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Understanding the Origin of Homochirality in Amino Acids and Polypeptides

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Abstract

Origin of Life (OoL) research has produced an amazing amount of scientific experimentation, but no consensus has emerged on any viable naturalistic path from chemical compounds to living, reproducing cells. One example of the accomplishments, optimism, and then futility of OoL research is the search for a prebiotic, naturalistic origin of homochirality in α-amino acids and polypeptides. This review surveys the current research on the significance of homochirality in proteins, the rivalries within OoL research, the abiotic sources of α-amino acids and polypeptides, their chiral amplification, their prebiotic stability, and the difficulty of finding a naturalistic explanation for the origin of homochirality.

Introduction

Homochirality is an essential physical-chemical characteristic of amino acids, proteins, sugars, polysaccharides, and DNA in all biochemical systems and living organisms. Since Louis Pasteur's discovery of molecular chirality in the 1840s, the homochirality of biological molecules has been recognized as a significant demarcation line between living and nonliving matter, a signature of life (Gol'danskii, 1997; Blackmond, 2010). If there were no naturalistic route to homochirality, then chemical evolution is stopped in its initial steps. In the early twenty-first century, what progress in chemistry, biology, geology, astronomy, and physics supports a naturalistic origin of homochirality in amino acids and polypeptides? The scientific community may never know if a naturalistic route to homochirality in biochemical molecules was possible, but an assessment of research published over the last 15 years or so should indicate whether a naturalistic route is even remotely possible. The recent article "Left-Handed Puzzle Remains" (Coppedge, 2012) whet appetites for a more comprehensive review of the latest research toward understanding the origin of homochirality in α-amino acids and polypeptides. This paper is written to review the origin of life (OoL) research to date regarding homochirality.

OoL researchers have produced elaborate scientific results without solving any of the profound difficulties of a naturalistic explanation for life's origin. Modern OoL publications are filled with optimism, speculation, and awareness of the significance of their research. Here are a few examples. Bergman (2000) noted that abiogenesis, the theory

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that life can arise spontaneously from nonlife molecules, has many scientific obstacles to overcome, including the origin of homochirality. Meinert et al (2010) concluded that scientific studies on the origins of life in general and on the origin of biomolecular homochirality are of interdisciplinary interest and will continue producing important and highly intriguing data on our origins. Meierhenrich (2009) wrote that the inability to link chemical and biological evolution is one of the unsolved fundamental mysteries in modern natural science that continues to puzzle scientists. Colonna et al (2009) noted that the emergence of homochirality in the prebiotic world is on the one hand a major open problem, while on the other hand it provides a fascinating challenge. Powner et al (2011) remain optimistic that the basis in organic chemistry contains a system of chemical transformations that can provide all the vital ingredients of life. Ávalos (2000) stated that the origin of life on earth is linked to the origin of enantiomerically pure compounds (homochiral compounds). Percec (2011) highlighted the significance of the homochirality problem by concluding that questions about the origin of homochirality in biological systems are almost synonymous with questions related to the origin of life.

Rivalries within Origin-of-Life Research

Because no scientific consensus exists on any critical step in the OoL, including the origin of homochirality in α-amino acids and polypeptides, researchers with competing explanations continue to advocate for their positions while simultaneously pointing out the weaknesses in their rivals' theories. Life consists of two key, interdependent biopolymers: DNA and proteins. DNA is the genetic biopolymer that stores information and directs the biosynthesis of proteins. Proteins provide a diversity of structure, metabolism, and catalysis. Benner (2002) stated that since it is difficult to envision a naturalistic mechanism that would allow either proteins or DNA to emerge spontaneously, it is highly improbable that both proteins and DNA arose simultaneously and spontaneously, and as an encoder-encoded pair. Menor-Salva and Marin-Yaselli (2012) argued that any proposed intermediate or transitional OoL system creates a rivalry between a genetics-first and a metabolism-first model. No transitional, remotely plausible system is known to exist today, nor has any specific abiogenic transitional system been proposed.

RNA is the leading "single-biopolymer" model proposed for OoL that may have preceded the current two-biopolymer system. RNA entities can exhibit both self-replication and catalytic properties (Luisi et al, 1999). Benner and Hutter (2002) concluded that catalysis and information storage place competing and contradictory demands on molecular structure. Plankensteiner et al (2005) and others advocate a metabolism-first origin model and propose a peptide/protein world as a precursor to the "RNA world" scenario. They argue that RNA or DNA is not a suitable starting point for the OoL due to the very limited stability of RNA or DNA in a primordial ocean (Plankensteiner et al, 2005). Jakschitz and Rode (2012) have proposed polypeptides as a way to transport information and to provide stability under the harsh conditions of the primordial ocean.

Another rivalry among OoL researchers is the abiotic–biotic dichotomy for the origin of homochirality of biological molecules. In the abiotic position, homochirality precedes life—either metabolic, genetic, or both. In the biotic position, homochirality is not a requisite for life or some intermediate chemical system evolving towards life (Ávalos et al, 2010). In the biotic proposal for homochirality, prebiotic amino acids and sugars did not evolve completely to chiral purity before the formation of the first "living" biopolymer systems. Blackmond (2010) speculated that perhaps chiral selectivity increased as the complexity of "life" increased. Percec and Leowanawat (2011) and others postulated that early life on earth was racemic and/or heterochiral and then slowly evolved over time at the biological level to homochiral. Coveney et al (2012) emphasized that intermediate metabolic-only or genetic-only phases toward "living systems" have not been found in nature, have not been verified experimentally, and no specific intermediate systems have been proposed, though theoretical research and modeling continues.

What were the likely sources of the prebiotic molecules necessary for the OoL? Three chemical reaction conditions have been the focus of the abiotic source of α-amino acids and proteins in research: (a) early earth atmospheric conditions (oxidizing or reducing), (b) the extreme conditions of hydrothermal vents on the ocean floor, and (c) a wide range of extraterrestrial environments (Evans et al, 2012). The famous Miller-Urey experiment was a milestone in origins research, showing that organic compounds necessary for life, including amino acids, could be synthesized from a gaseous mixture of water, ammonia, methane, and hydrogen. An electric spark provided the energy for bond formation (Miller, 1953). While there is much controversy regarding the composition of early earth atmosphere (oxidizing vs. reducing), the consensus is that the reducing environment necessary for Miller's experiment was not likely ever present (Coveney et al, 2012; Chen and Chen, 2005).

An early OoL hypothesis was the "warm little pond" idea attributed to Darwin. Coveney and Maurel and Décout argue that the traditional concept of a "warm little pond" or a "prebiotic soup" suffers from (i) the absence of geological evidence, (ii) the lack of a free energy source, (iii) a high dilution of the critical

organic materials, (iv) vulnerability of the biopolymers to hydrolysis, and (v) a lack of favorable selection for monomer sequences (Coveney et al, 2012; Maurel and Décout, 1999). The "prebiotic soup" model has been essentially abandoned.

Another possible source of organic compounds for life is hydrothermal vents on the ocean floor, which postulates a reducing, aqueous environment with elevated temperatures (Podlech, 2001). One interesting possibility with the "vent theory" is the formation of thioester derivatives of amino acids, which are "activated" alternatives to amino acids, as a route to polypeptides. Plankensteiner et al (2005), however, argued that the localized nature of hydrothermal vents probably would not allow large-scale abiotic syntheses of α-amino acids and polypeptides.

The panspermia theory proposes an extraterrestrial source of critical organic materials for the OoL. Over eighty amino acids have been detected in the Murchison meteorite from Australia in 1969, but only eight are the standard α-amino acids found in proteins (Sephton, 2002; Burton et al, 2012). Amino acid precursors also have been observed in meteorites, which could hydrolyze once they reached the earth's ocean. Terrestrial contamination and the complex mixture of materials complicate the chemical analyses of meteorites. Burton et al (2012) argued that isotope analysis has strengthened the argument that some amino acids on earth could have had an extraterrestrial origin. Menor-Salva and Marin-Yaselli (2012) postulated that extraterrestrial delivery could compensate for a possible lack of availability of materials from terrestrial synthesis of life. Extraterrestrial sources allow researchers to explore a wide range of temperatures, chemical building blocks, reaction conditions, and electromagnetic radiation energy for potential abiotic syntheses (Gol'danskii, 1997). Pizzarello (2007) noted a significant challenge for the panspermia theory: the selection problem, i.e., how small amounts of standard α-amino acids or their precursors (<100 ppm total) were separated and preserved from the vast amount of other chemical compounds also transported by meteorites.

Importance of Chirality in Biochemical Materials

A linear sequence of α-amino acids joined by peptide bonds constitutes the primary structure of a protein. For polypeptides to become biologically significant enzymes, hormones, muscles, etc., a protein's three-dimensional secondary, tertiary, and quaternary structural features must be meticulously and precisely bonded, folded, and coiled. Three important characteristics of the standard α-amino acids are harnessed to achieve precise and diverse functionality in proteins: (i) ionic charge (anionic, neutral, cationic), (ii) hydrophilic-lipophilic balance (water soluble, oil soluble), and (iii) molecular shape and size. The simplest aspect of the molecular shape and size of α-amino acids and proteins is chirality or "handedness." Nineteen of the twenty standard α-amino acids are chira; i.e., they can exist as either left-handed or right-handed, mirror-image enantiomers that are nonsuperimposable (Hames, 2000). Only L α-amino acids are found in the proteins of living animals. The precise L α-amino acid sequence (primary structure) in a polypeptide is a necessary but not sufficient requirement to define the shape and size of a protein. All four structural aspects (primary, secondary, tertiary, quaternary) must be correctly designed to direct and achieve a protein's intended structure and functionality.

Figure 1 shows a pair of mirror-image structures with four groups (A, B, D, E) tetrahedrally oriented around a central (C) group. These structures model the orientation of the four groups chemically bonded to a tetrahedral carbon atom, including the amino group and carboxylic acid group in α-amino acids. The two structures in Figure 1 have the same five groups, but the geometric relationships of these five groups are distinct. These two structures are different in a way that your right hand is distinct from your left hand. In proteins, this subtle spatial difference is magnified as each α-amino acid in the polypeptide sequence adds another chiral distinctiveness to the protein.

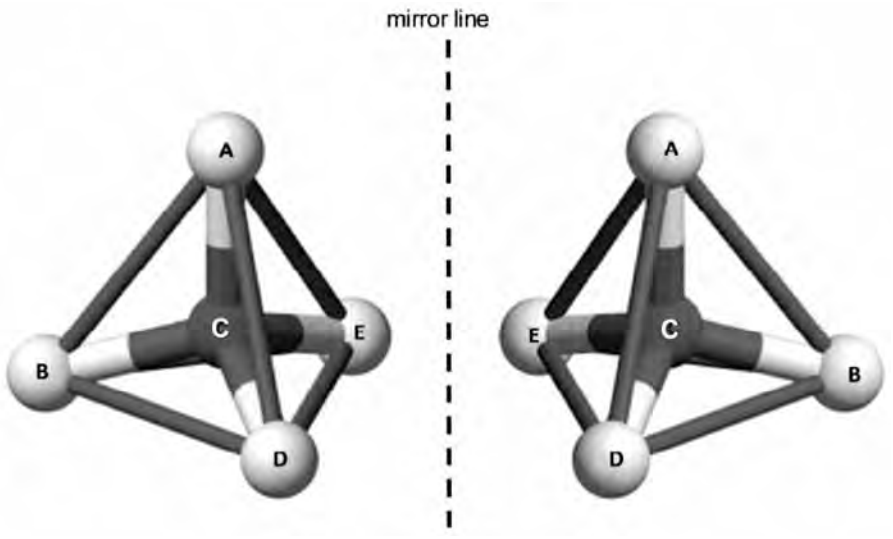

Figure 1. Mirror images demonstrating chirality around a tetrahedral carbon atom (C)

Individual α-amino acid are either D or L, but mixtures of D and L α-amino acid isomers can range from 100% D to 50/50 D/L to 100% L. The enantiomeric excess (EE) of the L α-amino acid is the difference between the amount of the two isomers, divided by the total amount of the two α-amino acids. If EE=0, then the α-amino acid mixture is racemic with equal amounts of both isomers. If EE=10%, then the α-amino acid mixture has 55% of the L α-amino acid and 45% of the D α-amino acid. Each α-amino acid in a polypeptide sequence can be either D or L. Polypeptide chains can therefore vary in chiral composition from 100% D to 50/50 D/L to 100% L. In all living systems, apart from very rare exceptions, peptides and proteins consist of entirely L α-amino acids. Proper structure and function for proteins strongly depend on the enantiomeric purity of each α-amino acid. Jakschitz and Rode (2012, p. 5487) stated, "If only one amino acid is replaced by its optical (chiral) counterpart the formed protein will not fulfill its tasks properly because of destabilization effects induced by the distorted structure of σ-helices and β-sheets." Amino acids synthesized by ordinary methods invariably result in 50/50 D/L mixtures (EE=0).

Roadmap to Chiral Polypeptides

Colonna et al (2009) have outlined the generally accepted scheme for abiotic generation of homochiral polypeptides, which consists of four fundamental steps: (i) the abiotic formation of racemic α-amino acids; (ii) symmetry breaking leading to chiral α-amino acids having small EE; (iii) the chiral amplification to enantiomerically pure substances; and (iv) their organization into self-sustaining systems. Figure 2 is a chemical roadmap to L α-amino acid polypeptides (V). This chemical roadmap is not comprehensive but emphasizes chirality and provides an overview of the kinetic and thermodynamic challenges to synthesize homochiral L α-amino acid polypeptides (V), especially in a prebiotic environment.

Many different organic and inorganic compounds (I) can be converted to vari-

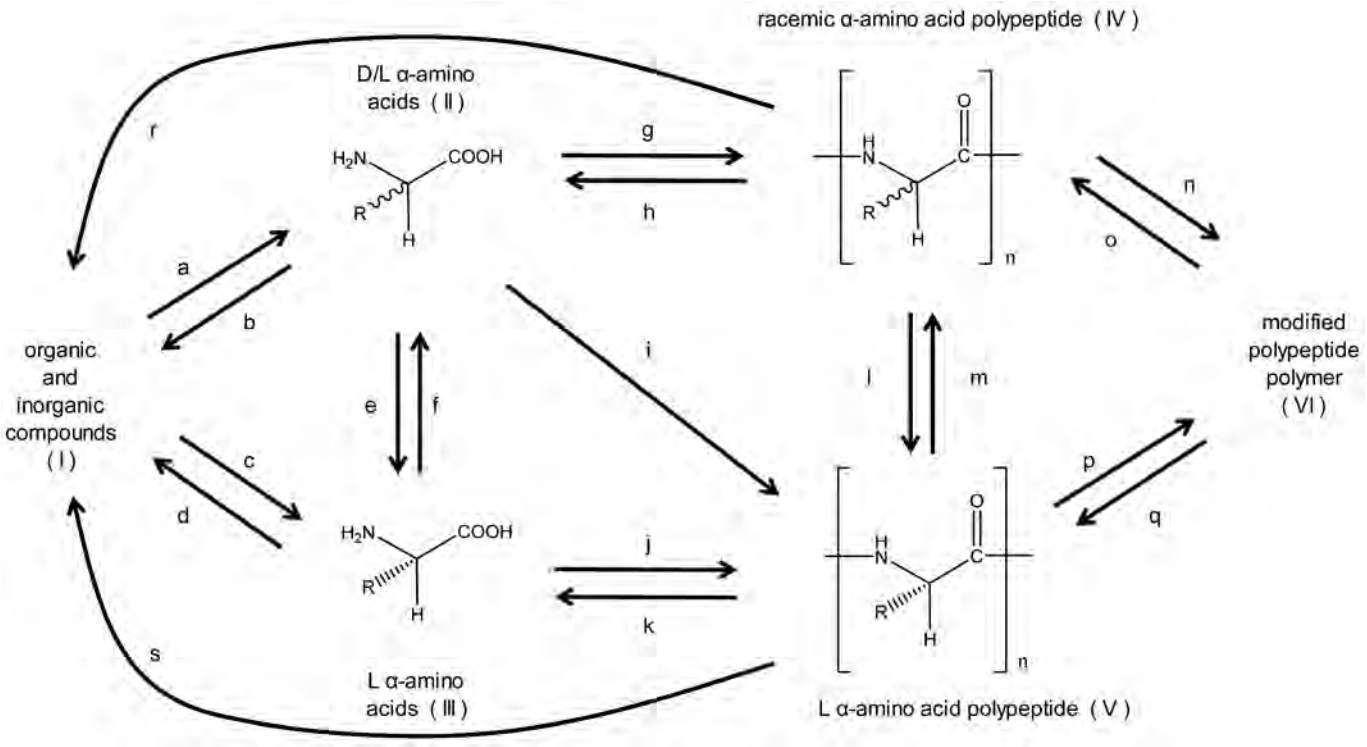

Figure 2. Roadmap to L α–amino acid polypeptides. (a) racemic amino acid synthesis, (b) racemic amino acid decomposition, (c) L amino acid synthesis, (d) L amino acid decomposition, (e) chiral separation or transformation, (f) racemization, (g) racemic polypeptide formation, (h) racemic polypeptide hydrolysis, (i) chiral L polypeptide formation, (j) L polypeptide formation, (k) L polypeptide hydrolysis, (l) chiral separation or transformation, (m) epimerization, (n) racemic polypeptide conversion, (o) racemic polymer transformation, (p) L polypeptide conversion, (q) L polymer transformation, (r) racemic polypeptide degradation, (s) L polypeptide degradation.

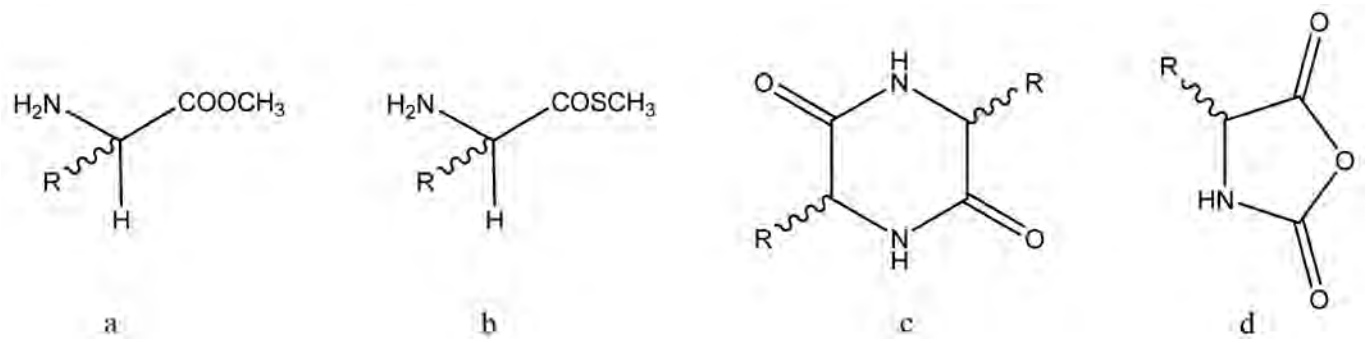

Figure 3. Examples of activated α–amino acid: a) ester, b) thioester, c) diketopiperazine (DKP), d) N-carboxyanhydride (NCA)

ous α-amino acids (routes a and c). Both D and L α-amino acids are vulnerable to decomposition (routes b and d). Amino acids (II and III) can be anionic, cationic, or zwitterions, depending on solvent, pH, concentration, solution salinity, phase, temperature, etc. Amino acids exist as zwitterions at or around physiological pH. "Activated" derivatives of amino acid (e.g., thioesters in Figure 3) can also form polypeptides, and consideration of the chirality of their syntheses and decompositions would parallel the Figure 2 chemical roadmap. Activation of amino acids *in vivo* involves ATP and specific transfer RNA molecules. Route e emphasizes that chiral separation is necessary to transform a racemic mixture of D/L α-amino acids to chirally pure L α-amino acid. Route f shows the effect of racemization on chirally pure L α-amino acids (III) to the racemic mixture (II). Polypeptides (IV and V) are formed by the dehydration between two α-amino acids in routes g, i, and j. Hydrolyses of polypeptides to α-amino acids are shown in routes h and k. As with α-amino acids, polypeptides can undergo chiral separation or transformation (route l) or epimerization (route m) as the D/L configuration of individual α-amino acids interconvert. Polypeptides can be transformed into other polymers (VI) or degraded directly to various organic and inorganic compounds (I).

The challenge for the naturalistic origin of homochirality in α-amino acids and polypeptides is to demonstrate a plausible, prebiotic route from various, available organic and inorganic compounds (I) to chirally pure L α-amino acid polypeptides (V), and to stabilize those chirally pure L α-amino acid polypeptides (V) against back reactions to reactants, oxidation, decomposition, hydrolysis, and racemization. Providing an abiogenic origin of homochirality is essential to a naturalistic worldview of life's origin. However, this does not begin to solve the naturalistic problems for the origins of the primary, secondary, tertiary, and quaternary structures of the diverse proteins necessary for living creatures.

Synthesis of α-Amino Acids

Many OoL experiments demonstrate potential prebiotic routes to amino acids, polypeptides, and other biochemical building blocks, but the yields for these syntheses are generally less than 3% even for glycine (the simplest amino acid). In all cases, prebiotic routes to amino acids (terrestrial or extraterrestrial) give racemic product mixtures that contain many impurities; note Figure 2, route a (McNichol, 2008; Pizzarello, 2006). Meierhenrich (2009) gives a survey of the leading prebiotic routes to amino acids, and a few routes are worth highlighting. The Strecker-cyanohydrin synthesis utilizes the reaction of ketones or aldehydes with ammonia, then with HCN, and finally hydrolysis (Smith and March, 2007). Photochemical syntheses from amines and carbon dioxide can yield amino acids (Meinert et al, 2010). Several syntheses of amino acids from carbon monoxide, water, and nitrogen are catalyzed by high-energy particles, UV irradiation, or electrical discharge (Chen and Chen, 2005). Debates about which synthetic pathway is more "prebiotic" abound. Regardless of their source, Ávalos (2010) argued that it is unclear how many α-amino acids could have been formed, preserved, and concentrated for further reactions in significant amounts and formed polypeptides or proteins in the early earth by any known route.

Synthesis of Polypeptides

The abiotic linking of monomers to form polymers is an important step in the naturalistic vision for life's origin. Danger et al (2012) have summarized many of the reaction conditions that have been proposed for the formation of peptide bonds between α-amino acids (Figure 2, routes g, i, and j). Proposals include hydrothermal systems, catalytic surfaces (e.g., clays, minerals), salt-induced peptide formation, condensation agents, and "activated" α-amino acids. Thermody-

namically, the formation of polypeptides from α-amino acids is mildly unfavorable. The free energy of hydrolysis of an internal peptide bond into two α-amino acid segments is favored (ΔG) by about -2 to -6 kJ/mole (Figure 2, routes h and k). The formation of long chain polypeptides in aqueous solution from realistic concentrations of α-amino acids remains highly unfavorable (Danger et al, 2012). The concentration of monomers for polymerization to proteins, polysaccharides, DNA, and RNA is a difficult OoL problem within prebiotic limits. Importantly, the linking of a particular sequence of α-amino acids into the primary structure of a protein followed by coiling and folding into a protein requires extremely complicated processes far from thermodynamic equilibrium (Hames, 2000). These processes are separate and distinct from the mere kinetics and thermodynamics of homochiral polypeptide synthesis discussed in this review.

One approach to overcoming the thermodynamic barrier to prebiotic peptide formation, which is considerable, involves postulating the participation of condensation reagents, such as cyanamide (H_2NCN) or cyanoguanidine ($NC-N=C(NH2)_2$) (Menor-Salva and Marin-Yaselli, 2012). None of the commonly used condensation reagents for modern polypeptide synthesis have been postulated in the early earth environment. Other potential prebiotic activating agents for the formation of polypeptides include urea (NH_2CONH_2), carbonyl sulfide (COS), carbon monoxide (CO), pyrophosphate ($P_2O_7^{-4}$), fulminic acid (HCNO), hydrogen cyanide (HCN), carbodiimide (NHCNH), acetylene (HCCH), and N-carboxyanhydrides (Danger et al, 2012; Chen and Chen, 2005). There is still a sizable gap between the proposed syntheses and the experimental verification for the role of condensation agents in the abiotic formation of polypeptides from α-amino acids.

Podlech (2001) and others have proposed "activated" α-amino acid monomers to form polypeptides in a prebiotic environment: for example, the condensation of α-amino acid esters or thioesters (see Figure 3). Activated α-amino acids are analogous to α-amino acids (II and III) in Figure 2 with similar synthesis and decomposition reaction pathways and chiral characteristics. Danger et al (2012) have shown that activated α-amino acid monomers can accelerate polypeptide synthesis and improve polymer yields, but these activated compounds are also increasingly likely to undergo decomposition reactions. In condensation polymerization, monomers can either form long polymer chains or can cyclize into various-sized rings. Any two α-amino acids can dehydrate and cyclize into a six-membered diketopiperazine (DKP) ring, which can hydrolyze back to the pairs of α-amino acids or can undergo ring-opening polymerization directly into a polypeptide, in which DPK acts as an activated α-amino acid monomer (Danger et al, 2012).

Amino acid polymerization to polypeptides will be thermodynamically favored only under highly dehydrating conditions (Saladino et al, 2012). Salt-induced peptide formation (SIPF) depends on high concentrations of salt, especially sodium chloride, to absorb the water formed between amino acids forming polypeptides (Plankensteiner et al, 2005). Evaporation in tidal pools can produce SIPF conditions, which are further favored by elevated temperatures and/or transition metal catalysts (e.g., copper) to give good yields of polypeptides. SIPF works well with a wide range of amino acids, favoring α-amino acids over the β-, γ-, or other analogs (Jakschitz and Rode, 2012). SIPF does not provide a selective route to the required homochiral L polypeptides and demonstrates that polypeptide polymer end groups (amines and carboxylic acids) can undergo condensation reactions with a variety of compounds that compete with the formation of polypeptides. Most of the standard amino acids have chemically reactive side-chain groups, which would compete with the normal bonding pattern of polypeptides.

The effects of reaction temperature create a challenge for the abiotic syntheses. Menor-Salva and Marin-Yaselli (2012) asserted that higher reaction temperature gives better yields of polypeptides from α-amino acids, but higher temperatures also accelerate decomposition of α-amino acids, chiral racemization, and hydrolysis of polypeptides. Prebiotic chemistry in eutectic frozen solutions and at liquid water–ice interfaces (terrestrial or extraterrestrial) has been studied to overcome the ambient concentration and stability problems and may provide enhanced polypeptide synthesis reaction rates and/or yields, diminution of racemization, and the suppression of side reactions (Menor-Salva and Marin-Yaselli, 2012). Research continues to postulate and to pursue a role for low-temperature chemistry in the naturalistic routes for life's origin.

Chiral Symmetry Breaking

While individual α-amino acid molecules are either D or L, mixtures of α-amino acids synthesized from achiral precursors, without chiral catalysts and without a chiral template, are racemic mixtures of D and L α-amino acids. Finding the initial source of chiral symmetry breaking that tips the balance toward L α-amino acids remains a critical goal in abiogenesis research. Sephton (2002) reported that some α-amino acids and amino acid precursors of extraterrestrial origin have shown a very slight EE (<1%). Circularly polarized light (CPL) across the UV-visible spectrum interacts differently with each isomer of a pair of enantiomers. Podlech (2001) postulated that chiral symmetry breaking in extraterrestrial amino acids could be due to exposure to one or more of the different

extraterrestrial sources of CPL: β-decay cosmic radiation, ultraviolet CPL, or infrared CPL. The theory that ultraviolet CPL provided the initial enantiomeric enrichment in the universe is a popular one in abiogenesis research. Evans et al (2012) summarized the three ways that CPL can potentially produce a chiral symmetry break: (i) photolysis, preferential destruction of one enantiomer; (ii) isomerization, preferential conversion of one enantiomer to the other; and (iii) synthesis, preferential creation of one enantiomer. Research continues to seek experimental verification of the role of CPL in the chiral symmetry break in amino acids. The photolysis/decomposition route to EE requires a high photolysis rate from CPL. Meinert et al (2010) concluded that to reach an amino acid EE of even up to 10%, a photochemically initiated decomposition of at least 99.99% would be necessary. Extraterrestrial α-methyl amino acids with higher EE (up to 15%) have been found on meteorites. The EE for these α-methyl amino acids may be due to a favorable chiral synthesis mechanism, a chiral bias in photolysis/degradation, or some other chiral separation process. Research continues in order to understand how these nonstandard amino acids could induce EE in the standard α-amino acids through an amplification or template mechanism (Meinert et al, 2010; Pizzarello, 2006).

In his book, Meierhenrich (2009) summarizes how differences in physical properties between D and L α-amino acids have attracted attention as a source of chiral symmetry breaking and challenged the long-held belief that enantiomers have completely identical physical properties except for interactions with other chiral materials or with polarized light and other polarized electromagnetic energy. Blackmond (2010) claimed that enantiomer partitioning via sublimation for α-amino acids in space is a possible extraterrestrial origin of chiral symmetry breaking. However, serine, the α-amino acid giving the highest initial enantio enrichment in sublimation, has not been observed in meteorites or in space (Blackmond and Klussmann, 2007). Also, the parity violation of the weak nuclear force results in extremely minor thermodynamic differences between D and L α-amino acids, which might contribute to the origin of their homochirality, but experimental verification has not been obtained (Evans et al, 2012).

Mineral catalysts are effective in the synthesis of polypeptides from α-amino acids. The "mineral basis" for the OoL describes the syntheses of homochiral sequences of small polypeptides formed from racemic mixtures of amino acids in the presence of quartz, sand, clay, or other minerals (Zaia, 2004; Chen and Chen, 2005). This line of research seeks to synthesize a chirally pure, L α-amino acid peptide from a racemic mixture of α-amino acids (Figure 2, route i). So far, these experiments usually have been performed with a single amino acid, with ionic amino acids, and in distilled water. The "mineral basis" for the origin of homochirality in peptides has not yet been generalized to mixtures of amino acids, salt/seawater conditions, or nonpolar amino acids.

The solubility and crystallization of α-amino acids have been studied for the effects of solvent, temperature, pH, concentration, additives, and mixtures as a possible source of their chiral symmetry breaking. Under carefully controlled conditions, chiral symmetry breaking can lead to either an enantiometric enrichment of the soluble, solution phase or the insoluble, solid phase. Blackmond (2007) described "chiral amnesia" as the formation of solid-phase homochirality from a racemic mixture of rapidly racemizing enantiomers. An initial precipitation of an enantiometrically pure or enriched solid phase leaves a solution depleted in that one enantiomer. Subsequent solution-phase racemization reestablishes the balanced racemic mixture, which leads to further precipitation of the pure enantiomer, and so on. Solution-phase racemization becomes the postulated driving force that leads to enantiomeric purity in the solid phase.

While the mechanism has intrigued and puzzled chemists, aspartic acid and a few amino acid derivatives have undergone chiral enrichment using cycles of crystallization and dissolution (Viedma and Cintas, 2011; Viedma et al, 2010). One explanation is Ostwald ripening, the diminishing of small crystals as large crystals increase, combined with solution racemization leading to enantiomeric purity. Chiral symmetry breaking and/or amplification of α-amino acids by crystal grinding can occur when the racemic α-amino acid mixture crystallizes into two enantiomerically pure α-amino acids. So far, a crystallization-grinding mechanism for chiral separation has been demonstrated only for aspartic acid and threonine (Budin and Szostak, 2010). The effects of contaminants and conditions (solvent, concentration, temperature, pH, etc.) on chiral symmetry breaking and on chiral enrichment using cycles of crystallization and dissolution in a prebiotic world remain controversial and not well understood.

Since current explanations for chiral symmetry breaking in prebiotic environments are not universally convincing, some researchers postulate a random or statistical source for the initial chiral symmetry break in nature, including α-amino acids and proteins. Coveney (2012) and others theorize that nonlinear effects caused an initial instability in the racemic state with random fluctuations selecting one handedness over the other, and further nonlinear interactions resulting in chiral amplification ultimately drive the system to chiral purity.

Chiral Amplification of Amino Acids and Polypeptides

No synthesis of any enantiomerically pure α-amino acids or polypeptides from

racemic or achiral starting materials has been discovered or postulated (see Figure 2, routes c and i). Therefore, the origin of homochirality in α-amino acids or polypeptides requires prebiotic chiral amplification of any small EE, coupled with the preservation of that chiral purity as EE increases. Chiral symmetry breaking and chiral amplification share many characteristics, but their dual importance to life's origin is unmistakable. "Whether or not the imbalance in enantiomers came about by chance, arising on earth or elsewhere, an amplification mechanism remains the key to increasing EE and ultimately to approaching the homochiral state" (Blackmond, 2010, p 2).

Solubility-based chiral amplification of α-amino acids depends on the solubility properties of the different racemic mixtures relative to their corresponding enantiomerically pure D and L α-amino acids (Ávalos et al, 2010). Klussman (2006) has shown that repeated cycles of dissolution-precipitation-separation produced chiral amplification of one enantiomer from a racemic mixture of the two enantiomers, including for some α-amino acids. Blackmond (2010) reported that several of the standard α-amino acids form relatively insoluble D,L crystals in water and therefore show high eutectic EE values, including serine (>99%), histidine (93%), phenyl alanine (88%), leucine (87%), and methionine (85%). Eutectic EE values are dependent on temperature, pH, salinity, and other components in the solution. Many other standard α-amino acids have not shown a significant eutectic EE value, and much more research is suggested on chiral amplification of α-amino acids using prebiotic conditions to understand the versatility of this mechanism. Kojo (2010) showed that chiral enhancement in one α-amino acid or chiral material can impart chiral enhancement in other α-amino acids through recrystallization of a mixture of the materials. Chiral enhancement through recrystallization does not appear to be general, and a unique set of conditions may be necessary for each standard α-amino acid (Kojo, 2010). The role of impurities in chiral symmetry breaking and chiral amplification remains controversial.

The Frank model for chiral amplification postulated that synthesis of one enantiomer would catalyze its own production while simultaneously suppressing the production of its mirror image. The only experimental verification of the Frank model is the Soai reaction for the anhydrous synthesis of secondary alcohols (not amino acids) from aldehydes and dialkyl zinc compouds (Ávalos et al, 2010; Blackmond, 2004). While the Frank model has been proposed for an abiotic amplification by stereoselective autocatalysis and inhibition for the synthesis of L α-amino acid or L polypeptides, no experimental results have demonstrated a Frank-like synthesis route to chiral enrichment for either α-amino acids or polypeptides. The Soai reaction does not directly translate to any known prebiotic abiogenesis reaction conditions, whether terrestrial or extraterrestrial.

Since chirally pure enantiomers are very far from thermodynamic equilibrium, much research has focused on kinetic approaches to chiral amplification. Various α-alkyl amino acids with slight EE were found on carbonaceous chondritic meteorites. Extraterrestrial α-alkyl amino acids could be the origin of terrestrial homochirality if certain abiogenesis conditions were met: (i) their chiral EE was preserved, (ii) their chiral EE was transferred to standard α-amino acids or polypeptides; and (iii) their modest chiral EE was amplified to very large EE in standard α-amino acids or polypeptides (Breslow and Levine, 2006). Research continues toward experimental verification.

Some OoL research focuses on aggregates of α-amino acids for chiral symmetry breaking and/or chiral amplification. Ávalos (2010) reported that right-handed α-helix seed composed of L α-amino acids incorporates L-configured monomers around 18 times faster than D-amino acids. Nanita and Cooks (2006) noted that the α-amino acid serine can undergo repeated crystallization-dissolution, forming stable octomer clusters with high enantiomeric enrichment. Experiments have shown that mixtures with other α-amino acids give serine with mixed octomer clusters leading to their enantiomeric enrichment. No convincing prebiotic chiral amplification process for L α-amino acids or L polypeptides has yet emerged.

Degradation of Amino Acids and Polypeptides

Schwartz (2007) admitted that in prebiotic chemistry, unwanted by-products often consume most of the starting material and lead to nothing more than an intractable mixture, or "gunk." Chemical degradation and side reactions always compete with reactions that produce synthetic targets. Toward the goal of synthesizing homochiral L α-amino acid polypeptides, Figure 2 (V), any chemical reaction of the α-amino acids or the polypeptides that moves the chemical composition away from the intended product diminishes the yield. Chemical degradation is a serious concern in OoL research. "The conditions in primitive earth are very atrocious, so even if early life could be generated, how could it survive is a problem" (Chen and Chen, 2005, p. 995). At least three types of degradation reactions shown in Figure 2 compete with the abiotic formation of L α-amino acid polypeptides: (1) chemical decomposition (routes b, d, n, p, r, s), (2) polypeptide hydrolysis (routes h and k), and (3) racemization or epimerization (routes f and m). Some by-products of these degradation reactions may be recycled to α-amino acids or to polypeptides, but all reaction kinetics and thermodynamics requirements must be met in a quest for a naturalistic origin

of homochirality in α-amino acids and polypeptides.

While the chemistry of α-amino acids and polypeptides is extensive (Hughes, 2009), a few important abiogenic degradation reactions shown in Figure 2 are highlighted here, specifically routes b, d, n, p, r, and s. While the terrestrial origin of α-amino acids and proteins could have occurred in the small amount of available freshwater on earth (the conditions used in most OoL experiments), Deamer (1997) points out that the more abundant terrestrial seawater is a mixture of relatively high ionic-strength mineral salts, giving conditions adverse to the formation and persistence of α-amino acids and proteins. One common example of the decomposition of proteins and α-amino acids is the family of Maillard reactions that occur between sugars and proteins. Maillard reactions are responsible for much of the browning and flavor development in food (Nursten, 2005). Formic acid decomposition reactions of amino acids and polypeptides have recently been reviewed (Boudreaux and DeMassa, 2013).

Amino acids are highly susceptible to ultraviolet (UV) photochemical decomposition, even under exposure to relatively low energy UV-visible photons. Ehrenfreund et al (2001) argued that amino acids in the diffuse gas phase, in ice crystals, in aqueous solution, or in any substance that can be penetrated by UV photons have a limited stability against photolysis. Extraterrestrial delivery of amino acids to the early earth required that amino acids were shielded from UV radiation in protected environments such as the interiors of comets or meteorites (Ehrenfreund et al, 2001). Thermal degradation of amino acids is also a critical problem for extraterrestrial delivery of OoL materials through the earth's atmosphere.

Polypeptide hydrolysis (the back reaction of synthesis) can occur between any pairs of α-amino acids in a polypeptide chain. Danger et al (2012) add that the half-life of the uncatalyzed hydrolysis of polypeptides to α-amino acids in neutral water varies from about 100 to 1000 years, depending on the amino acid and its position on the polypeptide chain (Figure 2, routes h and k). Metal ions (such as iron, copper, and zinc), aqueous base or acid, and elevated temperatures can accelerate polypeptide hydrolysis. Decomposition of polypeptides to diketopiperazines (DPKs) is direct decomposition route to organic and inorganic compounds (I) (Figure 2, routes r and s, and Figure 3; Danger et al, 2012).

Any emerging EE in amino acids or polypeptides is constantly jeopardized by spontaneous racemization (Jaakkola et al, 2008), which has been described as the "catastrophe of racemization" (Pizzarello 2006, p. 236) Klabunovskii (2012) estimated that early earth racemization of any EE of L α-amino acids could be *complete* in about 1000 years. Danger et al (2012, p. 5424) questioned how the chiral imbalance in α-amino acids or polypeptides "could be maintained in aqueous solution over long periods," and declared that this "remains to be explained."

In biological environments, the racemization of biological L-amino acids toward D-amino acids starts when counteractive biological processes involving D-amino acid oxidase metabolism becomes inactive after the death of a living organism. The increase of the proportion of D-amino acid in living organisms is used for archaeological and geochemical dating by a method called "the amino acid clock" (Meierhenrich, 2009; Grun, 2008; Miller et al, 2013). The amino acid clock has a considerable margin of error, because the rate of racemization of all α-amino acids is influenced by temperature, pH, humidity, and their position in a polypeptide. Csapó et al (1998) concluded that the half-lives of racemization of α-amino acids in proteins from biological systems generally range from a few thousand years to more than a hundred thousand years. While these racemization half-lives seem long, chiral preservation is a critical unsolved problem in abiogenesis research that postulates and requires millions and billions of years of naturalistic chemical evolution. Helmick (1976), writing from a creationist perspective, reviewed the significance of L-isoleucine racemization and presented a mechanism for both acid and base catalyzed racemization of this key amino acid.

Conclusion

In this early twenty-first century, no comprehensive, naturalistic explanation exists for life's origin, including even the relatively minor but essential challenge of the origin of homochirality in biological materials. Scientific research, instead of advancing the possibility of an abiogenic origin, actually continues to eliminate many mechanisms and reaction pathways as potential prebiotic routes to homochirality in α-amino acids and proteins. As all naturalistic routes to the OoL become more unreasonable and more unbelievable, fiat creation by God remains the realistic and sensible explanation for our existence. While many scientists remain nearly universally optimistic about the significance and future success of their own research, serious OoL researchers are expressing the scientific difficulty of finding a naturalistic explanation for life's origin, and even for just the small step on the origin of homochirality.

The existence of homochirality in all organisms on earth raises a question not satisfactorily explained in any current theory. We understand fundamental biomolecules better than ever, but the transition from chemicals to biochemicals in life is one that is elusive (McNichol, 2008). Work funded by the National Natural Science Foundation of China concluded that "in fact, there is no known way by which life could have arisen naturalistically" (Chen and

Chen, 2005, p. 996). "The ultimate origin of asymmetry in the universe is an unanswered question. … the large gap between molecular chirality and molecular evolution has become painfully clear" (Avalos et al, 2000, p. 891). The topic of the origins of life on earth is still largely one of theory and conjecture, given the vast period of time separating us from those key events (Coveney et al, 2012).

Meierhenrich (2009) opined that the problem (of the origin of homochirality of biological systems) may remain unsolved for a long period of time, if not forever. It is a shared opinion that we will never know exactly how life started on this planet (Saladino et al, 2012). Viedma and Cintas (2011) remarked that the genesis of enantiomer purity in nature (e.g., amino acids) has fascinated scientists for more than 150 years and the most that researchers can state with conviction is that we know what we do not know. A re-creation of the life's origin on earth will likely remain merely a surmise. Orgel (1998) concluded that it is not currently possible to decide issues of life's origin: not rejecting any theory out of hand, but admitted no theory is compelling and definitive answers will always be elusive.

Recent publications lead us to conclude that a scientific search for a naturalistic explanation for the origin for homochirality in amino acids and polypeptides will continue to fail for the foreseeable future. Many other aspects of the origin of life also remain unexplained by naturalistic science, including the irreducible complexity of living systems from the smallest biochemical systems to the largest ecosystems. It is important to realize that researchers assume evolution must have occurred in order to pursue experimentation that seems doomed to fail. Creationists assert that everything living is by God's command, "Let there be…" Even if a natural explanation for chirality (after all the failures mentioned above) becomes plausible, this still is a very minor step toward showing that life came from nonlife. With Louis Pasteur, creationists can boldly state that life comes only from life. The creationist explanation for the origin and preservation of life remains by far the only believable one.

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Fifty Years of Physics: Some Observations Regarding Radiohalos and Magnetic Fields

Eugene F. Chaffin*

Abstract

Some important evidence regarding tiny, spherical discolorations in rocks, seen in photographs as radiohalos, was reported in the *Creation Research Society Quarterly* in Volume 3, 1966. In 2002, another report was made regarding the decrease in energy in the earth's magnetic field over historical time. In retrospect, both of these papers were highly successful in advancing the creation model, and their significance will be reviewed here in honor of the 50-year anniversary of the Creation Research Society and its technical journal, the *Creation Research Society Quarterly*.

Introduction

When Creation models, or models of origins, are published, there is always some risk involved, the same as in studies of science that do not have much to do with origins. By "risk" I mean the likelihood that the proposed explanations may turn out to have little to do with reality. Subsequent observations or experiments may show that proposed explanations do not work or were based on assumptions that turned out to contradict other known results. So, in any scientific journal, there will be articles in the older issues that were based on sincere work by the scientists involved, but the results of that work are now mostly discarded. In this summary, I will review a few physics articles published during the 50 years of existence of the *Creation Research Society Quarterly* and will concentrate on a couple of articles I view as having been largely successful, at least in the furthering of Creation models.

Parentless Polonium Halos

In volume 3 of the *Quarterly*, issue 2, there appeared an article by Robert V. Gentry that brought the subject of radiohalos to the attention of the creationist community and showed that certain halos due to polonium isotopes were difficult to explain in the traditional uniformitarian paradigms (Gentry, 1966). Gentry did extensive observational and experimental work on radiohalos over his career and is arguably the world's leading expert on this subject. Halos are formed when small radiocenters of the size of a few microns are accumulated in rocks, and over time the subsequent radioactive decays send alpha particles out in all directions, forming a spherical region of damage to the crystalline structure of the surrounding mineral, which may be mica, corderite, sphene, etc. These spherical deformation regions are typically tens of microns in size and show up in photographs as circular, colored "halos." For creationists, Gentry reported the importance of halos due to Po-210 (half-life 138 days), Po-214 (half-life 164 microseconds), and Po-218 (half-life 3 minutes), which are distinguishable by the number of rings in the halo—one for Po-210, two for Po-214, and three for

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fully developed Po-218 halos, as shown in Figure 1.

The sizes of these rings are correlated with the predominate energies of the alpha particles emitted in the decay of the parent nuclei. Using various advanced experimental techniques, Gentry and his colleagues at Oak Ridge National Laboratory cast doubt on the idea that the polonium was a result of the accumulation of uranium-238 or any other radioactive precursor at the radiocenter that subsequently formed the radiohalo. He instead favored the hypothesis that these halos were the result of the Creator forming them along with host granite rocks during the six-day Creation week. After all, numerical simulations of the accumulation of the polonium at such sites could not result in the formation of a halo, since that would require somewhere around 10^8 to 10^9 decays, and the halo rings due to the progenitors such as radon are not found and the half-lives of the polonium isotopes in question are much too short for them to accumulate in the short times that are necessary. Snelling (2005) favored the hypothesis that many of these halos were formed during the Genesis flood and cited overwhelming geological evidence that these halos are found in Flood rocks (Phanerozoic rocks) rather than Creation-week rocks. However, Snelling (2005) did not offer a way for these halos to form on the time scales involved, instead he appealed to other evidence uncovered in the RATE (Radioisotopes and the Age of the Earth) project that half-lives may have changed over earth history and particularly at the time of the Genesis flood.

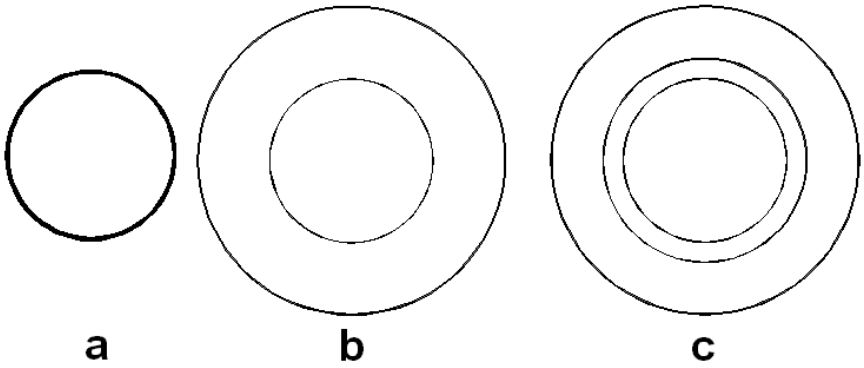

Figure 1 Polonium halos. Part a represents a Po-210 halo, which has a radius of 18.8 microns. Part b is a Po-214 halo, which includes the Po-210 ring plus another ring of radius 34 microns. Part c is a Po-218 halo, which adds a ring of radius 22.5 microns to the Po-214 halo. The corresponding alpha-particle energies are 5.30 MeV for Po-210, 6.00 MeV for Po-218, and 7.69 MeV for Po-214.

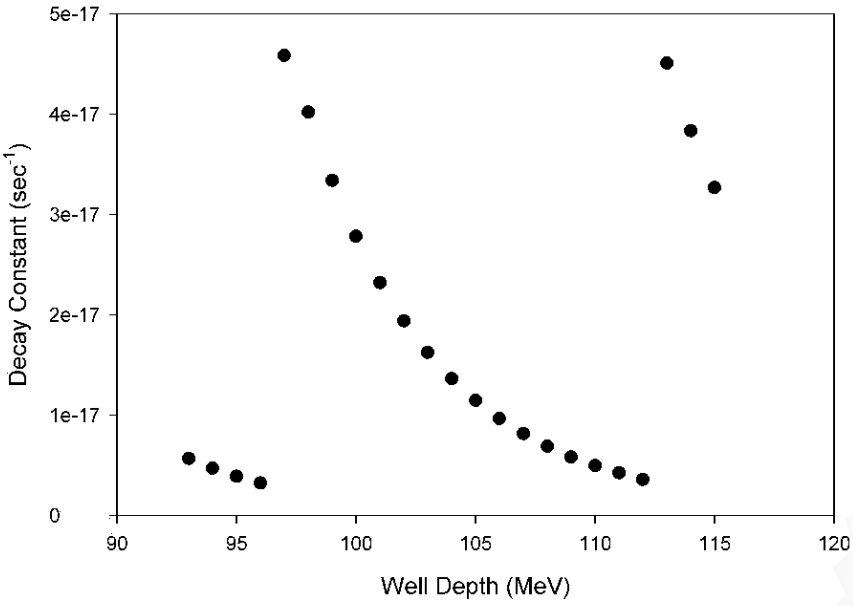

Figure 2. The decay constant, which is the fraction of the nuclei decaying per unit time, is plotted versus the nuclear well depth for the alpha particles. If the well depth, which measures the strength of the nuclear force, were to change over earth history, then there could be either increases or decreases in the decay constant, depending on the initial value of the well depth.

My own work (Chaffin, 2000, 2005, 2008), which was done along with some former students of mine, offered possible mechanisms for the accelerated decay that was involved. In the case of alpha-decays, the proposed mechanism involving a change in the strength of the nuclear force over earth history could also result, for some isotopes, in a decrease in the half-life, while others would have an increase in half-life. The work showed that the half-life for alpha-decay, proceeding by quantum mechanical tunneling, could radically change as a function of the strength of the nuclear force. Figure 2 shows a plot of the decay constant, which is the fraction of the

nuclei decaying per unit time, versus the nuclear well depth, which measures the strength of the nuclear force. I also presented experimental evidence, based on studies of double-beta-decay, which indicate a change in beta-decay half-lives at the onset of the Genesis flood (Chaffin, 2009, 2013) and, by implication, alpha-decay half-lives also.

The mechanism of halo formation supported by Snelling's work could not occur unless the very short half-life polonium isotopes had a prolonged half-life during the time they were being formed, i.e., while the polonium precursors were being transported by hydrothermal flows to the sites where the halos formed.

One should also mention the helium diffusion work of Humphreys (2005), which continues to offer evidence for a period of accelerated decay in order to explain the amounts of helium in zircons from the Jemez Mountains boreholes, New Mexico. This work was originally begun by Gentry, Glish, and McBay (Gentry, et al., 1982).

Thus, in spite of the questioning of the model that Gentry put forward to explain his halos (Brown, 1990; Gentry, 1990; Snelling, 2005), I still consider his work to be highly successful, since it brought the relevance of these polonium halos to the attention of creationists and offered the results of various very technical procedures as supporting data. Gentry's article in the *Quarterly* was a milestone that deserves applause.

Earth's Magnetic Field Is Fading Away

Another example of a successful model is a 2002 scientific paper by D. Russell Humphreys showing that Creation models of the decrease in the earth's magnetic field were not guilty of neglecting higher order effects. Barnes (1973) had originally proposed a test of origins models based on the observationally observed decrease in the earth's magnetic dipole. A simple dipole consists of a north pole and a south pole, a short distance apart. The earth's magnetic field, at least in the first approximation, can be represented by imagining a dipole located deep within the earth. Observational data, beginning with measurements of the earth's magnetic dipole dating back to the early 1800s, showed that the earth's dipole strength has been decreasing exponentially over time.

When we try to represent a magnetic field that is only approximately a dipole field, the necessary next-to-leading order correction is called the *quadrupole term*. We add the field produced by the quadrupole term to correct the dipole field found at each point. Prior to the 2002 work of Humphreys, an anticreationist could have claimed that the decrease in the earth's dipole field was compensated for by an increase in the quadrupole term. Humphreys, however, gathered the necessary data and actually did the calculations of the total energy in the earth's field due to both dipole and quadrupole contributions. His results showed that the non-dipole is increasing, but the energy gained by the total non-dipole contributions is not nearly as much as the energy lost by the total dipole contribution. This net decrease in the energy is a fact that has not been successfully explained by advocates of the traditional evolutionary timescale. According to their model, the total energy should not decrease appreciably except over a timescale of millions of years. Hence, the earth's magnetic field offers evidence of a timescale of only thousands of years, not billions of years, for Earth history.

Conclusion

The Gentry work on radiohalos is very difficult to explain, unless radioactive decay rates have varied over Earth History. Andrew Snelling's work speaks in favor of a large amount of change in decay rates during the Genesis flood, since rocks attributable to the Genesis flood contain numerous halos due to polonium isotopes. If it is possible to explain these halos as due to hydrothermal flows, it is only by also involving changes in decay rates after their formation. Humphreys' work on energy contained in the earth's magnetic field indicates a much more rapid decline in this energy than should be occurring if the field were due to the mechanisms offered by the old-earth advocates. Those interested in accurate views of Earth history would do well to consider these results.

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