, the authors reported the formation of two of the four nucleotides that comprise RNA [33]. They then have shown that the same starter chemicals, if treated differently, can also produce precursors to proteins and lipids [34]. They also identified methyl isocyanide as a selective phosphate activating agent, which drives the conversion of nucleoside monophosphates to phosphorimidazolides under potentially prebiotic conditions. Importantly, the isocyanide is further released upon irradiation, thus allowing for repeated reactivation cycles and non-enzymatic oligomerization processes [35]. More recently, diamidophosphate and imidazole were found to promote the formation of longer RNA chains from canonical ribonucleoside 3'-monophosphates under conditions of freezing aqueous solutions. Similar non-enzymatic condensation processes are thought to have been possible at some locations of the early Earth [36].

While noting that formamide, HCONH_2 , can easily form in the atmosphere both from the interaction of water with hydrogen cyanide $\text{H}_2\text{O} + \text{HCN}$ and from a combination of carbon monoxide and ammonia $\text{CO} + \text{NH}_3$, Saladino et al. [37] showed in their extensive review many chemically viable routes of condensation reactions of formamide (which remains liquid between 4 and 210 °C and can be concentrated on evaporation of aqueous

solutions). On the surface of different minerals (zeolite, calcium carbonate, alumina, titanium oxides, clays, olivines, phosphates, iron-sulfur-copper minerals, zirconium minerals, and borates), the condensation of formamide proceeds in different directions, leading to all possible nucleic bases. According to the authors, it is also plausible to assume the further syntheses of nucleosides and nucleoside phosphorylation as well as more complicated phosphodiester-promoted ligation and abiotic RNA chain extension to finally form RNA in prebiotic conditions [38,39]. The same group also reports the formation of various aliphatic acids and hydroxy acids by heating formamide in the presence of catalytically active zirconium minerals and borate minerals [40]. The authors consider formamide HCONH_2 as an ideal chemical precursor that is widely distributed in the universe and contains all the universal atomic components of living matter H, C, N, and O. “The prebiotic chemistry of formamide affords in a single and simple physical–chemical frame nucleic bases, acyclonucleosides, nucleotides, biogenic carboxylic acids, sugars, amino sugars, amino acids and condensing agents” [40]. Under similar conditions, formic acid and probably higher organic acids are easily formed from formaldehyde H_2CO , one of the oxidation products of methane. The acids facilitate the nucleation of cloud droplets and contribute to the acidity of clouds and rainwater [41].

Many other examples can be found in the literature claiming the formation of basic elements of living matter, amino acids, carboxylic acids, and nucleotides from the simplest possible molecules. However, no collection of these small molecules could form any living protocell. Only polymeric molecules could acquire a self-replication ability and construct any framework for structuring cell plasma. We must accept that the polymeric form is compulsory for living matter. While RNA is most useful for storing information and polysaccharides—for supporting a cell matrix, proteins are essential for both construction and chemical metabolism within the cell. Depending on the composition of the polypeptide and protein molecules and the sequence of comprising amino acids (primary structure) proteins can form alpha-helix, two-dimensional sheets, or coils and globules (secondary structure). Unfortunately, we only can speculate about how the increasingly complex macromolecules were produced in wet–dry (ebb–tide) cycles of concentrated mixtures of starting compounds under the action of heat, irradiation, and mineral catalysts.

Possible roots for the non-enzymatic nucleotide self-condensation and template-directed synthesis of RNA were extensively treated in reviews by Monnard [42] and a Danish group [43]. There are many possible methods of condensation, but, in the end, authors had to confess that “our knowledge of self-condensation and template-directed condensation remains sketchy at best”.

Facilitated by some clay-catalyzed condensation processes, Oparin supposed rather early [7] the emergence of polypeptides and protein-type self-replicating systems by condensation reactions in a warm primordial soup rich in amino acids. Indeed, saturated aqueous solutions of NaCl or KCl are reported to facilitate the condensation of two amino acids to a dipeptide with the elimination of a water molecule already at 60–80 °C [44]. A French group of researchers investigated repeated cycles of reacting nitrogen oxides with a mixture of amino acids (Gly, Ala, Val, and Glu) that resulted in the preliminary formation of N-carboxyanhydrides and the final formation of up to tetrapeptides. Production of NO could be assured by lightning in volcanic plumes from N_2 and CO_2 (more probably, H_2O). Remarkably, strong selectivity was recorded with respect to the amino acid sequence in the final peptides [45]. “With continuous amino-acid input, further cycles would therefore lead to progressive accumulation, elongation, and complexification of the peptides.” N-Carboxyanhydrides of amino acids were also found to be involved in the acylation of amino acids with aliphatic acids. Products of the acylation acquire properties of surfactants and form micelles in aqueous solutions. The latter easily cooperate with proteins and RNA to form something resembling protocell membranes [46,47].

In addition to the dominating Oparin’s “protein world” suggested above, alternative “polynucleotide world” [42,48,49] and even “polysaccharide world” [50] and “lipid world” [11,51] have been considered. Much attention has been paid to the idea of the

simultaneous growth of polynucleotide and polypeptide chains in the form of simple “progenes” [52].

While the above life-related compounds and aggregates incorporating amino acids, nucleotides, carbohydrates, and lipids can be considered as rather universal initial building blocks for composing living matter, the roots of their self-assembly into micelles, vesicles, protocells, and “protoliving systems” are so numerous and diverse that the emergence of final “ancestral organisms” on Earth might be regarded as a matter of chance. Reviewing the wealth of papers that emerged in this crucial area of research and speculations is beyond the scope of this paper. We could only note that the roots of the tree of life and the evolution of biochemical entities from “less-than-living” to “more-than-nonliving” have also been treated from the general philosophical perspective [53]. More recently, historical and philosophical issues in the study of the origins of life were discussed at full length by Mariscal’s [54]. Additionally, it is worth mentioning the original “gyre-theory” applicable for all matter categories from energy quanta and subatomic particles to living matter, developed by Andrulis [55]. The author claimed to “have compiled and unveiled an axiomatic, experimentally testable, empirically consistent, heuristic, and unified theory of life”. Remarkably, “this theory not only predicts but also proves that the Universe is teeming with life—a result of omnidirectional universal evolution.”

In spite of the great progress in understanding the obvious productivity of the global chemical reactor [10] that produced millions of organic compounds and accumulated them in a “Darwin’s warm little pond soup” [56], we still fail “to answer two simple questions: (1) What is the minimum number of parts that are essential for a living organism to survive? (2) By what mechanism do these parts get assembled together?” [57]. In view of this fact, Shanta states “Sorry, Darwin: Chemistry never made the transition to Biology”, since sentience, “purpose and meaning are inseparable aspects of life. We cannot expect those in dead molecules” [57]. In the end, we cannot exclude the situation that somewhere a peptide-oligonucleotide molecular system accidentally emerged, one part of which served as a catalyst and the other as a template [58]. In this way, life may have originated only once and then evolved into the myriad forms we now know today [9]. On the other hand, modern molecular biology and genome study [59], too, fail to contribute decisively to bridging the opposite side of the huge gap “between the origins of life per se and the simplest and most primitive life forms we currently know of.” Thus, “being already an extremely sophisticated mechanism of some 250–300 genes, such a minimal genome would not (yet) be the backbone of some of the earliest forms of life” [60].

5. Origins of Biological Homochirality

Surprisingly, only very few papers dealing with “prebiotic organic chemistry on Earth” mention the problem of the obligatory homochirality of amino acids and carbohydrates, which could prove suitable for constructing the first self-reproducing organic system. Good exceptions are the review papers [56,61] and, especially, the recent very informative monograph by Nikitin [44]. In fact, achieving the required homochirality of biomolecules presents the most problematic step of the evolution to life.

The estimated age of our planet Earth is 4.54 billion years. Traces of water withering on some rocks 4.3 billion years old imply the existence of condensed waters, i.e., oceans, above the solid surface of the planet. In some zircon crystals that are 4.1 billion years old, carbon-rich inclusions have been discovered, which allows us to suspect the existence of primitive living cells at that early time. Though the origin of these carbon inclusions has been questioned [62], scientists generally agree that it did not take long, just a few hundred million years, for life to emerge on the young Earth. In any case, “it is amazing to realize how fast complex biological structures arose in the early time of earth” [63]. Indeed, it is difficult to conceive the emergence of a molecule capable of replicating itself by random chemical reactions in the pool of primordial soup of millions of organic molecules. The molecule must have been rather long and complex in its composition and shape. According to Rouch [63], in an RNA world, “the first genome was limited to a size of about 200

base pairs". Bernhardt [64] writes: "the best ribozyme replicase created so far ... is ~190 nucleotides in length, far too long a sequence to have arisen through any conceivable process of random assembly".

For a protein world, Davankov [65,66] tried to estimate the probability of an accidental emergence of a peptide composed of 100 amino acid units. There exist many dozens of alpha-amino acids. Though only four primitive amino acids, namely glycine, alanine, aspartate, and serine, are supposed to initially dominate [63], nature finally used twenty items to form the construction proteins and catalytically active enzymes. With the exception of glycine, all of them incorporate an asymmetric alpha-carbon atom and exist in enantiomeric L- and D-forms. Let us suppose that the first self-reproducing molecule presented a peptide of 100 units selected from 20 natural AAs. Theoretically, there are 20^{100} variants of such a peptide possible. If we assume that 95 (other than glycine) units of the chain are chiral, the above number of variants must be multiplied with an additional huge factor of 2^{95} . Only one of the enormous series of peptides could possess catalytic abilities. It is clear that the probability of an accidental emergence of such a peptide is zero. There must exist several general factors favoring the formation of that single proper peptide (or nucleotide) that started life.

First of all, in order to eliminate or at least radically reduce the above factor 2^{95} , all amino acids should predominantly belong to one and the same configurational series. In other words, the pool of initial organic molecules must be homochiral; i.e., all amino acids must (predominantly) belong to the L-enantiomeric series and carbohydrates to the D-series. (Note that chemical synthesis of chiral species from achiral starting molecules always produces equal amounts of L- and D-enantiomers.) Chandrasekhar [67] reasonably notes: "It is indeed sobering—if not depressing—to consider the fact that, to the extent that a firm answer to the question on the origin of molecular chirality does not emerge, the origin of life will remain a mystery."

As early as the end of 1960th, seminal works of Gil-Av [68] and Davankov [69] have introduced long-awaited techniques for separating enantiomers and analyzing enantiomeric composition of organic compounds by means of gas and liquid chromatography, respectively. Chiral chromatography paved the way for numerous stereochemical studies. Since those times, hundreds of papers have appeared dealing with the problem of generating some spontaneous or induced chirality of amino acids by so-called "chance mechanisms". They basically include spontaneous resolution of enantiomers by sublimation or crystallization (with or without Viedma ripening), asymmetric autocatalysis, and enantioselective adsorption on chiral quartz crystals. Some of these processes, indeed, generate a rather high enantiomeric enrichment of individual compounds in the experiments, but such processes are unthinkable in a complex matrix of the primordial soup. Moreover, they proceed in small locations and produce enrichment of enantiomers of an undetermined sign. None of these chance processes could ever result in a *global* predominance of L-enantiomers for the whole class of alpha-amino acids and D-isomers for sugars. (For these reasons, in spite of the abundance of the literature dealing with the chirality multiplication processes, we do not consider them in the present review.) Therefore, we are left with theories of induced extraterrestrial homochirality of initial organic matter.

Indeed, it is now a well-established fact that meteorites bring to our Earth numerous organic compounds in the form of non-racemic mixtures of enantiomers. As summarized in the review by d'Hendecourt and Meierhenrich's group [70], extensive studies of the Murchison and Murray meteorites "revealed the presence of a series of alkyl-substituted bicyclic and tricyclic aromatic compounds, aliphatic compounds ranging from C1 to C7, including both saturated and unsaturated hydrocarbons, more than 80 amino acids, including diamino acids, N-alkylated amino acids and iminodiacids, small amounts of aldehydes and ketones up to C5, a wide spectrum of carboxylic acids and hydroxycarboxylic acids, several nucleobases, and sugar acids". It is noteworthy that all amino acids were enriched in isomers of the same L-series [70]. Enantiomeric analysis of α -substituted amino acids revealed especially high enantiomeric excess values: up to 60% for D-alloisoleucine [71]

and 18% for L-isovaline [72]. On the contrary, the groups of aliphatic amines and carboxylic acids were found to be racemic with the exception of α -hydroxypropionic (lactic) acid [71].

The often-considered physical chiral natural factor that could operate in a space at least as large as our Solar system and thus cause enantiomeric imbalance in the organics of meteorites is circularly polarized irradiation. The latter was shown to predominantly destroy one of the two enantiomers of racemic amino acids such that the last traces of the product achieve some optical activity (of no more than a few percent) [73]. As summarized in detailed reviews by Barron et al. [74] and Davankov [66,75], similar small effects of deracemization of synthetic amino acids were also observed on the action of spin-polarized electrons emitted by the β -decay of radioactive nucleons, of polarized beams of electrons, as well as due to the influence of a strong magnetic field (e.g., of a nascent neutron star from a core-collapsed supernova). Importantly, the supernova-derived neutrino irradiation is also expected to result in a small chiral imbalance of the same sign of chirality for all different amino acids [76]. In recent reviews from Meierheinrich's group [77,78], a crass contradiction becomes evident between the very insignificant enantiomeric enrichment caused by "chirality transfer from chiral photons to amino acids involving the two major processes of asymmetric photolysis and asymmetric synthesis", on the one hand, and the extremely high optical activity of biomolecules found in chondritic meteorites. Thus, intensive irradiation of ice grains incorporating some achiral organics resulted in the formation of 16 distinct amino acids, five of which were found to be chiral— α -alanine, 2,3-diaminopropionic acid, 2-aminobutyric acid, valine, and norvaline—with values ranging from $ee\ L = -0.20\% \pm 0.14\%$ to $ee\ L = -2.54\% \pm 0.28\%$ [79]. The sign of the induced chirality depended on the helicity and the wavelength of circularly polarized light. The ee values achieved by cosmic chiral fields and radiation are much smaller than those found for amino acids buried in the bodies of meteorites—up to the above-mentioned ee 60% for D-alloisoleucine. Another problem with the cosmic factors displaying a noticeable degree of chiral polarization and a proper energy is that they are thought to emerge only on rare occasions. All the other times, the constant hard unpolarized irradiation would gradually diminish the small induced chiral imbalance of organic molecules if not totally destroy the latter.

A fundamentally new conception of a direct absolute enantioselective synthesis of organic molecules was recently suggested by Davankov [66,75]. It is based on his statement that all fundamental particles of our matter are chiral (asymmetric) and each of them may have an enantiomeric counterpart, which is the antiparticle [66,80]. The two partners differ from each other not only in the sign of their electric charge but in all other characteristics as lepton charges, spins, and other properties reflecting, in one way or another, their spatial orientation. Whereas primary particles compose all the atoms of our matter, the antiparticles compose the antimatter. Theorists suppose that some 13.8 billion years ago, the Big Bang gave birth to equal amounts of barions, antibarions, and high-energy photons. The first two types of particles are annihilated, i.e., converted into energy quanta or photons. Sakharov [81] was the first to suggest that the number of barions happened to be slightly greater, such that after annihilation all antibarions vanished while a small part of the initial barions survived and presents nowadays the matter that forms the Universe. We know now that the number of photons exceeds the number of barions by a factor of 10^6 , and we do not see any antimatter. (In fact, the modern theory does not exclude the existence of antimatter galaxies in some remote parts of the Universe. By observing just their electromagnetic irradiation, we are not in a position to distinguish them from normal galaxies).

The idea of an inherent asymmetry of all primary particles of our matter goes back to the discovery of parity violation on the beta decay of radioactive nucleus, which is caused by a chirality of weak nuclear currents [82,83]. A series of arguments in favor of the chirality of subatomic particles, in particular barions (as protons and neutrons), leptons (e.g., electrons), and bosons (as individual photons), can be found in Davankov's original papers [66,80]. Notably, the author states that, contrary to the above-mentioned homochirality of elementary particles, namely barions and leptons, each individual photon

and each energy quantum are asymmetric but can exist in both left-rotating and right-rotating forms. Indeed, more recently, using accelerator-produced neutrino beams [84], asymmetry and parity violation was experimentally observed in the sector of leptons (electrons, muons), namely by comparing probabilities of muon neutrinos with electron neutrino oscillations and the corresponding antineutrino oscillations. Actually, these parity violations in leptons could be also considered as the cause of the matter–antimatter disparity through a process called leptogenesis.

The transmission of the inherent complete homochirality of all primary particles to the spatial structure of species belonging to higher hierarchies of matter complexity does not need to be perfect. Thus, atoms being composed of protons, neutrons, and electrons are known to be chiral, which was proven by the experimental measuring optical activity of hot vapors of heavy elements such as lead, bismuth, and thallium [85]. Molecules, being composed of chiral atoms, manage to inherit homochirality of weak nuclear currents in each atom's nucleus to only a tiny degree. Thus, the excess of L-amino acids over their enantiomeric counterparts due to the effect of parity violation is too small to be measured experimentally. According to theoretical calculations by Tranter [86] and Quack [87], our terrestrial L-alanine is expected to be more stable than D-alanine by about 10^{-14} to 10^{-11} J/mol. Our terrestrial racemic D,L-alanine must thus be enriched by the L-component with an enantiomeric excess *ee* of 10^{-6} to $10^{-5}\%$. Similarly, D-glyceraldehyde and all derived D-monosaccharides are supposed to be more stable than the corresponding L-isomers by the same tiny extent [88]. These initial energy imbalance values are really too small to cause homochirality of the starting molecular pool for creating living matter. Even the most powerful mechanism of chirality amplification acting in the unique asymmetric autocatalytic Soai reaction would not result in the preferential formation of desired enantiomers [89]. Thus, parity violations of nuclear weak forces, when acting on the molecular hierarchy level of matter, cannot account for one chirality to be favored over the other in prebiotic reactions of organic molecules.

Nevertheless, Davankov supposed that the immediate self-assembling of asymmetric organic molecules from homochiral elementary particles and atoms could result in greater values of enantiomeric imbalance of biologically related molecules, as compared to the formation of the same molecules from achiral or racemic molecular precursors. This type of direct synthesis of organic molecules was shown to proceed from super-high-velocity impacts of meteorites on heavier cosmic bodies. At an impact velocity over 5 km/s, both the projectile and some parts of the target convert into a plasma torch composed of totally atomized and ionized species. Dissipation and cooling down of the plasma brings about a series of synthesis and recombination reactions. Model experiments by Managadze showed the formation of hundreds of various compounds in the condensation products of such plasma torch, among them amino acids [90].

To prove or disprove the asymmetry of the absolute synthesis of amino acids suggested above, a large international group of researchers [91] started with carbon black composed of pure stable ^{13}C isotope. Under high pressure and high temperature, it was converted into diamond crystals of about 1.5–2.0 mm in diameter. The latter were used as projectiles in a gas gun against a target pellet composed of ammonium nitrate NH_4NO_3 . The pellet was positioned on a massive natural carbon ^{12}C graphite plate. Being accelerated to the velocity of about 5 km/s, the diamond crystals generate an impact energy that results in complete atomization and ionization of both the target pellet and diamond bullets, as well as a certain part of the graphite support. The emerging plasma torch contains all the elements— ^{13}C , H, N, O—that could produce amino acids upon dissipation and cooling of the plasma matter. Indeed, from the solid precipitate on the container walls, fractions could be extracted that contained a wide variety of organic compounds, among them glycine and alanine, the simplest amino acids. Mass-spectrometric analysis revealed a high content of non-natural ^{13}C isotope in amino acid molecules, thus proving the plasma reactor as their synthetic source. Most importantly, a careful enantiomeric analysis of alanine (after its conversion into a volatile derivative and gas-chromatography on a chiral stationary

phase) showed a significant isomeric imbalance of the product. Very cautious calculations of chromatographic and mass-spectrometric data proved that L-alanine dominated over the D-isomer with an “enantiomeric excess values between 7 and 25%, which is similar to *ee* values found in meteorites and outperforms by far the values expected for all deracemization effects under the action of cosmic polarized irradiations” [91].

The collision of cosmic bodies with super high velocities is, moreover, one of the common mechanisms of formation and accretion of planets. The above experiment proves that the impacts may generate plenty of organic compounds with the stereochemistry directly induced by the invariant chirality of the weak force, one of the four fundamental forces that govern the behavior of elementary particles and atoms. This initial enrichment of the prebiotic organic matter with enantiomers of self-consistent configurations must have contributed radically to the formation of the first homochiral polymeric structures prone to self-reproduction.

Another fundamental conclusion that can be derived from the above experiments is that the same mechanism of generation of homochirality of the starting organic matter must operate everywhere in the Universe, so life in any other world must also exploit L-amino acids and D-carbohydrates, though not necessarily in the same combinations as on our Earth.

Still, we must admit that the hypothesis discussed above on the emergence of the starting self-consistent homochirality of organic compounds by their direct asymmetric synthesis from homochiral elementary particles does not cover the following enhancement and further preservation of the optical purity of biomolecules at the required nearly 100%. The issue on homochirality, just like that on the assembly of the first protocell, thus remains the most problematic step in understanding the origin of life.

6. Life and Oxygen in the Atmosphere

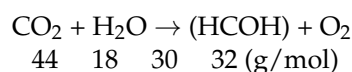
Since the discovery of the photosynthesis reaction some 120 years ago, the mystery of the origin of oxygen in our Earth’s atmosphere seems to be solved. In fact, free oxygen was not detected in the atmospheres of any other planet. Nor was it found in its free state among the components of the interstellar gas in our galaxy (almost 90% hydrogen and 10% helium with only traces of other heavier atoms). Oxygen is extremely reactive and exists almost entirely in the form of chemical compounds. With hydrogen dominating in the matter of our Universe, the major form of existence of oxygen is water, the most abundant compound. Other oxides, especially those of silicon, iron, and other metals, are rather stable and less abundant, so if free oxygen emerges somewhere in measurable amounts, its source must be water and only water. Moreover, oxygen cannot accumulate unless all other elements and compounds in this particular domain of space are oxidized to higher degrees, which would guarantee their tolerance to free oxygen under given environmental conditions.

When applied to the Earth’s situation, the above consideration means that oxygen did not participate in the formation of the primary atmosphere and could not emerge there until the complete elimination of reductive atmospheric gases such as H_2 , CH_4 , H_2S , NH_3 , CO , and HCN and almost complete oxidation of ocean-dissolved ions such as S^{2-} and Fe^{2+} , as well as oxidation of atmosphere-accessible minerals in the upper parts of continents. Indeed, the first signs of free oxygen appeared in the atmosphere somewhere about 2.3 billion years ago, in the middle of Earth’s age [92]. Nevertheless, long before this Great Oxidation Event on Earth, intensive oxidation processes took place. Indeed, the formation of Banded Iron Formations (or BIF) in the oceans started more than 3 Gyrs ago [93–95]. These dark brown layered sediments present alternating silica-rich bands and water-insoluble iron(III) oxides, magnetite (Fe_3O_4), and hematite (Fe_2O_3). They are formed by the oxidation of large amounts of iron(II) salts accumulated in the oceans. However, there was no oxygen in the atmosphere and no oxygen-generating cyanobacteria in the illuminated layers of oceans at that time.

The first signs of life emerged on Earth much earlier—already in Archean—approximately 3.8–4.0 Gyrs ago [96], and, in principle, the above oxidation processes in the oceans could be accounted for by the action of the first purple bacteria. They lived near oceanic hydrothermal vents and exploited infrared photons as an additional source of energy [97,98] in order to reduce CO₂ to cell materials and oxidize soluble Fe(II) salts to precipitates of Fe(III) oxides. The photosynthesis mechanism of these cells is anoxygenic, which means that they transfer two H atoms of a water molecule to CO₂ and convert the latter to organic matter, e.g., -HC(OH)-; simultaneously, they direct the excess O₂ for oxidation of Fe²⁺ or S²⁻ instead of releasing oxygen to the environment. Therefore, the Precambrian BIFs may be, at least partially, of an anoxygenic origin [99]. An alternative path of an abiogenic and anoxygenic BIF formation is extensively discussed in a series of works by Marie-Paule Bassez [100,101]. The author showed that the alkaline supercritical state waters near oceanic hydrothermal vents easily oxidize Fe(II)Mg-silicates and Fe(II)-sulfides to Fe(III)-minerals. In this process, H₂ molecules are released, as well as under radioactive irradiation. They can be partially consumed by purple bacteria or even trigger the formation of biomolecules such as glycine and other amino acids and peptides, provided that the anoxic waters contain dissolved CO, CO₂, CH₄, and N₂.

Importantly, cyanobacteria, which developed an oxygenic photosynthesis mechanism, were beginning to dominate Earth's oceans only 2.7 Gyrs ago, almost one billion years later than the supposed date of the emergence of life [102]. They indeed generated free oxygen, which started to appear in the atmosphere some 400 million years later. Plants appeared on the continents rather late, only some 600 Myr ago, since they needed the ozone layer to be formed in the atmosphere to protect life from the hard UV irradiation.

How much oxygen managed to produce the green algae and continental forests since that moment? The current atmosphere of Earth generates, on the sea level, a pressure of 1 kg cm⁻². This implies that each square meter of the surface bears 10 tons of air, including 2.3 tons of oxygen! According to the stoichiometry of the photosynthesis reaction:



production of the above amount of oxygen is unavoidably combined with the accumulation of equal amounts of organic matter. The two tons of dry biomatter are equivalent to one 100-year-old oak tree on each square meter of the surface, including oceans and glacier regions. (Interesting information on the biomass distribution on Earth can be found in [103].) Considering the present and estimated spent amounts of biomatter and oxygen, Davankov [104,105] questioned for the first time the generally accepted belief that photosynthesis in green cells is the only source of Earth's oxygen. Unfortunately, any correct correlation of the total amounts of organic matter and oxygen is impossible. Indeed, at least 95% of oxygen generated on Earth has been irreversibly spent [49] long ago for the oxidation of the initially reductive primordial atmosphere (H₂, CH₄, NH₃, H₂S, etc.) and conversion of ions such as Fe²⁺ or S²⁻ into oxygen-compatible compounds. On the other hand, a major part of the organic matter is dispersed in huge amounts of sediments. Still, Davankov assumes that the above balance is distorted in favor of the present and consumed oxygen, and therefore, there must be another source operating, in addition to photosynthesis, that generates substantial amounts of oxygen.

Current achievements in planetary science and physical chemistry unambiguously point to the photolysis of water molecules as the constant and powerful source of oxygen. Indeed, water molecules are lighter than other components of the atmosphere: molecular weights of H₂O, N₂, and CO₂ are 18, 28, and 44 Da, respectively, so water must always be presented in the upper layers of the atmosphere. Being exposed there to UV irradiation and bombardment by solar wind, water easily decays into hydrogen and oxygen. The former preferably dissipates into space, whereas oxygen atoms, which are 16 times heavier, largely are retained by the Earth due to its gravity. The intensity of the photolysis reaction varies with the solar activity, but altogether, water photolysis results in dramatic losses

of water and oxidation of all sensitive components of the atmosphere, hydrosphere, and surface layers of the lithosphere, before oxygen accumulated in its free state in the air in the amounts of 2.3 tons per m² stated above.

Recent estimations of water losses that correspond to the retained oxygen are impressive: 1.4 Earth's oceans [106] and even 8.5 Earth's oceans [107]. At first sight, these values seem to be overestimated, but we know for certain that there used to be much more water on our planet, which accounts for the abundance of ocean's sediments covering most parts of today's continents. We also must remember that the above-mentioned reactions of metallic (e.g., iron) meteorites with water as well as the anoxygenic photosynthesis of biomass during the first half of Earth's existence proceeded without the direct participation of free oxygen but with consumption of large amounts of water.

The ideas of water photolysis developed in [105,108], when applied to the situation of our neighboring planets Venus and Mars, logically explain both the practically complete loss of their initially acquired water and the drastic difference in the mass and composition of their atmospheres. Specialists in astrophysics have already accepted our photolysis hypothesis in their recent studies and publications [109].

7. Concluding Remarks

When considering life on our Earth as a logical result of a long and complicated evolution process of the matter accumulated by the planet, rather than a unique divine phenomenon in the Universe, it is advisable to try formulating basic regularities of the evolution and incidents on its pathway, according to our current knowledge and imagination. Let us present these ideas in a short summary.

- Because of the invariant chirality of weak interactions, all primary particles compose a homochiral pool of building elements for the construction of atoms and molecules. In contrast, all leptons (photons and muons) exist as a racemic form of energy quanta.
- Plasma reactors resulting from the super-high-velocity collisions of cosmic bodies generate mixtures of organic compounds, whose amount and composition are determined by the occasional content of the plasma torch-involved material.
- All organic compounds synthesized in a plasma torch acquire preferred configurations that correspond to the invariant chirality of fundamental weak interactions; the forms dominating everywhere are L-amino acids and D-carbohydrates.
- The mechanisms further enhancing the extent of homochirality in the complex mixture of organic compounds remain unclear.
- The presence of large amounts of water in its liquid state on any planet is the essential prerequisite for life to emerge, since water is the only unique natural solvent compatible with both polar organic compounds and mineral electrolytes.
- Any living matter must be based on the abundant light elements C, H, O, N, S, and P, for the reason that they are able to interact with each other and form chains; many other elements are also needed, though in small numbers.
- Life most likely emerged in a small aqueous pool that received, from time to time, additional portions of the globally produced from and distributed in the ocean; the pool frequently evaporated, which resulted in concentrating the primordial soup and enhancing contacts of the compounds with solid minerals.
- The organic compounds most useful and available in numerous variants are alpha-amino acids, nucleic bases, carbohydrates, and, carbonic acids, since they are prone to form polymeric chains or large associates. The selection of particular compounds and polymers for composing the first self-reproducing scaffolded protocell is a matter of pure chance and remains a complete black box of early evolution.
- Water vapors are constantly subjected to photolysis by cosmic irradiation, followed by hydrogen escaping to space and oxygen largely retained within the planet; under certain conditions, oxygen may form, an oxygenating the atmosphere, but this is not a clear indication of the existence of living organisms on the planet.

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