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Homochirality Through Photon-induced Melting Of Rna/dna: Thermodynamic Dissipation Theory Of The Origin Of Life

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Abstract

The homochirality of the molecules of life has been a vexing problem with no generally accepted solution to date. Since a racemic mixture of chiral nucleotides frustrates the extension and replication of RNA and DNA, understanding the origin of homochirality has important implications to the investigation of the origin of life. Theories on the origin of life have generally elected to presume an abiotic mechanism giving rise to a large prebiotic enantiomer enrichment. Although a number of such mechanisms have been suggested, none has enjoyed sufficient plausibility or relevance to be generally accepted. Here we suggest a novel solution to the homochirality problem based on a recently proposed thermodynamic dissipation theory for the origin of life. The ultraviolet absorption and dissipation characteristics of RNA/DNA point to their origin as photoautotrophs, their replication assisted by UV light and temperature, and acting as catalysts for the global water cycle. Homochirality is suggested to have been incorporated gradually into the emerging life as a result of asymmetric right- over left-handed photon-induced denaturation of RNA/DNA occurring when Archean sea surface temperatures became close to the denaturing temperatures of RNA/DNA. This differential denaturing success would have been promoted by the somewhat right-handed circularly polarized submarine light of the late afternoon when surface water temperatures are highest, and a negative circular dichroism band extending from 220 nm up to 260 nm for small segments of RNA/DNA. A numerical model is presented demonstrating the efficacy of such a mechanism in procuring 100% homochirality of RNA or DNA from an original racemic solution in less than 500 Archean years assuming a photon absorption threshold for replication representing the hydrogen bonding energy between complementary strands. Because cholesteric D-nucleic acids have greater affinity for L-amino acids due to a positive structural complementarity, and because D-RNA/DNA+L-amino acid complexes also have a negative circular dichroism band between 200 - 300 nm, the homochirality of amino acids can also be explained by the theory.

Introduction

Molecules that have no plane of symmetry come in two distinct geometrical, but energy degenerate, forms, or mirror images, called "enantiomers", which are labeled as being left (L)- or right (D)-handed. This chirality in biological molecules is a result of the tetravalent nature of carbon atoms, often associated with a so-called "alpha-carbon atom" that attaches to a functional group. Energy degeneracy implies that enantiomers have essentially equal formation and degradation probability under near equilibrium conditions (except perhaps for one part in 10¹⁷, due to the parity non-conserving weak force). However, life has an overwhelming preference for one enantiomer over the other, and thus non-equilibrium biochemical reactions are chirality biased. For example, RNA, DNA, ribose, and deoxyribose are right-handed, while the amino acids of life are left-handed.

Today, incorporation of only the correct enantiomer of the nucleotides into RNA/DNA is guaranteed by an unflinching chiral enzymatic selection process. Such enzymes, however, could not have been available at the very beginnings of life. Without enzyme selection, RNA template extension is severely adversely affected in a racemic (equal concentration of both enantiomers) solution of nucleotides, principally because incorporated nucleotides of the wrong chirality act as extension terminators [1]. Orgel [2], has suggested that this frustration during the copying of polynucleotides is one of the greatest obstacles to an understanding of the origin of life.

The simplest potential solution to the puzzle of biotic homochirality has been to suggest an initial overwhelming predominance of one enantiomer over the other in the original prebiotic soup, or, perhaps, a smaller initial enantiomer excess subsequently amplified by asymmetric autocatalysis [3] or other similar mechanisms. Although many mechanisms for such an original bias and amplification have been proposed, none has come to be generally accepted for lack of demonstrated relevance or plausibility.

In the following section we briefly review the mechanisms hitherto proposed for enantiomer enrichment. Equally briefly, we describe the problems

associated with the efficacy of each mechanism. In section 3 we describe how homochirality could have arisen gradually within the first replicating organisms due to an asymmetry in the UV photon-induced denaturation of RNA or DNA [4], without the need to invoke a prebiotic enantiomer excess or catalytic amplification mechanism. Section 4 presents a simple model demonstrating the efficacy of the proposed mechanism. Section 5 reviews the evidence for how D-nucleic acid could have selected for L-amino acids.

Prevalent Homochirality Theories

Many theories for homochirality have proposed a prebiotic enantiomer excess of the biological molecules, either generated at the Earth's surface or in space. Potential mechanisms for generating this excess are; circularly polarized light either photolysing, photocatalysing, or photoreacting the molecules; inorganic chiral clay or crystalline template selectivity; magnetochirality; and the parity violating weak interaction. Terrestrial circularly polarized light can be generated by distinct mechanisms [5,6]. In order of importance these are: 1) Sunlight scattered at depth in water becomes linearly polarized. If this light is then totally internally reflected at the water-air interface, its vertical component undergoes a phase shift. As observed from below, near the surface, one sees partially circularly polarized light outside Snell's window of up to 10% [5,7], 2) Molecular (Rayleigh) atmospheric scattering produces linearly polarized light and a subsequent aerosol (Mie) scattering ($r \gg \lambda$) gives circular polarization. Right-handed circularly polarized light has been measured at twilight up to a maximum of about 0.5% [8,9]. 3) The intrinsic circular polarization of sunlight itself, about one part in 106 [10]. 4) Sunlight interacting with the Earth's magnetic field gives circular polarized light through the Faraday effect with an anisotropy factor of 10⁻¹⁰ [6].

The maximum optical purity (enantiomer excess) that could be obtained through photocatalysing or photoreacting is given by $g/2$ with $g = \Delta e/e$ where $\Delta e = e_R - e_L$ and e_R and e_L are the molar absorption coefficients for right and left circularly polarized light, and $e = (e_R + e_L)/2$ is the average of these. Empirical studies suggest that the values of $g/2$ for many different reactions are such as to result in optical purity of usually less than 1% [11]. It is improbable, therefore, that circularly polarized light could have given rise to homochirality on Earth through photocatalysing or photoreactions without

some kind of post amplification. On the other hand, optical purity is not limited to $g/2$ for photolysing, and thus this has been the mechanism most studied. However, there are three basic difficulties with enantiomer enhancement on Earth through photolysing. First, because the circular polarization of sunlight is small, and since the differential left- or right-handed photolysing capacity is small, a very large amount of basic RNA/DNA material would have to be destroyed in order to obtain 100% chirality. Experiments with camphor, for example, suggest that 20% chirality can be achieved by photolysing 99% of the original racemic material [12]. Homochirality would thus require essentially complete destruction of the original material. Secondly, averaged over the full diurnal cycle, the net circular polarization of sunlight is zero. Finally, high temperature, metal ions, radiation, and ultraviolet light itself, all have the tendency to cause racemization, and this effect is enhanced if the molecules are in water [13].

The smallness of the terrestrial circular polarization of sunlight, and its averaging to zero over the diurnal cycle, has led investigations into considering an extraterrestrial origin of the basic molecules of life and their chirality. Astronomical sources of potentially much greater circular polarization and intensity have been proposed, such as synchrotron radiation from neutron stars with large magnetic fields [11,14]. However, very few such circularly polarized light sources have been found to date, and all, so far, have only been identified in the infrared (albeit, presumably because shorter wavelength light does not penetrate as well the extensive dust clouds of space). Furthermore, the synchrotron radiation from these sources is generally white, and non-trivial frequency dependent dispersion properties of the organic molecules means that circular dichroism (differential absorption of left- over right-handed circularly polarized light) is both positive and negative in different regions of the spectrum. In fact, integrated over the whole spectrum circular dichroism sums to zero, the "Kuhn-Condon zero sum rule" (see section 3 and [15]). Therefore, a net enhancement of either chirality could only be entertained if additional arguments restricting the extraterrestrial light to a relevant frequency range could be found [16].

Finally, it is known that gamma rays, high energy particles, unpolarized UV light itself, and the heat of meteoritic entry into the atmosphere, all cause radioracemization (equalization) of the original enantiomer excess [17,18], so further mechanisms would have to be identified which could keep the molecules in their chiral state during their trip to Earth. Notwithstanding these difficulties, however, up to 15%

enantiomer excess has been claimed for some non-biological amino acids delivered to the Earth in carbonaceous chondrite meteorites such as Murchinson. Biological amino acids found in these meteorites have little, if any, enantiomer excess [19].

It has been suggested that inorganic elements crystallizing with a preferred chirality could have acted as templates for generating the chirality bias of the molecules of life. Bonner et al. [20,21] found that amino acids are enantioselectively adsorbed on chiral, enantiopure quartz crystals. For example, D-Alanine is bound selectively to D-quartz with an enantiomer excess of up to 20%. Results of several groups claiming to have found a selective adsorption of amino acids on the surfaces of achiral clays have been controversial [20,21]. Although there is evidence of a very small chiral selectivity by clay minerals, it has been argued that such a small effect may be due to previous absorption of optically active biomolecules produced by living organisms [22]. It is still uncertain, but unlikely, that prebiotic clays could have had a chiral bias.

Illumination of a racemic mixture of chiral molecules in a magnetic field by non-polarized light induces an enantiomer excess through the Faraday effect [23,24]. This so called "magneto-chiral dichroism" is operative on Earth, generating circularly polarized light from the interaction of unpolarized sunlight with the terrestrial magnetic field. However the anisotropy factor is small, of order 10^{-10} [6]. A further problem is that the magneto-chiral dichroism effect has opposite sign on opposite sides of the equator. Very young stars have a large magnetic field due to high rotation rates and are also sources of intense UV light. Such an astronomical magneto-chiral effect would be larger than that due to a terrestrial source, but still small, giving rise to an enantiomer excess of only about 10^{-6} [6].

The weak force is parity violating, resulting in a breaking of the energy degeneracy of the right- and left-handed enantiomers, thus favoring one over the other. This was first proposed to be the source of biomolecular homochirality by Ulbricht [25]. However, a comparison of the weak energy to thermal energy at the Earth's surface gives $\Delta E/k_{BT} = 10^{-17}$ [14], much too small to be a plausible solution in itself to homochirality. Vester et al. [26] proposed a somewhat different mechanism for an enantioselective reaction originating from the parity violating weak interaction. According to the Vester-Ulbricht hypothesis, the longitudinally polarized beta-decay electrons would, when decelerated in matter, lead to circularly polarized bremsstrahlung photons, promoting enantioselective reactions. However, as mentioned previously, enantiomer excess is limited to $g/2$, which, for most

relevant reactions, is very small.

In summary, although many mechanisms can be conceived which could have given rise to a small enantiomer excess locally during some finite time interval, these alone would not have been sufficient to lead to the homochirality of life. An additional auto-catalytic amplification mechanism [3], or far from equilibrium condition [27,28] would have been needed to bring the effect to the level of homochirality. Amplification mechanisms rely on different barrier heights in chemical reactions involving chiral catalysts of a small enantiomer excess. However, in true thermodynamic equilibrium, the products must necessarily be racemic, independently of barrier heights, but if the reaction is incomplete, or driven out of equilibrium, then one of the product enantiomers could be produced, at least in the short term, in much greater quantity than the other [29]. Still other far-from-equilibrium theories rely on spontaneous symmetry breaking, a type of second order phase transition involving a control parameter which passes through a critical value. Spontaneous symmetry breaking through amplification of a microscopic fluctuation in non-equilibrium systems with non-linear kinetic laws has been demonstrated by Prigogine [30]. Amplification, by whatever mechanism, therefore requires

non-equilibrium situation. Indeed, since life is an out of equilibrium phenomena, it is not surprising that many of life's enzymatic promoted chemical reactions are chirality biased. Although such non-equilibrium ideas for homochirality have been argued to apply in general, and although there exists experimental evidence validating the idea for certain out of equilibrium chemical reactions (see Podlech [29] and references therein), there has as yet been no demonstration of the principle in association with the putative original molecules of life; the amino acids or the nucleic acids RNA and DNA.

Homochirality through photon-induced melting of RNA and DNA

The Earth's surface during the Archean (3.8-2.5 Ga) was subjected to intense ultraviolet light within the 200-300 nm wavelength region [31,32], the result of a young Sun [33] and the lack of UV absorbing oxygen and ozone in the Earth's atmosphere. RNA and DNA are extraordinary absorbers and dissipators of UV light within this spectral region [34]. According to the thermodynamic dissipation theory of the origin of life

[4], life arose as a catalyst for the water cycle by absorbing this light and transforming it into heat, thereby augmenting the daytime temperature of the ocean surface and evaporation. Circumstantial evidence exists indicating that RNA and DNA were photoautotrophs, obtaining their free energy for assembly and reproduction from the intense ultraviolet light, while at the same time, by coupling to the water cycle, producing much more entropy than attributable to their metabolism and replication alone [4]. Such a view connects the visible light dissipation by plants and cyanobacteria today with UV light dissipating RNA/DNA in the Archean, and emphasizes life's continued involvement in the water cycle.

Geochemical evidence in the form of $^{18}\text{O}/^{16}\text{O}$ ratios found in cherts of the Barberton greenstone belt of South Africa point to an Earth's surface temperature of around 70 ± 15 OC during the 3.5--3.2 Ga. era [35]. These temperatures, near the beginnings of life (ca. 3.8 Ga), are close to the melting temperatures of RNA and DNA. An enzyme-free mechanism for replication can therefore be imagined in which absorption and dissipation of UV light into heat by the nucleic acids during the day increased the local sea-surface temperatures to beyond the denaturing temperature of RNA or DNA, allowing the separated strands to act as templates for extension during the cooler periods overnight [4]. Such ultraviolet and temperature assisted replication (UVTAR) bears similarity to polymerase chain reaction which is used to amplify particular segments of RNA or DNA in the laboratory [36]. Photon-induced RNA/DNA denaturation has been experimentally observed [37,38].

Replication of RNA and DNA could therefore have been promoted by the local diurnal variation of the sea surface temperature, due in large part to the absorption and dissipation of UV light by RNA and DNA at the ocean surface. Enzymes, and thus information content and reproductive fidelity, were not required until the sea surface temperature had cooled to somewhat below the melting temperature of RNA and DNA. Longer RNA or DNA segments that began to code for simple denaturing enzymes could continue replicating at colder temperatures, thereby initiating evolution through natural selection in response to a cooling ocean surface [4].

Scattering of unpolarized UV sunlight from water molecules and suspended particles and a subsequent total internal reflection of this light at the air-water interface, would have led to a component of about 5 % right-handed circular polarization during the afternoon near the sea surface [5], independently of the hemisphere, season, or terrestrial magnetic polarization reversals. Since the sea surface

temperature would be greatest in the late afternoon, this fact could have contributed to a gradual enhancement of RNA/DNA with D-enantiomer nucleotides because of the greater absorption cross sections for right- over left-handed circularly polarized light for these chiral molecules. Double strands containing L-enantiomer nucleotides would have been at a disadvantage since they would absorb less well the right-handed circularly polarized light of the late afternoon, and thus could not raise local water temperature as often for denaturation. These, therefore, would suffer from a somewhat lower probability of reproduction through UV and temperature assisted replication. RNA/DNA containing predominantly L-enantiomer nucleotides would tend to become locked in the double strand formation, effectively removing them as templates for facilitating further reproduction. Those with mainly D-enantiomer nucleotides could have continued replicating, and thus evolving.

The nomenclature, "left-" or "right-handed", is often not related to the true optical chirality of molecules. Optical chirality is collective to many asymmetric centers while the nomenclature refers to usually only one of them. Therefore, a quantitative theory of homochirality, based on differential absorption of circularly polarized light, requires a careful look at the full circular dichroism (CD) spectrum as a function of wavelength for RNA and DNA and their complexing with amino acids.

The CD spectrum of DNA and RNA depends on temperature, salinity, and pH. Higher temperature has the effect of reducing the amplitude of the circular dichroism with little effect on peak positions or zero crossings [39]. At neutral pH, the CD spectrum of DNA shows a negative band (greater absorption of right-circularly polarized light) with a maximum at 245 nm, extending to about 260 nm, and a positive band with a maximum at approximately 275 nm [40]. The negative band has been shown to be a result of base stacking [41] and is relatively independent of base content and secondary structure, while the positive band depends on these characteristics [40]. The CD spectrum of shorter polynucleotides shows a wider negative CD band spanning the region of 220 to 260 nm at neutral pH [39]. It is thus probable that this negative CD band was responsible for the gradual accumulation of homochirality in RNA/DNA through photon-induced melting in the ultraviolet and temperature assisted mechanism of replication described above.

Model Simulations

A racemic mixture of single strand RNA/DNA segments produced by UV photochemical reactions on atmospheric gases probably floated on the surface of a hot prebiotic Archean ocean (see [4] and references therein). These segments could begin to act as templates for reproduction as soon as the sea surface temperature at night dropped below their melting temperature. We now present a simple model, ignoring all unnecessary details, to estimate how rapidly chirality would have grown in the population due to the slightly greater melting probability for absorption of a right- over a left-handed circularly polarized photon of 255 nm where RNA/DNA absorb most strongly.

For a fixed ocean surface temperature, melting of RNA/DNA, and therefore the possibility for replication, would be, in first approximation, proportional to the amount of UV light absorbed. In reality, an energy threshold exists due to the hydrogen bonding between strands. (This threshold has important consequences and will be considered in an extension of the model given below.) The following recursion relations then give the number of left-handed and right-handed strands (nL_i and nR_i) at any given diurnal cycle i ,

$$nL_i = nL_{i-1}(1+c(P_{\{LL\}} + P_{\{LR\}})),$$

$$nR_i = nR_{i-1}(1+c(P_{\{RR\}} + P_{\{RL\}})), \dots\dots\dots(1)$$

Where $P_{\{LL\}}$ and $P_{\{LR\}}$ are the average (over all existing strands) relative probabilities that a left-handed RNA/DNA absorbs a left- and right-handed photon respectively. $P_{\{RR\}}$ and $P_{\{RL\}}$ are similarly defined, but for absorption on a right-handed RNA/DNA. All probabilities are taken relative to that of right-handed circularly polarized light absorption on right-handed DNA, $P_{\{RR\}}$, being this the largest since most melting would occur in the afternoon when surface temperatures were highest, and afternoon light is somewhat right-handed circularly polarized. Also, D-RNA/DNA have a negative circular dichroism band between 220 and 260 nm where RNA/DNA absorb strongly. Therefore,

$$P_{\{RR\}} = 1.0,$$

$$P_{\{LL\}} = \{(1.0 - \Delta_{\{RCPL\}})/(1.0 + \Delta_{\{RCPL\}})\},$$

$$P_{\{LR\}} = \{(1.0 - \Delta_{\{RCD\}})/(1.0 + \Delta_{\{RCD\}})\},$$

$$P_{\{RL\}} = \{(1.0 - \Delta_{\{RCPL\}})/(1.0 + \Delta_{\{RCPL\}})\} \times \{(1.0 + \Delta_{\{RCD\}})/(1.0 + \Delta_{\{RCD\}})\}. \dots\dots\dots(2)$$

where $\Delta_{\{RCPL\}}$ is the right-handed circular polarized light excess of the afternoon, and $\Delta_{\{RCD\}}$ is the right-handed circular dichroism excess. The $\Delta_{\{RCPL\}}$ of visible light in the afternoon today is only about 0.5% [8,42]. However, that due to multiple scattering in water and totally

internally reflected at the water-air interface is much greater, about 5% [5]. According to Gray et al. [39] the differential absorption of right- over left-handed photons $\Delta_{\{RCD\}}$ due to circular dichroism at 250 nm for short polynucleotides is about 4/6000. The "c" in equation (1) is a normalization constant that would depend on both denaturation factors (daytime intensity of the incident UV light, sea-surface temperature) and extension factors (the length of RNA/DNA strand, the concentration of nucleotides available at the sea-surface at night, the sea-surface temperature at night, duration of night, etc.). Until such values for the Archean are better constrained, an exact calculation cannot be made. However, for the sake of argument, we consider segments of up to 10 nucleotides in length, and take as a plausible value for "c" of one in 1,000 RNA/DNA segments reproducing through the UVTAR mechanism during each diurnal cycle, i.e. $c=0.001$ (For example, this is the probability that 10 nucleotides chosen at random from a racemic solution would have the same chirality, i.e. $(0.5)^{10}= 0.001$. In polymerase chain reaction with an unlimited supply of nucleotides, primers, and the enzyme polymerase, but much shorter extension times, this value is very close to one).

Using these values in the recursion equation ([ref{eq:recurs}](#)) together with an equation for the homochirality as a function of diurnal cycle i

$$HC_i = (nL_i - nR_i) / (nL_i + nR_i),$$

gives curve (b) plotted in figure 1. Given racemic initial values, nL_0 and nR_0 , the curve is independent of these initial values.

Fig. 1: Homochirality as a function of number of Archean days. (a) Including an energy threshold for denaturation related to the complementary strand binding energy, (b) assuming denaturation probability is simply proportional to the number of photons absorbed.

Since an Archean day was about 1/2 the length of an actual day, and assuming the orbit of Earth has not changed, figure 1 implies that practically 100% homochirality can be obtained in less than 50,000 Archean years.

The model can be refined by including an energy threshold for denaturation. Such a cut-off exists due to the specific temperature dependent hydrogen bonding energies between the two complementary strands. The threshold would be larger in the morning than afternoon because of a cooler surface temperature. Denaturation of right-handed RNA/DNA would therefore be further favored by this threshold since there is more right-handed circularly polarized light available in the afternoon. This threshold can be included in the model by randomly varying the $P_{\{RR\}}$,

$P_{\{LL\}}$, etc. by 5% about their nominal values (to mimic the statistical fluctuations of photon absorption) and setting the combined probabilities for denaturation $P_{\{LL\}} + P_{\{LR\}}$ and $P_{\{RR\}} + P_{\{RL\}}$ to zero if they fall below a specified limit. Such a threshold dramatically increases the rate of obtainment of homochirality, giving times as short as 500 Archean years (curve (a) of figure 1). A 1% replication rate, $c=0.01$, leads to obtainment of homochirality in only 50 Archean years (not shown). A greater right-handed circular polarization of submarine UV light during the afternoon, than that assumed of 5%, would decrease this time further.

Homochirality of the Amino Acids

If homochirality had been obtained for all the 20 amino acids of life before incorporation into the first replicating organism, through, for example, photolysing by circularly polarized light in space, then a spectral window for the circularly polarized UV light in which the circular dichroism band was large and of the same sign for all the amino-acids would have to exist. An analysis of the CD data of amino acids by Cerf and Jorissen [43] suggests that such a mechanism could not have been operating if tryptophan or proline were among the original amino acids. Furthermore, stability of the amino acids against racemization would have to be demonstrated. The alpha-methyl amino acids found with non-negligible enantiomer excess in meteorites have sufficient stability against racemization [44], but the alpha-hydrogen amino acids composing the 20 natural amino acids of today's proteins do not [45]. Furthermore, experiments on photolysing of the amino acids have demonstrated only weak enantiomer excesses of a few percent ([44] and references therein). Uncertainty also remains as to whether life based amino acids have yet been detected in space, where photolysing possibilities may be greater than on Earth.

A more plausible alternative for the homochirality of the amino acids is chiral discrimination by D-nucleic acids, resulting from its structural complementarity with L-amino acids. Evidence of chiral selectivity of activated L-amino acids by DNA through protein intercalation between adjacent base pairs has been obtained by Barton et al. [46]. Reich et al. [47] have demonstrated experimentally that D-nucleic acid in the cholesteric form (with the molecule folded in on itself) has greater affinity for the poly-L-lysine than for poly-D-lysine. Also, using molecular modeling

techniques, Bailey [48] has shown that D-RNA constrained to a surface selects preferentially for L-amino acids. Such post chiral selectivity for the amino acids has resonance with the thermodynamic dissipation theory of the origin of life because in this theory enzymes are postulated to have arisen later in life's history as the Earth's surface temperature cooled and conditions began to stray from those favorable to UV and temperature assisted replication of RNA/DNA. As sea surface temperatures cooled and its salinity increased, longer RNA/DNA segments would spontaneously take on cholesteric forms [47] in which the right-handed double-helix folds in on itself to produce a supra-molecule with enhanced right-handed asymmetry. The circular dichroism of these cholesteric forms is positive within the 200-300 nm region [47] and these by themselves would therefore not absorb as well the right-handed circularly polarized light of the afternoon. However, Reich et al. [47] have also shown that L-amino acids have a significantly larger affinity to D-DNA in the cholesteric form than do D-amino acids, and thus L-amino acids would have been naturally selected by these. These D-DNA+L-amino acid complexes have, in fact, a negative circular dichroism over the whole 200 to 300 nm region [47], implying greater absorption efficiency for the right-handed circularly polarized light. These D-DNA+L-amino acid complexes would then be more able at raising the local water temperature to beyond the denaturing temperature, providing the templates for reproduction during cooler periods.

Conclusions

Hitherto proposed mechanisms for the homochirality of the biomolecules, invoking an abiotic mechanism for producing a prebiotic enantiomer enrichment, have not been generally accepted for lack of plausibility or relevance. The thermodynamic dissipation theory for the origin of life offers a novel possibility in which the mechanism for the obtainment of homochirality is an integral part of the replication mechanism for emerging life, promoted through asymmetric right- over left-handed photon-induced melting of RNA/DNA due to a negative circular dichroism band extending from 220 nm up to 260 nm for small segments. Photon-induced melting would be much more effective in producing homochirality than photoreaction, photocatalysing, or photolysing because it deals with weak hydrogen bonds rather than strong covalent bonds. Further, since the mechanism operates close to the denaturing temperature of RNA/DNA, there exists a temperature dependent threshold related to

the strength of these bonds which becomes greater as the sea surface cools, thereby favoring D-RNA/DNA. The mechanism, in analogy with polymerase chain reaction, but unlike previously proposed mechanisms, produces an exponential increase in chirality in the population with diurnal cycle. Homochirality, the ratio of the difference of populations to their sum, thus increases linearly while the enantiomer populations are similar (Fig. 1). This is a case of a far-from-equilibrium process operating under varying boundary condition, rather than an example of a non-equilibrium spontaneous symmetry breaking process.

The most plausible scenario for the homochirality of the amino acids is that of chiral selectivity of D-nucleic acid for L-amino acids due to complementarity of structure, particularly when DNA is in its folded cholesteric form, of relevance to longer strand RNA/DNA. This, in turn would have relevance to post origin of life colder sea surface temperatures when enzymes to aid denaturation became necessary [4]. D-DNA+L-amino acid complexes have negative circular dichroism over the entire 200 to 300 nm region, while D-DNA+R-amino acid complexes have positive circular dichroism over this region [47]. D-DNA+L-amino acid complexes would thus have greater replication probability under the UV and temperature assisted replication theory.

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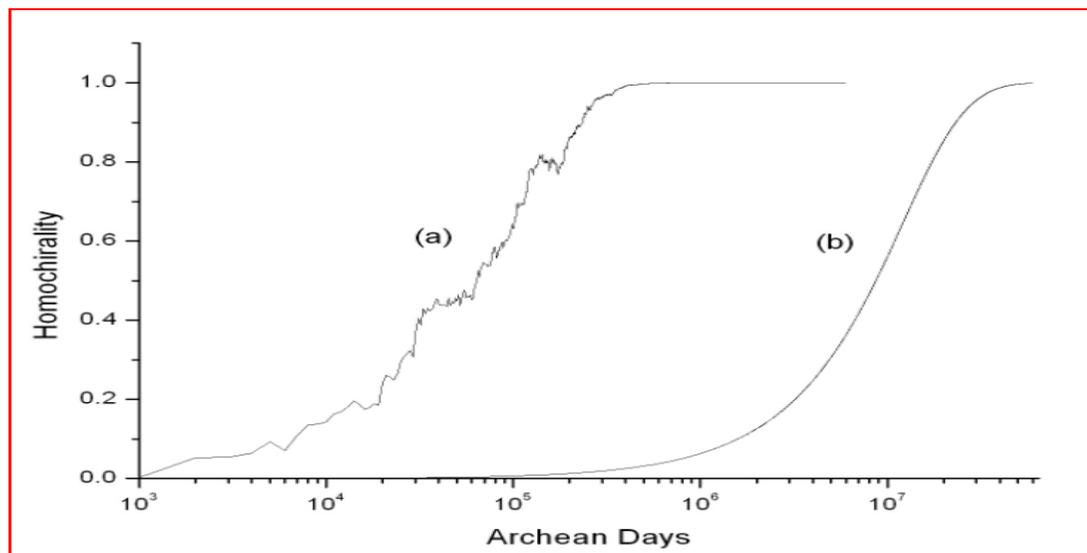
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Illustrations

Illustration 1

Figure 1

Homochirality as a function of number of Archean days. (a) Including an energy threshold for denaturation related to the complementary strand binding energy, (b) assuming denaturation probability is simply proportional to the number of photons absorbed.



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