

Article

Astrophysical Sites that Can Produce Enantiomeric Amino Acids

Michael Famiano ^{1,2,*} , Richard Boyd ³ , Toshitaka Kajino ^{2,4,5} , Takashi Onaka ⁶
and Yirong Mo ⁷ 

¹ Department of Physics, Western Michigan University, Kalamazoo, MI 49008, USA

² National Astronomical Observatory of Japan, Division of Science, Mitaka, Tokyo 181-8588, Japan; kajino@nao.ac.jp

³ Department of Physics, Department of Astronomy, The Ohio State University, Columbus, OH 43210, USA; richard11boyde@comcast.net

⁴ Department of Physics, Graduate School of Science, University of Tokyo, Tokyo 113-8654, Japan

⁵ School of Physics, Beihang University, Beijing 100083, China

⁶ Department of Astronomy, Graduate School of Science, University of Tokyo, Tokyo 113-8654, Japan; onaka@astron.s.u-tokyo.ac.jp

⁷ Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008, USA; yirong.mo@wmich.edu

* Correspondence: michael.famiano@wmich.edu; Tel.: +1-269-387-4931

Received: 28 November 2018; Accepted: 23 December 2018; Published: 28 December 2018



Abstract: Recent work has produced theoretical evidence for two sites, colliding neutron stars and neutron-star–Wolf–Rayet binary systems, which might produce amino acids with the left-handed chirality preference found in meteorites. The Supernova Neutrino Amino Acid Processing (SNAAP) model uses electron antineutrinos and the magnetic field from source objects such as neutron stars to preferentially destroy one enantiomer over another. Large enantiomeric excesses are predicted for isovaline and alanine; although based on an earlier study, similar results are expected for the others. Isotopic abundances of ¹³C and ¹⁵O in meteorites provide a new test of the SNAAP model. This presents implications for the origins of life.

Keywords: origin of life; amino acid handedness; nucleus–molecular coupling; chirality

1. Introduction

Recent studies [1–4] have identified two astrophysical sites in which the combination of intense magnetic fields and high fluxes of electron antineutrinos could produce amino acids with a high probability of favoring left-handed chirality.

Enantiomeric excess ee is defined as $ee = (N_L - N_D)/(N_L + N_D)$, where $N_{L(D)}$ is the number of left- (right-)handed molecules in a population. An ensemble of amino acids with $ee = 1$ are purely left-handed, while those with $ee = -1$ are purely right-handed. The ensemble is racemic if $ee = 0$, having equal left- and right-handed molecule parts.

Our studies have shown that ees of the order of a percent or higher could be produced from two-neutron-star coalescence, and somewhat lower, but still appreciable ees could arise from a close binary system consisting of a massive star and a neutron star. Note, though, that this latter site might ultimately evolve into a two-neutron-star coalescence site.

Amino acids are essential for the continuing existence of life, and may have even enabled its formation. The basic steps by which life might have developed from these basic molecules are not fully known, though much progress has recently been made for understanding them [5–7]. All amino acids (except for achiral glycine) used by Earth’s living creatures are homochiral ($ee = 1$), to the near exclusion of right-handed forms. Molecular chirality was originally studied by Pasteur [8], and the

homochirality of the amino acids was subsequently deduced. However, the origin of amino acid chirality is still a mystery.

Mid-20th century experiments [9,10] suggested that organic molecules, including amino acids, may have been assembled in an early earthly lightning storm. However, this result does not explain how amino acids achieved homochirality. Possible mechanisms to explain the conversion of racemic amino acids to purely left-handed ones in terrestrial processes have been reviewed by Bonner [11]. It was concluded that these processes would likely not result in amino acids of a single chirality. Additional evaluations have been made by Mason [12] and Barron [13].

Furthermore, it was concluded by Goldanskii and Kuzmin [14], and by Bonner [11], that amino acid homochirality is essential for the perpetuation of life.

Amino acids have been found in meteorites, and are therefore produced in outer space [15–20]. Further, some of these have been found to have nonzero *ees*, of typically a few percent, and to mostly be left-handed, suggesting a possible cosmic origin of amino acids. Earth may, therefore, have been seeded with chirally selected amino acids. The observed *ees*, however, require amplification, presumably via autocatalysis [14,21,22], to achieve earthly homochirality. Autocatalysis is thought to have converted small *ees* to the homochirality observed today. Autocatalytic processes have been demonstrated in laboratory experiments [23–26] to produce homochiral populations from very small *ees*. Although attempts have been made to sample *ees* of amino acids on objects in outer space [27,28], those missions have not yet provided definitive results.

The production of enantiomeric amino acids in space could possibly be explained by multiple models. One possible model explains a production of chiral amino acids with ultraviolet circularly polarized light (CPL). Mie scattering from an extremely hot star was suggested by Flores et al. [29] and Norden [30]. This has been extensively studied [31–36]. This model has the advantage that its chiral selectivity can be experimentally demonstrated with beams of polarized photons from an accelerator. However, significant molecular selectivity also requires the destruction of most pre-existing amino acids of both chiralities. The CPL model can produce either positive or negative *ees*, whereas the Supernova Neutrino Amino Acid Processing (SNAAP) model is capable of producing only one enantiomeric excess in a single site.

Another model, Magneto-Chiral Anisotropy (MCA), has been developed by Wagniere and Meier [37], explored experimentally by Rikken and Raupach [38], and extended by Barron [39]. In this model, the interaction between photons from an intense light source, for example, a supernova, and molecules in a magnetic field, possibly from the supernova's nascent neutron star, would produce a chirality-dependent destruction effect on the amino acids. The dielectric constant of a medium depends on $\mathbf{k} \cdot \mathbf{B}$, where $\mathbf{k}$ is the wavevector in the direction of travel of the incident light, and $\mathbf{B}$ is an external magnetic field. The dielectric constant increases (decreases) when incident light travels in the same (opposite) direction as the external magnetic field. This effect has opposite signs for L- and D-enantiomers. The net result is that one enantiomer absorbs more of the incident light (and is thus preferentially destroyed) than the other. Experimental studies on this effect have resulted in *ees* on the order of 10^{-4} for chiral molecules [40]. The MCA model can also produce *ees* of either sign.

Other models exist, but these are generally less developed than the MCA or CPL models [40,41]. The SNAAP model [3,4,42], described below, utilizes intense magnetic fields and electron antineutrinos to create enantiomeric amino acids. Quantum molecular calculations indicate that the SNAAP model can produce enantiomeric amino acids with significant positive *ees* [4]. A particularly viable astrophysical scenario for this model was suggested [2] to be a neutron-star–Wolf–Rayet-star binary system.

In this work, we discuss the SNAAP model as it applies to three systems. The first is a core-collapse supernova that, albeit problematic, does illustrate some of the basic features of the model. The second is a neutron star and massive star binary system. The third is one with two neutron stars that merge. We estimated the *ees* produced in each site for the alanine and isovaline amino acids over

a range of parameters within the sites, applying the quantum molecular calculations developed for previous studies.

SNAAP model basics are described in Section 2. Application of the SNAAP model to various sites is discussed in Section 3, followed by a discussion of the simulations relevant to their development in Section 4. Section 5 presents the results for each site. Section 6 discusses how the SNAAP model might explain the isotopic abundances observed in the meteorites, and Section 7 gives our conclusions.

2. SNAAP Model

In this model [1–4,42], amino acids contained within meteoroids in the vicinity of an intense magnetic field and electron antineutrino (hereafter denoted ‘antineutrino’) flux are processed. As a result of the parity-violating weak interaction induced by antineutrino interactions with the ^{14}N nuclei of the amino acids, one enantiomer is destroyed over another.

The relevant nuclear reaction is:



where $\bar{\nu}_e$ is an electron antineutrino, and e^+ is an antielectron—a positron. If the ^{14}N spin (1, in units of $\hbar$, where $\hbar$ is Planck’s constant divided by 2π) is antiparallel to the $\bar{\nu}_e$ spin (spin 1/2), the total quantum mechanical angular momentum of the reaction can be 1/2. This must be equal to the sum of the spins of ^{14}C (spin 0) and the positron (spin 1/2) in order to conserve angular momentum so that this reaction can proceed. Alternatively, if the ^{14}N spin is aligned parallel to the $\bar{\nu}_e$ spin, the total angular momentum can only be 3/2, and, for angular momentum to be conserved, one unit of angular momentum must be provided by the wavefunction of either the incoming $\bar{\nu}_e$ or the outgoing positron. This process is known from basic nuclear physics [43] to occur at a much smaller rate (roughly one order of magnitude) than the antialigned case.

Although this transition must be between nuclear states of opposite parity, for $^{14}\text{N} \rightarrow {}^{14}\text{C}$, both ground states have positive parity. Thus, two units of angular momentum must come from the antineutrino or positron wave functions for that transition to occur. Thus, the inhibition may be closer to two orders of magnitude. This is the origin of the preferential destruction postulated by the SNAAP model.

The energies of the antineutrinos from some of the sources we considered are sufficiently large that it might be possible for a transition to occur between the ^{14}N ground state and the negative-parity ^{14}C first excited state. However, transitions to the negative-parity states in ^{14}C all require not only the weak interaction, but also excitation of one of the nucleons in ^{14}C from the p-shell to the higher lying sd-shell. Such reactions would thus have their own additional level of inhibition, and would therefore probably not be more likely than the ground state to ground-state transition.

Molecular interactions with the external magnetic field have been studied via quantum molecular calculations [1,4]. Such a field can come from a neutron star. In the molecular rest frame, an electric field is produced by the motion of the meteoroids in the magnetic field. This produces a truly chiral environment [13]. In this situation, more right-handed amino acids are destroyed by the interaction of the ^{14}N nuclei with the $\bar{\nu}_e$ s than left-handed ones [4].

The destruction mechanism is nuclear, but amino acid chirality is molecular, so it must be shown how the nucleus and molecule are coupled. The external magnetic field aligns the ^{14}N nuclei via their nuclear magnetic moments, whereas the effective electric field aligns the molecular electric dipole moments, which depend on chirality. The external magnetic field, however, is modified at the nucleus by the effects of the orbital electrons, known as shielding—a phenomenon central to nuclear magnetic resonance. The rank-2 shielding tensor (i.e., a two-dimensional relationship, expressed in the form of a matrix, which relates each vector component of the external field to each vector component of the shift in the local field) depends on the electron orbital configuration. Because the electron orbital configuration depends on the molecular geometry, the shielding tensor depends on the

chirality of the molecule. As a result, off-diagonal elements in the shielding tensor are asymmetric under parity transformation, meaning that they are asymmetric under a change in chirality [1,3]. A chirality-dependent magnetization (a bulk property) is created.

The vectors associated with this scenario are illustrated in Figure 1. Here, a scenario for a meteoroid at or near the equatorial plane of the magnetic dipole is studied. There, it can be seen that the external electric field vector E_{TS} (which is coming out of the page in this diagram) is induced by the meteoroid's velocity vector v_m through external magnetic flux B . Here, an antineutrino velocity vector $v_{\bar{\nu}}$ makes an angle θ with respect to the meteoroid velocity vector. The bulk magnetization vector is M for a meteoroid at rest. For moving meteoroids, the induced electric field creates additional transverse magnetization components ΔM_{χ} , where χ represents the chiral state. This induced magnetization is chirality-dependent, and results in net-positive and -negative spin components aligned along the magnetization vectors. The population of nuclei with spins along these components is labeled as $N_{+,-}$ in the figure. The angle 2ϕ is the separation of net magnetization vectors M_{χ} , where $\phi = \tan^{-1}(\Delta M/M)$. The difference in angle between net magnetization and neutrino velocity results in a different reaction rate for each chiral state [3,4].

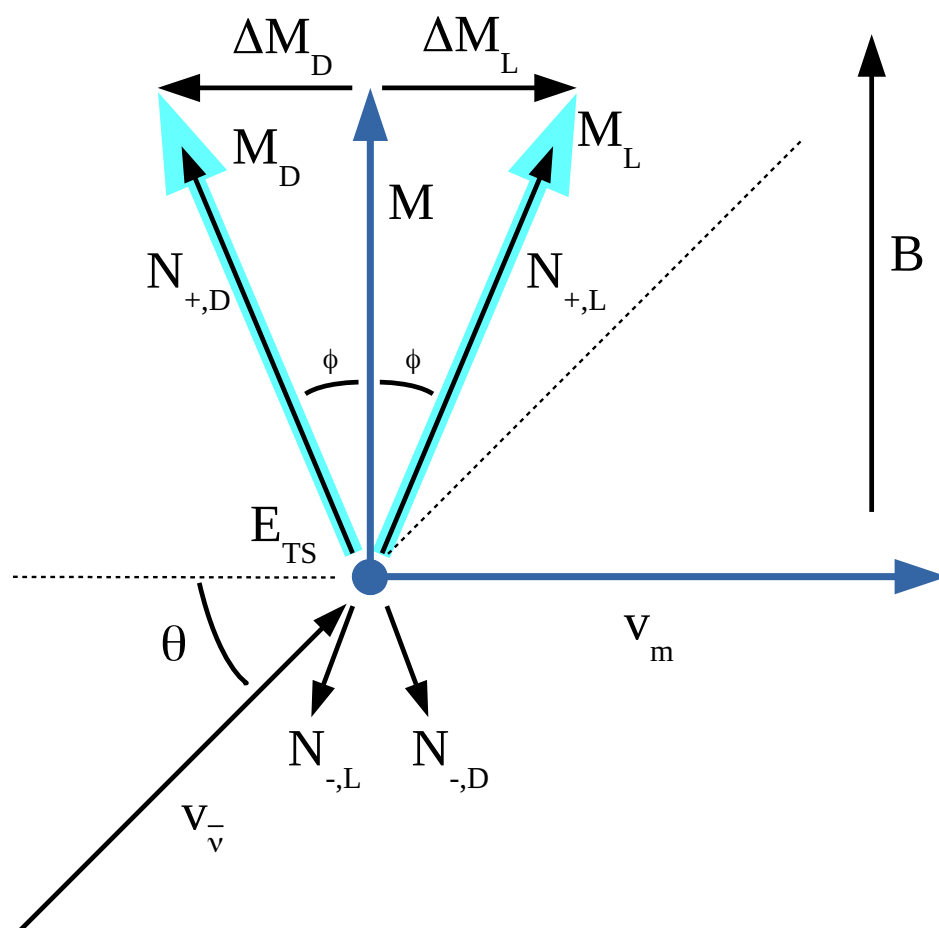


Figure 1. Vectors relevant to the processing of amino acids in this model. The vectors and labels are explained in the text [1]. Used with the permission of Astrobiology.

The external electric field enhances this asymmetry by aligning the molecule along its electric dipole moment [44], thus coupling the nuclear spin and the molecular chirality to result in the selective destruction of one enantiomer [4]. The destruction rate of individual enantiomers and spin states can be used to determine the evolution of the *ee* in time.

Figure 1 shows that the net magnetization, which is an average of the ^{14}N spins, is not necessarily parallel or antiparallel to the antineutrino velocity (and spin) vector. Thus, the antineutrino/nucleus wavefunction consists of a mixture of antialigned and aligned states. The interactions are a result of the projection of the nitrogen spin onto the antineutrino spin vector. However, because of the splitting of the magnetization vector, the components of this mixture are chirality-dependent. In Figure 1, it can be seen that the nuclei of the D enantiomers have a net magnetization that is more antialigned with the antineutrino spin than those of the L enantiomers. This is because the magnetic field for D enantiomers shifts in the direction toward the incoming neutrino and shifts in the opposite direction for the L enantiomer. This results in a higher number of spins of the D enantiomer pointing toward the neutrino. Thus, on average, the nuclei of the D enantiomers are subject to larger destruction cross-sections than the nuclei of the L enantiomers. To take into account this splitting, we adopted the factor in which the value of the reaction rate is proportional to $1 - \cos \Theta$, where Θ is the angle between the antineutrino spin vector and the magnetization vector [45], a good approximation for the considered geometries.

It is also possible that the electron neutrinos could interact with ^{14}N to produce ^{14}O . However, the energy threshold of this reaction is much higher (greater than 5 MeV compared to the order of 1 MeV). Because the cross-section for neutrino-capture processes increases as the square of the energy above threshold, and the antineutrino energies expected [46] from one of the sites, we consider, that coalescing neutron stars are predicted to be much larger for antineutrinos than neutrinos (16 MeV versus 10 MeV), this reaction does not have a significant result in producing a negative enantiomerism from the combined flux from antineutrinos and neutrinos—at least in the two-neutron-star coalescence model.

The size of the meteoroid or planetoid in this model is not constrained, as the antineutrinos are able to pass through the intervening material. They simply must be large enough to survive the passage through space and atmospheric entry. Possible candidates that may provide the necessary conditions for this model include massive-star-neutron-star binaries, magnetars, Wolf-Rayet stars, or “silent supernovae”. These are stars massive enough to collapse into black holes. In this process, they create magnetic fields large enough for this model to work. They also create a very large antineutrino flux, but very few photons. Another possible candidate is the site of merging neutron stars, which also produces these same conditions, but with greater magnetic field strength and antineutrino flux at the location of the meteoroid than in the other sites, primarily due to the meteoroid’s closer proximity to the event [47,48].

3. Amino Acid Processing in Various Possible Sites

3.1. Processing from a Core-Collapse Supernova

The most obvious candidate for enabling the SNAAP model is a core-collapse supernova from a single massive star. The magnetic field produced by the nascent neutron-star remnant and the antineutrino flux are both enormous. However, this site has a fatal flaw: when the massive star goes into its red-giant phase of stellar evolution, its periphery expands out to about 1 AU. However, our calculations have shown that, because the magnetic field decreases significantly with radius, amino acids would not be significantly affected beyond about 0.01 AU [43,49]. The amino acids that could be processed are therefore inside the star, and would surely be incinerated. Note that the same problem exists for the MCA model; a single isolated supernova cannot work there either.

3.2. Processing from a Close Neutron-Star–Massive-Star Binary

A system such as this would presumably have been born from two massive stars in close proximity. When the more massive one completed its stages of stellar evolution and became a supernova, it would create a neutron star, assuming it wasn't so massive so as to collapse into a black hole. If those two stars remained together, the neutron star would attract the outer one or two layers from the remaining massive star, creating a Wolf–Rayet (WR) star. It would continue its stages of stellar evolution, and would eventually become a core-collapse supernova, known as a Type Ib or Ic.

The material that had been attracted to the neutron star would form an accretion disk around the neutron star. These have been studied in detail, and have been found to enable the formation of dust grains, meteoroids, and even planets [50]. The cooler outer regions could presumably also permit the creation of amino acids, possibly on the dust grains that have formed. These may be shielded from radiation from the WR star, for the portions of their trajectory that are closest to the WR star, by more outward facing regions of the disk. Amino acids have been shown to form on dust grains [51], although under different conditions than would be expected in the outer regions of an accretion disk.

An important consideration is the region in which amino acids might be formed in the accretion disk around one of the neutron stars. Most disk simulations do not extend to temperatures at which molecules might form, but they agree that the temperature falls off roughly as $r^{-3/4}$. D'Alessio et al. [50] found that the midplane temperature depends on the assumed grain size, but was typically several hundred K at 1 AU for the system they considered. Thus, molecules might begin to form around an AU from the central object. However, this is outside the region in which the nuclei could be oriented by the magnetic field from the neutron star.

Although there may be considerations that would allow amino acids to exist closer to their parent neutron star, this might be a long-term prospect that would result in the destruction of the formed amino acids in all but the largest meteoroids. As smaller objects with amino acids agglomerated into larger ones, the material in the disk would impede their velocity, reducing it to less than that required for them to maintain a stable orbit. Thus, they would gradually sink toward the neutron star. Although it might be difficult to have very many amino acids existing within 0.01 AU, the maximum distance within which they would experience a sufficiently large magnetic field to sustain a selection between chiral states, some might survive their trek to that radius if they were in large meteoroids.

3.3. Processing from the Merger of Two Neutron Stars

The two neutron stars in close orbit might have begun their existence as two massive stars. When the first exploded as a supernova, it became a neutron star that drew the outer one or two shells off of the remaining massive star, creating an accretion disk around the neutron star, leaving the other as a WR star. However, when the second star exploded, the result might well have been a two-neutron-star system, with the two in close proximity. One of them would also probably retain some semblance to the accretion disk it had before the WR star exploded.

What is known from GW170817 [52], simultaneously observed by the FERMI [53] and INTEGRAL [54] gamma-ray detectors, and by the CHANDRA [55] X-ray detector, as well as by many optical telescopes, is that a lot of heavy nuclides were synthesized via the rapid-neutron-capture process resulting from the merger of the two neutron stars. While the details of this depend on the masses of the two stars prior to the merger, the final-state neutron star or black hole may not be of great consequence to our considerations. The actual amount of created heavy nuclides has been estimated [56] to be several tenths of a solar mass. Since this was made largely from neutron matter, a huge flux of electron antineutrinos must have been produced by the process that converted the essentially pure neutron matter to the neutron-rich progenitors of the r-process nuclei. (Here, "r-process nuclei" are isotopes thought to be produced via neutron-capture reactions in explosive environments. The r-process is responsible for production of nearly all of the elements heavier than iron [57].)

Fortunately, enough theoretical work [46,58] has been done on two-neutron star mergers that good estimates of the needed parameters to perform SNAAP model calculations exist. In particular,

the maximum magnetic field generated at the composite neutron star is around 10^{17} G [46]. That permits the magnetic-field orientation region to extend nearly an order of magnitude beyond what it would be for the supernova from a neutron-star–WR-star binary system.

Perego et al. [58], and Rosswog and Liebendorf [46] calculated both the expected fluxes for electron neutrinos and antineutrinos, and their energies. The electron antineutrinos are the dominant species, and their total flux is expected to exceed 10^{53} ergs in the fraction of a second during which they would be emitted. Their mean energy is predicted to be 16 MeV.

However, for creating enantiomeric amino acids, it is important to consider the disk. When the second neutron star began to converge on its companion to a distance where it would begin to intercept the outer regions of the disk, the disk would be disrupted by the gravitational field of the second neutron star. Amino acid-laden meteoroids might be pulled into a close orbit with the second star, or might be deflected into elongated orbits. As the second star continued to plow through increasingly dense regions of the disk, it would thoroughly mix the disk material, dragging some of the meteoroids from the outer disk regions into regions closer to one or the other neutron star and sending others into orbits that would allow them to pass by the central objects after longer, and highly variable, times. As the two stars grew even closer, this disk material would begin to orbit both stars, and would be compressed under the increased gravitational pull of the two stars.

Presumably, many of the amino acids, especially those enclosed in larger meteoroids with highly elongated orbits, could survive the higher temperatures in which they would find themselves for some time, in some cases long enough for the two stars to complete their spiral into an object. The huge magnetic field of the resulting neutron star, along with the enormous flux of electron antineutrinos, would also surely produce *ees* in many of these amino acids. The expanding “butterfly” inner disk of matter that is predicted to occur [46,59] would presumably eventually push the outer disk into outer space, there to seed the surrounding volume with enantiomeric amino acids.

4. Simulations

Approximations have been performed of the level of conversion of amino acids that might have existed in the accretion disk from racemic to enantiomeric. Important factors include the gravitational field, the magnetic field, the meteoroid orbital characteristics, and the electron antineutrino flux. Many of these factors are dependent on the meteoroid distance from the neutron star. This includes the meteoroid velocity, which is closely linked to the distance from the star. The details of the calculation are described in prior work [1], so we only summarize them here.

We have computed the shielding tensors and electric dipole moments in each enantiomer of isovaline and alanine using the Gaussian16 [60] quantum chemistry code [4]. The environmental conditions that approximate the expected environment in the space surrounding a neutron-star merger were simulated. For a typical merger event, the two stars of 1 solar mass each, with a net surface field of 10^{11} T, are assumed. Because the dynamics of the fields (gravitational and magnetic) and the neutrino flux can be complicated in a typical event, we assumed a spherical mass of $2 M_{\odot}$ with a dipole field. A constant antineutrino flux of $10^{57} \text{ cm}^{-2}\text{s}^{-1}$ was assumed at the surface of the merger event for one second with an average cross-section for the $^{14}\text{N}(\bar{\nu}, e^+)^{14}\text{C}$ of 10^{-40} cm^2 . The net antineutrino interaction rate, f , relative to half the ^{14}N relaxation time, T_1 , is defined by a unitless fraction [1]:

$$f \equiv 2 \frac{\lambda_{\bar{\nu}}}{\lambda_R} = 2\lambda_{\bar{\nu}}T_1 \quad (2)$$

Using the computed shielding tensor, the nuclear magnetic polarizabilities for cationic isovaline and alanine were computed with a density functional theory (DFT) calculation using a pcS-2 basis set [61]. Prior to this, the initial electronic wavefunctions were optimized using an HF + MP2 [62] computation with the aug-cc-pVDZ basis.

With the resultant shielding-tensor asymmetries, the difference in magnetic field vector for each enantiomer was determined, $\mathbf{B}_{\chi} = \mathbf{B}_o + \Delta\mathbf{B}_{\chi}$, where χ represents the chirality of a particular

enantiomer. The antineutrino-interaction rates vary as $\sigma \cdot \mathbf{B}_\chi \rightarrow \mathbf{v} \cdot \mathbf{B}_\chi$ [63], where σ and $\mathbf{v}$ are the antineutrino spin and velocity vectors, respectively. Assuming a massless antineutrino, its spin vector points in the same direction as its momentum vector.

5. Results

Several simulations were run, in which the ee s of multiple amino acids were computed as a function of time in the vicinity of a neutron-star merger.

The net ee as a function of time and orbital radius is shown in Figure 2 for isovaline. Because the merger event is so fast, it can be assumed that the orbital radius changes little over the course of an event. Disk viscosity, however, is an unknown parameter in this model, so a constant meteoroid velocity of 1% of the vacuum orbital velocity was assumed for all orbital radii. Larger velocities commensurate with close radii would result in a higher computed ee .

In Figure 2, a plot of the ee up to 1 s, the assumed duration of the antineutrino pulse, is also shown for various assumptions of the meteoroid velocity at a constant orbital radius of 1500 km from the merger event. It can be seen that the achieved ees can become large, comparable to those observed in meteorite analyses, at least at that assumed radius. For lower velocities or greater distances from the resultant neutron star, ees of the order of a percent can still be achieved.

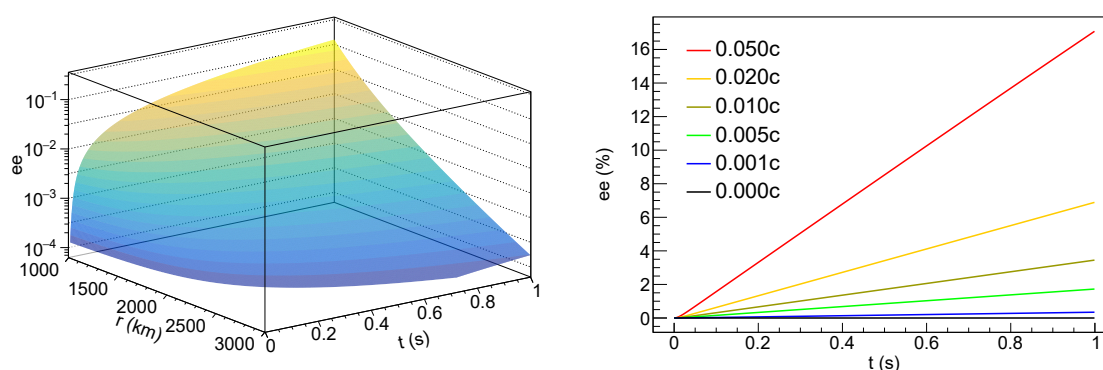


Figure 2. Left: ee as a function of time and radius from a neutron binary merger for isovaline. Velocity for a circular orbit is assumed to be damped to 1% of the orbital velocity of a circular orbit. Right: ee as a function of time for various meteoroid velocities at a fixed distance of 1500 km from the merger, where c is the velocity of light.

The conditions in Figure 2 are a result of large magnetic fields. This model also produces large electric fields; these may possibly exceed the dielectric strengths of the amino acids. However, this effect could be mitigated in several ways. A strong magnetic field and a weak electric field can result in the same chiral selection. Additionally, this effect could work if the amino acids were contained in crystalline structures for which a much smaller electric field may suffice.

In prior work, it was shown that, if the antineutrino flux continues for too long, a total destruction of both L- and D-enantiomers could result, and a sudden drop in ee occurs as all amino acids are destroyed. This is partially due to their thermalization. In the case of the NN merger event, the antineutrino pulse is so short that the ee rapidly increases and the antineutrino flux stops well before all of the amino acids are destroyed.

The results for alanine are shown in Figure 3. Here, it is seen that the ee as a function of time and distance is similar to that of isovaline. It is noted that, after 1 s, the ee of isovaline is slightly larger than that of alanine. As explained in previous work [4], the product of the asymmetric components of the shielding tensor and the electric dipole moment is larger for isovaline than for alanine. It is seen, however, that a sizable ee can still result for alanine. Although the present results were only achieved for isovaline and alanine, our previous work [4] strongly suggests that similar results would be obtained for most other amino acids.

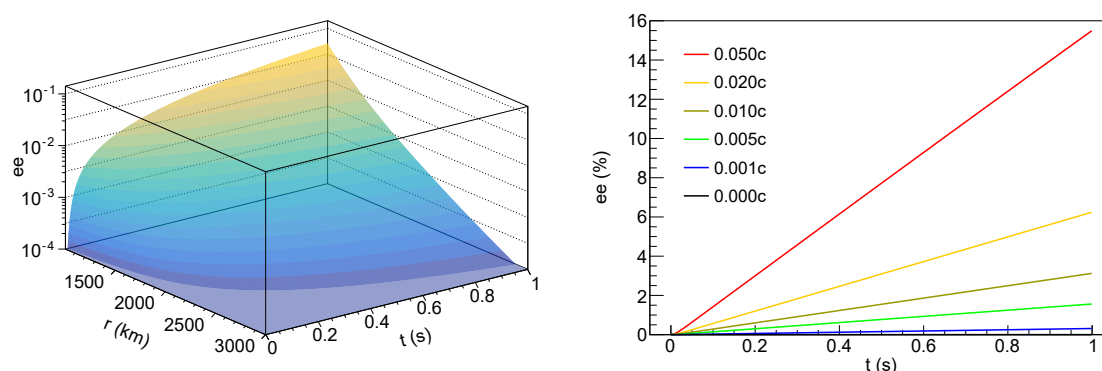


Figure 3. Left: ee as a function of time and radius from a neutron binary merger for alanine. Velocity for a circular orbit is assumed to be damped to 1% of the orbital velocity of a circular orbit. Right: ee as a function of time for various meteoroid velocities at a fixed distance of 1500 km from the merger, where c is the velocity of light.

The results for the neutron-star–WR-star binary system are not as impressive as those from the two-neutron-star merger model, but appear to produce viable ees nonetheless. We estimate those to be roughly four orders of magnitude less than those for the two-neutron-star merger case. In this case, the amino acids would obviously require amplification via autocatalysis to reach the levels found in meteorites, but their ees are still competitive with those from other models of chiral selection. Note, though, that these two sites are sufficiently different that other issues may affect the ratio of achievable ees . For example, the magnetic field for the two-neutron-star merger may be so high that processing of the amino acids cannot occur as close to the merged object (because the resulting electric field might destroy the molecules) as it could to the neutron star in the neutron-star–WR-star site. As noted above, though, that site might well evolve to the two-neutron-star case when the WR star explodes, in which case considerably higher ees would be achieved.

The single supernova is problematic, though, because its red-giant phase would envelop any amino acids that could be processed by its electron antineutrinos. We estimate that the maximum ee it could achieve would be 10^{-10} or even less. This is probably not a viable site for providing Earth's enantiomeric amino acids.

6. Test of the SNAAP Model

Recent analyses of amino acids in meteorites [64,65] have presented an interesting test of the SNAAP model. The relative abundances of ^{15}N and ^{13}C , both stable nuclides with low normal relative abundances (^{15}N is 0.366 percent of natural N and ^{13}C is 1.11 percent of natural C) were observed to be enhanced in meteoritic amino acids. The abundance of ^{15}N is considerably larger, about a factor of 10, than that of ^{13}C , although the actual enhancement factor considerably varies from one amino acid to another.

We developed a simple model to see if the SNAAP model is consistent with these isotopic enrichments. Both charged-current and neutral-current reactions can change the mass numbers of nuclei if they go to sufficiently highly excited states in the residual nucleus that they can decay by proton or neutron emission. We assume in the following discussion that neutral-current reactions perform the transitions, although the results would not be different if charged-current reactions were included. Then, the relative abundance of ^{15}N to ^{14}N is enhanced both by ^{15}N production from antineutrino reactions on ^{16}O and by ^{14}N destruction by antineutrino reactions. Similarly, the ^{13}C to ^{12}C abundance ratio is enhanced by production from antineutrino reactions on ^{14}N and destruction of ^{12}C by antineutrinos.

In order to simulate the neutral-current reactions, we approximated the antineutrino energy distribution, which has a mean energy of 16 MeV [46,58], with a flat distribution from 8 to 24 MeV,

and assumed the reactions varied with the square of the energy. (The results from our model are rather insensitive to the details of the distribution.) This model produced relative destruction rates for ^{16}O : ^{14}N : ^{12}C of 8.3:22.7:2.3, with the destruction rate of ^{14}N being the largest because it has the lowest energy threshold of all the possible reactions. In each case, the yields from the two possible reactions were added to produce the result, since the two reactions produce the same final nucleus following the beta decay of the unstable member. For example, the interaction of an antineutrino with ^{16}O can produce either ^{15}O plus a neutron or ^{15}N plus a proton, but ^{15}O decays to ^{15}N .

To determine the enhancement of ^{15}N to ^{14}N from the destruction rates on ^{16}O and ^{14}N , one must take into account the relative abundances of ^{16}O and ^{14}N , and similarly for determining the production of ^{13}C to ^{12}C . The natural relative abundances are, roughly, for O:N:C = 10:1:4 [66] (these depend on whether they are galactic or solar abundances, so the numbers given are a rough average of those from the two sets of values). However, these may not be the abundances in the meteoroids when they get processed. The abundances of the three elements are more likely to be comparable in amino acids, but those are not the only molecules formed in the meteoroids. Indeed, there would most likely be some water, and that would enhance oxygen abundance. In the absence of better information, we have just assumed the natural abundances. When these are included, they give a relative enhancement factor of ^{15}N to ^{13}C of about 8.5.

This calculated ratio of the rare isotope enhancements is similar to the observed enhancements in meteorites of rarer isotopes (~ 2 –10) to well within the observed fluctuations for different amino acids [64,65]. Since both the charged-current and neutral-current interactions would affect most of the nuclides other than hydrogen in the amino acids, they produce atomic detritus that have insufficient recoil energy to move very far from where it is produced. Thus, after the neutrino burst ends, it would be expected that these atoms would recombine into new molecules, some of which would be amino acids. It should also be noted that the dust grains on which much of the interstellar chemistry is thought to occur have both carbon and water, that is, oxygen. The neutrinos certainly produce more nitrogen from the oxygen that was not part of the original amino acid inventory, but might well be when recombination occurs. If antineutrino exposure results in a production of nitrogen, then it might be possible to produce more amino acids afterward, as more nitrogen is available for their production, assuming that available nitrogen is the limiting factor in amino acid production. Given the possibility of autocatalysis, that might well increase the *ees*.

7. Conclusions

The present results suggest that NN-star mergers are a potentially ideal site for producing appreciable enantiomeric excesses in meteoroids that were nearby when the merger occurred. Furthermore, the ability of the SNAAP model to reproduce the ratio of the isotopic enhancements of ^{13}C and ^{15}N does lend confidence in the basic features of the SNAAP model. Finally, the SNAAP model may well explain the enantiomeric excesses observed in meteorites and even, possibly, the origin of life on Earth.

Author Contributions: M.A.F. performed the calculations and wrote the descriptions thereof; R.N.B. did the calculations of the isotopic abundances and wrote their description; M.A.F. and R.N.B. wrote the rest of the paper jointly; T.K., T.O., and Y.M. edited the draft of the manuscript.

Funding: This research was funded by Moore Foundation grant #7799, a Western Michigan University Faculty Research and Creative Activities Award, and by Grants-in-Aid for Scientific Research of JSPS (15H03665, 17K05459). The APC was funded by Moore Foundation grant #7799.

Acknowledgments: M.A.F. is supported by a Moore Foundation, grant #7799, and by a Western Michigan University Faculty Research and Creative Activities Award. T.K. is supported by Grants-in-Aid for Scientific Research of JSPS (15H03665, 17K05459).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

AU	Astronomical Unit
CPL	Circularly Polarized Light
ee	enantiomeric excess
MCA	Magneto-Chiral Anisotropy
SNAAP	Supernova Neutrino Amino Acid Processing
WR	Wolf-Rayet (star)

References

1. Famiano, M.A.; Boyd, R.N.; Kajino, T.; Onaka, T. Selection of Amino Acid Chirality via Neutrino Interactions with ^{14}N in Crossed Electric and Magnetic Fields. *Astrobiology* **2018**, *18*, 190–206. [[CrossRef](#)] [[PubMed](#)]
2. Boyd, R.N.; Famiano, M.A.; Onaka, T.; Kajino, T. Sites that Can Produce Left-handed Amino Acids in the Supernova Neutrino Amino Acid Processing Model. *Astrophys. J.* **2018**, *856*, 26–30. [[CrossRef](#)]
3. Boyd, R.; Famiano, M. *Creating the Molecules of Life*; IOP: London, UK, 2018.
4. Famiano, M.; Boyd, R.; Kajino, T.; Onaka, T.; Mo, Y. Amino Acid Chiral Selection Via Weak Interactions in Stellar Environments: Implications for the Origin of Life. *Sci. Rep.* **2018**, *8*, 8833. [[CrossRef](#)] [[PubMed](#)]
5. Rode, B.; Fitz, D.; Jakschitz, T. The First Steps of Chemical Evolution towards the Origin of Life. *Chem. Biodivers.* **2007**, *4*, 2674–2702. [[CrossRef](#)] [[PubMed](#)]
6. Pennisi, E. The power of many. *Science* **2018**, *360*, 1388–1391. [[CrossRef](#)] [[PubMed](#)]
7. Sadownik, J.; Mattia, E.; Nowak, P.; Otto, S. Diversification of self-replicating molecules. *Nat. Chem.* **2016**, *8*, 264–269. [[CrossRef](#)] [[PubMed](#)]
8. Pasteur, L. Mémoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de la polarisation rotatoire. *C. R. Acad. Sci. Paris* **1848**, *26*, 535–538.
9. Miller, S. The Production of Amino Acids Under Possible Primitive Earth Conditions. *Science* **1953**, *117*, 528. [[CrossRef](#)]
10. Miller, S.; Urey, H. Organic Compound Syntheses on the Primitive Earth. *Science* **1959**, *130*, 245–251. [[CrossRef](#)]
11. Bonner, W. The origin and amplification of biomolecular chirality. *Orig. Life Evolut. Biosph.* **1991**, *21*, 59–111. [[CrossRef](#)]
12. Mason, S.F. Origins of biomolecular handedness. *Nature* **1984**, *311*, 19–23. [[CrossRef](#)] [[PubMed](#)]
13. Barron, L. Chirality and Life. *Space Sci. Ser.* **2008**, *135*, 187–201. [[CrossRef](#)]
14. Goldanskii, V. Spontaneous mirror symmetry breaking in nature and the origin of life. *Orig. Life Evolut. Biosph.* **1989**, *19*, 269–272. [[CrossRef](#)]
15. Kvenvolden, K.; Lawless, J.; Perring, K.; Peterson, E.; Flores, J.; Ponnampereuma, C. Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite. *Nature* **1970**, *228*, 923–926. [[CrossRef](#)] [[PubMed](#)]
16. Bada, J.; Cronin, J.; Ho, M.S.; Kvenvolden, K.; Lawless, J.; Miller, S.; Oro, J.; Steinberg, S. On the reported optical activity of amino acids in the Murchison meteorite. *Nature* **1983**, *301*, 494–496. [[CrossRef](#)]
17. Cronin, J.; Pizzarello, S. Enantiomeric excesses in meteoritic amino acids. *Science* **1997**, *275*, 951–955. [[CrossRef](#)] [[PubMed](#)]
18. Cronin, J.; Pizzarello, S.; Cruikshank, D. Meteorites and the Early Solar System. In *Meteorites and the Early Solar System*; University of Arizona Press: Tucson, Arizona, 1998; pp. 819–857.
19. Glavin, D.; Dworkin, J. Enrichment of the amino acid L-isovaline by aqueous alteration on CI and CM meteorite parent bodies. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 5487–5492. [[CrossRef](#)]
20. Herd, C.; Blinova, A.; Simkus, D.; Huang, Y.; Tarozo, R.; Alexander, C.; Gyngard, F.; Nittler, L.; Cody, G.; Fogel, M.; et al. Origin and evolution of prebiotic organic matter as inferred from the Tagish Lake meteorite. *Science* **2011**, *332*, 1304–1307. [[CrossRef](#)]
21. Frank, F. On spontaneous asymmetric synthesis. *Biochim. Biophys. Acta* **1953**, *11*, 459–463. [[CrossRef](#)]
22. Kondepudi, D.K.; Nelson, G.W. Weak neutral currents and the origin of biomolecular chirality. *Nature* **1985**, *314*, 438–441. [[CrossRef](#)]

23. Klussmann, M.; Iwamura, H.; Mathew, S.P.; Wells, D.H.; Pandya, U.; Armstrong, A.; Blackmond, D.G. Thermodynamic Control of Asymmetric Amplification in Amino Acid Catalysis. *Nature* **2006**, *441*, 621–623. [[CrossRef](#)] [[PubMed](#)]
24. Breslow, R.; Levine, M.S. Amplification of enantiomeric concentrations under credible prebiotic conditions. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12979–12980. [[CrossRef](#)] [[PubMed](#)]
25. Arseniyadis, S.; Valleix, A.; Wagner, A.; Mioskowski, C. Kinetic Resolution of Amines: A Highly Enantioselective and Chemoselective Acetylating Agent with a Unique Solvent-Induced Reversal of Stereoselectivity. *Angew. Chem. Int. Ed.* **2004**, *43*, 3314–3317. [[CrossRef](#)]
26. Soai, K.; Kawasaki, T.; Matsumoto, A. The Origins of Homochirality Examined by Using Asymmetric Autocatalysis. *Chem. Rec.* **2014**, *14*, 70–83. [[CrossRef](#)] [[PubMed](#)]
27. Goesmann, F.; Rosenbauer, H.; Bredehöft, J.H.; Cabane, M.; Ehrenfreund, P.; Gautier, T.; Giri, C.; Krüger, H.; Le Roy, L.; MacDermott, A.J.; et al. Organic compounds on comet 67P/Churyumov-Gerasimenko revealed by COSAC mass spectrometry. *Science* **2015**, *349*. [[CrossRef](#)] [[PubMed](#)]
28. Kitajima, F.; Uesugi, M.; Karouji, Y.; Ishibashi, Y.; Yada, T.; Naraoka, H.; Abe, M.; Fujimura, A.; Ito, M.; Yabuta, H.; et al. A micro-Raman and infrared study of several Hayabusa category 3 (organic) particles. *Earth Planets Space* **2015**, *67*, 20. [[CrossRef](#)]
29. Flores, J.J.; Bonner, W.A.; Massey, G.A. Asymmetric photolysis of (RS)-leucine with circularly polarized ultraviolet light. *J. Am. Chem. Soc.* **1977**, *99*, 3622–3625. [[CrossRef](#)]
30. Norden, B. Was photoresolution of amino acids the origin of optical activity in life? *Nature* **1977**, *266*, 567–568. [[CrossRef](#)]
31. Bailey, J.; Chrysostomou, A.; Hough, J.H.; Gledhill, T.M.; McCall, A.; Clark, S.; Ménard, F.; Tamura, M. Circular Polarization in Star-Formation Regions: Implications for Biomolecular Homochirality. *Science* **1998**, *281*, 672–674. [[CrossRef](#)]
32. Takano, Y.; Takahashi, J.I.; Kaneko, T.; Marumo, K.; Kobayashi, K. Asymmetric synthesis of amino acid precursors in interstellar complex organics by circularly polarized light. *Earth Planet. Sci. Lett.* **2007**, *254*, 106–114. [[CrossRef](#)]
33. Takahashi, J.I.; Shinojima, H.; Seyama, M.; Ueno, Y.; Kaneko, T.; Kobayashi, K.; Mita, H.; Adachi, M.; Hosaka, M.; Katoh, M. Chirality Emergence in Thin Solid Films of Amino Acids by Polarized Light from Synchrotron Radiation and Free Electron Laser. *Int. J. Mol. Sci.* **2009**, *10*, 3044–3064. [[CrossRef](#)] [[PubMed](#)]
34. Meierhenrich, U.J.; Filippi, J.J.; Meinert, C.; Bredehöft, J.H.; Takahashi, J.I.; Nahon, L.; Jones, N.C.; Hoffmann, S.V. Circular Dichroism of Amino Acids in the Vacuum-Ultraviolet Region. *Angew. Chem. Int. Ed.* **2010**, *49*, 7799–7802. [[CrossRef](#)] [[PubMed](#)]
35. de Marcellus, P.; Meinert, C.; Nuevo, M.; Filippi, J.J.; Danger, G.; Deboffe, D.; Nahon, L.; Le Sergeant d'Hendecourt, L.; Meierhenrich, U. Non-racemic Amino Acid Production by Ultraviolet Irradiation of Achiral Interstellar Ice Analogs with Circularly Polarized Light. *Astrophys. J. Lett.* **2011**, *727*, L27–L32. [[CrossRef](#)]
36. Meinert, C.; Hoffmann, S.V.; Cassam-Chenaï, P.; Evans, A.C.; Giri, C.; Nahon, L.; Meierhenrich, U.J. Photonenergy-Controlled Symmetry Breaking with Circularly Polarized Light. *Angew. Chem. Int. Ed.* **2014**, *53*, 210–214. [[CrossRef](#)] [[PubMed](#)]
37. Wagnière, G.; Meier, A. The influence of a static magnetic field on the absorption coefficient of a chiral molecule. *Chem. Phys. Lett.* **1982**, *93*, 78–81. [[CrossRef](#)]
38. Rikken, G.; Raupach, E. Enantioselective magnetochiral photochemistry. *Nature* **2000**, *405*, 932–935. [[CrossRef](#)] [[PubMed](#)]
39. Barron, L.D. Chirality, Magnetism, and Light. *Nature* **2000**, *405*, 895. [[CrossRef](#)]
40. Guijarro, A.; Yus, M. *The Origin of Chirality in the Molecules of Life*; RSC Publishing: Cambridge, UK, 2009.
41. Meierhenrich, U. *Amino Acids and the Asymmetry of Life: Caught in the Act of Formation*; Springer-Verlag: Berlin/Heidelberg, Germany, 2008.
42. Boyd, R.; Kajino, T.; Onaka, T. Supernovae and the chirality of the amino acids. *Astrobiology* **2010**, *10*, 561–568. [[CrossRef](#)]
43. Boyd, R.N. *An Introduction to Nuclear Astrophysics*; The University of Chicago Press: Chicago, IL, USA, 2008; pp. 126–132.
44. Buckingham, A.; Fischer, P. Direct chiral discrimination in NMR spectroscopy. *Chem. Phys.* **2006**, *324*, 111–116. [[CrossRef](#)]

45. de Shalit, A.; Feshbach, H. *Theoretical Nuclear Physics I: Nuclear Structure*; John Wiley & Sons, Inc.: New York, NY, USA, 1974.
46. Rosswog, S.; Liebendörfer, M. High-resolution calculations of merging neutron stars - II. Neutrino emission. *Mon. Not. R. Astron. Soc.* **2003**, *342*, 673–689. [\[CrossRef\]](#)
47. Tian, J.Y.; Patwardhan, A.V.; Fuller, G.M. Neutrino flavor evolution in neutron star mergers. *Phys. Rev. D* **2017**, *96*, 043001. [\[CrossRef\]](#)
48. Price, D.J.; Rosswog, S. Producing Ultrastrong Magnetic Fields in Neutron Star Mergers. *Science* **2006**, *312*, 719–722. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Famiano, M.; Boyd, R.; Kajino, T.; Onaka, T.; Koehler, K.; Hulbert, S. Determining Amino Acid Chirality in the Supernova Neutrino Processing Model. *Symmetry* **2014**, *6*, 909–925. [\[CrossRef\]](#)
50. D'Alessio, P.; Calvet, N.; Hartmann, L. Accretion Disks around Young Objects. III. Grain Growth. *Astrophys. J.* **2001**, *553*, 321–334. [\[CrossRef\]](#)
51. Muñoz Caro, G.M.; Meierhenrich, U.J.; Schutte, W.A.; Barbier, B.; Arcones Segovia, A.; Rosenbauer, H.; Thiemann, W.H.P.; Brack, A.; Greenberg, J.M. Amino Acids From Ultraviolet Irradiation of Interstellar Ice Analogues. *Nature* **2002**, *416*, 403–406. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Abbott, B.; Abbott, R.; Abbott, T.; Acernese, F.; Ackley, K.; Adams, C.; Adams, T.; Addesso, P.; Adhikari, R.; Adya, V.; et al. GW170817: Observation of Gravitational Waves from a Binary Neutron Star Inspiral. *Phys. Rev. Lett.* **2017**, *119*, 161101. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Goldstein, A.; Veres, P.; Burns, E.; Briggs, M.; Hamburg, R.; Kocevski, D.; Wilson-Hodge, C.; Preece, R.; Poolakkil, S.; Roberts, O.; et al. An Ordinary Short Gamma-Ray Burst with Extraordinary Implications: Fermi-GBM Detection of GRB 170817A. *Astrophys. J. Lett.* **2017**, *848*, L14. [\[CrossRef\]](#)
54. Savchenko, V.; Ferrigno, C.; Kuulkers, E.; Bazzano, A.; Bozzo, E.; Brandt, S.; Chenevez, J.; Courvoisier, T.J.L.; Diehl, R.; Domingo, A.; et al. INTEGRAL Detection of the First Prompt Gamma-Ray Signal Coincident with the Gravitational-wave Event GW170817. *Astrophys. J. Lett.* **2017**, *848*, L15. [\[CrossRef\]](#)
55. Troja, E.; Piro, L.; van Eerten, H.; Wollaeger, R.; Im, M.; Fox, O.; Butler, N.; Cenko, S.; Sakamoto, T.; Fryer, C.; et al. The X-ray counterpart to the gravitational-wave event GW170817. *Nature* **2017**, *551*, 71–74. [\[CrossRef\]](#)
56. Kasen, D.; Metzger, B.; Barnes, J.; Quataert, E.; Ramirez-Ruiz, E. Origin of the heavy elements in binary neutron-star mergers from a gravitational-wave event. *Nature* **2017**, *551*, 80–84. [\[CrossRef\]](#)
57. Arnould, M.; Goriely, S.; Takahashi, K. The r-process of stellar nucleosynthesis: Astrophysics and nuclear physics achievements and mysteries. *Phys. Rep.* **2007**, *450*, 97–213. [\[CrossRef\]](#)
58. Perego, A.; Rosswog, S.; Cabezón, R.; Korobkin, O.; Käppeli, R.; Arcones, A.; Liebendörfer, M. Neutrino-driven winds from neutron star merger remnants. *Mon. Not. R. Astron. Soc.* **2014**, *443*, 3134–3156. [\[CrossRef\]](#)
59. Fernández, R.; Kasen, D.; Metzger, B.; Quataert, E. Outflows from accretion discs formed in neutron star mergers: effect of black hole spin. *Mon. Not. R. Astron. Soc.* **2015**, *446*, 750–758. [\[CrossRef\]](#)
60. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 16 Revision A.03*; Gaussian Inc.: Wallingford, CT, USA, 2016.
61. Jensen, F. Basis Set Convergence of Nuclear Magnetic Shielding Constants Calculated by Density Functional Methods. *J. Chem. Theory Comput.* **2008**, *4*, 719–727. [\[CrossRef\]](#) [\[PubMed\]](#)
62. Jensen, H.; Aa, J.; Jørgensen, P.; Ågren, H.; Olsen, J. Second-order Møller-Plesset perturbation theory as a configuration and orbital generator in multiconfiguration self-consistent field calculations. *J. Chem. Phys.* **1988**, *88*, 3834–3839. [\[CrossRef\]](#)
63. Morita, M. *Beta Decay and Muon Capture*; Benjamin: Reading, MA, USA, 1973.
64. Chan, Q.H.S.; Chikaraishi, Y.; Takano, Y.; Ogawa, N.O.; Ohkouchi, N. Amino acid compositions in heated carbonaceous chondrites and their compound-specific nitrogen isotopic ratios. *Earth Planets Space* **2016**, *68*, 7. [\[CrossRef\]](#)
65. Glavin, D.P.; Elsila, J.E.; Burton, A.S.; Callahan, M.P.; Dworkin, J.P.; Hilts, R.W.; Herd, C.D.K. Unusual nonterrestrial L-proteinogenic amino acid excesses in the Tagish Lake meteorite. *Meteorit. Planet. Sci.* **2012**, *47*, 1347–1364. [\[CrossRef\]](#)
66. Anders, E.; Ebihara, M. Solar-System Abundances of the Elements: A New Table. *Meteoritics* **1982**, *17*, 180.

