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Connections Between Nuclear Physics and the Origin of Life

Examining the Origin of Biomolecular Chirality

Michael Famiano[1,2,3,*], *Richard* Boyd[4,**], *Toshitaka* Kajino[2,3,5,***], *Satoshi* Chiba[3,6,****], *Yirong* Mo[7,†], *Takashi* Onaka[5,8,‡], and *Toshio* Suzuki[2,9,§]

[1]Western Michigan University, Department of Physics, Kalamazoo, MI 49008-5252 USA
[2]National Astronomical Observatory of Japan, Mitaka, Tokyo, Japan 181-8588
[3]School of Physics, Beihang Univ. (Beijing Univ. of Aeronautics and Astronautics), Beijing 100191, P.R. China
[4]The Ohio State University, Department of Physics and Department of Astronomy, Columbus, OH 43210 USA
[5]Graduate School of Science, Univ. of Tokyo, Bukyo-ku, Tokyo 113-0033 Japan
[6]Laboratory for Advanced Nuclear Energy, Institute of Innovative Research, Tokyo Institute of Technology, Meguro-ku, Tokyo, 152-8550, Japan
[7]Western Michigan University, Department of Chemistry, Kalamazoo, MI 49008-5252 USA
[8]Meisei University, Department of Physics, Hino, Tokyo 191-8506, Japan
[9]Nihon University, 3-25-40, Setagaya-ku, Tokyo 156-8550, Japan

Abstract. The discovery of bio-molecules in meteorites with an excess of one chiral state has created one of the biggest questions in astrobiology today. That is, what is the origin of bio-molecular homochirality? Studies of this question are highly interdisciplinary, and while several phenomenological models exist, we examine the relationship between fundamental symmetries at the particle level and the macroscopic formation of bio-molecules. A model has been developed which couples fundamental interactions with the formation of molecular chirality. In this magneto-chiral model atomic nuclei bound in amino acids interact via the weak interaction in stellar environments. Nuclei are coupled to the molecular geometry (chirality) via the shielding tensor, the same interaction responsible for NMR identification. Associated with this is the fact that isotopic abundances vary from solar system values. Interactions with leptons can selectively destroy one chiral state over the other while changing isotopic values. Possible sites are proposed in which this model may exist.

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[*] e-mail: michael.famiano@wmich.edu
[**] e-mail: richard11boyde@comcast.net
[***] e-mail: kajino@nao.ac.jp
[****] e-mail: chiba.satoshi@nr.titech.ac.jp
[†] e-mail: yirong.mo@wmich.edu
[‡] e-mail: onaka@astron.s.u-tokyo.ac.jp
[§] e-mail: suzuki@chs.nihon-u.ac.jp

1 Introduction

Because they are asymmetric, amino acids have two chiral states - or mirror images - referred to as “left-handed” and “right-handed” forms, prefixed with L- and D- respectively. With very few notable exceptions, nearly all life on earth utilizes only left-handed amino acids, a phenomenon referred to as biomolecular homochirality.

The discovery that *meteorites not only contain amino acids, but can have amino acids favoring left handed chirality* [1–8] is a possible indicator that amino acid chiral selection may have extra-terrestrial origins and has led to several theories and models [9–17].

After selection of a particular chirality within a meteorite, successive synthesis or evolution of the molecules via autocatalysis can amplify this enantiomeric excess [6], which is defined to be the relative difference in numbers of left and right handed enantiomers; $ee = (N_L - N_R)/(N_L + N_R)$. While the *ee*s within meteorites are small, on the order of a few percent, chemical autocatalysis can ultimately to result in homochirality, $ee = 1$. It may be possible that non-zero *ee*s in meteorites may have influenced terrestrial homochirality. In such scenarios processing of amino acids within interstellar dust and planetary bodies could result in non-zero *ee*s within those objects. Meteorites with non-zero *ee*s would then be delivered to earth - possibly during the Late Heavy Bombardment [18]. The excess left-handed amino acids within these meteorites could then influence the *ee*s of existing amino acid populations on the earth and be amplified via terrestrial autocatalytic mechanisms [19, 20].

However, the mode by which the initial imbalance is produced is not well understood. This enigma has been discussed in numerous reviews in the past [21–28]. Current theories include the interactions of molecules with circularly polarized ultraviolet light [29], ultra-violet radiation [30], weak interactions [31–37], and other mechanisms. Many of the proposed solutions to this problem either fail in their abilities to produce a sufficient amount of amino acids in a chiral state, or they fail to identify sites that would supply the conditions which their explanation requires. *The question of the origin of biomolecular homochirality is one of the top questions in astrobiology today, despite the fact that it is nearly 170 years old* [38].

From an observational perspective, a large segment of astrobiological exploration today is focused on locating and quantifying amino acids in stellar environments. This includes astronomical observations and theory [30, 39–41] as well as space missions to search for amino acids in comets and asteroids [42, 43].

An emergent model has been developed in which amino acid chirality may be formed via a selective destruction mechanism in which nuclear spin is coupled to the molecular chirality. Destruction of nuclear spin states via the weak interaction with external leptons proceeds at rates which depend on the relative lepton-nuclear angular momentum vectors and, hence, the molecular chirality. The primary goal of the work presented here is to explore the fundamental physics involved in the origin of biomolecular homochirality and to answer the question, *Is there a nuclear physics origin of biomolecular homochirality?*

2 Magnetochiral Model of Chiral Selection

One possible model for amino acid chiral selection involves an emergent phenomenon in which molecules in crossed electric and magnetic fields. In this model, which is described in detail in references [32–37], molecules are polarized in an electric field via the interaction of their electric dipole moments and the external field, $\mu_E \cdot \mathbf{E}$. Because the dipole moment is molecular shape-dependent, the polarization reverses sign under a parity transform; it is thus chiral.

When an external magnetic field $\mathbf{B}^{(0)}$ is introduced, the magnetic field at individual nuclei is shifted by the interactions of the molecular orbitals with the magnetic field. This creates a

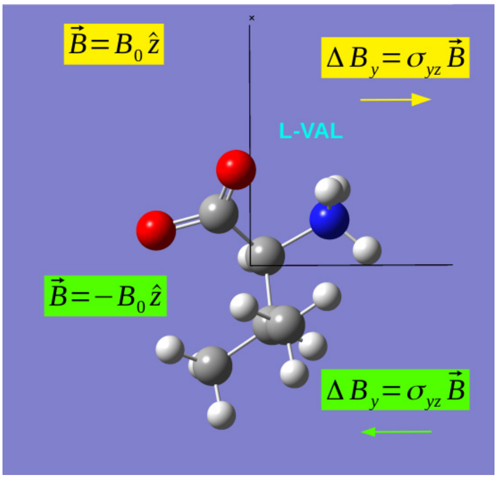

Figure 1. The shift in local magnetic field for L-valine for a magnetic field in the positive and negative z-direction. For D-valine, the shift in the magnetic field is in the opposite direction.

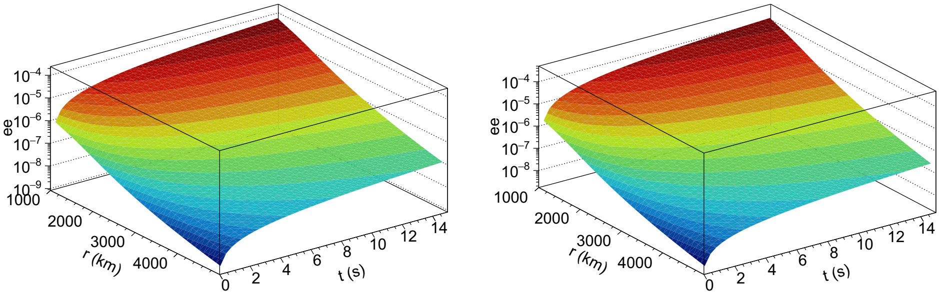

Figure 2. Enantiomeric excesses of zwitterionic alanine (left) and cationic isovaline (right) as a function of time and orbital radius of meteoroids about a neutron-star merger.

"shielding" effect, in which the magnetic field at the nucleus, $\mathbf{B}^{(N)}$ is shifted in both magnitude and direction. This shift is represented by the shielding tensor [44, 45]:

$$\Delta B^{(N)}_{\alpha} = -\sigma_{\alpha\beta} B^{(0)}_{\beta} \tag{1}$$

where the Greek subscripts indicate Cartesian coordinates and matching subscripts imply a sum.

Because the shielding tensor depends on the electronic orbital configuration, the off-diagonal elements are sensitive to a parity transform, and thus one rectangular element changes sign with chirality. That is, $\sigma_{z\alpha,L} = -\sigma_{z\alpha,R}$ and $\sigma_{\alpha z,L} = -\sigma_{\alpha z,R}$.

In an isotropic medium, the molecules tumble freely, and the average over the shielding tensor elements in a magnetic field is quite small. However, for molecules polarized in an external electric field, the temperature-dependent shift can be written (in the linear approximation) as [44]:

$$\Delta\mathbf{B}^{(N)} = \frac{1}{6kT}\varepsilon_{\alpha\beta\gamma}\sigma_{\alpha\beta}\mu_{E,\gamma}\mathbf{B}^{(0)} \times \mathbf{E} \tag{2}$$

where ε is the permutation operator. This shift is of opposite sign for left-handed and right-handed molecules. The shift is also perpendicular to the external B and E fields. For meteoroids in motion about a highly magnetized body, an electric field is created in the molecular rest frame. Thus, the molecules are polarized, and the sign of $\Delta\mathbf{B}^{(N)}$ for nuclei within the molecule depends on the molecular chirality.

For molecules embedded in meteoroids in motion about a highly magnetized source of anti-neutrinos (e.g., a type II supernova or neutron star merger), the nitrogen within the molecules has a magnetic polarization resulting from its nuclear spin (equal to 1 in units of $\hbar$) that is then chirality-dependent. Nitrogen nuclei in right-handed amino acids have spins that point more towards the star, while those in left-handed amino acids have spins that point away from the star. The interactions of the anti-neutrinos with the ^{14}N have a higher cross-section than the anti-neutrino interactions because of the lower Q-value. Further, because of the selection rules for weak interactions in nuclei [46], they also have a higher cross-section for the nuclei that are polarized with their spins oriented towards the star. Because the ^{14}N nuclear alignment is now chirality-dependent, the interaction rate for nuclei in right-handed molecules is higher. Thus the right-handed amino acids are preferentially destroyed. This results in a net positive enantiomeric excess.

An example of the shift in the magnetic field for L-valine is shown in Figure 1. Here, the shift in the magnetic field $\Delta\mathbf{B}$ is shown from a single off-diagonal component of the shielding tensor for a magnetic field in both the positive and negative z directions. For D-valine, the shifts are in the opposite direction.

In order to evaluate this model, the shielding tensors for all 20 α-amino acids were computed using a quantum chemistry code. Using these results, it was then possible to evaluate the nitrogen polarization within the molecule. It was then possible to determine the relative anti-neutrino interaction rates, λ, via the estimation [47]:

$$\lambda \propto 1 - \cos\phi \tag{3}$$

where ϕ is the angle between the anti-neutrino momentum vector and the nitrogen spin.

3 Results

In order to compute the shielding tensor, a quantum chemistry code [48] was used. The molecular geometry,taken from the Cambridge Structural Database [49], was first optimized using a second order Möller-Plesset (MP2) computation [50] with the `aug-cc-pVDZ` basis set. The shielding tensor components were then computed with the optimized geometry using a density-functional calculation with `B3LYP` functionals and the `pcS-2` basis set [51].

Using this model, the enantiomeric excess of several amino acids have been computed for meteoroids moving in the vicinity of several sites. In addition, we have also evaluated the possible correlations between amino acid *ee*s and variations in isotopic ratios within amino-acid-containing meteoroids.

3.1 Enantiomeric Excesses of Amino Acids

The enantiomeric excesses (*ee*s) of amino acids orbiting several sites which vary by magnetic field and anti-neutrino flux have been evaluated.

As an example, the *ee*s for alanine and isovaline in meteoroids in close proximity to a neutron star merger are shown in Figure 2. In this figure, the *ee*s as a function of time and meteoroid distance from the merger are shown after the neutrino burst.

In either case shown in Figure 2, the *ee* is positive and increases with integrated neutrino flux. It is also noted that the *ee* increases at a faster rate with proximity to the merger event. This is due to the increasing anti-neutrino flux as well as the larger magnetic field. While the anti-neutrino flux increases the rate at which the *ee* changes in time, the magnetic field increases the difference in reaction rates between chiral states and, ultimately, the maximum possible *ee* that is formed [16].

3.2 Isotopic Anomalies

Because this model for amino acid chiral selection relies on neutrino interactions in meteoric bodies, then the same neutrino source could result in weak current and neutral-current interactions in the meteoric body and its embedded organic material. Thus, we have also examined differences in isotopic abundance ratios in meteorites.

Using neutrino and anti-neutrino flux models from reference [52] and a nuclear reaction network spanning nuclei with $0 \leq Z \leq 10$ including neutral-current interactions, charged-current interactions, and neutron captures, the abundance evolution of individual isotopes was computed within meteoric bodies with various initial abundance distributions [53].

In each simulation, using the results of the nuclear reaction network for neutrino, antineutrino, and neutron interactions, the isotopic abundance ratios δD, δ^{7}Li, δ^{10}B, δ^{13}C, and δ^{15}N were evaluated as a function of time after the start of the neutrino burst. Here, the abundance ratio δX for an isotope is defined as:

$$\delta X \equiv \left(\frac{(Y_X/Y_Z)_s}{(Y_X/Y_Z)_{ref}} - 1 \right) \times 1000‰ \tag{4}$$

where Y_X and Y_Z represent the isotopic species of interest and the most abundant species in an isotopic chain, respectively. The subscripts s and ref indicate ratios for a meteoric sample and a reference sample.

An example of the results from this evaluation is shown in Figure 3. This figure presents calculations of δD vs. δ^{15}N for three neutrino luminosity models from reference [52] (labeled *C*, *D*, and *E*). Each dot in the figure represents a time step in the computation assuming a constant neutrino luminosity and temperature in each model. We note that δD and δ^{15}N increase in time, and the computation is run out to 10 s. Thus the largest values of δD and δ^{15}N correspond to a 10 s exposure to the merger source, while the intermediate values (for models *C* and *E*) correspond to an exposure of 0.5 to 2 s.

The red markers with errors bars in Figure 3 correspond to measurements of amino acids in actual meteorites [54]. In these measurements, organic biomolecules were evaluated from within the meteoric material. We note that the scatter in the measurements is large. However, the fact that the computations pass through the locus of measurements is promising, though there is still a significant amount of work left in evaluating these computations and measurements. It is important to note that the calculations here only represent results from the nuclear physics calculations, and effects from cold chemistry and diffusion have been ignored.

In addition to the isotopic ratios within meteoric organic material, abundance ratios for isotopic Li and B nuclei were also evaluated and compared to measurements of meteoric rock and grains. These are discussed in a future paper [53].

4 Conclusions

A model in which amino acid chiral selection via the interaction of anti-neutrinos with ^{14}N in amino acids in external magnetic fields has been presented. Four components are necessary

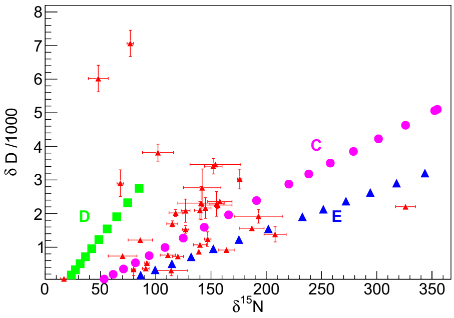

Figure 3. Evolution of δD vs δ^{15}N in a meteoroid with an initial isotopic abundance distribution with an abundance distribution closely matching that of the early solar system and slightly depleted in H, N, O, and Ne [53].

for such a phenomenon to occur. These include external electric fields and external magnetic fields which couple the molecular chirality to the nuclear spin. An electric field is produced in the reference frame of the meteoroid by its motion through a magnetic field. The magnetic field may be uniform, though that is not necessary, and a non-uniform field can produce some additional effects.

Another necessary component of this model is anti-neutrino interactions. Weak interactions with the polarized nitrogen nucleus selectively destroy nuclei of particular spin states coupled to the molecular chirality.

The final component in this model is the non-zero spin of the nitrogen nucleus. In a magnetic field, the spin polarization then results in different reaction rates between the nuclei and anti-neutrinos.

The model presented is also capable of inducing isotopic ratio variations in meteoroids. Though measurements and computations suffer from significant uncertainties, the model does provide some qualitative success. In that it appears to predict *ee*s comparable to those observed for objects passing close to an extreme cosmic event such as a neutron star merger while simultaneously producing excess abundances of various isotopes. Subsequent autocatalysis of the amino acids in this model can drive the produced enantiomeric excesses to significant values.

Interestingly, the selective destruction of amino acids is also predicted to produce a large significant enhancements of D, ^{15}N, and ^{11}B but little to no enhancement of ^{13}C, which is consistent with observations.

While there is a significant amount of work to be done in evaluating the astrophysical plausibility of weak interactions in producing amino acid enantiomeric excesses, the initial results are promising. Future work can concentrate on autocatalysis mechanisms, refinement of the weak interaction mechanism, and studies of molecular effects. Experimental work is underway to simulate the environment necessary for this model to work in NMR-type experiments while confirming the shielding tensor calculations. In addition, polarized beam and target experiments are being planned to study and simulate the effects of the weak interaction on polarized molecules.

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