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The origin of homochirality in nature: a possible version

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The proper axial rotation and right-handed helical orbital rotation of Earth are the simplest and persistent factors of chiral influence on the Earth. These types of motion are treated as basic to the selection of L-amino acids and D-sugars (homochirality) as 'building blocks' for constructing right-handed helical biomacromolecules. The role of agent for transfer of chiral influence of the factors mentioned above on the molecular level can be played by tides and wind waves. The rise and fall of the waves leads to formation of mainly right-handed helical water associates that favour the formation of right-handed helical biomolecules. Biological indications of the existence of such water associates are discussed.
The bibliography includes 175 references.

Contents

I. Introduction 121
II. Abiogenic reactions on the Earth, resulting in racemic mixtures of amino acids and sugars 122
III. Physicochemical factors of asymmetric influence 122
IV. Physical factors of asymmetric influence 123
V. Homochirality and helicity of key biomacromolecules 126
VI. Water as agent for transfer of asymmetric information 128

I. Introduction

Homochirality,† or configurational homogeneity, manifests itself in that living organisms are built of L-amino acids and D-monosaccharides only. There are numerous hypotheses of the choice of L-amino acids, D-nucleotides and D-monosaccharides for biological reactions,[1–18] but all of them still have no commonly accepted explanation. Prelog[19] even believed that the phenomenon provides a basis for molecular theology. Chandrasekhar[20] noted 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'. Besides, Carroll[21] suggested that the origin of homochirality and the origin of life were the same event.

There are three different routes to the explanation of the origin of homochirality.[22] One of them follows Pasteur[23] and involves attempts to relate prebiotic homochirality to the asymmetric influence of a certain physical agent. The second route to the explanation of the appearance of prebiotic asymmetry is based on the following arguments. Equal proportions of the right and left enantiomers represent statistically averaged values, whereas instantaneous values may significantly deviate from the average values in, *e.g.*, the Soai reaction (see reviews[1,3]) or during crystallization.[24,25] As a result, an accidentally emerged enantiomeric imbalance in a small system that gave birth to life on the Earth will automatically spread obeying the laws of catalysis. The authors supporting the third route propose to treat the germ of life as not a unique event and to consider 'D-life' and 'L-life' in the areas with predominant concentrations of D- or L-amino acids, respectively. Competitive fighting led to complete disappearance of 'D-life'. This homochirality and life scenario was, in particular, proposed by Goldanskii and co-workers.[26–28] In this case, the onset of homochirality follows the advent of life, which casts some doubt. Also, domination of one of the two physically and chemically identical 'chemical machines'‡ based on L- and D-amino acids§ can be interpreted as a result of a stochastic process. Therefore, the third version of homochirality scenario is unlikely. Even less probable is simultaneous utilization of both enantiomeric forms of amino acids in the initial steps of evolution. Indeed, experiments showed that amino acid chains containing both L- and D-amino

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† Other names used in scientific literature: biochirality, biomolecular chirality, biomolecular homochirality, biological homochirality and biomolecular asymmetry.
‡ The definition of life according to Volkenstein.[29,30]
§ There is an opinion of minor distinctions between L- and D-amino acids and their polymers.[10]

acids cannot form a regular *P*-helix (α-helix), which is of great importance for catalytic functions of proteins. With no homochirality, the catalytic activity of a protein will be much lower. It is hard to imagine how complex living structures could develop in these conditions. Similar considerations are also applicable to nucleic acids.[12,18] Thus, homochirality and α-helicity of the key molecules had to precede the origin of life.

This review is devoted to the hypothesis of the onset of homochirality and helicity of key biomolecules under the influence of asymmetric physical factors that acted on the Earth since its formation as planet. According to this hypothesis, the onset of homochirality and the origin of life are not accidental.

II. Abiogenic reactions on the Earth, resulting in racemic mixtures of amino acids and sugars

Reactions resulting in key biomolecules on the primeval Earth have long attracted the attention of researchers (see recent reviews[31–34]). In 1955, Miller and co-workers[35–38] reported the presence of α- and β-amino acids and organic acids in gaseous mixtures containing H_2, CO, CH_4, N_2 and NH_3 exposed to electric discharge and UV irradiation.¶ Similar experiments led to the discovery of racemic amino acids, polypeptide-like and polysaccharide-like molecules in cold plasma,[41] upon electric discharge and on exposure to radioactive radiation,[42] as well as on heat treatment.[43,44] The formation of amino acids,[45–47] their dimers[48] and more complex molecules[49–54] was observed upon UV irradiation of organic acids in aqueous ammonia.

Examples of prebiotic synthesis of adenine, purine, cytosine and pyrimidin-4(3*H*)-one from formamide,[55–57] cyanamide[58] and other condensing agents[59–62] were also studied. Catalytic action of montmorillonite[63] and apatite[64] in these reactions was established. Supramolecular structures based on guanine and cytosine were investigated.[65]

Gabel and Ponnamperuma[66] reported that polymerization of formaldehyde under the action of Al_2O_3 in boiling water led to pentoses (22%), tetroses (17%), trioses (38%) and glycolaldehyde. A similar reaction catalyzed by various minerals resulted in tetroses, hexoses and pentoses including ribose.[67] Thus, three groups of key molecules for living organisms can be synthesized in the form of racemic monomers under conditions that could occur on the primeval Earth.

III. Physicochemical factors of asymmetric influence

Many hypotheses of the origin of homochirality are based on the primary formation of racemic molecules which provided a necessary amount of chiral key biomolecules in the biosphere only after enantiomeric enrichment.[68] Asymmetric reactions without formation of racemates are also possible. They include, *e.g.*, sublimation,[17] crystallization,[11,13,24,25,69,70] action of adsorbent surface,[10,71] autocatalysis,[7,18,72] catalysis,[73] spontaneous symmetry violation,[18] chiral amplification,[74] action of magnetic field,[1,3] some other processes[8,9,16] and, finally, Soai-like reactions.[70,75] However, the maximum enantiomeric enrichment is achieved only in the stochastic Soai reaction[3] representing a kind of a one-and-only process (see reviews[1,3]). An example of primeval asymmetric catalysis could be provided by the catalytic reaction in the presence of achiral catalyst in a nematic liquid crystal whose right- or left-handedness is due to a small additive of a chiral compound of, *e.g.*, meteorite origin (see below).[76–78] Asymmetric induction with an achiral catalyst can be provided by the helical structure (molecular arrangement) of a cholesteric liquid crystal. Indeed, induced circular dichroism studies[79,80] of cholesteric liquid crystals revealed helical ordering of the reactant and catalyst molecules in the temperature interval corresponding to the existence of the mesophase. Amino acid precursor hydrogenation in the presence of achiral Wilkinson's catalyst $[RhCl(PPh_3)_3]$ in an optically active cholesteric liquid crystal occurs enantioselectively (Fig. 1).[79,80] Clearly, this reaction is only an example of a rough approximation to primitive conditions for enantiomeric enrichment; it could hardly occur on the primeval Earth.

Chiral amino acids can also be delivered to the Earth by meteorites.[1,3–5,14,32,81] Indeed, six α-methyl-α-amino acids found in meteorites contain corresponding L-enantiomers in a small excess (up to 15%). However, they are very rare to occur on the Earth and are not involved in living metabolism. The fact that these compounds are contained in meteorite matter can be explained by the impossibility to undergo racemization. The answer to the question whether these compounds, during the earliest steps of evolution, can play some role in the induction and stabilization of chiral α-H-amino acids and subsequently polypeptides remains unknown. Racemization of chiral α-amino acids, provided that they are delivered to the Earth by meteorites, occurs much faster taking into account the temperature difference between the interstellar space and Earth. Summing up, mention may be made that all enantiomeric enrichment processes mentioned above can hardly create a molecular environment enriched with just L-amino acids and D-sugars in considerable enantiomeric excess.

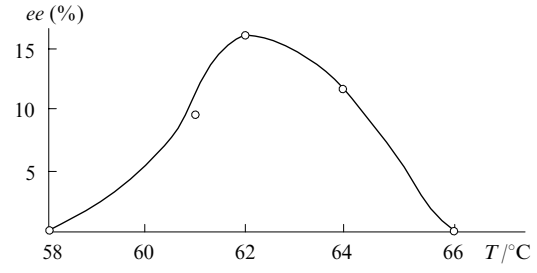


Figure 1. Enantiomeric excess of hydrogenation product of α-*N*-acetylaminocinnamic acid in cholesteryl tridecanoate in the presence of $RhCl(PPh_3)_3$ as catalyst plotted *vs.* temperature.[79,80]

¶ We observed (unpublished data) the formation of important α-amino acids upon UV irradiation of formaldehyde in an aqueous solution of a mixture of KNO_3, $NaNO_3$ and NH_4NO_3 (formaldehyde-^{14}C was used for convenience to analyze amino acids after 2D paper chromatography). Formaldehyde can form in a photochemical reaction in a mixture simulating the primeval Earth atmosphere and containing gaseous N_2 and CO_2, water vapour and traces of H_2 and CO.[39] A similar experiment was also repeated under fog conditions in a more recent, independent study.[40]

IV. Physical factors of asymmetric influence

IV.1. Chirality of moving objects: elementary particles

Selective photolysis of racemic amino acids on exposure to elliptically and circularly polarized light can indeed lead to enantiomeric enrichment.[82–84] Experiments on deracemization of DL-leucine irradiated with circularly polarized light led to enrichment with L-leucine (enantiomeric excess, *ee*, was 4.68%).[85] However, powerful extraterrestrial sources of circularly polarized light[86,87] imply delivery of enantiomerically enriched amino acids to the Earth. Meanwhile, the *ee* values for L-alanine and L-valine (both compounds were found in the Murchison and Murrey meteorites) were at most 2.2%.[1,3] Therefore, the conclusion drawn at the end of the preceding Section is also valid in this case.

In 1956, Lee and Yang[88] discovered parity violation † of elementary particles in weak nuclear forces also called Z-forces (see also Ref. 13). Experimental observation showed that β-particles emitted from radioactive nuclei have an intrinsic asymmetry, *viz.*, the number of left-handed electrons is slightly larger than the number of right-handed electrons; in other words, there is no mirror symmetry and chirality exists at the level of elementary particles. Weak nuclear currents act on right-handed and left-handed electrons in different manner; therefore, the spin – orbit coupling in right-handed helical molecules leads to an excess of left-handed electrons and *vice versa*. As a result, enantiomers ‡ have different energies.[89] Since Z-forces are very weak, their influence on the chemical properties of molecules has not been reported so far. A theoretical estimate of the preference of an L-amino acid over corresponding D-amino acid (*i.e.*, the *ee* value) is estimated as 1×10^{-17}%, which goes far beyond the detection limits. Therefore, negligible distinctions between different amino acid and sugar enantiomers, due to weak nuclear interactions, have no effect on the enantiomeric composition of reaction products for both synthesis and decomposition of racemates (however, see Ref. 13).

An interesting hypothesis was proposed by Davankov.[6] He assumes[90] that chirality is an intrinsic property of matter on all hierarchical levels including elementary particles, atoms, molecules, macromolecules and supramolecular aggregates, cells and living organisms, galaxies and the Universe.§ Probably, for some systems this should be considered in the dynamical sense because a sphere moving along its axis of rotation exhibits true chirality.[92] Thus, a stationary spinning electron is not a chiral system, whereas an electron executing translational motion along the axis of rotation parallel or antiparallel to the spin direction exhibits true chirality (Fig. 2).

Using data[93] on possible formation of organic matter upon a super-high-velocity (SHV) meteorite impact (Fig. 3),

† Terminologically, 'parity' is equivalent to 'chirality', *i.e.*, the property of an object of not being superimposable with its mirror image.

‡ Enantiomers can be graphically represented as twisted in right-handed helix and left-handed helix.

§ As to the family of helical galaxies and the Universe as a whole, Longo[91] catalogued the direction of rotation of ten thousands of helical galaxies photographed in the framework of the Sloan Digital Sky Survey. It was found that galaxies mainly rotate counterclockwise, thus being left-handed (assuming a top view from the North Pole of the Milky Way Galaxy where the Solar System is located. The excess is small (~7%), but the probability of such a cosmic accident is one part per million. This is a nontrivial result because until now it was commonly accepted that the Universe is isotropic.

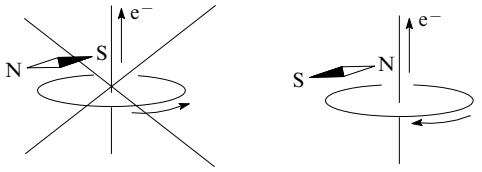


Figure 2. A moving electron generates circular magnetic field of a particular configuration, thus indicating an inherent chirality.[6]

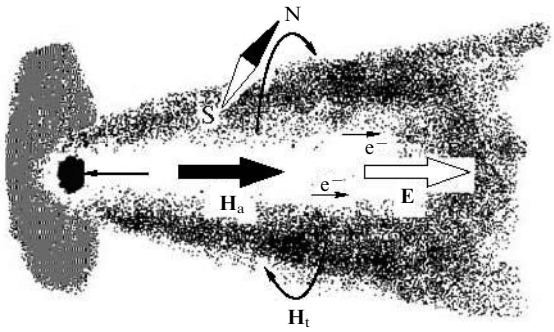


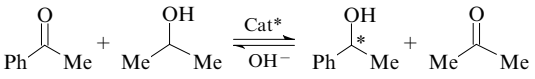
Figure 3. A schematic of plasma torch generated by super-high-velocity impact of a solid body on a solid target. Chiral combination of electric field **E** with axial magnetic field $\mathbf{H}_a$ and toroidal magnetic field $\mathbf{H}_t$.[6]

Davankov assumed that organic molecules influenced by chiral electrons can be enantiomerically enriched under these conditions. No attempts to experimentally confirm this hypothesis have been undertaken as yet.

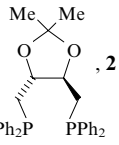
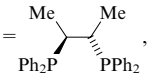
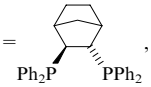
Prior to discussing this hypothesis, one should answer the question of whether all chiral systems can perform asymmetric induction. Recall that asymmetry is characterized by the absence of symmetry elements, except C_1 symmetry axis, in the system in question. Chirality is a more general term; a chiral system can have C_n (n = 1, 2, 3, ...) or D_n (n = 2, 3, ...) symmetry which includes the case for asymmetric systems (C_1 symmetry). However, chiral molecules (intermediates) having both C_1 and C_2 symmetry differ in the asymmetric induction step.[94–96] This step controls transfer of stereochemical information from the inductor (catalyst) to the acceptor molecule (product). More than 250 asymmetric reactions catalyzed by chiral complexes were analyzed from the standpoint of symmetry of the molecules (intermediates) involved in the reactions. It was shown that two factors significantly influence the enantioselectivity of the process. These are (i) one-, two- or three-point coordination of substrate (reactant) in the catalyst – substrate intermediate and (ii) C_1 or C_2 symmetry of the intermediate responsible for the asymmetric induction.[94–96] For instance, in the case of reactions of simple monofunctional prochiral substrates (acetophenone, benzaldehyde, thioanisole, styrene, *etc.*) coordinated by only one (reacting) group (single-point coordination), the key intermediate inherits the symmetry of the starting chiral catalyst complex. In these processes, C_2 symmetry of the key intermediate is responsible for the low enantioselectivity (for the catalyst complex with C_2 symmetry).[95]

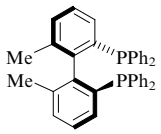
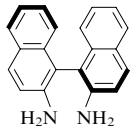
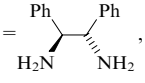
For instance, hydrogenation of acetophenone in the reaction with hydrogen transfer (Scheme 1) and reduction of benzaldehyde with dialkylzinc (Scheme 2) occurs with different enantioselectivity depending on the symmetry of

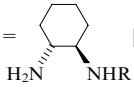
Scheme 1



Ligand	Symmetry	Metal	*ee* (%)	Product configuration	Ref.
1	C_2	Ru	1–4	*S*	97, 98
2	C_2	Rh	<1		99
2	C_2	Ir	4–28	*S*	100
3	C_2	Ru	28	*R*	101
4	C_2	Ru	15	*R*	101
5	C_2	Rh	0		102
6	C_2	Rh	17	*R*	99, 100
7	C_2	Rh	12	*S*	102
8	C_1	Rh	97	*R*	103
8	C_1	Ir	96	*R*	103

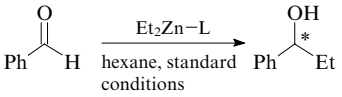
1 = , **2** = , **3** = ,

4 = , **5** = , **6** = ,

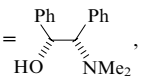
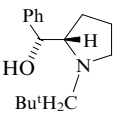
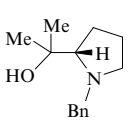
7, **8** =  [R = H (**7**), 4-MeC$_6$H$_4$SO$_2$ (**8**)]

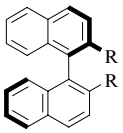
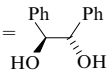
the catalyst. For the first reaction (see Scheme 1), the optical purity of reaction products increases by almost an order of magnitude on going from the complexes with ligands **1**–**7** having C_2 symmetry to the complexes with asymmetric ligand **8** (C_1 symmetry). This trend is also observed for the second reaction, *viz.*, the optical purity of reaction products is much higher for the complexes with asymmetric ligands **9**–**11** than for the complexes with ligands **6** and **12**–**15** having C_2 symmetry (see Scheme 2).

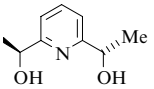
Scheme 2



Ligand	Symmetry	*ee* (%)	Product configuration	Ref.
9	C_1	97	*R*	104
10	C_1	100	*R*	105
11	C_1	99	*R*	106
12	C_2	8	*S*	107
6	C_2	26	*S*	107
13	C_2	8	*R*	108
14	C_2	20	*R*	107
15	C_2	4	*S*	109

9 = , **10** = , **11** = ,

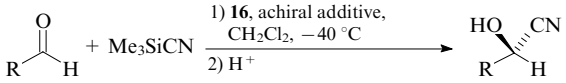
12, **13** =  [R = OH (**12**), NMePh (**13**)], **14** = ,

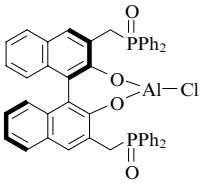
15 = 

If the substrate is coordinated to two or three groups, the key intermediate, in the case of the complex with the C_2-ligand, loses this symmetry and becomes asymmetric. High enantioselectivity of such reactions is well known (see, *e.g.*, a review[94]). Indeed, according to the mechanism proposed by Landis and Halpern[110] and by Imamoto and co-workers,[111] hydrogenation of amino acid precursors (three-point coordination) under the action of complexes with C_2 symmetry involves the formation of an intermediate with C_1 symmetry.

From the standpoint of comparison of the symmetry of the key intermediates, an experimentally more evidential example is provided by the cyanosilylation under the action of complex **16** with C_2 symmetry in the presence of achiral additive (Scheme 3).[112] Possible intermediates of this reaction include structures **17** with C_2 symmetry and **18** with C_1 symmetry.[113, 114] Unlike the reaction with no achiral additive, the intermediate of the reaction proceeding in the presence of achiral additive loses its C_2 axis, which leads to a tenfold increase in enantioselectivity.

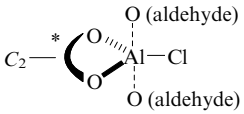
Scheme 3

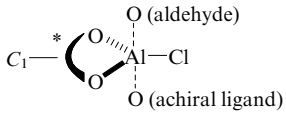


16 = 

R	Achiral additive	*ee* (%)
$Ph(CH_2)_2$	Bu^n_3PO	99 (*S*)
$Ph(CH_2)_2$	is absent	9 (*S*)
Pr^i	Bu^n_3PO	90 (*S*)
Pr^i	is absent	25 (*S*)

Structures 17, 18

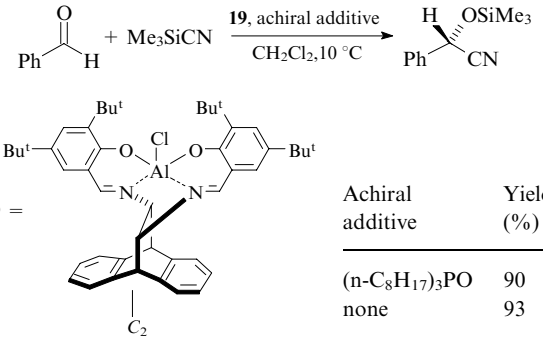

17


18

Yet another illustration of the sensitivity of the enantioselectivity of a catalytic reaction to the presence of achiral additives is cyanosilylation of benzaldehyde in the presence of complex **19** (Scheme 4).[115] Abrupt increase in enantioselectivity in the presence of achiral additive in this reaction is probably of the same nature as in the preceding reaction. There is a variety of other catalytic reactions characterized by similar results (see, *e.g.*, Refs 116–119).

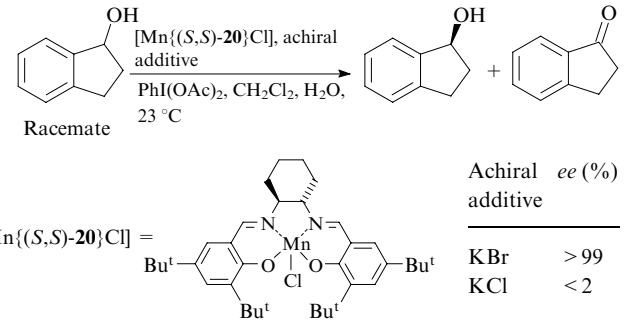
A common feature of these reactions leading to low or zero enantiomeric enrichment of products consists in C_2 symmetry of the intermediates responsible for asymmetric induction. A well-studied example of such reactions is provided by the oxidation of a racemic secondary alcohol in the presence of a manganese(III)–salen complex (Scheme 5).[120] Brown *et al.*[120] proposed a reaction pathway involving transformation of the catalytic complex **A** to

Scheme 4



Achiral additive	Yield (%)	*ee* (%)
$(n\text{-}C_8H_{17})_3PO$	90	86 (*S*)
none	93	0

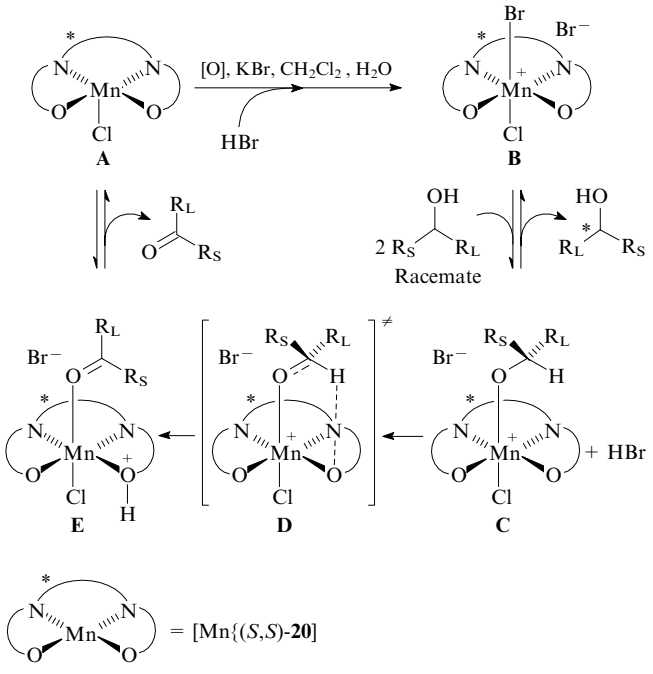
Scheme 5



Achiral additive	*ee* (%)
KBr	> 99
KCl	< 2

asymmetric intermediate **B** in the presence of [O]–KBr–H_2O system (Scheme 6). It is the intermediate that is responsible for the asymmetric induction in the **B** → **C** step. The catalytic cycle is closed *via* transition state **D** and intermediate **E**. Replacement of KBr by KCl as achiral additive causes the enantioselectivity of the reaction to abruptly decrease because the key intermediate **B** adopts C_2 symmetry.

Scheme 6



These experimental observations suggest that molecules of higher symmetry (C_2, C_3, C_n and D_2) cannot be efficient asymmetric inductors in the formation of molecules of lower symmetry (C_1). This agrees with the opinion of P Curie,[121] who noted that only asymmetric factors can cause asymmetric effects.¶

Getting back to Davankov's hypothesis, one can assume that a chiral electron with helical symmetry can hardly be a chiral inductor in the synthesis of chiral molecules of lower symmetry (C_1). Nevertheless, this hypothesis needs thorough experimental revision.

IV.2. Chirality of moving bodies. Cosmic bodies: Earth–Sun–Solar System–the Milky Way Galaxy

Extending Barron's concept[92] of the chirality of spinning spheres executing translational motion along the axis of rotation (see Section IV.1) not only to elementary particles, but also cosmic bodies (in excellent agreement with Davankov's idea of the chirality of matter on all hierarchical levels), one can suggest that the Earth revolving around the Sun is also a chiral system. It is just the conclusion drawn by He *et al.*,[122–125] who hypothesized that biomolecular homochirality originated from the chiral influence of the axial and orbital rotation of the Earth (Fig. 4). The authors concluded that (i) any point on the Earth surface (except the poles) moves along a super helix in space and time, all things being considered, and (ii) this right-handed helical motion is responsible for the right-handed helical structure of polypeptides and DNA molecules. Thus, helicity of the key biomolecules was directly related[122–125] to handedness of the axial and orbital rotation of the Earth.

Indeed, consider the Earth–Moon system moving around the Sun along a right-handed helix.† The axes of

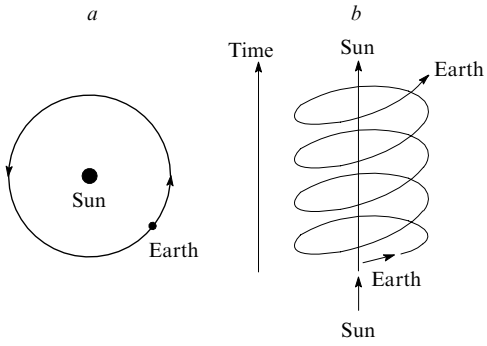


Figure 4. Orbital chirality of the Earth: a schematic description.[125]
Orbital (circular) motion of the Earth around the Sun (*a*) and right-handed helical motion of the Earth around moving Sun (*b*). Combination of circular and helical motion of any point on the Earth surface (except the poles) around the axis of rotation of the Earth (not shown) also corresponds to Figs *a* and *b*.

¶ 'No dissymmetry can manifest itself in a physical property which does not already exist in the system'.

† When considering the problem of homochirality, apparent incomparability of the size of molecules and cosmic bodies raises the question. However, if we discuss the chiral influence of elementary particles, that of cosmic bodies should also not be ignored because from, the standpoint of size, key biomacromolecules occupy an intermediate position between elementary particles and cosmic bodies. Indeed, the rest mass of a photon is zero[126] (also, $m = 1.6 \times 10^{-47}$ g), that of an electron is 9.11×10^{-28} g,[127–129] a DNA macromolecule has a mass of $1.66 \times 10^{-22} - 6.64 \times 10^{-21}$ g,[130] the mass of the Earth is 5.974×10^{27} g and that of the Moon is 7.35×10^{25} g.

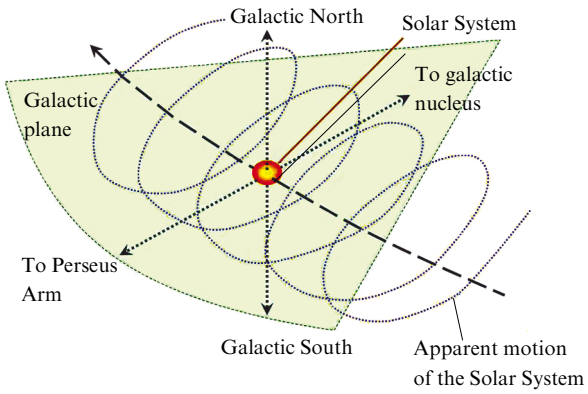


Figure 5. Motions of the Solar System in the Milky Way Galaxy.[131 – 135]

rotation‡ of both partners are tilted to the plane of the motion. The entire system undoubtedly is a system with asymmetric structure and asymmetric gravitational field.§ In turn, the Solar System spins and moves along a right-handed helix in the gravitational field of our Galaxy (Fig. 5).[131 – 135]

Our Galaxy represents a double 'snail' and the 'snails' have different enantiomeric configurations. There is a symmetry plane between the 'snails'. Thus, being a symmetric system, the Galaxy consists of two asymmetric fragments. The plane of rotation of the planets of the Solar System is tilted by 90° to the symmetry plane of the Galaxy. The helical orbit (dashed line in Fig. 6) of the Solar System passes across the galactic North. From the standpoint of symmetry, the structure of our Galaxy to some extent resembles that of meso-tartaric acid (inner racemate containing two asymmetric carbon atoms of different configurations).

Thus, the asymmetric system Earth – Moon is in asymmetric gravitational field composed of the contributions of the proper motion and right-handed helical orbital motion of the system in question, of the right-handed helical motion of the Solar System, and of the gravitational field of the right-handed chiral (Northern) Galactic 'snail', which also executes right-handed rotation. Quite probably, these chiral cosmic motions are interrelated¶ (although the authors of this review are also familiar with the opinion of uniqueness of the Solar System).

‡ The Moon also executes axial rotation. Only one hemisphere of the Moon faces the Earth because the orbital and rotational periods of the Moon are the same.

§ From the standpoint of mass ratio, the planet – satellite (Earth – Moon) system is rather the only double planet in the Solar System. Each planet experiences a considerable asymmetrizing influence of the partner. For Earth, this influence manifests itself in periodic variations of the symmetry of water surface (tides and tide ebbs). The Sun also causes tides and tide ebbs. Although the Sun is distant from the Earth, its large mass allows Sun-induced tides and tide ebbs to be only 2.5 times weaker than corresponding Moon-induced phenomena. From the standpoint of symmetry of gravitational field, the Earth – Moon system is also asymmetric; elliptic motion of the Moon around the Earth occurs in the plane of the ecliptic rather than in the equatorial plane, as is the case for satellites of other planets in the Solar System.

¶ Only Venus, unlike other planets, executes counterclockwise axial and orbital rotation.

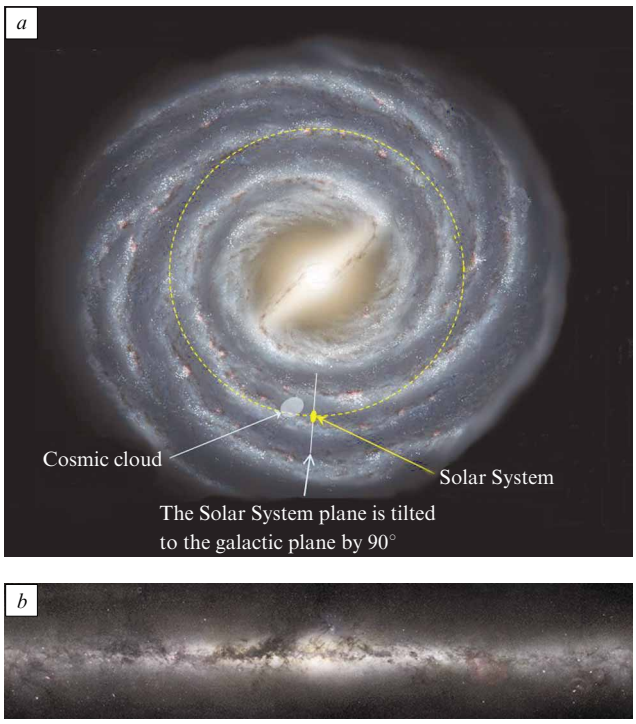


Figure 6. The Milky Way Galaxy: top view from the Galactic North (*a*) and side view (*b*).[131 – 135]

Prior to discussing possible mechanisms of transfer of asymmetric 'cosmic' influence on the molecular level, one should consider the onset of homochirality as a result of the formation of helical polymer molecules.

V. Homochirality and helicity of key biomacromolecules

On the primeval Earth, many (but not all) of the reactions mentioned above usually lead to a small excess of L-amino acids in the resolution of racemates or in an asymmetric reaction; these amino acids can also be delivered by meteorites and comets. There exist mechanisms for selection (accumulation) of D-sugars by L-amino acids (*e.g.*, L-serine and D-glucose,[136, 137] L-dipeptides and D-sugars[138]). However, all these reactions compete with the racemization of amino acids. Racemization can be precluded by the polymerization of homochiral L-amino acids and D-monosaccharides affording a *P*-helix† (Fig. 7) whose configuration is stabilized by inter-coil hydrogen bonds.‡ Probably, it is the *P*-helix formation that is the limiting stage in the origin of homochirality and it is this reaction that underlies the choice of L-amino acids and D-monosaccharides as monomers for constructing self-regulating structures (living organisms).

Experimental conditions have relatively little effect on the formation of *P*-helices from L-amino acids and double

† *P*-helix and *M*-helix (from 'plus' and 'minus') are the right-handed and left-handed helix, respectively.

‡ D-Amino acids and L-monosaccharides can also undergo polymerization resulting in enantiomeric *M*-helix. However, there exists a mechanism favouring the reaction affording the *P*-helix (see Section VI).

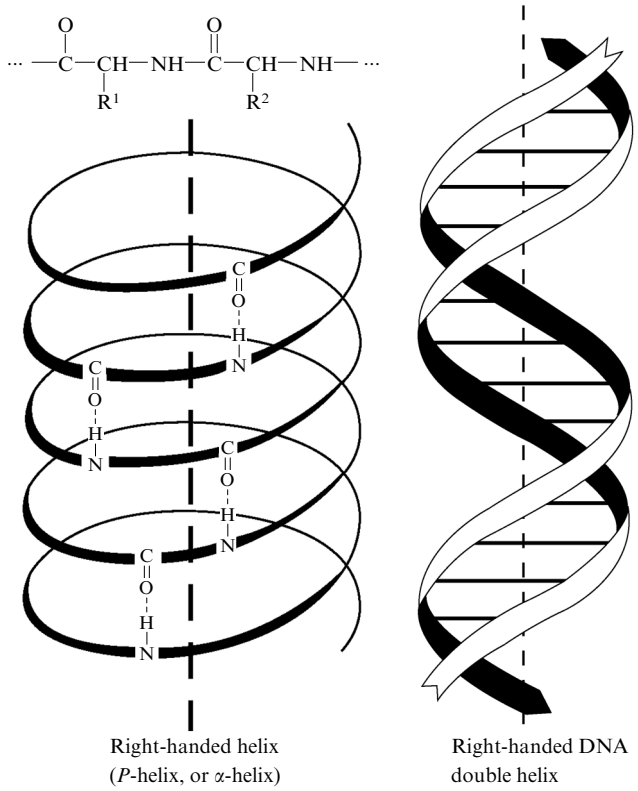


Figure 7. Polymers of homochiral molecules.

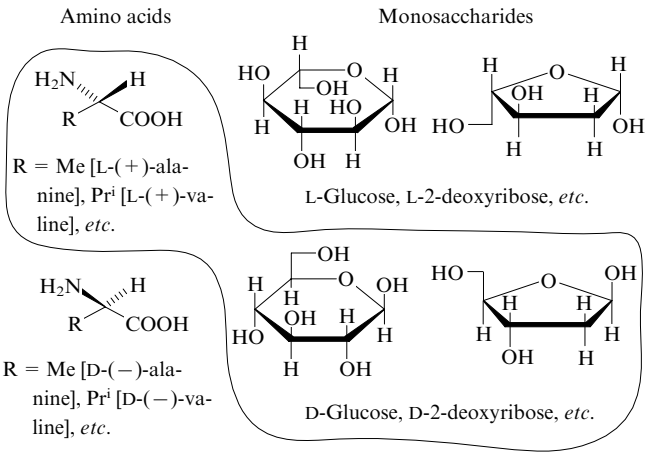


Figure 8. Homochiral molecules.

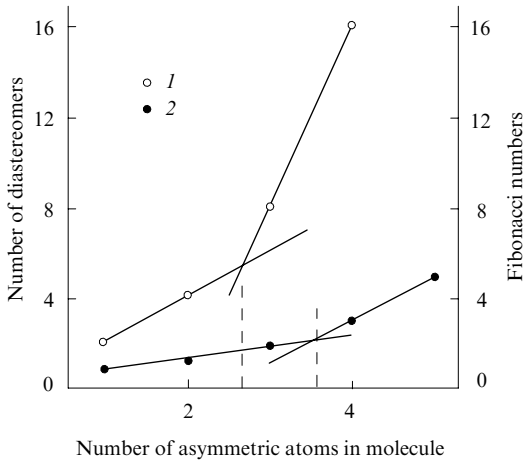


Figure 9. Magnitude of 'configurational error' as function of the number of asymmetric atoms in the monomer molecule. Number of diastereomers (*1*) and Fibonacci numbers (*2*).

P-helices based on D-deoxyribose; however, D-monosaccharides can form either right-handed or left-handed helices depending on the experimental conditions. Moreover, the configuration choice, which is very strict in the case of the polymers based on L-amino acids and D-deoxyribose, is violated for some polysaccharides by, *e.g.*, a small additive of L-galactose in the snail galactans (Table 1).[139] L-Galactose (11% – 15%) was also found in the galactans of 9 different snail species (family *Helicidae*, group *Pulmonata* and phylogenetic subclass of *Prosobranchiata*).[140] Seemingly, this can be explained by an increase in the 'configurational error' with increasing the theoretically possible number of diastereomers. Indeed, amino acids, deoxyribose and hexoses contain one, three and five asymmetric carbon atoms, respectively (Fig. 8). If a monomer molecule contains three or more asymmetric atoms, the number of possible diastereomers abruptly increases. The plot of the number of diastereomers *vs.* number of asymmetric atoms (n) exhibits a kink at $n > 3$ (Fig. 9). A similar kink is observed in the plot of the Fibonacci numbers§ *vs.* number of asymmetric atoms in the monomer molecule (see Fig. 9). In the latter case, the kink can be associated with transition from helical symmetry to snail symmetry, which can also be interpreted as 'configurational error'. Probably, it is not accidental that the choice of key biomolecules responsible for information transfer with minimization of errors is limited to the monomers containing from one to three asymmetric atoms, that is, amino acids and deoxyribose (see also Refs 10 and 141). The possibility for 'configurational error' to occur in building polymer molecules from hexose molecules containing five asymmetric atoms is substantiated by the examples given above.[139, 140]

Studies of the helical configuration of linear polysaccharides based on hexoses, *e.g.*, amylose [α-(1 → 4)-D-glucopyranose], showed that the sign of the helix depends on

Table 1. Compositions of the snail galactans determined from specific rotation and after oxidation by D-galactose oxidase.[139]

Snail species	Galactan configuration (%)	
	D	L
Helix pomatia	74.4	13.0
Arianta arbustorum	73.2	15.2
Cepala nemoralis	68.0	14.7
Biomphalaria glabrata	79.0	12.2

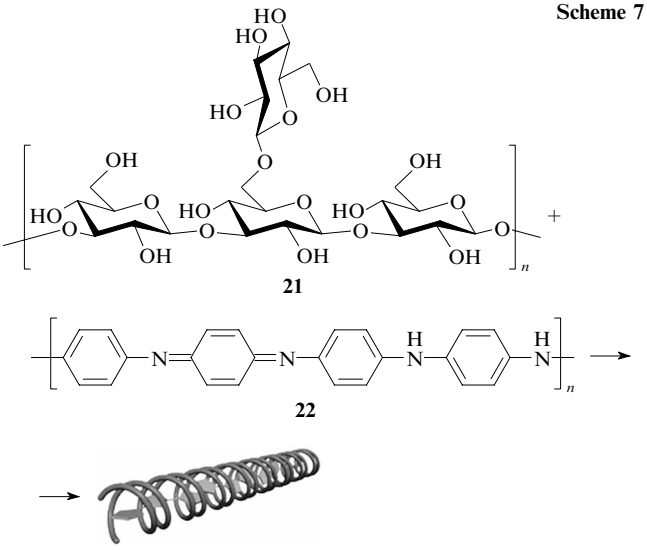
§ The simplest asymmetric structure (a snail) obeys the principle of constructing the Fibonacci sequence of numbers (each subsequent natural number is the sum of the previous two).

Table 2. Helix handedness of linear polysaccharide amylose as function of the solvent used for crystallization (according to X-ray data).

No.	Notation	Solvent for crystallization	Helix sign	Ref.
1	Amylose A [a]	water	*P*	142
2	Amylose B [a]	water	*P*	143
3	Amylose V	–	*M*	144
4	KOH – amylose	water, KOH	*M*	145
5	Amylose $V_{propan\text{-}2\text{-}ol}$	propan-2-ol, water	*M*	146
6	Amylose	water	*M*	147

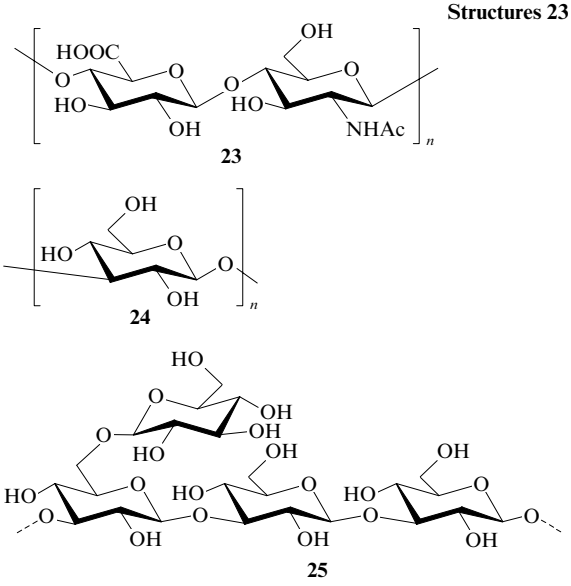
[a] Double helix.

Scheme 7



the crystallization conditions (Table 2). It follows that the use of the same solvent does not ensure the formation of same-sign helices (see items 1, 2 and 6 in Table 2).¶ A

Structures 23 – 25



¶ Probably, the sign of the helix is also influenced by the nature of monosaccharide and chemical bonds used in the formation of a linear polysaccharide. For instance, α-(1 → 2)-mannan forms only a left-handed helix, whereas β-(1 → 3)-glucan forms a right-handed helix.[148]

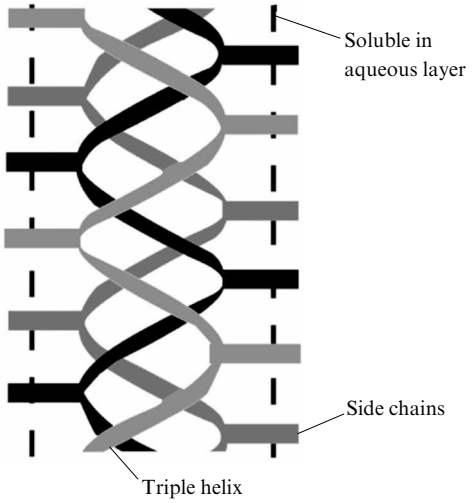


Figure 10. Schematic of triple *P*-helix formed by some polyglucans.

possible stabilizing factor of the *P*-helix is the double helix (see Table 2, items 1 and 2). Indeed, linear polysaccharides ι-carrageenan (X-ray data) [149] and xanthan (circular dichroism data) [150] do form double helices (the formation of *P*-helix in the former case was proved). According to circular dichroism data,[151, 152] branched polysaccharide schizophyllan (**21**) (Scheme 7) forms a double *P*-helix with encapsulated polyaniline molecule (**22**). This results in a supramolecular compound. However, the double helix is not necessarily *P*-helix. For instance, hyaluronic acid (**23**), a linear polymer, forms a double *M*-helix.[152]

Curdlan (**24**),[151] the simplest β-(1 → 3)-D-glucan, as well as two more glucans, lentinan (**25**) [153] and scleroglucan,[154] and other branched glucans [155 – 161] form triple *P*-helices (Fig. 10).

A large group of polysaccharides form double *P*-helices with polypeptides.[162 – 167] Thus, unlike polypeptides and DNA, polysaccharides form various helical structures. *P*-Helices are mainly formed in the case of double and triple helices.

VI. Water as agent for transfer of asymmetric information

Wind waves and tide waves may act as the simplest inductors and transfer agents of asymmetric influence of the orbital and proper rotation of the Earth – Moon system (and other cosmic bodies) to the molecular level. Indeed, water molecules are dipoles that can form various associates, *e.g.*, clusters and helical structures (Fig. 11). Water in wind-generated waves or tide waves obeys handedness

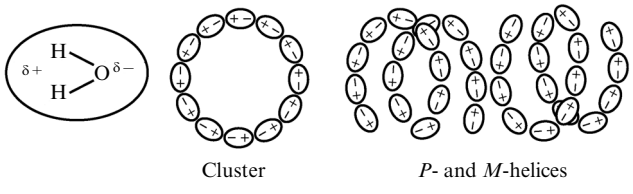


Figure 11. High-molecular-mass associates of water molecules.

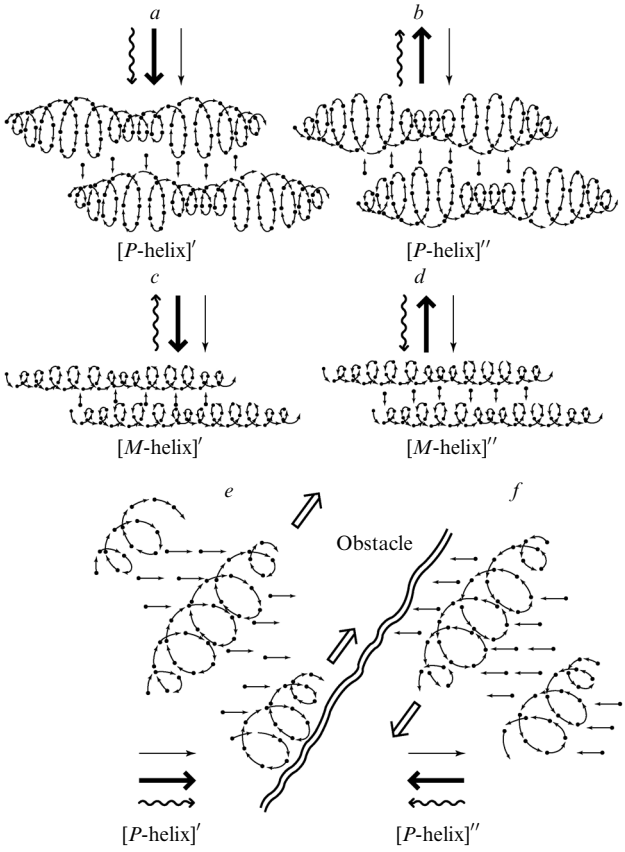


Figure 12. Helicity of large water waves (see text).[168]
⟶ — direction of the proper rotation of the Earth,
➡ — tide or wind direction,
⇝ — wave propagation direction,
•⟶ — direction of the motion of water molecules,
⇒ — water momentum (if the wave propagation direction is not normal to the obstacle (beach, ground, flow).

conventions for circularly polarized travelling waves.[168] Namely, a circularly polarized travelling wave is called right-handed if its angular momentum is along the propagation direction and is called left-handed if the angular momentum is opposite to the propagation direction. If the angular momentum of a travelling wind-generated wave or a tide wave (the wind or tide direction) coincides with the propagation direction of the wave, one deals with mainly right-handed motion of water molecules (Fig. 12 *a*,*b*). Otherwise (see Fig. 12 *c*,*d*), left-handed helical motion occurs. If there is an obstacle to the wave (see Fig. 12 *e*,*f*), mainly right-handed helical motion occurs.

It should be noted that, seemingly, the contribution of the axial rotation of the Earth manifests itself after a long time;† otherwise, concentric waves created when a stone is thrown into a body of water should not be highly symmetric (Fig. 13). Indeed, the waves shown in Fig. 12 (*a* and *b*, *c* and *d*, *e* and *f*) are visually identical. Also, a left-handed helical wave is relatively weak (see Fig. 12 *c*,*d*) if its propagation direction is opposite to the wind or tide direction. Likely, the largest water *P*-helices can be observed only if the wind or breaking direction coincide with the propagation direction of the wave and the direction of the proper rotation of the Earth (see Fig. 12 *a*).

† For instance, prolonged influence of axial rotation of the Earth leads to formation of high right bank for south-flowing rivers and, *vice versa*, high left bank for north-flowing rivers. This 'experimental' fact can also evidence for preference of the right-handed component of river water (wave).

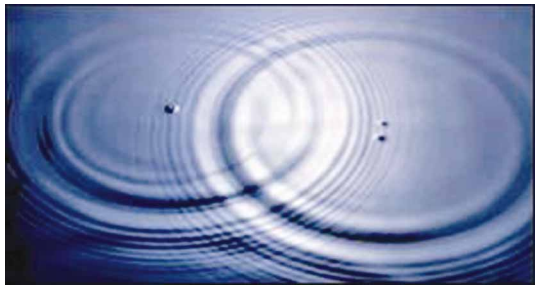


Figure 13. Concentric waves.[168]

It should be noted that helical motion of water molecules is characterized by the angular momentum whose direction does not coincide with the wind or breaking direction. This occurs if there is an obstacle to the wave (see Fig. 12 *e*,*f*). An illustration is provided by the motion of a surfer (Fig. 14) across a well-defined *P*-helical wave.

As mentioned above, right-handed helical motion is more preferable than left-handed motion; therefore, the inequality [*P*] > [*M*] is valid (quantities in brackets denote the corresponding concentrations). Taking into account the long-term 'memory effect' of water,[169 – 173] mainly right-handed helical structure of water associates also persists after wind- or tide-generated waves. A drawback of this theoretical consideration is the difficulty of experimental proof of the existence of water associates in the form of mainly *P*-helices. Indeed, the absorption band of water is in the 200-nm region and therefore the detection of water associates with some circular dichroism spectrometers faces problems. Also, it seems not improbable that the total concentration of *P*-associates is low compared to that of *M*-associates and thus the circular dichroism effect of the *P*-associates goes beyond the detection limits of modern circular dichroism spectrometers. Nevertheless, there are indirect indications of the existence of water *P*-associates.



Figure 14. Motion of a surfer on a tidal wave.[168]
The rise of water *P*-helix is clearly seen.



Figure 15. Right-handed shells of mollusks *Busycon coarctatum* (*1*), *Lambis lambis* (*2*), *Murex ramozus* (*3*), *Hexaplex chicoreus* (*4*) and a left-handed shell of mollusk *Busycon contrarium* (*5*).[174]



Figure 16. Arbitrary taken shells of gastropod mollusks *Turbinella anqulata*, *Cassis cornuta*, *Babylonia areolata*, *etc*.[174]
Bottom line: a total of 134 shells studied (*1*), 38 (*3*), 313 (*3*), 58 (*4*), 14 (*5*), 8 (*6*), 26 (*7*), 54 (*8*), 28 (*9*) and 136 (*10*). All shells are right-handed (*P*-forms).

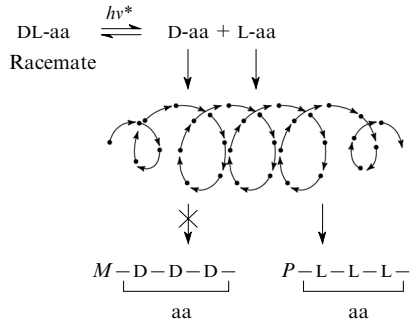
Water exhibits an amazing 'structural memory' effect.[169, 170] It was also reported that water can act as memory device and store more complicated information.[171 – 173] Therefore, mainly right-handed helical structure of water associates, which is due to wind waves and tide waves, can probably persist for rather long periods of time in the form of *P*-helical macromolecular associates and supramolecular structures. This may influence the symmetry of marine organisms.[173] Indeed, unlike terrestrial mollusks, which have both right-handed and left-handed shells (*P*- and *M*-forms, respectively) occurring in the same area, marine mollusks mainly have same-type shell symmetry and the shell handedness is dependent on the area. Most of them have right-handed shells.[174] Left-handed shells are rare to occur. Only two species of mollusks are characterized by more or less comparable proportions of right-handed and left-handed shells. These are *Achatinella mustelina* (the island of Oahu, Hawaiian Islands, a total of 223 shells studied)[175] and *Partula suturalis* (the island of Mo'orea, Windward Islands, a total of 58 shells studied),[175] whose *P*- and *M*-forms were found in different water areas near the corresponding islands. Figure 15 presents shells of the next two close species of different symmetry: right-handed shells of *Busycon coarctatum* (*1*) and left-handed shells of *Busycon contrarium* (*5*),‡ found in the Bay of Campeche (Mexico) and in the Gulf of Mexico, respectively.§ A feature of the four species¶ is that particular shell symmetry occurs in different areas of the body of water. The probability to find both *P*- and *M*-forms in the same area is very low.[175]

Figure 16 demonstrates arbitrarily chosen shells of the marine mollusks *Turbinella angulata*, *Charonia sauliae*, *Cassis cornuta*, *Cymbiola nobilis*, *Cymbiola imperialis*, *Pleuroploca trapezium*, *Architectonica trochlearis*, *Bursa bubo*, *Murex indivia*, *Murex brassica*, *Mitra mitra*, *Babylonia areolata*, *Strombus sinatus*, *Murex hausellum*, *Trochus conus*, *etc*. from Caribbean Islands, South Vietnam, China, Philippines, India and Sri Lanka. Most of these shells are right-handed; the proportion of left-handed shells is very small (see Figs 15 and 16 and a manual for the identification of seashells[174]). Thus, one deals with a correlation between preferred formation of *P*-helical wind waves and tide waves (see Fig. 12) and the right-handed (*P*-form) shells of marine mollusks (see Fig. 16). Probably, this is an example of a deep intimate relationship originating from the existence of mainly *P*-helical water associates. Yet another indirect indication of such a correlation is area-specific occurrence of the symmetry of seahells. Namely, left-handed and right-handed shells of the four species mentioned above (*Acatinella mustelina, Partula suturalis, Busycon coarctatum* and *Busycon contrarium*) are very rare to simultaneously occur in the same area.[175] This is probably due to specific features of wind waves and tide waves that form water associates of different handedness in corresponding areas.

These coincidences indirectly confirm the existence of helical water associates that are reflected in the symmetry of seashells. If this is the case, prevailing right-handed helical water associates (*P*-form) can serve a kind of a filter to hamper the formation of the *M*-form on the molecular level in favour of the *P*-form, as is, *e.g*., shown in Fig. 17 taking amino acids as an example. The formation of a coil of a *P*-helix from a minimum number of L-amino acids in a solution of sea water is probably the limiting step of the onset of homochirality on the primeval Earth. Further evolution leading to the formation of the *P*-form of the double helix based on water-soluble D-2-deoxyribose resembles the formation of the *P*-form of the double helix based on D-amylose.[142, 143] An analogy with amino acids and the symmetry filter based on the *P*-form of helical water associates is also possible in this case.

Based on the concept formulated in this Section (sea water as agent for transfer of asymmetric influence), one can draw an interesting conclusion that, among all planets

‡ Figure 15 also demonstrates right-handed shells with left-handed 'fingers' ('symmetry hermaphrodites') of the following mollusks: *Lambis lambis* (*2*), *Murex ramozus* (*3*) and *Hexaplex chicoreus* (*4*).
§ Data by Hugo Kubinyi, www.kubinyi.de (Museo de Ciencias Naturales, Buenos Aires, Argentina).
¶ Probably, *Busycon coarctatum* and *Busycon contrarium* belong to the same species and differ only in shell symmetry.



aa is amino acid

Figure 17. A possible aqueous 'symmetry filter' for preferred formation of a *P*-helix of the polymer based on L-amino acids compared to the *M*-helix of the polymer based on D-amino acids.

in the Solar System,† only the Earth provided ideal conditions for the onset of homochirality (germ of life). Indeed, the Moon causes very intense tide waves (unidirectional motion); tide ebb occurs in a much more calm manner and creates no waves. Therefore, among the wind waves and tide waves, the latter are more stable and more admissible for the formation of helical water associates in the *P*-form.

* * *

In this review, we formulated and substantiated the hypothesis, according to which homochirality (configuration uniformity in the construction of living organisms from L-amino acids and D-sugars only) can be explained by the simplest and persistent asymmetric influence existing on the Earth. This influence originates from right-handed helical orbital motion and from the proper motion of the Earth – Moon system (see also Refs 133 – 136). In addition, the Earth is in asymmetric gravitational field created by the right-handed helical motion of the Solar System in the Northern (chiral) part of the Milky Way Galaxy. This right-handed helical asymmetric combination of fields is reflected in the right-handed helical structure of polypeptides based on L-amino acids, DNA double helices based on the monosaccharide D-2-deoxyribose, as well as double and triple helices of polysaccharides based on D-hexoses. The compounds listed above specify the configuration choice of L-amino acids and D-sugars. The role of an agent for transfer of asymmetric influence of gravitational fields created by cosmic bodies to the molecular level can be played by right-handed helical water associates formed by water waves and tide waves that reach maximum amplitudes if their direction coincides with the direction of the angular momentum of the Earth. The existence of right-handed helical water associates is supported by the biological data presented above.

† If the Moon and Moon-induced tide waves on the Earth are of importance for the onset of homochirality (germ of life), hypothetical corresponding phenomena on the primeval Mars when (if) there were water oceans, were much less probable compared to the Earth conditions. Indeed, the Moon : Earth mass ratio is 1 : 81, being incomparably larger than the Phobos : Mars and Deimos : Mars mass ratios equal to $1 : 50 \times 10^6$ and $1 : 35 \times 10^7$, respectively. Correspondingly, tide waves that would be expected in the hypothetical primeval Martian oceans should have much smaller amplitudes. Besides, astronomers hypothesized that both Martian moons were caught a long time since the formation of the planet Mars. This casts doubts on the possibility of existence of tide waves induced by Martian moons (not by Sun).

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