Computational Models of the Transmission of Chirality: The Chemical Evolution of Homochirality, A Biosignature of Life

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ABSTRACT

At the current point in time, there is still no complete understanding of how life formed on early Earth. One mystery is the evolution of homochirality; many biologically important molecules have two stereoisomers: L- and D- . For reasons we do not yet understand, all 20 amino acids, the building blocks of proteins, are L-amino acids. How did this happen?

We designed computational models of chemical systems to understand the transmission of chirality from a molecular template. In the model, we found conditions showing that with an exceedingly small excess of the L-form of precursors, there was a large production of L-molecules; we learned that breaking of chiral symmetry to yield a homochiral environment might well be expected from simple chemical systems.

INTRODUCTION

The emergence of homochirality is still a huge question in the explanation of how life evolved on Earth; indeed, homochirality is thought to be a biosignature of life, a requirement for chemical building blocks wherever life might arise. Chirality can be explained in terms of handedness, L- and D- (or R- and S-), which are mirror images that cannot be superimposed. This handedness in structure determines how molecules may behave and function. In simple chemical systems, typically, both stereoisomers, L- and D-, are produced in equal quantities. However, in living systems, there are exclusively L-amino acids and D-sugars, showing that a split in symmetry at some point in time on early Earth. [1]

In earlier studies, we showed how one stereoisomer might have predominated on the prebiotic Earth [2]. We now asked how such a breaking of chirality might have been transmitted to other molecules. Could an initial molecule behave as a template for other molecules such as the amino acids? Could this explain why all twenty amino acids have the same L- form? Our results are consistent with the work of others suggesting that such a template mechanism could have led to homochirality on prebiotic Earth. [3]

METHOD & MATERIALS

Kintecus™, a kinetic software used to run equations based on kinetics was used to run systems and determine the outcome of the reactions based on specific settings. Reactions were developed based on a previous SURF project with Dr. Schwartz and Dr. Barrett by Brandy Morneau and Jackie Kubala [2].

Based on those reactions, a more complex system was created using one molecule, R, as a template to find conditions where chirality was transferred from this structure to other molecules. The model can be seen to the right.

The value for the activation energy was arbitrary and chosen to give the best set of reactions. In the model, X was used to represent an achiral precursor, which is necessary for the reaction to take place. R represents the template molecules being used throughout the system. R_n and S_n represent the chirality of the other molecules, treating the reactions exactly the same with the same initial conditions, so neither chirality appeared favored. By reacting with a template, the achiral substrate binds to the template and reacts following the initial reaction so it results in a molecule with a structure that favors one of the structures.

RESULTS

The goal was to learn if conditions could be found that supported the notion that homochirality could evolve from an initial template molecule. Many different models were tested with arbitrary activation energies. The output from Kintecus was a data sheet, which was produced showing the concentrations of all involved species as well as a graph showing the concentrations of the R and S chirality. We found conditions documenting the break in symmetry yielding the favorable chirality (R) for each individual group. Temperature was critical for breaking chiral symmetry but inconsistently favored different stereoisomers.

The most important finding was that whenever the initial concentrations for the R_n molecules was greater than the initial concentrations of the S_n molecules, the chemical system favored homochirality for the R forms. Even when the difference between R1 and S1, for example, was as small as 1×10^{-14} M, breaking symmetry favored the R form throughout the model.

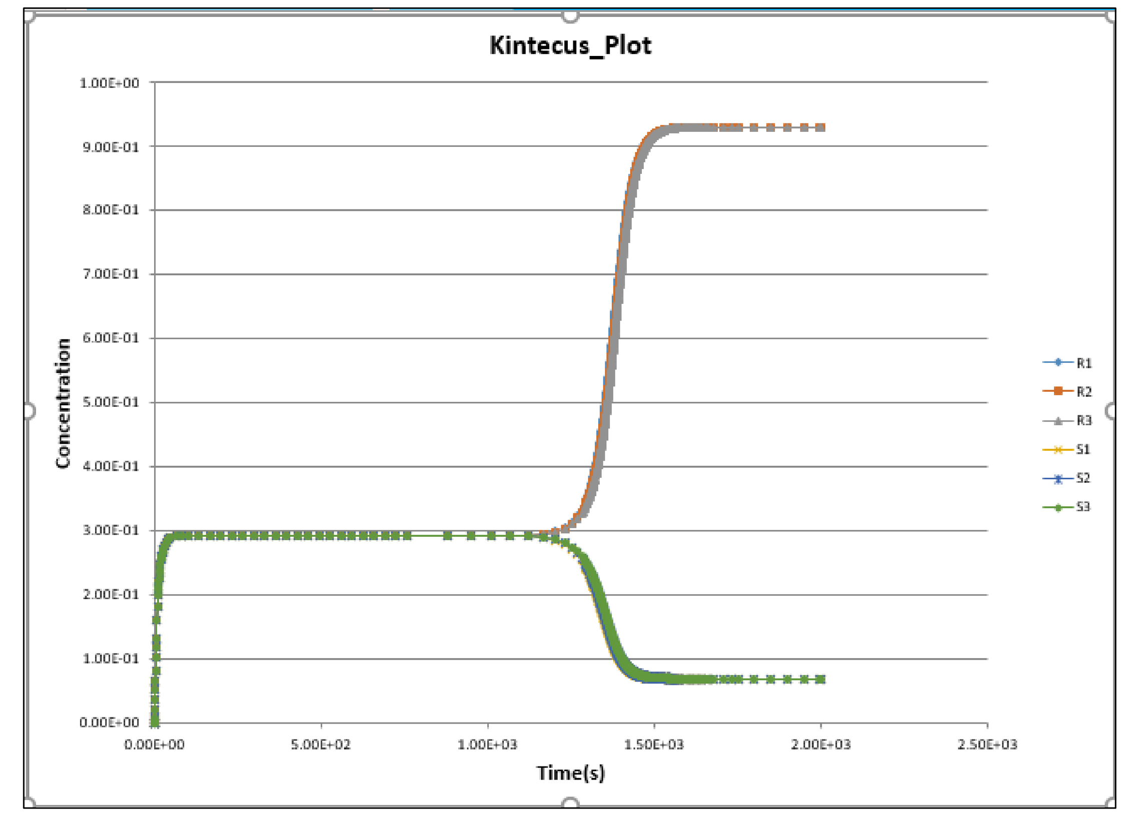
In the present model, only three different sets of R_n and S_n were used. Further investigation would need to be done in order to determine if this would hold true for more molecules, such as the 20 L-amino acids.

#	Model Description SpreadSheet		
# A	T^m	Ea	Reaction
1.00E+03	0	35	X1+R==>X1R
1.00E+03	0	35	X1R==>R1R
1.00E+03	0	35	X1R==>S1R
1.00E+03	0	25	R1R+R1==>R1R+X1
1.00E+03	0	25	S1R+S1==>S1R+X1
1.00E+03	0	10	R1R+S1==>S1R+X1
1.00E+03	0	10	S1R+R1==>R1R+X1
1.00E+03	0	15	R1R==>R1+R
1.00E+03	0	15	S1R==>S1+R
1.00E+03	0	35	X2+R==>X2R
1.00E+03	0	35	X2R==>R2R
1.00E+03	0	35	X2R==>S2R
1.00E+03	0	25	R2R+R2==>R2R+X2
1.00E+03	0	25	S2R+S2==>S2R+X2
1.00E+03	0	10	R2R+S2==>S2R+X2
1.00E+03	0	10	S2R+R2==>R2R+X2
1.00E+03	0	15	R2R==>R2+R
1.00E+03	0	15	S2R==>S2+R
1.00E+03	0	35	X3+R==>X3R
1.00E+03	0	35	X3R==>R3R
1.00E+03	0	35	X3R==>S3R
1.00E+03	0	25	R3R+R3==>R3R+X3
1.00E+03	0	25	S3R+S3==>S3R+X3
1.00E+03	0	10	R3R+S3==>S3R+X3
1.00E+03	0	10	S3R+R3==>R3R+X3
1.00E+03	0	15	R3R==>R3+R
1.00E+03	0	15	S3R==>S3+R
END			

R1 & S1

R2 & S2

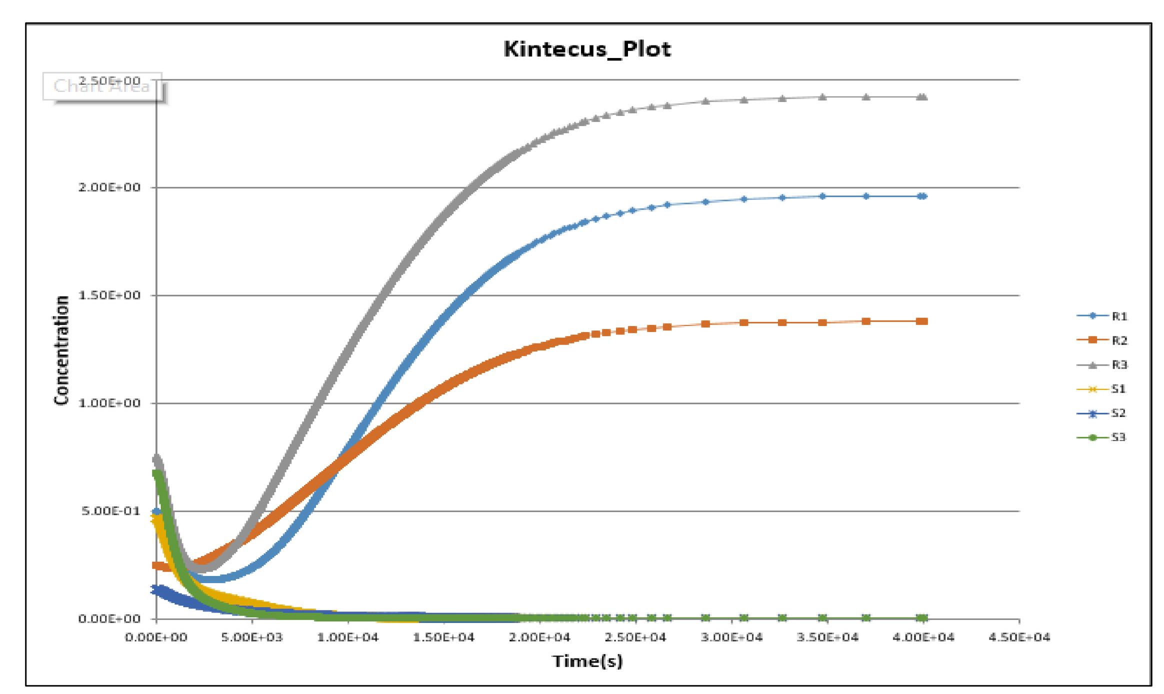
R3 & S3



The graph shows homochirality in favor of R at 300K with concentrations R1=R2=R3= 1 x 10^{-14}M and S1=S2=S3=0.0M .

Time	R1	R2	R3	S1	S2	S3
7.22E+04	1.34E-01	1.34E-01	1.34E-01	1.34E-01	1.34E-01	1.34E-01
7.93E+04	1.35E-01	1.35E-01	1.35E-01	1.34E-01	1.34E-01	1.34E-01
8.42E+04	1.35E-01	1.35E-01	1.35E-01	1.33E-01	1.33E-01	1.33E-01
8.74E+04	1.37E-01	1.37E-01	1.37E-01	1.32E-01	1.32E-01	1.32E-01
9.14E+04	1.43E-01	1.45E-01	1.44E-01	1.26E-01	1.25E-01	1.26E-01
9.40E+04	1.54E-01	1.57E-01	1.55E-01	1.17E-01	1.15E-01	1.16E-01
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
9.70E+04	1.87E-01	1.95E-01	1.90E-01	9.43E-02	8.97E-02	9.24E-02
9.71E+04	1.88E-01	1.96E-01	1.91E-01	9.40E-02	8.93E-02	9.20E-02
9.71E+04	1.88E-01	1.97E-01	1.92E-01	9.37E-02	8.90E-02	9.17E-02
9.71E+04	1.88E-01	1.97E-01	1.92E-01	9.36E-02	8.88E-02	9.16E-02
9.72E+04	1.89E-01	1.98E-01	1.93E-01	9.30E-02	8.82E-02	9.10E-02
9.72E+04	1.90E-01	1.99E-01	1.94E-01	9.26E-02	8.78E-02	9.06E-02

This table shows the concentrations of each molecule, where the initial concentrations were R1=R2=R3= 1 X 10^{-14} M and S1=S2=S3=0.0 M. Homochirality can be seen in the final concentrations



The graph to the left shows the different concentrations when R1=0.5 M, R2=0.25M, and R3 = 0.75M, while S1=0.47M, S2=0.14M, and S3=0.68M. As time passes, an excess of R molecules can be seen.

DISCUSSION

As can be seen on the graph, after a successful run was performed, the symmetry would break and the lines representing three of the species went up while the other three went down, approaching zero. The lines that went up represented an excess of that particular species. The greater the difference between the two lines of the plot, the greater the enantiomeric excess and the higher probability of the model being successful in prebiotic earth. By examining the thresholds of the system, it was determined that it is possible for the reaction to occur over a wide range of temperatures. This means that depending on the location and the stage of the Earth's cooling or if perhaps a reaction occurred in a hydrothermal vent with a large variety of temperatures. When homochirality was achieved, it showed that there was a viable possibility a similar reaction happened millions of years ago, leading to first life.

One of the issues encountered was the unpredictability of the model at varying temperatures. However, as previously stated, with an initial concentration in which R1 is greater than S1, etc. was always homochiral in favor of R. Recently there have been studies in which meteorites have ben studied after landing on earth. When looking at the composition of the meteorites, frequently there is an excess of L amino acids, which is synonymous with R chirality, and thus can answer the question as to whether or not it was possibly that the earth already had a small concentration of L – amino acids. [4]

CONCLUSIONS

A possible chemical model of reactions has been developed that shows a system of reactions under specific conditions that suggests that once symmetry broke on early earth, that first amino acid was used as a template for all other amino acids. This is significant because it gives a possible explanation for how despite nature's tendency toward equal concentrations of each chirality, life developed with specifically L – amino acids.

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