than the dot on this *i*, with a complex of aeropyles for diffusion of oxygen that comprises a mystery[2]; and the motivating power and design initiated by—oops—I almost said "by a Divine Creator!" But then, that would be nit-picking, wouldn't it? Surely if a miniscule butterfly egg can produce such wonders of development from gene to genius, it shouldn't need any outside help, should it?

But nitting is just like knitting; for every design there must be a Designer. For every plan there must be a Planner; and for even the lowliest nit there is the evidence of a sacred knitting. "For the invisible things of Him from the creation of the world are clearly seen, being understood by the things that are made, even His eternal power and Godhead, so that they are without excuse." Romans 1:20.

References

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AMINO ACID RACEMIZATION IN MARINE SEDIMENTS

LARRY S. HELMICK *

The spontaneous diagenesis which occurs after death of an organism results in hydrolysis of the peptide bonds in proteins and racemization of the amino acid residues. The extent of racemization of amino acids has therefore been suggested as a potential dating method for samples containing proteins, such as marine sediments. In order for the method to be useful, however, three general requirements must be met: (1) the environmental conditions since deposition must be known; (2) the experimental method must provide accurate quantitative data concerning the extent of racemization which has occurred; (3) the mechanism of diagenesis must be known under the environmental conditions. The problems associated with each of these topics are discussed in detail. The existing data are then reinterpreted in a teleological framework and shown to be in agreement with the Genesis account of a worldwide flood.

Introduction

Living organisms are known to contain proteins consisting almost exclusively of L-amino acid residues. During the spontaneous diagenesis process which occurs after the death of the organism, the proteins are hydrolyzed and the L-amino acid residues are racemized to thermodynamically more stable racemic modifications consisting of equal quantities of the L- and D-amino acids. If environmental conditions are such that racemization occurs at a rate which can be determined, then the extent of racemization observed in material of biogenetic origin might provide an indication of the length of time which has passed since the death of the organism.

Consequently, the extent of racemization of amino acids has been suggested as a new and independent method for determining the age of biogenetic material. Since the basis of the method was first reported in 1967, it has been used to determine the ages of ocean sediments, shells, bones, and corals.[1]

Independent dating of marine sediments by the racemization of amino acids is based on five assumptions: (1) proteins contained amino acid residues of only the L-configuration when deposited; (2) no alteration of the sediments has occurred since deposition; (3) the extent of racemization can be accurately determined; (4) the mechanism and rate of racemization are known; (5) the mechanism of diagenesis is known.

In this paper each of these assumptions will be examined in detail, the problems associated with the application of this dating method to marine sediments will be analyzed, and a reinterpretation of existing data, consistent with the Genesis account of a recent worldwide flood, will be presented. Some of the problems associated with the amino acid racemization dating method have been presented recently.[2,3]

Original Configurations of Amino Acids

It has been assumed that amino acid residues preserved in sediments originally consisted of only the L-enantiomers. Racemization then produces increasing concentrations of D-enantiomers with time. The extent of racemization is, therefore, proportional to the length of time since formation of the sediment. Presence of D-enantiomers in the sediment at the time of formation, however, would cause the sediment to appear older than it actually is.

Consequently, the magnitude of the calculated age is highly dependent on the enantiomeric purity of the original amino acids in the sediment. For accurate results this purity must be known.

Amino acids are preserved primarily in the form of proteins. The proteins of living organisms are known to consist almost exclusively of L-amino acids although D-amino acids have been reported to occur in small quantities in bacteria, insects, worms, and algae.[4] D-amino acids are also formed in equal quantities with L-amino acids in all synthetic reactions not involving chiral reaction conditions. Furthermore, D-amino acids are continuously being formed by spontaneous racemization of biogenetic L-amino acids.

The extent to which D-amino acids from any of these sources have been included in marine sediments, however, appears to be small. Bound amino acid[5] and total amino acid[6] analyses of the top few centimeters of marine sediments, which are apparently of recent origin and therefore would contain very small amounts of D-amino acids produced by racemization after the sediment was formed, indicate that they contain L-amino acids almost exclusively.

Thus it may be assumed that deeper sediments also contained only L-amino acids when they were formed, unless there has been a marked change in the stereochemistry of the proteins in living organisms in the recent history of the earth. Such a change is not predicted by use of either the evolutionary or teleological theory.** Furthermore, the complexity of the chemistry of living cells makes this alternative seem highly unlikely.

Alteration of Marine Sediments

Alteration of marine sediments may involve either large-scale mixing of old and new sediments or diffusion of

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**Teleology refers to the study of evidence relating to design of natural processes, as opposed to a purely mechanical causation. The teleological theory of origins refers here to a recent highly ordered divine creation, followed by degeneration and a worldwide flood, as described in Genesis.

amino acids into or out of the undisturbed sediments. Neither method has been investigated in detail, but either one could result in serious problems for researchers using the racemization dating method. The possibility of mixing of gross sediments on a worldwide scale is undoubtedly the most serious and will be considered shortly.[7]

Studies on the diffusion of amino acids into or out of shells[8] indicate that both can occur to some extent under simulated geological conditions, and thus might also occur in sediments. Similarly, diffusion of free amino acids into or out of fossil bones[9] has been suggested in order to explain anomalous results, and a method has been developed for determining whether contamination has actually occurred. However, the validity of the method has not yet been confirmed, and disagreement exists as to whether some bones are actually contaminated when data are analyzed by this method.[10,11]

Contamination by recent amino acids has also been suggested in order to explain the lack of racemization and the presence of thermally unstable amino acids in much of the geologic column,[12] including Precambrian strata such as the supposedly three billion-year-old Fig Tree chert[13] and two billion-year-old Gunflint chert.[14] Nevertheless, "to what extent these materials can move around in the geologic column is not clear."[15] In fact, these observations may be more consistent with a teleological theory of origins than with an evolutionary theory.[16]

Since the teleological theory is based on a recent creation, it is not necessary to suggest that extensive contamination has occurred in order to explain the data. Yet the potential for contamination of marine sediments exists, and the effects need to be considered.

Since free amino acids in sediments are known to be more extensively racemized than peptide or protein-bound amino acids, preferential diffusion of free amino acids into or out of the sediment would alter the extent of racemization observed for the total amino acid analysis of the sample. Due to lower solubility, the peptide and protein fractions would presumably be much less susceptible to alteration by diffusion. However, as the concentration of amino acid residues in a sample decreases, as it does with increasing age, the potential effect of alteration increases.[17]

Both diffusion of highly racemized free amino acids out of the sediment and contamination by recent L-amino acids would serve to lower the ratio of D- to L-amino acids found in the total amino acid analysis and cause the sediment to appear younger than its true age. Except for very old sediments, however, alteration by diffusion is probably insignificant. Although laboratory blanks are often run in order to detect contamination during processing, they reveal nothing about *in situ* contamination before collection.[18]

Major Factors Affecting Analytical Data

In order to use the extent of racemization of amino acids for determination of absolute ages of sediments, quantitative data are required. Thus the investigator must be able to determine accurately the precise concentration of each stereoisomer of the amino acid of interest in the sample.[19] The ratio of concentrations of D- to L-amino acid then gives the degree of racemization. At this point, several major analytical problems have been encountered.

In any given sample, amino acids exist in at least three different states (protein, peptide, and free) due to incomplete hydrolysis of the proteins. Some investigators have not distinguished between these three states but simply reported the ratio of D-alloisoleucine to L-isoleucine for only the bound, free, or total amino acids present. However, one attempt has been made to determine the extent of epimerization[20] of L-isoleucine for all three states of amino acids.[21] Thus is is now known that the extent of racemization increases with the extent of *in situ* hydrolysis. Protein exhibits very little racemization while free amino acids are highly racemized.

Although data undoubtedly would be more meaningful if they were all separated in this way, accuracy and reproducibility appear to suffer when they are. While results by different workers on the same core are only slightly different for total amino acids, they are grossly different for the free amino acid fraction.[22-24] This difference has been attributed to the use of a new method of analysis involving esterification of the free amino acids.[25] This method may have also resulted in hydrolysis and esterification of some of the peptides present in the free amino acid fraction. Since peptides have a lower degree of racemization than free amino acids, this would greatly lower the apparent extent of racemization in the free amino acid fraction. It still remains to be determined whether this is indeed the case.

Furthermore, Wehmiller and Hare[26] have reported that racemization in the free amino acid fraction of core V23-110 decreases with depth, rather than increases. Yet Kvenvolden *et al.*[27] reported increasing racemization with depth for the same core. In addition, Bada[28] has reported that the D-alloisoleucine/L-isoleucine ratio in the free amino acid fraction is only 0.61 for a 20,000-year-old sample and 0.81 in a 93,000-year-old sample, while Wehmiller and Hare[29] reported much larger ratios for supposedly younger samples (1.3 for a sample greater than 0 years old and 1.0 for one 3,000 years old).

The validity of the independent geological dating methods used to verify the racemization dating method is also highly significant. For example, Bada originally thought that ages for sediments could be calculated directly from laboratory data on the rate of racemization of free amino acids and the present ocean bottom temperature.[30] In this way, the age for the bottom of a sediment core from the Mid-Atlantic ridge was determined and thought to be in agreement with the age determined by paleomagnetic and radionuclide decay techniques.[31]

However, the age was later revised downward from 1.23 million years to 96,000 years for two reasons: (1) it had been demonstrated that racemization in shells[32] and sediments[33] occurs at elevated temperatures about an order of magnitude faster than free amino acids under similar conditions, and (2) the extent of racemization in other supposedly younger cores dated by magnetic reversals, paleontology, and radionuclide decay had been found to be considerably greater than in Bada's core.[34] Thus the original results from the paleomagnetic and radionuclide decay methods were assumed to be invalid.

In addition, the elevated temperature data and geological data were thought to provide concordant ages.[35] Nevertheless, as will be noted later, there are problems associated with determining rates of racemization at elevated temperatures and extrapolating to determine rates at environmental temperatures. Furthermore, application of ^{14}C dating to sediments does not always give consistent results,[36] and results from application of the various geological dating methods on fossil bones has been termed "strongly discordant."[37] Finally, use of radionuclide decay dating methods to empirically calibrate the amino acid racemization method[38,39] results in a secondary dating method. This approach would simply magnify the uncertainties already noted in the radionuclide decay methods ,[40,41] and would not result in independent dates.

Minor Factors Affecting Analytical Data

Three minor factors affecting the accuracy and reproducibility of the analytical data have also been identified. While some work has involved analysis of the gross sediment from a core segment, other studies have been done on only the foraminifera fraction. Application of these two procedures to the same core segment (400 cm segment of core CH96-G12), however, resulted in detection of slightly different degrees of racemization.[42,43] Although the differences are small, the exact extent of racemization detected may depend somewhat upon the fraction of the core segment selected for analysis.

Secondly, the concentration of amino acids may be extremely low under certain conditions and difficult to measure accurately. Consequently, results may not be reproducible.[44] This generally occurs for D-amino acids in young sediments, due to insufficient time for extensive racemization to occur, and for both D- and L-amino acids in old sediments. Extremely low concentrations can result in relatively large percentage errors in measurement and thus large errors in the calculated extent of racemization.[45]

Even at higher abundances, 30% errors in determination of concentrations in duplicate analyses have been reported[46], although the error in the ratio of D- to L-amino acids was considered to be only 5%. To reduce the possibility that minute amounts of amino acids in reagents might dominate the analysis of samples with low amino acid concentrations, reagent blanks are often run.

Finally, acid hydrolysis of proteins to free amino acids is necessary in order to identify the amino acids and determine the extent of racemization which has occurred in the sample. Any racemization which occurs during hydrolysis must be deducted from the observed degree of racemization in order to determine the extent of *in situ* racemization which has occurred. However, the literature contains contradictory reports as to whether racemization occurs to any appreciable extent during acid-catalyzed hydrolysis of proteins in refluxing 6N hydrochloric acid.

Bada reported that no detectable racemization occurred,[47] although a latter report claimed that a small amount is produced.[48] Hare reported that "insignificant" amounts of D-amino acids are formed from either free L-amino acids or shell protein under acid-catalyzed hydrolysis conditions.[49] Yet Wehmiller and Hare stated that "significant" racemization occurred in three out of four samples of marine sediments tested.[50] Perhaps the following discussion of the mechanism of acid-catalyzed racemization of free amino acids and the mechanism of acid catalyzed hydrolysis of proteins would help to resolve this question.

In solutions more acidic than pH 1, racemization of free amino acids proceeds by protonation of the carbonyl oxygen, followed by enolization (Figure 1).[51] Experiments designed to detect hydrogen exchange and thus racemization, using tritium labeling, indicated that ten free amino acids, including isoleucine, racemize less than 3% when refluxed for 22 hours in 6N hydrochloric acid.[52] Although this demonstrates the stability of amino acids after hydrolysis, it reveals nothing concerning the potential for racemization during the hydrolysis reaction itself.

> Some amino acid residues in peptides are racemized to the same extent as the corresponding free L-amino acids. This may indicate that protonation of the peptide bond, which is favored over formation of the conjugate acid of the free carboxylic acid group, results first in hydrolysis followed by racemization of the free amino acids which are released. Increased racemization of amino acid residues compared with that observed with free amino acids may be due to an interaction between adjacent residues, as in bacitracin A, or to an increased ease of protonation of the *a* - CO_2H group of a peptide caused by the decreased tendency of protonation of the adjacent peptide group.[53]

Several of racemization during hydrolysis of peptides have been reported. Thirteen percent racemization of glutamic acid in myoglobin, and 9% racemization in insulin have been attributed to acid hydrolysis. Approximately 8% racemization of the two phenylalanine residues in bradykinin has been attributed primarily to the residue in the L-Phe-L-Ser sequence. "Acid hydrolysis of one of the ergot alkaloids causes complete inversion of configuration of a L-proline residue."[54]

Twelve percent racemization of the only leucine in bacitracin A may be due to interaction with the adjacent cystine. One of the L-isoleucine residues in bacitracin A "forms a thiazoline ring with the adjacent cystine" and is completely epimerized during acid hydrolysis. Since there are three isoleucine residues in bacitracin A, the observed[55] degree of epimerization for isoleucine is 33%.

Since L-isoleucine has been used more extensively than other amino acids in dating marine sediments, epimerization of L-isoleucine when bonded to cystine demonstrates that a potential problem exists for the racemization dating method. Even a small degree of racemization during hydrolysis would result in apparent ages which are older than the correct ages.

Thus there are presently several unresolved analytical problems involving primarily accuracy and reproducibility of data. Some of the problems may originate in the different analytical methods used for determination of the extent of racemization. Still others may originate in the dates which have been determined for the cores by other geological dating methods.

Mechanism and Rate of Racemization

The importance of knowing the rate constant for racemization under environmental conditions cannot be overestimated. "Obviously, the rate constant for the reaction must be known accurately if age is to be calculated, but its value is difficult to assess."[56] The major factors generally considered to influence the rate constant for racemization of amino acids in sediments are peptide bonds and temperature.

In order to determine the rate constant for racemization under environmental conditions, it is necessary to have an understanding of the mechanisms by which racemization occurs in free amino acids, peptides, and proteins. Each of these might be expected to have a particular mechanism and rate of racemization, and also a specific set of factors which would influence the rate. Thus far, only the factors involved in controlling the rate of racemization of free amino acids have been determined quantitatively. Qualitative results on the racemization of peptides are also available. However, little is known concerning the racemization of proteins under environmental conditions.

In solutions between pH 1 and pH 13, three different species of free amino acids are generally involved in racemization: $\overset{+}{N}H_3CHRCO_2H$ (+0), $\overset{\pm}{N}H_3CHRCO_2^-$ (+–), $NH_2CHRCO_2^-$ (0–).[57,58] Due to formation of carbanions of different stability, racemization proceeds at different rates for each species. The cation (+0) is most reactive while the anion (0—) is least reactive. The observed rate (k_{obs}) is the sum of the individual rates of racemization: k_{obs} =

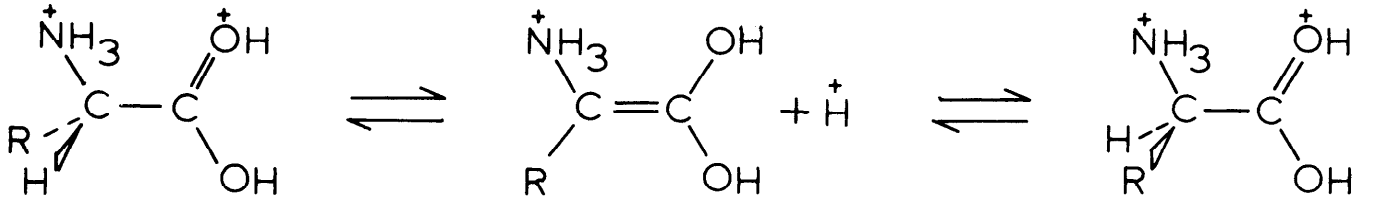

Figure 1. Acid-Catalyzed Racemization of Free Amino Acids.

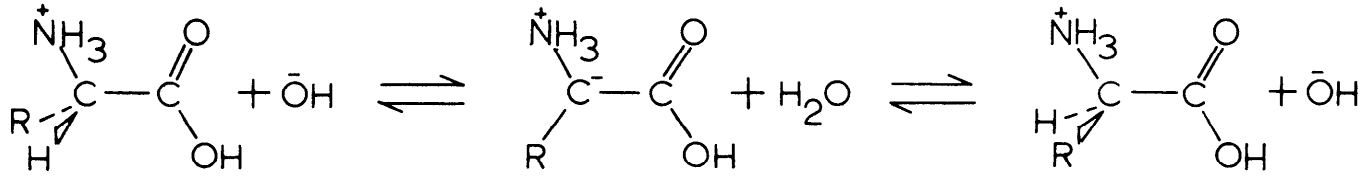

Figure 2. Base-Catalyzed Racemization of Free Amino Acids.

$(k_{+0}\ [+0] + k_{+-}\ [+-] + k_{0-}\ [0-])\ [OH^-]$, where k is the rate constant and [ ] is the concentration of each species.

Carbanion stability and thus rate constants for racemization of different free amino acids have been found to be dependent upon the relative inductive effects of the corresponding substituents, R.[59] Similar effects of substituents in aromatic nitrogen heterocycles have been observed.[60]

The rate-determining step of the reaction involves abstraction of the α-hydrogen by hydroxide[61] (Figure 2). Racemization is, therefore, a second-order reaction. If the hydroxide concentration is constant, first-order kinetics is observed. However, since the relative concentration of each species is also dependent on the hydroxide concentration, the observed rate of racemization appears to be independent of hydroxide between pH 5 and 8.

Consequently, racemization occurs at a minimum but nearly constant rate in the environmental pH range from 5 to 8 and increases as the medium becomes either more acidic or more basic.[62] Since ocean bottom environments have probably not experienced extreme fluctuations from their present pH of 7.6, it is unlikely that changes in acidity would have any major effects on the rate of racemization of free amino acids in sediments. However, small local fluctuations would probably serve to increase the rate, making the sediment appear older than its true age.

The rates of base-catalyzed hydrogen-deuterium exchange, and consequently racemization,[63] have been determined for individual residues in peptides using nuclear magnetic resonance spectroscopy.[64] At room temperature and pH 13.1, it was found that the central residues of tri- and tetrapeptides showed considerable exchange after only a few hours. For example, in Gly-Gly-Gly, the half-time for exchange of the middle Gly was approximately 5 hours. The terminal residues were inert.

Futhermore, free glycine and the dipeptide, Gly-Gly, showed no exchange of the α-hydrogens in 21 hours. For comparison, the half-time for racemization of free aspartic acid at 25° and pH 12.0, calculated from elevated temperature data, is 4×10^6 hours.[65] Thus it appears that racemization occurs at considerably faster rates in the central residues of polypeptides than in terminal residues or in free amino acids in strongly alkaline solutions.

This tremendous reactivity difference may be attributed primarily to stabilization of the intermediate carbanion by two peptide bonds. Indeed, the strongly activating effects of acylation of the amino group and conversion of the carboxylate group to a carboxamide have been demonstrated.[66] From this, the following order of reactivity can be established: $RCONHCHRCONHR > RCONHCHRCO_2^-$, $NH_2CHRCONHR > NH_2CHRCO_2^-$. Thus racemization occurs at reasonable rates under these conditions only for amino acid residues which are activated by two peptide bonds.

The mechanism for base-catalyzed racemization of free amino acids has been shown to change from rapid racemization of $NH_2CHRCO_2^-$ at pH 12.5[67] to rapid racemization of $\overset{+}{N}H_3CHRCO_2H$ at pH 7.5.[68] Thus the mechanism of racemization in peptides might also be expected to depend on acidity and to change when the pH is lowered from 12.5 to 7.5. This increase in acidity would have two effects.

One would be to greatly decrease the rate of racemization of the central residues due to the 10^5 fold decrease in hydroxide concentration. The second would be to increase the concentration of the protonated N–terminal residues. Since the protonated amino group has been shown to be a stronger activating group than the acetamido group,[69] the protonated N–terminal residues should then be the most reactive residues present ($\overset{+}{N}H_3CHRCONHR > RCONHCHRCONHR$). Consequently, these two effects would result in a change from rapid racemization of the central residues of peptides at pH 12.5 to rapid racemization of the N–terminal residues at pH 7.5.

Qualitative Rate Comparison

A qualitative comparison of the rate of racemization of N-terminal residues with free amino acids may also be made. It has been shown that $\overset{+}{N}H_3CHRCONHR$ and $\overset{+}{N}H_3CHRCO_2H$ have approximately the same rates of racemization.[70]

Although $\overset{+}{N}H_3CHRCO_2H$ is the major species contributing to the rate of racemization at pH 7.5, it represents only one part in 10^5 of the total amount of amino acid present. The rest exists as $\overset{+}{N}H_3CHRCO_2^-$, which is much less reactive.[71]

In the case of N–terminal residues, however, essentially all of the material is present in the more reactive form, $\overset{+}{N}H_3$CHRCONHR, since ionization of a carboxyl group is not possible. Thus the N–terminal residues of a peptide should be subject to racemization at a rate which is considerably faster than that for either central residues, C-terminal residues, or free amino acids, under environmental conditions.

This mechanism is in agreement with previous suggestions that racemization in marine sediments may be occurring via the N-terminal residues of peptides.[72] It also would explain the rapid rate of racemization which is thought to be occurring during hydrolysis of proteins to free amino acids under environmental conditions,[73] but for which no satisfactory mechanism has yet been proposed.[74]

Effect of Temperature

The effect of temperature on the rate constant for racemization also has been investigated. The rate of racemization of free amino acids is highly temperature dependent, generally doubling for each 4 to 5°C rise in temperature.[75] Attempts to determine the effect of temperature on the rate of racemization of *in situ* amino acid residues in sediments have not been as successful.[76]

Apparent first-order rate constants for racemization were determined by heating samples with water in sealed tubes at various temperatures.[77] An Arrhenius graph of these rate constants appeared to give a straight line from which the apparent energy of activation for racemization was calculated.

However, this method for determining the energy of activation for racemization of *in situ* amino acid residues is acceptable only if racemization of proteins is fast relative to hydrolysis or if hydrolysis of proteins and peptides is fast compared with racemization of free amino acids, and only if the rate constant for racemization can be determined. As will be noted shortly, there is evidence that neither one of these mechanisms of diagenesis is correct.

Furthermore, for one sediment sample heated at 148.7°C, it was clearly shown that a plot of the kinetic data was not linear. The reaction did not follow first-order kinetics. Consequently, the first-order rate constant could not be determined. Instead, only the initial rate was estimated from the graph and used to determine the Arrhenius energy of activation. Kinetic data were not reported at other temperatures, but apparently only the initial rates were estimated and reported for the same reason.

Consequently, it is not at all clear just what is represented by the energies of activation which have been determined. It is clear, however, that these energies of activation may result in invalid rate constants for racemization of amino acid residues in sediments under environmental conditions. Obviously, use of an inaccurate rate constant to calculate the length of time required to produce the observed degree of racemization in a sediment core would result in an inaccurate age for the sediment.

In any event, the maintenance of a constant known temperature is necessary to obtain rates of racemization from which ages may be calculated. Consequently, only samples such as marine sediments, which are assumed to have experienced minimal temperature fluctuations during their history, are selected for racemization dating. The temperature fluctuations represented by the well-established and recent worldwide warm climate,[78] and an even more recent ice age,[79] are generally ignored. Instead, the present temperature is considered to be representative of the average temperature during the history of the sample, and is used in age calculations.[80]

Although average temperatures in the southeastern United States may have dropped as much as 15°C during the glacial period,[81] cooling effects during a short glacial period would be expected to introduce minimal errors in the calculated ages for marine sediments, since the ocean bottom temperatures are already 2° to 4°C and could not become much colder. (Ocean water freezes at −1.5°C.)

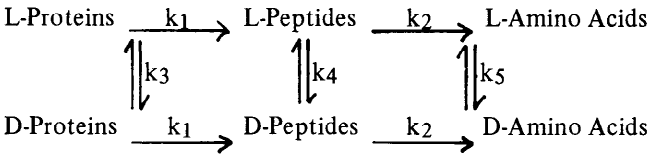

Figure 3. Diagenesis of L-Proteins to Racemic Free Amino Acids.

However, considerably higher ocean bottom temperatures, and thus faster rates of racemization, may have been experienced due to the absence of cold bottom water flowing from the Arctic and Antarctic during the period of a worldwide warm climate.[82] Consequently, any errors in this assumption would tend to make marine sediments appear older than they actually are.

Mechanism of Diagenesis

"In any event, the use of racemization as a chronological tool will depend on a thorough understanding of the diagenetic reactions of amino acids in the particular system under study." However, "the kinetics of racemization observed in hydrolysates of fossil or sediment samples depend on a variety of time constants, none of which is easily evaluated."[83] Consequently, determination of the mechanism of diagenesis is a significant but complex problem.

Several mechanisms for diagenesis of proteins to racemized free amino acids (Figure 3) are conceivable: (1) fast racemization of proteins followed by slow hydrolysis to peptides and free amino acids ($k_3 > k_1, k_2$); (2) fast hydrolysis of proteins and peptides followed by slow racemization of free amino acids ($k_1, k_2 > k_5$); (3) slow hydrolysis of proteins and peptides followed by fast racemization of free amino acids ($k_5 > k_1, k_2$); (4) slow hydrolysis of proteins and peptides followed by fast racemization of N-terminal residues of proteins and peptides.

Two kinds of evidence eliminate the first mechanism (racemization followed by hydrolysis), but support the remaining three (hydrolysis followed by racemization): (1) the large extent of racemization observed in the free amino acid fraction relative to the protein and peptide fractions of sediments,[84] and (2) the absence of racemization in fossil bones preserved under anhydrous conditions,[85] and in shells heated without water.[86] The following data concerning the relative rates of hydrolysis and racemization are significant when considering the remaining three mechanisms:

> Partial hydrolysis of proteins has generally been found to produce a fairly specific set of peptides under a given set of conditions.[87] This is because some peptide bonds are considerably more susceptible to cleavage than others. Rates may vary over two or three powers of ten.[88] Hydrolysis of the most labile bonds occurs rapidly, then the rate decreases as less labile bonds remain to be hydrolyzed. This decreasing rate of hydrolysis of protein has been cited to explain the presence of incompletely hydrolyzed proteins in presumably old samples.[89]
>
> Due to both acid and base catalysis, the rate of hydrolysis of amides depends upon the acidity of the solution. The reaction is fast in acidic solutions, decreases in rate as the acid concentration decreases, then increases in rate again as the solution becomes basic. The rate of hydrolysis of proteins to free amino acids via peptides may be similar, with minimum rates observed in neutral solutions.
>
> It is well known that hydrolysis of proteins is faster than racemization in strongly acidic solutions.[90] However, in basic solutions, hydrolysis is slower than

racemization.[91, 92] Thus the relative rates of hydrolysis and racemization reverse as the acidity decreases. In neutral solutions, little comparative data is available.[93, 94] However, in 50% deuteroacetic acid-deuterium oxide solutions, hydrogen-deuterium exchange of amides has been reported with no mention of hydrolysis.[95] Thus hydrolysis of peptides may still be slower than racemization in neutral and weakly acidic solutions.

Racemization of free amino acids is known to follow first-order kinetics[96] while hydrolysis of proteins does not.[97] If the *second mechanism* of diagenesis (fast hydrolysis of proteins and peptides followed by slow racemization of free amino acids) is correct, then rates of racemization determined at elevated temperatures on recent sediments would be expected to exhibit first-order kinetics. This has not been observed.[98] Consequently, the rate-controlling step in diagenesis at elevated temperatures appears to be hydrolysis rather than racemization. If this is the case under environmental conditions, then the second mechanism may be eliminated.

If the *third mechanism* of diagenesis (slow hydrolysis of proteins and peptides followed by fast racemization of free amino acids) is correct, then the rate of racemization in sediments should be slower than the rate determined for free amino acids. However, it has been shown that amino acid residues in sediments[99] and shells[100] racemize an order of magnitude faster than free amino acids under similar conditions. Thus it has been proposed that rapid racemization of free amino acids under environmental conditions is occurring by a mechanism involving metal ion catalysis.[101]

Catalysis of racemization of amino acids by metal ions such as Cu^{+2} and Al^{+3} has been reported in dilute alkaline solution.[102] Catalysis is produced by stabilization of the intermediate carbanion due to chelation of the amino group. Racemization of alanine and valine in the complex Co(ethylenediamine)$_2$ amino acid^{+2} is first order in hydroxide. Extrapolation of rate data obtained at 34.3°C indicates that chelated alanine is about 3000 times more reactive than nonchelated alanine at pH 7.6 and 0°C.

Thus such a mechanism involving metal ion catalysis may be able to account for the high degree of racemization observed in the free amino acid portion of older sediments if the amino acids are completely complexed. If only a small fraction of the amino acids is complexed,[103] the rate enhancement may be insufficient to account for the high degree of racemization found in the free amino acid portion of recent sediments.[104]

However, the *fourth mechanism* (slow hydrolysis of proteins and peptides followed by fast racemization of N-terminal residues of proteins and peptides) is able to account for the high degree of racemization in the free amino acid fraction even in recent sediments.

Peptides represent a general class of low molecular weight amino acid polymers including dimers, trimers, tetramers, etc. The process of hydrolysis to free amino acids may involve cleavage of the central peptide bonds of larger peptides to produce two smaller ones, or it may involve cleavage of either of the terminal peptide bonds to produce a free amino acid and a smaller peptide.

If racemization of the N-terminal residues is faster than hydrolysis of the N-terminal peptide bonds under environmental conditions, then the N-terminal residues should be highly racemized before hydrolysis to free amino acids occurred. Consequently, a high ratio of D- to L-amino acids in the free amino acid fraction should be observed even in young samples. However, whenever C-terminal residues are hydrolyzed, only L-amino acids would be produced. Thus the free amino acid fraction should not be completely racemized.

Furthermore, the ratio of D- to L-amino acids in the free amino acid fraction should be considerably higher than the corresponding ratio in the peptide fraction. This would be due to the large number of unracemized central and C-terminal residues relative to the number of racemized N-terminal residues in the peptide fraction. In addition, the ratio of D- to L-amino acids in the protein and peptide fractions should increase with time, as the larger proteins and peptides are hydrolyzed to smaller ones, producing a larger ratio of racemized N-terminal residues relative to unracemized central and C-terminal residues.

Observations are in agreement with all of these predictions.[105, 106] Consequently, the major features of this mechanism of diagenesis involving slow hydrolysis of proteins to peptides followed by fast racemization of N-terminal residues of peptides and slow hydrolysis of peptides to free amino acids appear to be in agreement with the geological data from marine sediments as well as the laboratory data on proteins, peptides, and free amino acids.

If this mechanism is correct, the concentrations and rates of racemization of peptides and free amino acids will be controlled primarily by a decreasing rate of hydrolysis of proteins. Therefore, the observed rate of racemization for the total system would not fit first-order kinetics. Consequently, observations of first-order kinetics for racemization in marine sediments over long periods of time under environmental conditions would not be expected.

Thus it is now difficult to understand how meaningful ages for sediments could be calculated from the extent of racemization observed for the total amino acid fraction of the sample and the first-order rate constant for racemization of either free or *in situ* amino acids, as has been attempted. Nevertheless, according to geological data, the degree of racemization is a function of depth, and this may have a significant impact on the evolutionary and teleological theories.

Reinterpretation of Data

Evolutionary theory is based upon the principle of uniformitarianism which involves the concept that processes have always occurred at rates which are similar to those observed today. Use of the racemization of amino acids as a dating method is no exception. It is assumed that the rate of sedimentation in a given locality during the last several million years has been nearly constant and can be determined by dating one or two levels of the sediment core.[107] Consequently, a direct relationship between depth in ocean sediment and age is presumed to exist.

Since the rate of racemization of amino acids in ocean sediments was expected to be constant, it was assumed that the extent of racemization was not only a function of depth in ocean sediment, but also of age.[108] Therefore, the extent of racemization has generally been plotted versus age determined by other methods, rather than depth. If the theory is correct, nearly linear plots of racemization versus age would be expected (Figure 4,A).[109] Use of such a graph has been suggested as a means for determining the age of sediment when other dating methods are unavailable.[110]

The teleological theory is based upon the Genesis account of a recent creation, degeneration, and worldwide flood. The worldwide flood has tremendous implications for dating methods,[111, 112] including those involving marine sediments.[113]

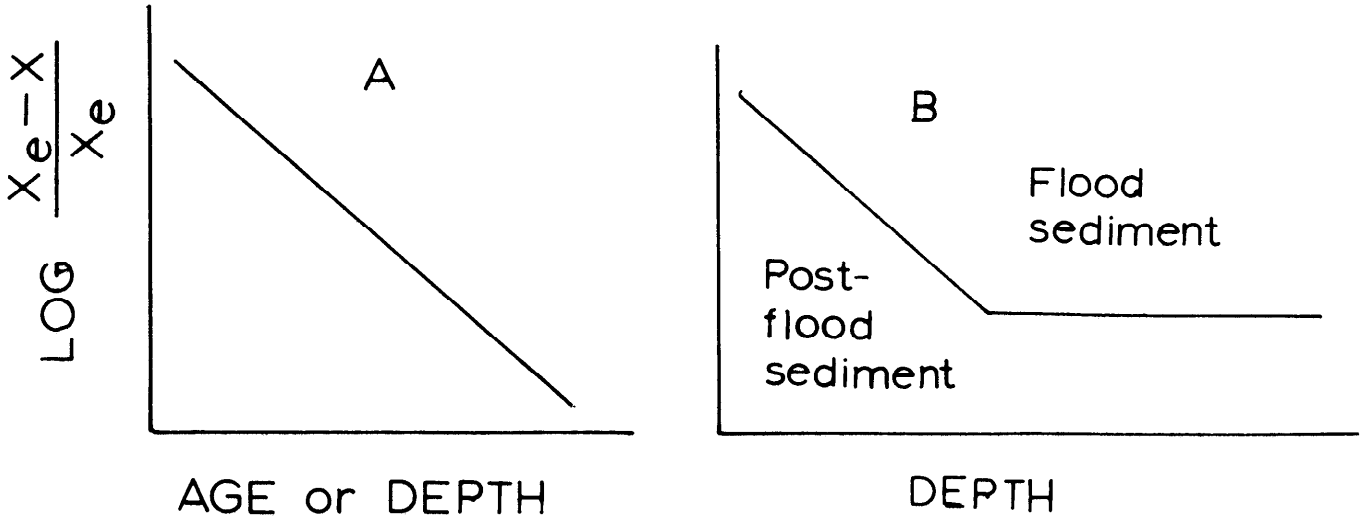

Figure 4. Extent of Racemization Versus Depth for Marine Sediments Predicted by (A) Evolutionary Theory, (B) Teleological Theory.[110]

Sediments laid down previous to the flood would have undergone more rapid amino acid racemization than is observed today, due to the higher ocean bottom temperatures produced by the worldwide warm climate. Rates of sedimentation during and immediately following the flood would also have been large,[114] but rapidly decreased as the earth adjusted to the new geological conditions after the flood. Consequently, it may be concluded that the rates of racemization and sedimentation during the recent history of the earth have not been constant.

In addition, the effects of extensive alteration of marine sediments during the flood must be considered. Mechanisms by which this may occur are known. The extensive reworking of marine sediments due to volcanic and seismic upheavals, tidal waves, and currents during the flood have been amply described.[115] Furthermore, the eroding effects of the first torrential rains, flooding rivers, and erupting subterranean waters would have introduced numerous layers of new sediment from land masses. Phenomena such as these might easily produce such vast and thorough mixing that little increase in the average extent of racemization would be observed for considerable depths. However, pronounced differences in the extent of racemization from one layer of sediment to the next might be expected.

These effects of a worldwide flood would result in plots of racemization versus depth in marine sediments which are not linear. Instead, it might be expected that the extent of racemization would increase with depth in present ocean sediments only for the period of time since the flood. Sediments laid down rapidly during the flood, which includes most of the geologic column, might show erratic changes from one layer to the next, but little increase in the average degree of racemization with depth. Consequently, the graph of racemization versus depth (Figure 4, B) predicted by use of the teleological theory would be strikingly different from the one predicted by the evolutionary theory (Figure 4, A).

This change in slope has actually been observed for one long sediment core (V23-110), and may be present in data from other cores (V16-39, RC8-93, V12-18, V16-205) as well.[116, 117] It also appears to be observed for fossil corals and shells,[118] and would account for observations of incomplete racemization throughout the geologic column.[119]

Such a change in slope is not predicted by use of the evolutionary theory and thus far has not been explained by it. However, it is predicted by the teleological theory, and would coincide with the termination of unprecedented marine turbulence and rapid sedimentation at the end of the Genesis flood. Consequently, the teleological theory appears to be superior to the evolutionary theory in accounting for the extent of racemization of amino acids in marine sediments.

Conclusions

Proteins preserved in marine sediments originally consisted almost exclusively of L-amino acids. Alteration due to diffusion of free amino acids into or out of the sediment is probably insignificant except in very old sediments. Mixing of gross sediments on a worldwide scale, however, must be considered.

Major factors affecting the accuracy and reproducibility of results include: (1) selection of the protein, peptide, free or total amino acid fraction for analysis, (2) the choice of experimental procedure for the analysis, and (3) the validity of the geological dating methods used for verification and calibration.

Minor factors include: (1) selection of the foraminifera fraction or the gross sediment for analysis, (2) the absolute concentrations of amino acids present in the sediment, and (3) the extent of racemization which occurs during acid-catalyzed hydrolysis of the proteins.

Under environmental conditions, base-catalyzed racemization occurs. Related kinetic data indicate that racemization probably involves the N-terminal residues of peptides rather than the central residues, C-terminal residues or free amino acids. N-terminal residues would be expected to racemize rapidly due to the extensive carbanion stabilization afforded by the protonated amino group and the peptide bond. Attempts to determine the first-order rate constant for racemization under environmental conditions by determining the energy of activation of *in situ* amino acids at elevated temperatures have not produced applicable results.

The mechanism of diagenesis probably involves slow hydrolysis of proteins to peptides followed by fast racemi-

zation of N-terminal residues of peptides and slow hydrolysis of peptides to free amino acids. If so, meaningful ages for sediments cannot be calculated from the extent of racemization observed for the toal amino acid fraction of the sample and the first-order rate constant for racemization of either free or *in situ* amino acids.

A graph of the extent of racemization versus depth in marine sediments is not linear. Instead, a change in slope has been detected which is not predicted by the evolutionary theory. Nevertheless, it is consistent with the teleological theory, and would coincide with the end of rapid sedimentation at the close of the Genesis flood. Thus the teleological theory appears to be superior to the evolutionary theory in accounting for the geological data.

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A CATASTROPHIST JOURNAL

Many readers of the C. R. S. *Quarterly* were no doubt familiar with the journal *Pensée*, though it is no longer being published. Another journal is now being published which contains much the same kind of material.

The new journal is called *Kronos*. Inquiries about it can be sent to Warner Sizemore, Glassboro State College, Glassboro, New Jersey 08028.

The items in *Kronos* relate especially to questions raised by Velikovsky. On some points creationists will disagree, but on others they will find some common ground. Velikovsky and his followers believe in catastrophism; and catastrophism is a natural counterpart of Creationism. Most creationists believe in at least one great castastrophe; and possibly several others, still extensive but not worldwide.

Moreover, while Velikovsky does not seem to hold a very strong doctrine of Biblical inspiration, yet in practice he uses the Scriptures with great confidence as trustworthy records. It is true that he uses other sources also; but it is likely that he uses Scripture as much as all of the other sources together.

Creationists, then, can likely find some things of interest in such a publication, and they will wish the publishers of *Kronos* success.

— Editor