Enantiomeric amplification of L amino acids: part 1—irrelevant and discredited examples

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Naturalist explanations for the origin of proteins based on only L-amino acids (AAs) have concentrated on the notion of an initial enantiomeric excess (e.e.) being amplified. The processes discussed here couldn't plausibly have occurred naturally. Amplification examples include chemical reactions irrelevant for living organisms, like Soai alkylation and cyclobutene polymerization. Examples of selective adsorption on minerals such as kaolinite and montmorillonite clay have been discredited by other researchers. Adsorption on chiral calcite and quartz would have produced identical amounts of D and L enantiomers overall. Causing a specific glycine crystal face to extract only L-AAs from a racemic solution required pure D leucine be adsorbed on a different face. Cleverly designed AAs with large alkyl groups formed conglomerates of single enantiomer chains but the products remained inseparably mixed, and the molecules are not relevant biochemicals. Using a Langmuir trough to form crystalline islands of opposite handedness required chemical transformations and laboratory processes not found in nature. In all the proposals there is no credible reason why separated AA enantiomers would not remix. Furthermore, any e.e. produced would racemize in water over time and combine with already racemized AA in the environment.

Key biomolecules such as proteins, RNA, and DNA can only function if their constituent monomers use a single enantiomer (mirror image variant). Truman explained in this journal how secondary structures, the basis for protein-reliable folded structure, won't form if poisoned by merely c. 5% randomly inserted D-amino acids (AAs).[1] Goldanskii and Kuzmin also showed, using molecular models, how inserting a few L-sugar nucleotides in double-stranded helices prevents H-bonding across the two strands of DNA.[2]

D-amino acid residues are included in proteins in some rare cases, to add structural and functional diversification or to provide chemical robustness. This opposite chirality is produced through posttranslational conversion of an L → D residue and not by incorporating D-amino acids from the environment.[3]

Given their symmetry with respect to each other, it is often assumed that the physical and chemical properties of AA enantiomers would always be identical, preventing their separation under natural conditions. However, as we will see in this series, this intuition is not correct for all circumstances.

The error arises from failing to recognize that homochiral dimers (L-L or D-D) and heterodimers (L-D) won't experience identical physical interactions. Diastereomeric aggregates occasionally possess different physical properties after chemical bonding or even when non-covalent packing interactions are strong.

Creation scientists must not be careless and claim that racemic mixtures of AAs and sugars must always be found under natural conditions.

Chemists know that when amino acids and sugar molecules possessing chiral carbon atoms are synthesized in a laboratory racemic mixtures are obtained unless a suitable template is used. This could be an asymmetric enzyme, reagent, or catalyst.[4] But then the question becomes: where do these pure enantiomeric substances come from?

As far as I am aware, no specialist in the Origin of Life (OoL) community argues that a prebiotic earth contained only L-AAs, which therefore would have had to be used when forming peptides. The current naturalist approach consists of trying to explain two complementary processes. In Process 1 discussed in detail below, an initial enantiomeric excess of the L isomer ($e.e._L$), defined by equation (1), is assumed to have been somehow produced.

$$e.e._L = ([L] - [D] / [L] + [D]) \quad (1),$$

where [L] and [D] are the concentration of each enantiomer.

After an initial e.e. has been produced, somehow Process 2 is assumed to have locally concentrated, or amplified, this excess. For L to be concentrated in one location, it must automatically be depleted from where it was extracted. The total amount of L remains unchanged. A key assumption is that the two nearby regions do not remix.

In this series, I will be focusing on Process 2 and showing that none of the proposals that I am aware of could have had an effect of any relevance for OoL purposes and, in most cases, couldn't plausibly have occurred naturally without intelligent guidance.

It is important to distinguish between natural conditions and expertly guided outcomes. Louis Pasteur was able to

physically separate two versions of hemihedral crystals formed from a racemic mixture of sodium ammonium tartrate by selecting each using a lens and tweezers.[5] In addition to the willful choice being made hundreds of times to separate both kinds of crystals, formation of these kinds of crystals is very difficult even when carefully guided in a laboratory by professional chemists.[6]

An important and recurring principle in this series is that any $e.e._L$ formed must be eventually made available in water to polymerize and form peptides. For example, if a technique produces solid crystals, then in this state they cannot contribute to an OoL model, since the subsequent necessary chemical processes would not occur. They must be first dissolved. In a series of papers, Truman argued that for thermodynamic and kinetic reasons, AAs in water would racemize faster than elongate to form large peptides, at all temperatures under natural conditions.[1,7–9] In all the experiments discussed in this current series, the conditions were optimized to shorten the time needed and to yield high enantiomeric excesses. Arguing that this was only for researcher convenience and that less optimal natural settings would be compensated for by enormous time overlooks that the long time periods would have permitted loss of e.e. through L- → D-AA conversion.

Process 1. Creation of a small enantiomeric excess

I already analyzed potential sources of an initial $e.e._L$ in this journal, and only mention a few naturalist proposals here which are often found in the evolutionist literature or were not mentioned before.[1]

Parity violation

In nuclear physics, the weak interaction produces β-decay of atomic nuclei.[10] Unlike the other fundamental interactions (gravitation, electromagnetism, and the strong interaction), its effect is not perfectly symmetrical.[11] The tiny energy difference of $\approx 10^{-14}$ Jmol^{-1} theoretically could lead to $\approx 10^{-15}$ % ee_L in an AA.[12]

Another quantum mechanical computational method developed by Quack predicted a slightly higher value for ee_L of $\approx 10^{-14}$ % for alanine, valine, serine, aspartate, and glyceraldehyde.[13,14] Quack and others have denied an energy preference at all in the case of L-alanine.[13,14]

Since [L] + [D] = 1 from eqn. (1), an $e.e._L \approx 10^{-14}$ % means that [L] – [D] $\approx 10^{-16}$. The greater likelihood of a particular L-AA interacting with another L instead of D enantiomer is less than a specific hair on the head of one person on the entire earth being correctly matched to another hair selected by chance.[15] Longer peptides consisting of hundreds, or thousands of only L-AAs couldn't have formed based on such a probability.

Quack is aware that a few more L- than D-AAs, generated over billions of years, cannot explain the origin of proteins. The miniscule excess would racemize with enough time, anyway. He warns that[16]

> "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."

Electric, magnetic, gravitational, and centrifugal fields

Many papers have been published over the last century claiming that a way has been found to preferentially produce an AA enantiomer. Creation of chiral molecules has been claimed using electric, magnetic, gravitational, and centrifugal fields, but the alleged successful outcomes could never be independently confirmed, so too much time won't be devoted to these reports. In a review article, leading OoL researcher Bonner summarized all these claims by starting that

> "… to date no experimentally substantiated asymmetric reactions have been observed under the external influence of any of the fields described above (electric, magnetic, gravitational and centrifugal fields)."[17]

Bremsstrahlung photons

Ulbricht pointed out, in 1959, that longitudinally polarized electrons emitted during β-decay produce so-called circularly polarized 'bremsstrahlung' photons. He suggested that these might induce stereoselective photochemical reactions.[18] However, none of the experiments ever found chiral products beyond the limitations of experimental error.[17]

Over the following years, Ulbricht and Vester carried out a variety of experiments and concluded that

> "No unequivocal rotations (measured at the sodium D line) were obtained, and any induced optical activity was probably less than 0.02%."[19]

Process 2. Amplification of enantiomer excess

Autocatalytic amplification

The principle that 'once a little reactant or product is formed this could facilitate more being produced' is well known. Max Bodenstein introduced the concept of a chain reaction into the chemical toolkit in 1913.[20] His insight was that an unstable chemical intermediate might sometimes be generated, rich in energy, which, on further reaction, gives

rise not only to a particular final product, but also to another intermediate, which thereby regenerates the same process, over and over.

An example is the hydrogen with chlorine chain reaction to produce HCl shown in figure 1.[21]

A similar concept involves polymerizations which consist of multiple monomer components. Once polymers begin to form, they can react with monomers to form larger polymers of the same kind. Many examples and applications are found in the industry.[22]

One of the simplest examples involves the commercial production of aliphatic polyethers generated by the ring-opening polymerization of epoxide monomers (figure 2).[23]

The driving force is the high ring strain of epoxides. This enables polymerization of epoxide monomers via base-initiated catalysis, acid-initiated catalysis, or by coordination polymerization.[22]

Although the preceding discussion helps to understand the underlying intuition behind how a bootstrap set of reactions might lead to amplification *per se*, none refer to the phenomenon of enantioselectivity. The examples do help demonstrate, though, the implausibility of the effect arising naturally. For example, high concentrations of pure H_2 and Cl_2, in the absence of radical quenchers such as oxygen, are not expected to arise naturally. High concentrations of high-energy pure epoxides will not arise naturally either. But we will see in this series of papers that examples proposed by evolutionists to amplify initial e.e.s for biologically relevant compounds are also implausible under putative prebiotic conditions.

Autocatalytic amplification (Soai alkylation)

Frank proposed, in 1953, the theoretical concept of autocatalytic amplification reactions as a mechanism to produce e.e.[24] The only experimental corroboration ever found of this concept is the astutely designed and often mentioned Soai alkylation of pyrimidyl aldehydes (see figure 3).[3,25] Remarkably, if a small excess of one of the activated enantiomers is provided to the reaction mixture it can preferentially autocatalyze creation of more of that enantiomer. However, this involves chemistry that has no prebiotic relevance, given the consensus that such dialkylzinc compounds would not have been generated in a putative aqueous prebiotic soup, far less in a pure and concentrated amount.[3,26]

A theme which will recur repeatedly in this series is that interesting artefacts can be designed under extreme or narrowly-controlled laboratory conditions which will not occur naturally. They have no direct relevance for OoL purposes. The Soia scheme illustrates this. Three exceedingly rare chemicals with very unstable moieties and which will not be naturally produced must be present and kept isolated. They

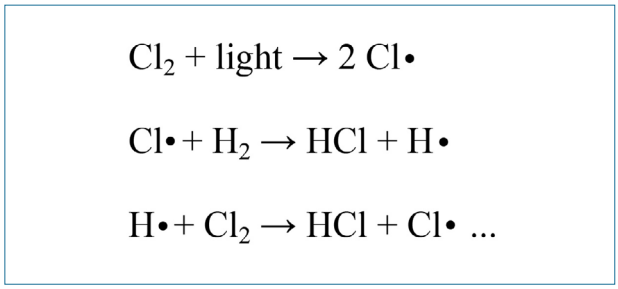

Figure 1. Hydrogen-chlorine chain reaction (from ref. 20)

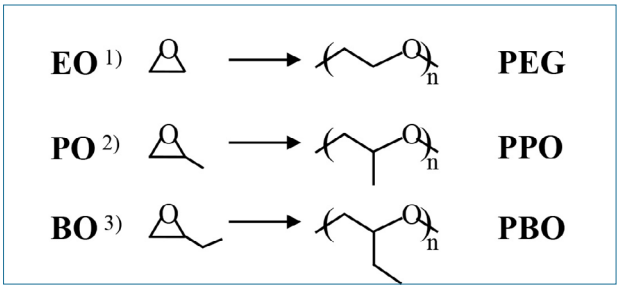

Figure 2. Polymerization of epoxide monomers (from ref. 22)
[1] EO: ethylene oxide
[2] PO: propylene oxide
[3] BO: butylene oxide

must be unable to diffuse away from each other. So, where would the steady influx of diisopropylzinc and pyrimidine-5-carbaldehydes come from to keep the reaction cycle going? And how would they be pumped into the isolated reaction environment? In addition, the solvent used was toluene or a mixture of ether and toluene, which are irrelevant for OoL purposes. Furthermore, after the repeated catalytic step, the final product required hydrolysis under acidic conditions.[28]

Nonetheless, the Soai reaction has kept hope alive in the OoL community since it

> "… proved that a chemical reaction exists in which very low enantioenrichment is amplified to almost enantiopure (>99.5% ee)."[28]

What is so special about the Soai reaction and what can be learned from it?

First of all, *autocatalytic reactions generally should not increase the enantiopurity of products.* Here is why.

Suppose that an asymmetric catalytic reaction led to a product having enantiomeric excess $e.e._{prod}$. In the ideal case where the catalyst is enantiopure ($e.e._{cat} = 1$) the product would have some enantiomer excess $e.e._0$.

For a simple catalytic reaction, $e.e._{prod}$ is a linear function of the $e.e._{cat}$:

$$e.e._{prod} = e.e._0 \times e.e._{cat} \quad [1]$$

Clearly, when $e.e._{cat} < 1$, *as is inevitably the case*, then $e.e._{prod} < e.e._{0}$.

Consider now what happens when this is an autocatalytic reaction starting with less than enantiopurity. The product formed will have a lower enantiomeric excess than its antecedent state. During each cycle the catalyst (which is also the product) would begin with a lower $e.e._{cat}$ than before. Over time the $e.e._{prod}$ would decrease relentlessly, converging to zero.

This led Dr Blackmond, a leading OoL researcher, to conclude that "any process of pure autocatalytic self-replication would lead inexorably to a racemic world!"[4]

But then why does the Soia reaction defy this expectation? To increase the e.e. through an autocatalytic scheme one enantiomer must somehow be able to suppress production of the other enantiomer.

This could happen in special cases when enantiomers *S* and *R* could interact to form *SS*, *RR* and *SR* dimers. Suppose *S* is present initially in excess. If *SR* is formed preferentially over the homodimers, then major enantiomer *S* would become enriched and relatively less *R* would participate in the self-catalysis.

Blackmond suggested a variant of this argument for the Soia reaction. Remarkably, the dimers and not the individual monomers seemed to be responsible for catalyzing the reaction, with the heterochiral *SR* being more effective than the *SS* or *RR* species. She pointed out that otherwise the product would have been racemic.[4]

The cleverly designed Soia scheme could only work in an exceedingly concentrated laboratory flask or the dimers would not form. Furthermore, more raw materials had to be added continuously at a rate which ensured autocatalysis faster than the end products could racemize naturally.

Autocatalytic inhibition (cyclobutane polymers)

Addadi and colleagues, from the Weizmann Institute of Science in Israel, devised a clever scheme to produce enantiomerically enriched chiral cyclobutane polymers from special dienes, which themselves are non-chiral.[29,30] Alignment between neighbouring C=C bonds led to two crystal versions, which, upon UV irradiation, yielded dimers, trimers, and higher oligomers, denoted by $[\ ]_d$ and $[\ ]_l$ in figure 4 in equal amounts. No net enantiomeric excess of product P_r or P_s was generated.

However, one of the crystalline variants was favoured when chiral dimers, trimers, or oligomers (i.e. P_r or P_s in figure 4) were present in excess during crystallization. In some experiments, the monomers were melted with 3–15% enantiomerically pure dimer, trimer, or oligomer and allowed to crystallize together. And in other experiments, crystallization was carried out using concentrated solutions in laboratory solvents (CH_2Cl_2, hexane, or ethyl acetate).[31]

Enantiomeric yields ranged from 30 to 100%, depending on the monomer used. Specifically, more D crystals were obtained when an excess of P_s was present, and more L crystals if the initial excess was of P_r.[28] Apparently one oligomer can replace several monomers at the growing site of a crystal having the same configuration, slowing down further crystallization. The authors showed that this kind of inhibition affects specific faces of crystals, modifying the rate of crystal growth and dissolution of that portion of the crystals.

This example shows that, at least in principle, autocatalysis of an enantiomer can be designed under carefully contrived conditions. In the final sentence of one paper, the researchers point out correctly that

> "The solution of the amplification problem will thus require very specially designed experiments."[30]

Experiments such as those described above illustrate the creativity and technical expertise of the thousands of researchers who have designed processes to isolate pure D-AAs. The fact that molecules structurally unrelated to AAs must be used is revealing. It demonstrates the decreasing lack of hope in finding a feasible naturalistic original for L-only AAs.

Nevertheless, creation scientists and ID supporters must avoid claiming that symmetry breaking can only occur with the help of pre-existing chiral enzymes. The next section summarizes why exotic designed systems like this one provide no evidence that L amino acids and D sugars could arise in enantiomeric purity under natural conditions. Although the objections are specific to this example, they are generally valid for most other schemes designed by OoL researchers.

Critique of these studies

Carefully designed schemes such as shown in figure 4 provide no evidence that pure L amino acids or D sugars could have been concentrated locally and naturally. This example cannot serve as a proof-of-principle, nor analogy, that e.e.s could have arisen without intelligent guidance for the following reasons:

- The materials displaying an enantiomeric excess have no resemblance to biochemical molecules used in living systems.
- The reactants are highly unlikely to be produced naturally under even speculative theoretical prebiotic conditions.
- The reactions are of very limited applicability. The stable inhibitor product required intense UV photolysis to produce an unusual cyclobutane ring having two possible enantiomeric configurations.

- The crystallization process required carefully guided conditions, including:
  - use of special laboratory solvents, since the reactants and products were not soluble in water
  - beginning with supersaturated pure solutions which were slowly cooled
  - control of pH, etc.
- Long exposure to UV light would have generated a variety of destructive radicals, but the researchers irradiated only D or L crystals at just the right time, wavelength, and duration to obtain the intended result.
- Extremely high concentrations of the pure dienes were necessary to form the crystals, at the same time and location.
- There is no reason why a significant excess of one inhibitor (P_r vs. P_s) would be present, and therefore the inhibitory effect would be symmetric, leading to no net enantiomeric excess.
- The effect was kinetically and not thermodynamically driven, and of only a short duration. Within only hours, the inhibitory action of P_r or P_s was no longer effective as more crystals developed and increased in size, exposing more surface to the free monomers. In addition, the crystals with inhibitor attached could simply redissolve. Without careful temperature and concentration control of the crystallization process, the just detached P_r or P_s would no longer have inhibited crystal growth.

What the experiments do show is how much expertise is required to know how to generate an e.e. But, instead of revealing that e.e.s could have arisen for AAs via natural processes, examples like these illustrate the opposite: intelligent organization was necessary.

We will conclude part 1 of this series with the main commonly cited, but absurd or irrelevant, claims of an $e.e._L$ produced naturally on various minerals.

Selective adsorption on various minerals

Kaolinite mineral clay

Claims of stereoselective adsorption of AAs on clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$) and of stereoselective polymerization of aspartic acid catalyzed by kaolinite have been discredited following re-examination by various researchers employing better analytical methods.[17,32,33]

Montmorillonite clay

L-leucine, L-aspartate, and D-glucose were claimed to bind in a stereospecific manner onto the montmorillonite clay ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$), which is the major component of the adsorbent swelling clay bentonite. The non-biological enantiomers D-leucine, D-asparatate, and L-glucose allegedly did not exhibit any selective adsorption.[34] However, Youatt and Brown demonstrated shortly afterwards that this was a misinterpretation of the experimental data.[35]

The two examples above illustrate a recurring principle in the OoL literature. A disconcertingly large number of publications alleging a break-through in the origin or amplification of homochirality pass peer review in leading journals like *Science* and *Nature*, but other teams can't replicate the claims. Many examples of this can be found in a review paper by evolutionist Standard University professor Bonner.[17]

Bonner summarizes all attempts to produce an enantiomeric excess with clay minerals with the sobering words:

> "Thus there is no experimental evidence whatsoever to date supporting any stereoselective effects on prochiral or racemic substrates attributable to clay minerals."[17]

The initial hype fades and is replaced with a new claim, but it seems that a feeling has developed that steady progress is

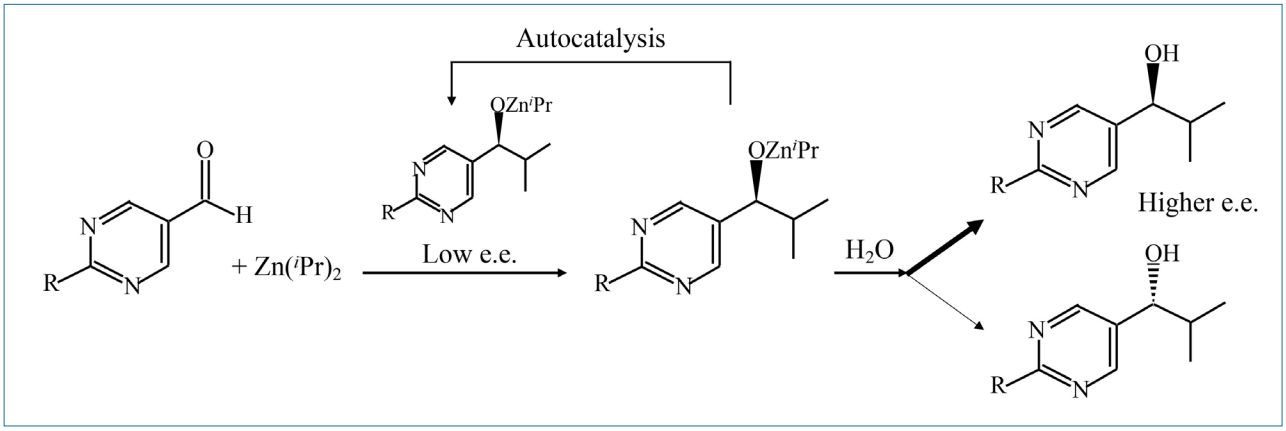

Figure 3. Autocatalytic amplification of enantiomeric excess in the Soai alkylation of pyrimidyl aldehydes. Diagram based on insights from refs 25 and 27.

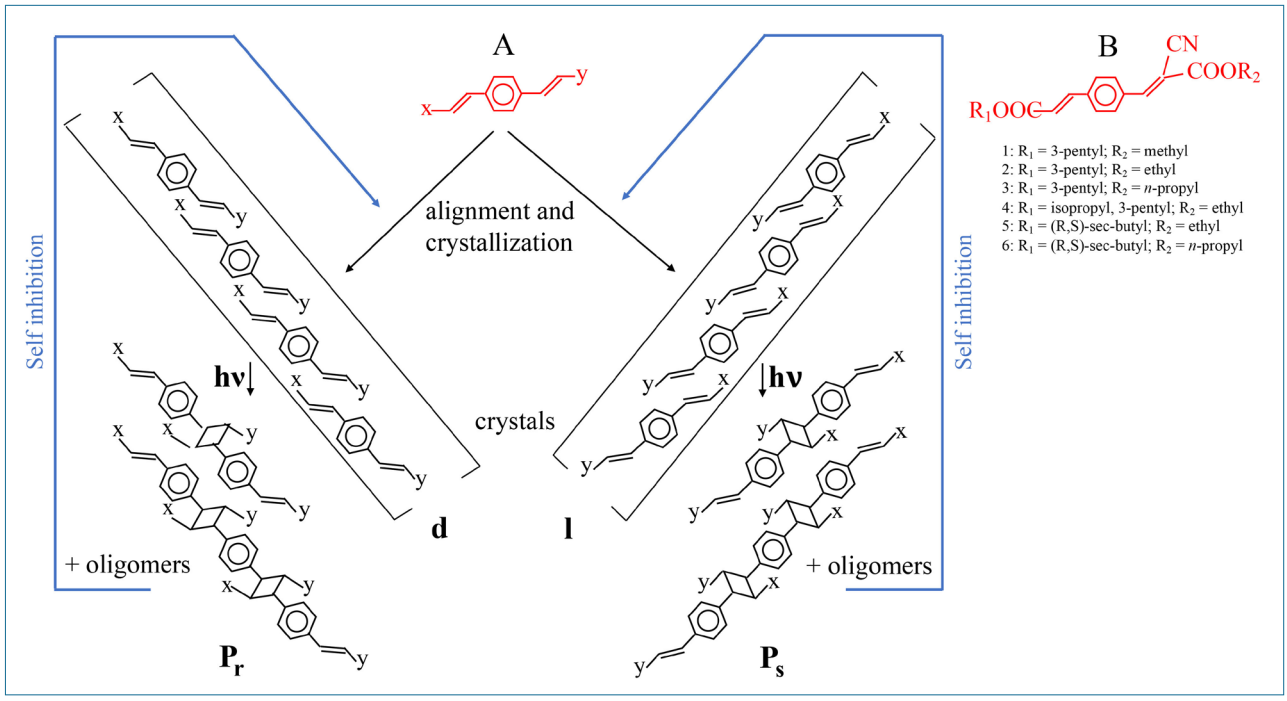

Figure 4. A. Feedback inhibition of enantiomer crystals during production of chiral cyclobutane derivatives from non-chiral dienes. B. Ester substituents used in ref. 29.

being made in explaining the original of pure L-AAs. Heavily marketed sensationalized claims are not easily forgotten, but reports of disproof do not receive the same fanfare.

I'll next mention some examples of small levels of e.e. obtained in carefully designed surfaces under special laboratory conditions. To evaluate their relevance for OoL purposes, one should always examine the concentrations of AA used, pressures, and avoidance of contaminants. But most importantly, in nature, both mirror-image surfaces would form in the same proportions, cancelling out any net e.e.

$CaCO_3$ (calcite) crystal

Calcite ($CaCO_3$) and other minerals form mirror-image surfaces on the same crystal. Hazen and co-workers immersed a rhombohedral calcite crystal in an aqueous solution of racemic AAs (aspartic acid or alanine) and found that crystal faces of a particular handedness selectively adsorbed the D- or L-AA enantiomer.[36] However, as anticipated the mirror-image crystal face selectively adsorbed the opposite AA.[37] Therefore, under natural conditions, no net e.e. could result. Furthermore, this effect was not observed with other amino acids tested, such as valine and lysine.[36]

Chemists have also succeeded in producing other kinds of crystals having chiral faces with which some enantioselectivity was obtained for some heterogeneous reactions and photodimerizations, both of which are however irrelevant for OoL purposes.[38–40]

Chiral minerals such as quartz

Some chiral minerals such as quartz can exist as in dextro- and levorotatory enantiomorphs. Preferential adsorption of one AA enantiomer on right-, (+)-, or left-handed, (−)-, crystal forms of quartz was first proposed as possibly producing chiral molecules in the 1930s.[41]

Bonner *et al.* were only able to generate low e.e.s ~20% for D-alanine adsorbed on d-quartz. This required using non-aqueous solvents irrelevant for OoL purposes with moisture carefully excluded.[36,42–46]

Extensive examination has shown that D- and L-quartz are present in equal amounts worldwide, and so no net selectivity would result.[17,47] In 1962, Palache *et al.* collected 17,738 samples worldwide and found 1.4% excess of (−)-quartz (50.7%) over (+)-quartz (49.3%) (i.e. a 1.4% excess).[48] This is within the expected statistical variability expected from a sample size so much smaller than the population of all suitable quartz crystals. The variance of a binomial distribution is given by

$$\sigma^2 = np(1-p) \qquad (2),$$

where n is the sample size (17,738) and $p = 0.5$ is the probability of obtaining a quartz of either form. This leads to a standard deviation of $\sigma = 66.6$. About half of the sample (8,869) should be found as each form of quartz and 2σ correspond to 133. Therefore, about 95% of random samples

of this size would have one quartz form in an amount of 8,849 ± 133, which is ±1.5% from the expected mean (±100 × 133/8,849). The reported 1.4% excess of (−)-quartz lies within the range of random sampling.

In a later, larger study Frondel examined 27,053 samples and found 50.17% (+)- and 49.87% (−)-quartz, which is also within the range of random sampling. But this time, a tiny excess of the *opposite* form of quartz was found over that found in the Palache study.[49]

Glycine crystals doped with D-amino acids

The faces of glycine crystals have been used to separate AA enantiomers at an air/water interface.[17,28,50,51] Plate-like crystals of glycine tend to float at the air/water interface, exposing the (010) or ($0\bar{1}0$) face to air in equal proportions.[28] Experiments with several chiral α-AAs revealed that (*R*) enantiomers are preferentially adsorbed at the (010) crystal face.[28,36]

Consequently, when the crystals were produced together with small amounts of pure D-leucine, D-phenylalanine, or D-α-aminooctanoic acid, the hydrophobic side chains caused the floating crystals to always expose the ($0\bar{1}0$) face to the air side. Since the other face is now exposed to the water phase, non-hydrophobic AAs also present would only attach there. Experiments showed that crystals grown in the presence of equal amounts hydrophobic D-leucine mixed with L-glutamic acid, L-methionine, L-alanine, or L-serine, continued to have platelets with the ($0\bar{1}0$) faces directed to the air. HPLC analysis showed that the aforementioned L-AAs occluded within the crystals were found in high e.e.

Critique of these studies

These kinds of experiments could find application for manufacturing purposes, for example by designing two-dimensional crystallites optimized to form chiral monolayers.[52–55] But there are many reasons why such a process could not have arisen naturally:

- The production of pure glycine crystals and then location to an air/water interface is not plausible.
- The amount of enantioenrichment which could have been created in the liquid phase would have been negligible, and the glycine crystals could redissolve and liberate the contained AAs. Consequently, an OoL scenario must involve the air phase only.
- Enantioenrichment in crystals on faces aimed towards air would serve no purpose. To form peptides, they would have to redissolve in water, where racemization would occur along with contamination with D-AAs. Note that any e.e. in the air phase could only have arisen from impoverishment in the solution phase, and so redissolving would undo the enantiomer separation.
- The process required the presence of pure D-AAs, which would have been devastating if proteins were to have arisen using only L-AAs.
- The minority of suitable hydrophobic D-AAs would have competed with other D-AAs at the same crystal phase, hindering orientation to the air side.
- The proportion of hydrophobic D-AA to L-AA would need to be close to 1:1 to produce a relevant $e.e._L$.

Crystal conglomerates using amino acids with large alkyl groups

Weissbuch *et al.* studied some racemic *α*-AA having the structure $RHC(NH_3^+)CO_2^-$ which form monolayers on water and on glycine aqueous solutions.[53] Heterochiral crystals were synthesized by using $R = C_nH_{2n}+_1$, n = 10, 12, 16 and homochiral crystals by using $R = C_nH_{2n}+_1CONH(CH_2)_4$, n = 11, 17, 21. In the latter case, adjacent hydrocarbon chains are held together due to N–H•••O=C hydrogen bonds between amide groups.

The long chains formed separate 2-dimensional islands having single (*R*) or (*S*) enantiomers. However, the individual crystalline domains are very small. For the long-chain amides, the lengths of a single island were about 170, 500, and 300 Å along the (0,1), (1,0), and ($1,\bar{1}$) lattice plane directions. Conglomerates of domains are formed; i.e. mixed enantiomorphous crystals. The overall amounts of (*R*) and (*S*) domains formed are identical. Thus, as typical of enantiomeric amplification examples, the enrichment refers to a tiny region which is not naturally separate from the mirror-image enantiomer.

Critique of these studies

- The AAs were first dissolved in unique laboratory solvents, chloroform/trifluoroacetic acid (v/v 98:2), then carefully spread on a concentrated glycine aqueous solution at 8°C. Compression of the monolayer using a Langmuir trough was accompanied by further cooling to 5°C. These are not relevant conditions for a putative prebiotic earth.
- Little evidence for any crystal formation was found in the absence of concentrated glycine.
- Even when using glycine in water, no islands were found for chains as short as $R = C_6$ and C_8, sizes relevant to the sidechains of biological AAs. In other words, the molecules used cannot have contributed to a natural origin of biological AAs.
- The formed conglomerates are an intimate mixture of (*R*) and (*S*) regions. No natural full separation of enantiomers was achieved.

Using a Langmuir trough

Racemic mixtures of amphiphiles, such as fatty acids, alcohols, amides, and amino acids, can sometimes be engineered to separate into left- and right-handed molecule islands at the air–water interface of a Langmuir trough.[56] The enantiomers separate into crystalline islands of opposite handedness. The various chemical structures organized are located at the air–liquid interface and the solution phase due to interaction with the monolayer.[54]

Griffith and Vaida claimed that similar environments could have existed on the ancient surfaces of lakes, oceans, and atmospheric aerosols. This is, at best, very wishful and unsubstantiated thinking. In a key paper, they describe how the amino acid leucine was first chemically activated by converting the end carboxyl group to an ethyl ester.[57] In addition, for the condensation to proceed, coordination to Cu^{2+} (copper(II) chloride) was necessary and the final solution was sonicated until a transparent solution resulted.[57] Finally, an unrealistically high externally applied pressure of 15 mN⁄m was applied to force the orientation of the molecules.

In natural conditions, a wide variety of chemicals could also mix with the amphiphiles. Solutes (including unnatural amino acids) can prevent or retard formation of monolayer crystallites and also dissolve them once formed.[54]

Critique of these studies

- Any substance related to an AA first had to be chemically modified. There would have been no steady supply of feedstock such as esterized AAs,
- Coordination of AAs with a high concentration of Cu^{2+} would have accelerated racemization, whereas the goal was to find a natural way to produce only L-AAs.[58]
- Careful experimental control by the experimenters was necessary, using a highly concentrated solution of pure substances at a high pressure, which was carefully increased in a way and rate which minimized turbulence.

Concluding comments

Several mechanisms to explain the origin of an enantiomeric excess or enrichment of one enantiomer have been proposed over the years. These were usually marketed with great fanfare and shamelessly oversold. The mechanisms discussed here were selected as being those clearly irrelevant for abiogenesis purposes. They continue to be referenced in the current OoL literature but rarely is the fact emphasized that they are no longer being actively researched nor that they were unfruitful.

In the next parts to this series, we will focus on the ongoing proposals which have not yet been demonstrated to be just as irrelevant to explain the origin of enantiomerically pure biochemicals.

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