Racemization of amino acids under natural conditions: part 1—a challenge to abiogenesis

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Three-dimensional structure is a minimum prerequisite for protein functions. I show that even for optimized amino acid sequences under ideal laboratory conditions only 5–10% randomly distributed D-amino acids would prevent polypeptides composed of L-amino acids from forming a stable structure in water. Parity violation and selective degradation of one amino acid enantiomer by circularly polarized light could not have produced the necessary L-amino acid excess. Carefully designed experiments to amplify an initial enantiomeric excess using partial sublimation, crystallization separation techniques, isolation of eutectic mixtures, chiral minerals, and chiral auxiliaries are not plausible naturalistic solutions for the origin of large enantiopure peptides.

Professor Bada pointed out, in 1991, that "Currently, considerable controversy exists about the source of the organic compounds necessary for the origin of life on Earth."[1] Only a limited variety of organic molecules would have formed and in at best only trace quantities given the insignificant amount of reducing gases thought to have been present in the early earth.[2–5] The alleged frequent impacts of objects 10–100 km in diameter on the early earth would have pyrolyzed all organics present and prevented the origin of primitive organisms.[5] Furthermore, the annual source of amino acids (AAs) into the oceans from micrometeorite and cosmic dust which survived pyrolysis during atmospheric passage would have been $< 3 \times 10^{-15}$ g/l per year.[1] The maximum accumulation time would have been about 10 million years, since the entire oceans would have circulated through the hydrothermal vents during this time period, completely destroying AAs. Bada concluded that the maximum concentration of AAs in ancient oceans would have been only about 10^{-8} g/l, which corresponds to a concentration of $\sim 10^{-10}$ M, using an AA average molecular weight of about 110 daltons.[1]

In this 4-part series I will document laboratory data to help quantitatively evaluate abiogenesis scenarios. Future papers will rely on these to make my critiques more precise.

The homochirality problem

All proteinogenic AAs except glycine can exist as D or L enantiomeric forms, which are non-superimposable mirror images of each other (figure 1). Since Louis Pasteur's discovery of chiral crystals in 1848, scientists have been searching for a naturalistic origin for the homochirality of biomolecules. Homochirality refers to the use of almost exclusively L-AAs to form proteins and of D-sugars (figure 2) for RNA and DNA polymers.

Enantioselective synthesis of chiral molecules has been researched intensively for two centuries, providing deep understanding and techniques for medical and industrial purposes. The rewards are high. Knowles, Noyori, and Sharpless won Nobel prizes in 2001 for their work on chiral catalysis. But for abiogenesis purposes the conditions must be naturalistic and not expertly designed.

The efforts to find a naturalist explanation of homochirality in biochemistry was summarized by Professor Quack at the ETH Zürich university:

> "We think that no clear answer to the question of the origin of biochemical homochirality exists at present or is to be expected in the near future. Minimal conditions for such an answer would be that 1) in each possible mechanism for a desired selection all possible control experiments for proving the opposite outcome must be carried out and 2) the precise mechanism by which the effect leads to a selection of homochirality must be theoretically understood. To our knowledge none of the numerous suggestions existing today come even close to satisfying these minimal requirements."[6]

In the same paper Quack added:[6]

> "Each time some new effect for some perhaps possible mechanism in chiral selection comes up in the literature, this is quickly praised as the 'solution to the problem' (sometimes with cautious remarks in very small print) in the popular science press. There was a considerable amount of speculation in relation to the early findings of the stabilization of L-amino acids and D-sugars by parity violation.[7–11] These results were, however, refuted by recent theory."[12–25]

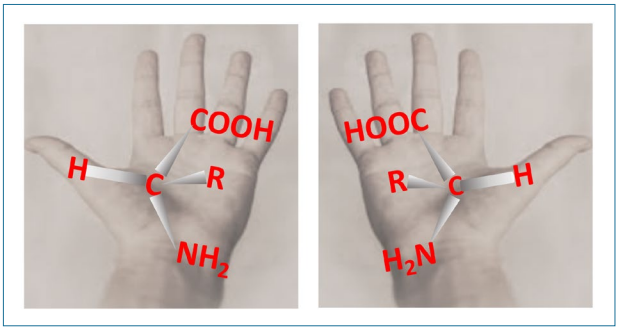

Figure 1. All proteinogenic AAs except glycine can exist as D- or L-enantiomeric forms, which are non-superimposable mirror images of each other.

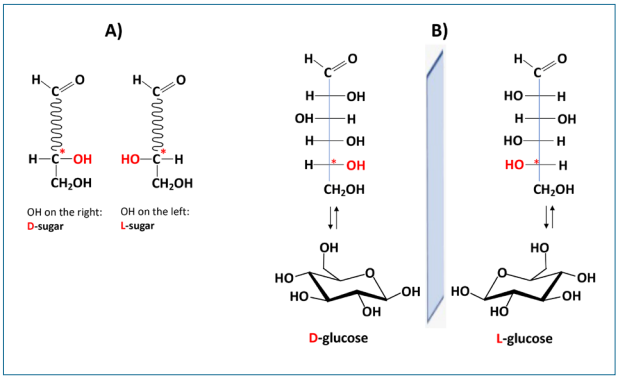

Figure 2. Nomenclature of D- and L-sugars. **A)** Using a Fischer projection locate the chiral carbon (C*) farthest from the carbonyl group (C = O). When the OH group is on the right side it is a D-sugar, otherwise an L-sugar. **B)** D- and L-linear and cyclic glucose.

He illustrates with an example:[6]

> "The alleged excess of L-amino acids found in meteorites is a fairly typical case with 'proof' and 'refutation' being repeated more than once."

I am planning to publish a detailed analysis of the key proposals elsewhere. The overview below will prepare the groundwork for understanding how rapid and inevitable AA racemization, covered in part 2, further discredits all of them under naturalistic conditions.

I. Potential sources of enantiomeric excess

Two approaches are used to attempt to explain the symmetry breaking: *parity violation* in otherwise identical molecules; and *selective degradation* of one enantiomer by circularly polarized light.[16] These hypothetical proposals lead to an enantiomer excess (ee)[17] much too small for abiogenesis purposes.

Parity violation

In nuclear physics, the weak interaction is one of the four fundamental interactions, and involves the interaction between subatomic particles, which produces β-decay of atomic nuclei.[18] Unlike the other fundamental interactions (gravitation, electromagnetism, and the strong interaction), it violates parity, i.e. symmetry rules.[19] The so-called z force interacts between the electrons and the atomic nucleus and can differentiate between right and left. This energy is called the parity violating energy difference (PVED).[20]

Enantiomeric excess of an L amino acid, ee_L is defined as (L – D) / (L + D). In practice, it is usually expressed as a percent. A tiny parity-breaking energy difference on the order of 10^{-14} J mol^{-1} could theoretically produce ≈ 10^{-15} % ee_L in a proteinogenic amino acid (AA).[16] This is based on parity differences in the weak interactions observed during radioactive decay of polarized ^{60}Co nuclei.[6,20–22] For biomolecules, *ab initio* theoretical calculations of the parity-violating energy difference predict that left-handed AAs and some D-sugars are more stable.[23] Symmetry violation cannot be unequivocally proved empirically, being below the current levels of detection.

Different computational techniques lead to different values, and so does the choice of conformation of molecules,[20] whereby the motivation is focused on finding and reporting the highest energy differences possible. Additional *ab initio* calculations by Mason and Tranter, in 1983, suggested a slightly larger energy difference.[20,24–27] They concluded that the parity-violating stabilization of an L-peptide, relative to the corresponding D-peptide, in the α-helix or the β-helix conformation is at most ~ –2 x 10^{-14} J mol^{-1} per amino acid residue, which suggests an enantiomeric excess of some 10^6 L-peptide molecules per mole (i.e. 6.0 x 10^{23} molecules) of racemate in thermodynamic equilibrium at ambient temperature.[28] This effect is still much too small for any chemical relevance.[29] The energy difference estimates for hydrated glyceraldehyde relevant for producing sugars range between 0.5–2.6 x 10^{-13}J mol^{-1}.[20]

Another method developed by Quack *et al.* called configuration interaction singles—restricted Hartree–Fock (CIS-RHF) to calculate parity violating potential E_{pv} also led to slightly higher values than the widely used SDE-RHF (single determinant excitations—restricted Hartree–Fock) method. This predicted an ee_L of ≈ 10^{-14}% for alanine, valine, serine, asparate, and glyceraldehyde.[30,31] These miniscule effects are contingent on the calculation technique used, and clearly there is a motivation to find and report examples of symmetry violation, although Quack and others have denied an energy preference in the case of L-alanine.[20]

To put things in perspective, Quack warns that[6]

> "The *de lege* (parity violation) community often expresses the belief that, because we know for certain that there is some preference at the molecular level that is caused by parity violation, there must 'somehow' be a connection to the evolution of biomolecular homochirality at the next higher level of organization. Such an argument can be easily refuted."

Selective degradation of one enantiomer by circularly polarized light

Theoretical considerations have led to the proposal that one enantiomer could be predominantly degraded by circularly polarized light (*CPL*), leading to an enrichment (under optimized conditions not expected to arise naturally) of ≈ 0.1% ee D or L, depending on the light source.[6,16,32,33] This can occur when a racemic mixture of molecules with sufficiently small excited electronic state barriers to enantiomer inversion is irradiated with CPL at a suitable wavelength.

The production of optical activity through CPL might occur through different mechanisms such as (i) the preferential decomposition of one enantiomer of a racemic mixture, (ii) asymmetric photosynthesis, or (iii) photo-interconversion of the enantiomers of a racemate.[34–36]

Selective degradation of leucine enantiomers on film

Chiral solid-state amino acids might have been exposed to circularly polarized vacuum ultraviolet (VUV) electromagnetic radiation before arriving on Earth. Meierhenrich *et al.* experimented with solid-state D,L-leucine 1-µm-thick films deposited on a MgF_2 window. These were irradiated with left circular polarized synchrotron radiation (l-CPSR) and right-CPSR (r-CPSR) at 170 and 182 nm in various experiments, inducing photochemistry via the (π^*, π_1)-electronic transitions.[37] Leucine was selected since it has the largest anisotropy factor g ($g = \Delta\varepsilon/\varepsilon$) among proteinaceous amino acids and therefore should provide the largest ee. This single-photon electronic excitation of AAs led to destructive photolysis, mainly by decarboxylation. Therefore, irradiating D,L-leucine with r-CPL (circularly polarized light) at the right wavelength was expected to produce an ee of the surviving L-leucine, and vice versa.[37]

A major drawback of direct photochemistry with CPL is that extremely low ee values are obtained unless a high-intensity source is utilized. After 70% photodecomposition, the highest ee reported was + 2.6% D-leucine when irradiating with only r-CPSR, but only at precisely 182 nm.[31,37] Remarkably, irradiation with l-CPSR, also at 182 nm, produced an ee of only 0.88% L-leucine.[31,37] The symmetric overabundance of the 'wrong' D-enantiomer is not very satisfying, and the authors attributed the difference to inexactitudes in the experimental setup. Table 1 summarizes their results. In three of the four experimental conditions the 'wrong' D-leucine is formed in excess, since at λ = 170 nm r- and l-CPSR both preferentially destroyed L-leucine.

What would happen naturally? The slight difference in absorption by D- or L-AAs has been shown experimentally to reverse at different wavelengths.[38] AAs would be exposed to a range of wavelengths, and a mixture of left and right-handed CPL sources will randomize the effect, tending to cancel out any ee.

Table 1. Enantiomeric excesses (averaged over three to six samples) obtained after irradiating D,L-leucine with l-CPSR (circular polarized synchrotron radiation) and r-CPSR[37]

Sample	λ [nm]	Irradiation	ee (d-leucine) [%]	CI_{95}[b]
1	182	l-CPSR	-0.88	0.28
2	182	r-CPSR	2.60	0.16
3	170	r-CPSR	0.75	0.36
4	170	l-CPSR	0.48	0.48

[b] CI_{95} = confidence interval at 95%.

II. Enantiomeric amplification

There is consensus in the pro-evolution community that there is no known process able to produce the necessary highly pure L-AAs required for abiogenesis purposes. Instead, much effort is being devoted in laboratory methods to 'amplifying' small excesses of L-enantiomer AAs. The concept is to concentrate one enantiomer and physically separate it from the other in some restricted location. Note, however, that this *automatically enriches the mirror enantiomer* elsewhere.

Partial sublimation

Partial sublimation of racemic AAs at very high temperatures can sometimes separate some D- and L-AAs.[39–41] However, D- and L-amino acids which are separated by a few millimetres could easily remix, especially once dissolved in water.

Separation of crystals

Some DL racemic crystals of AAs are less soluble than the pure D- and L-crystals, so, if one enantiomer is present in excess, the liquid phase can be enriched by carefully crystallizing out the racemic DL- form.[42–45] This can be enhanced by taking advantage of the fact that stabler, larger pure D- or L-crystals sometimes form when that enantiomer is present in higher proportion.[42–46] Viedma and others have argued that in a few rare cases a small initial ee_L of some AAs could be concentrated. The L-form crystals can form preferentially, benefitting from the larger number of initial L-crystal seeds made available by the researcher.

Under special conditions, this can be enhanced for some AAs using a carefully designed continuous abrasion-grinding process, which breaks smaller crystals preferentially.[43,47,48] However, forming L-enantiomer crystals would automatically enrich the solution phase in the D-enantiomer, quickly hindering formation of more crystalline L-form. Therefore, Viedma added a substantial amount of an appropriate aldehyde to a highly concentrated AA in an aliphatic acid such

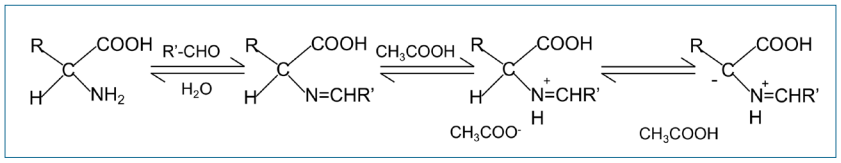

Figure 3. Racemization mechanism of amino acids with an aldehyde under acidic conditions[51]

as acetic acid at a high temperature.[49] Racemization thereby converted the excess D produced in the solution phase to L-form,[50] via the mechanism shown in figure 3. Protonating the imine produced by reacting AA with aldehyde is followed by proton abstraction from the α-carbon atom by the acetate anion, leading to the key planar carbanion intermediate which permits racemization.[50]

Suitable aldehydes presumably would have been present in adequate concentrations according to various abiogenesis scenarios, including influx from extra-terrestrial sources. But it is implausible that AAs with an excess of L-form would place themselves in a suitable hot mineral acid environment fortuitously co-located with an appropriate aldehyde, over and over, to produce a variety of L-amino acids in large quantities. Importantly, without intelligent organization the overall outcome would be devastating for naturalistic abiogenesis: faster indiscriminate racemization of *all* proteinogenic AAs. Viedma's solution provides yet another means to accelerate racemization throughout nature. The chemists who developed these laboratory and manufacturing enantiomer separation techniques before Viedma make no claim of relevance to abiogenesis.[50] (Traditional laboratory procedures, which can also be done in neutral or weakly alkaline conditions, use an aldehyde with a metal ion which forms a chelate compound with the initially formed Schiff base.[16])

Instead of removing DL-racemic crystals from an aqueous solution, Viedma showed, in 2001, that racemic aspartic and glutamic amino acid aqueous solutions can be made to crystallize as conglomerates under special supersaturated conditions. In conglomerates, D- and L-crystals form which are physically separated. The effect can be enhanced by partially immersing porous fire brick in the solutions to allow capillary rise.[52] Viedma does point out the obvious, that the spontaneous resolution mechanism over time will produce an equal number of opposing resolutions, with no net enantioselectivity.[52]

Among all proteinogenic AAs, asparagine and threonine form conglomerates spontaneously, which are pure separate D- and L-crystals.[28,53] For preferential crystallization to work, the homochiral interactions must be stronger than heterochiral interactions at the interface crystal–mother liquor. In theory, an excess of one enantiomer could be separated as a pure crystal.[54] Of course, for origin-of-life speculations an eternally frozen crystal of L-amino acid would serve no purpose. It would have to dissolve in water to form peptides at some point, racemizing to D-form and mixing with racemic amino acids from the environment.

Separation using the eutectic point of mixtures

Specific proportions of mixtures sometimes liquify/solidify at a lowest temperature called the eutectic.[55] Some combinations of amino acid enantiomers are indeed less soluble at various temperatures than pure D- or L-enantiomers, allowing separation in laboratories if done carefully.[56–58] Remixing occurs upon dissolving in water again, of course.

Use of chiral minerals

Some chiral minerals, such as quartz, can exist as dextro- and levorotatory enantiomorphic forms. But even carefully optimized laboratory experiments by Bonner *et al.* could only generate low ee values such as 20% for D alanine.[59–62] Extensive examination has shown, however, that D- and L-quartz are present in equal amounts worldwide, so once again no net enantiomeric preference would result.[63,64]

Use of chiral catalysts or auxiliaries

An approach to form L-AAs in excess involves mediation by chiral catalysts or chiral auxiliaries. This does not address the origin of their own optical purity, of course. One proposal involves the Strecker reaction using a mixture of D-pentose.[65] Breslow chirality transfer reactions via transamination have also been suggested.[66] However, the enantiomeric excesses of the products are much lower than that of the molecules from which they are transferred and would have to be co-located at the reaction location. For example, to obtain even a small excess of an AA, the fraction of pure sugar present had to be unrealistically high in one series of experiments.[65] Furthermore, some D-sugars increased, and others decreased the ee of the AAs tested, randomizing the net outcome.[65]

Breslow *et al.* found that non-proteinogenic α-methyl AAs found on meteorites could transfer their chirality during the synthesis of normal AAs.[66] (The α-methyl AAs differ from biological ones by having a methyl instead of hydrogen attached to the α-carbon.) However, they obtained the wrong products in excess (i.e. D-AAs) and had to experiment extensively to obtain the opposite outcome desired.

Their solution required using one equivalent of cupric sulfate, one equivalent of sodium pyruvate or sodium phenylpyruvate, and 4 equivalents of 96% pure L-α-methyl amino acid dissolved in water and vigorously stirred. All the reactants would need to be co-located in unrealistically high concentrations. (Anhydrous copper (II) sulfate is found naturally but as the very rare mineral chalcocyanite). The optimized and

unrealistic special conditions finally led to L-phenylalanine with 37% ee and L-alanine with up to 20% ee.

This experiment illustrates a principle encountered in virtually all abiogenesis work. Researchers set up the precise laboratory conditions which force the outcome desired, often terminating the reactions before the inevitable wrong things then take over. We saw above that Viedma's proposed addition of aldehydes would facilitate racemization of AAs throughout free nature, the last thing naturalists wish to demonstrate. Breslow introduced a high concentration of Cu^{2+}, which, we will point out in part 2, accelerates amino acid racemization in water everywhere.[67] Again, the opposite to what naturalists wish to demonstrate. Such special-purpose-designed intervention in abiogenesis papers is ubiquitous; one must always carefully examine the experimental details.

III. Minimum homochirality to form polypeptide structure

What proportion of D-residues could a protein tolerate and remain functional? 5% of an average sized 300-residue protein represents fifteen positions. Large proteins with one or multiple secondary structures such as α-helices and β-sheets (figure 4) offer many ways to be rendered nonfunctional through L → D replacements. Most functional proteins would not tolerate fifteen randomly occurring residue inversions. The percentage tolerable will decrease with increasing protein size. A 3,000-residue protein would be worthless long before 150 randomly located residue replacements occurred.

A collection of random-sequence racemic peptides would not provide the reliable three-dimensional structures necessary for life-like chemical activities. Neglecting the need for having the correct sequences, about what proportion of the AAs would need to be L-enantiomers? To provide a minimum structure for something functional to occur, at a minimum one secondary structure (α-helix or β-sheet) would be needed. We will use experimental data available to see what ee_L would be needed to produce the simplest realistic β-sheet reliably. Some have suggested that α-helical L-peptides can cope with some D contamination,[69] but this leads to distorted and unstable α-helices.[70] In any event, evolutionists claim β-sheet structures arose first,[70] and we have the necessary detailed experiments to perform some mathematical analysis. In aqueous solution, short amphiphilic peptides do not generally possess a complete helical structure, so surfactants or liposomes are needed to help form alpha helices as small as 12 or 13 residues. In one experiment a helix structure for $(Leu\text{-}Asp\text{-}Asp\text{-}Leu)_n$-Asp could be induced with the appropriate concentration of Zn^{2+} for peptides between 13 and 25 residues, but the sensitivity to L → D substitution was not determined.[71]

Brack and colleagues showed, in the 1970s, that $(Leu\text{-}Lys)_n$ β-sheets are very sensitive to the incorporation of about 5% D-isomer and will only form fleetingly at ambient temperatures with *seven or more* of the correct homochiral residues in a row. Even this was only possible under optimized conditions, such as including the right coordinating metals and an aqueous media with high ionic strength.[71–74]

Salt ($NaClO_4$) concentrations had to be set as high as possible to produce these structures but not so high as to cause precipitation. It is very difficult to dissolve large poly(Lys-Leu-Lys-Leu) molecules, known to be fully in the β-form in salted solution.[74] Based on his observations, Brack concluded that large soluble β-sheets won't arise naturally, even when a small excess of one enantiomer is present, since the side chains would be forced into the plane of the β-sheet, generating conflicting steric contacts.[74]

Brack pointed out that some proteinogenic amino acids have been identified in the Murchison meteorite: Glycine, Alanine, Proline, Leucine (Leu), Isoleucine, Valine, Aspartic acid (Asp) and Glutamic acid (Glu).[73] Notice, however, that Lysine (Lys), used in the study above, was not found, and Leu was only present in trace amounts, rendering the relevance to abiogenesis reasoning doubtful. Our review of the literature on meteorites confirmed that Asp and Glu were reported in all the key studies we examined, but no Leu nor Lys, for example in three Antarctic CR chondrite meteorites, EET 92042, GRA 95229, and GRO 95577[75]; Tagish Lake meteorite samples[76]; Sutter's Mill Carbonaceous Chondrite;[77,78] and Aguas Zarcas.[79]

Brack *et al.* then examined other oligomers of varying sizes, whereby Leu continued to be used (being a very effective hydrophobic residue and optimal to form β-sheets) with an equimolar amount of Asp, Glu, or Lysine (Lys) as the hydrophilic residue. Water-soluble β-sheets using $(Glu\text{-}Leu)_n$ and $(Asp\text{-}Leu)_n$ chains could be produced when prepared properly. In pure water large poly(Glu-Leu) exists only as a random conformation. Adding NH_4^+ ions to a final 0.1 M solution converted it to water-soluble β-sheets due to shielding of the charged side chains by the salt. Monovalent cations, such as Li^+, Na^+, K^+, Rb^+, or Cs^+ ions, were not suitable for this purpose.[73] However, divalent cations Ca^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, and Hg^{2+} did induce β-sheets if the metallic ion / Glu ratio did not exceed 0.3 to 0.5. Mg^{2+} ions led to less soluble β-sheet structures, and CdS, which was also tested, precipitated with the polypeptide.

For the smaller oligomer $(Glu\text{-}Leu)_9$, steady addition of increasing amounts of $CaCl_2$ from 0.1 to 0.3 equivalent increased the formation of β-sheet, but 0.5 equivalents totally precipitated the peptide. The smaller $(Glu\text{-}Leu)_2$ oligomer is very soluble in salts but never produced any β-structure under any conditions tested.[73] Addition of 0.5 equivalent of

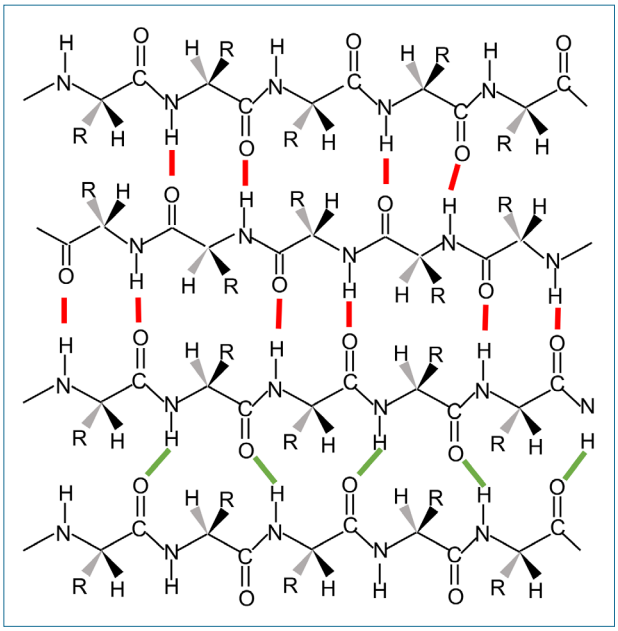

Figure 4. Schematic representation of a four-strand *β*-sheet. Hydrogen bonds are identified with red lines when the strands are antiparallel and green lines for parallel strands connecting the hydrogen and receptor oxygen. Based on an example from ref 68.

$CaCl_2$ to very large poly(Asp-Leu) also induced formation of a β-sheet.[73]

Notice that these peptides use an equal proportion of Leu and the hydrophilic partner. Is this reasonable? In an extensive study of the Murchison meteorite, reported in 2017, Koga and Naraoka found Asp, Glu, and Leu but no Lys.[80] To avoid the uncertainties introduced by considerable contamination from terrestrial L-enantiomers, we will consider only the reported concentrations of the D-form to calculate the relative proportion of Asp / (Asp + Leu) and Glu / (Glu + Leu) in the Murchison meteorite report. The former was 0.79 and the latter was 0.80. Therefore, the proportion of sequences having the minimum of 7-residues with a correct pattern (Leu-Glu-Leu-Glu-Leu-Glu-Leu) would be about $0.2^4 \times 0.8^3 < 10^{-3}$.

10^{-3} is an overestimate of the average homochiral proportion which would form, for several reasons. Multiple copies would be needed for abiogenesis purposes, and if the necessary AAs were fortuitously available in some isolated environment, the Leu would be steadily consumed, making each new copy ever less probable. If β-sheets were to form using the residues Asp and Glu, then matters are statistically even worse.[80] Now the proportion with the right pattern would be about $0.1^4 \times 0.9^3 < 10^{-4}$. Disruption by insertion of occasional glycyl is also known to decrease dramatically the tendency to form β-structures,[81] and Gly was about twenty times more abundant on the Murchison meteorite than the other L-proteinogenic AA. All this ignores the fact that the laboratory conditions necessary to produce the oligomers would never occur realistically.[82]

Nevertheless, Brack's work provides important insights to estimate how pure L-AAs must be for a polypeptide to possess a structural feature reliably, a minimum prerequisite for functionality.

Our goal is to determine how pure L must be to generate a seven-residue L-only pattern $(Glu\text{-}Leu)_3$-Glu by chance, with at least 50:50 odds.[83] For [L] = [D], p(L) = 0.5 we obtain $0.5^7 \approx 0.008$. A reliable supply of minimally functional β-sheets won't be produced from an amino acid mixture. Increasing the proportion to p(L) = 0.9 one obtains $0.9^7 = 0.48$, and now almost half the sequences would be L-AA and thus suitable in principle to generate a β-sheet.

p(L) = 0.9, meaning 90% L-AA in this abiogenesis environment, is not enough on average, since it only results in occasional and fleeting formation of a smallest-possible β-sheet under exceedingly unlikely conditions. We use other work published by Brack to illustrate. Asp side chains are more effective than Glu in forming β-sheets,[71] and $(Asp\text{-}Leu)_5$, $(Asp\text{-}Leu)_{10}$, and $(Asp\text{-}Leu)_{15}$ in water did not produce β-sheets at all. Cationic metal ions can interact with acidic side chains to inhibit charge repulsions, but no β-sheets were observed even if NH_4Cl, $CaCl_2$, or MgCl2 were added to $(Asp\text{-}Leu)_5$ and $(Asp\text{-}Leu)_{12}$.

β-sheets did form partially for $(Asp\text{-}Leu)_{15}$ in the presence of 0.5 molar equivalents Ca^{2+}/Asp residue, 1 equiv Mg^{2+}/Asp, or 0.3 equiv Fe^{3+}/Asp. Only addition of ~ 0.4 equiv Zn^{2+}/Asp was found to induce a complete random coil to β-sheet transition in the large $(Asp\text{-}Leu)_{15}$, but no β-sheet for $(Asp\text{-}Leu)_5$ and with $(Asp\text{-}Leu)_{12}$ only partially.[71]

The latter provides the data we need. Asp and Leu are optimal residues to form β-sheets and 0.4 equiv. Zn_2/Asp is an optimal condition, yet β-sheets only form partially. $(Asp\text{-}Leu)_{12}$ represents 24 L-residues; let us arbitrarily assume that two could be replaced by D-residues to favour the naturalist position in oligomers with optimal pattern $(X\text{-}Leu)_{12-1}$, where X = Asp, Glu, or Lys. The environment would require an L-proportion of ≈ 97% (i.e. $0.966^{20} = 0.50$). For comparison purposes, β-sheets in biological proteins consist of four to ten residues and are formed from three or more strands.[84]

Conclusions

No matter how an excess of L-AAs might be produced or resolved ('amplified') in some location, Bada points out that[85]

> '… racemization places an important restraint on any proposed mechanisms for the origin of optically active amino acids on Earth since racemization would rapidly convert any optically active amino acids back into an optically inactive or racemic mixture."

The concentration of AAs in a primitive ocean would have had to be very low, on the order of 10^{-10} M.[1] I propose that the presence of only 5–10% D-amino acids, or this amount of L → D conversion in peptides of size 20 or fewer residues, would prevent reliable secondary structures from forming, a minimum requirement for abiogenesis models. However, none of the proposed naturalist sources of ee_L proposed could produce anywhere near this level of purity.

In part 2, I will examine how fast amino acid racemization occurs. I will consider the effect of acceleration through chelation with dissolved metal ions like Cu^{2+}; temperatures above 0° C and occasional intense heating from volcanos or meteorite impacts. Initially pure L-AAs and those found in peptides would racemize quickly, and we now realize this needs to occur for only 5–10% of the material to render it worthless for abiogenesis models.

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