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Amino Acid Cosmogeochemistry

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SUMMARY

Amino acids are ubiquitous components of living organisms and as a result they are widely distributed on the surface of the Earth. Whereas only 20 amino acids are found in proteins, a much more diverse mixture of amino acids has been detected in carbonaceous meteorites. Amino acids in living organisms consist exclusively of the L-enantiomers, but in meteorites, amino acids with chiral carbons are present as racemic mixtures. Protein amino acids undergo a variety of diagenetic reactions that produce some other amino acids but not the unique amino acids present in meteorites. Nevertheless, trace quantities of meteoritic amino acids may occur on the Earth, either as a result of bolide impact or from the capture of cosmic dust particles. The ensemble of amino acids present on the early Earth before life existed was probably similar to those in prebiotic experiments and meteorites. This generates a question about why the L-amino acids on which life is based were selected.

1. INTRODUCTION

Amino acids are a substantial component of the $\sim 10^{17}$ g of organic matter produced annually on the Earth by photosynthesis. Although most of these amino acids are rapidly converted back to CO_2 by respiration and other oxidative processes, some small fraction escapes destruction and becomes part of the global organic carbon pool. It is thus not surprising that amino acids are widely distributed on the surface of the Earth; my estimates of the various amino acid reservoirs are given in table 1. Biospheric amino acids represent one of the smaller reservoirs on the Earth. Nevertheless, the amino acids in all other reservoirs are derived from this source.

The L-entantiomers (except for achiral glycine) of only twenty different amino acids are coded by mRNA even though a vast number of amino acids are synthetically possible. The discrimination against D-amino acids during protein biosynthesis is estimated to be greater than one part in 10^4 (Yamane *et al.* 1981). On the surface of the Earth, biogenic amino acids undergo reactions that produce a variety of products including other amino acids as well as racemic (D/L = 1.0) amino acid mixtures. Thus, although the biospheric biomass reservoir consists of a well-defined suite of amino acids, the other reservoirs in table 1 contain not only these amino acids, but also their degradation and alteration products.

Carbonaceous meteorites have been found to contain a diverse group of amino acids, most of which do not occur on the Earth. In the Murchison meteorite, an extensively studied carbonaceous chondrite, 74 amino acids have been identified with the protein amino acids accounting for only 10% (Cronin & Pizzarello 1983; Cronin *et al.* 1988). The most abundant non-protein amino acids in Murchison are shown in table 2. When free of terrestrial contaminants, meteoritic amino acids with a chiral carbon are racemic (Bada *et al.* 1983).

This contrast between terrestrial and extraterrestrial amino acids generates several interesting questions. How stable are protein amino acids and what are their decomposition pathways? How were the extraterrestrial amino acids in carbonaceous meteorites synthesized? Did this type of synthesis occur on the early Earth? Have extraterrestrial amino acids been added to the Earth's surface, and if so, by what processes? Why are only the protein L-amino acids used by life and on what bases was this selection determined?

2. TERRESTRIAL AMINO ACID DIAGENESIS

(*a*) *Peptide bond hydrolysis*

The peptide bond in proteins is thermodynamically unstable and is rapidly cleaved by the three competing hydrolysis reactions, with the simplest being the cleavage of an internal peptide bond. Peptide bonds containing aspartic acid, serine and threonine residues are the most rapidly cleaved, whereas those containing hydrophobic amino acids such as valine and leucine take the longest to break (van Kleef *et al.* 1975; Hare 1976; Inglis 1983). An internal aminolysis reaction, which yields a diketopiperazine (cyclic dipeptide), is likely to be the main hydrolysis pathway for amino acids at the N-terminal position of proteins (Steinberg & Bada 1983). Studies of small peptides in the neutral pH range have shown that this reaction is more rapid than internal cleavage, especially for peptides made up of hydrophobic amino acids. This reaction becomes more significant as an overall hydrolysis pathway as internal hydrolysis produces an increasingly larger number of peptide fragments. The final reaction is the

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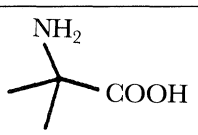
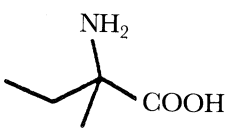
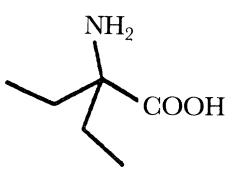
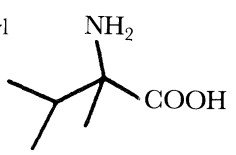
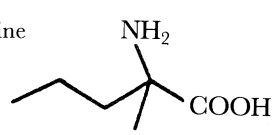
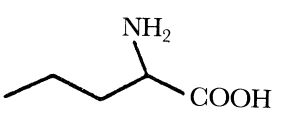
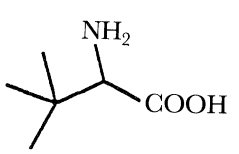
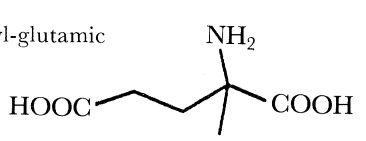
Table 1. *Amino acids on the Earth*

	carbon (Gt C)[a]	estimated amino acid content (%)	amino acids (Gt AA)[b]
biosphere	600–800	< 10	< 100
sea water organics	2000–3000	1	20–30
soil organics	1000	< 1	< 10
sediments			
organic matter	3×10^7	0.02–1	6000–300000
carbonates	10^8	0.002–0.03	1000–30000

[a] Gt C = 10^{15} g carbon
[b] Gt AA = 10^{15} g amino acids.

Table 2. *The most abundant non-protein amino acids in the Murchison meteorite (Cronin & Pizzarello 1983)*

name	structure	amount (nmol g^{-1})
α-aminoisobutyric acid (AIB)		91–145
isovaline		27–85
2-amino-2-ethyl butyric acid		6–21
2-amino-2,3-dimethyl butyric acid		8–35
2-methyl-norvaline		4–19
norvaline		2–4
pseudoisoleucine		3
2-methyl-glutamic acid		9

hydrolysis of an amino acid at the C-terminal position. This reaction is catalysed by acid and base, but between pH 5 and 9, it is independent of pH (Kahne & Still 1988). The half-life for the hydrolysis of glycine from the C-terminal position when the adjacent amino acid is phenylalanine has been estimated to be only 7 years in water at 25 °C (Kahne & Still 1988). The C-terminal hydrolysis pathway also increases in significance as internal hydrolysis proceeds.

As a result of these hydrolysis reactions, proteins and peptides are rapidly hydrolysed on the surface of the Earth. In biogenic carbonates the protein initially present in the matrix is 90% hydrolysed to smaller peptides and free amino acids in about 1 Ma on the ocean floor (Bada & Man 1980), and in around 100000 years in surface environments (Serban *et al.* 1987). In the bone matrix, hydrolysis of the main protein component, collagen, is much more rapid than for proteins in biogenic carbonates. Little collagen remains in bones after only 10000 to 30000 years, except for those in cool depositional environments (Bada 1985*a*). Proteins present initially as minor components of bone are more resistant to hydrolysis than collagen, and these may be the dominant proteins remaining in bones that contain little or no intact collagen (Masters 1987).

Because of their rapid hydrolysis under geochemical conditions, proteins are not preserved on the Earth's surface for periods greater than 1 Ma, except possibly in cool (and probably dry) environments. Thus the possibility of retrieving intact protein sequences from ancient biogenic materials is remote.

(*b*) *Decomposition*

Amino acids undergo decomposition both in proteins and in the free state, yielding a variety of products including other amino acids. Some of the decomposition reactions are extremely slow and would never take place on the surface of the modern Earth. Others can be observed directly in living mammals and in fossils. Catalysts, such as metal ions, carbonyl compounds and oxygen, greatly accelerate the decomposition of amino acids (Bada 1971). This discussion will mainly focus on the non-catalysed reactions because the rates of these reactions place an upper limit on amino acid stability under various conditions on the Earth.

Amino acids with alkyl substituents decompose by simple decarboxylation:

$$\text{amino acid} \rightarrow \text{amine} + CO_2. \qquad (1)$$

Leucine, valine and phenylalanine have the fastest decarboxylation rates, glycine and alanine the slowest. In all cases, decarboxylation is slow in the absence of oxygen, with half-lifes (time for half the amino acid to decompose) estimated to be in the range of 10^7 to 10^{10} years at 20 °C (Vallentyne 1964, 1968). The decarboxylation of alanine, which yields CO_2 and ethylamine, was first studied in the 1950s (Abelson 1954, 1956; Conway & Libby 1958) and is probably the most extensively investigated amino acid decarboxylation reaction. A summary of the rates of decarboxylation of alanine as a function of temperature are given

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

in figure 1. In the presence of oxygen, the decarboxylation rates increase by a factor of 10^3 (Conway & Libby 1958). Extrapolation of these measurements to present-day surface temperatures indicates that under anoxic conditions alanine would not undergo decarboxylation over the entire age of the Earth. Even in the presence of oxygen, alanine would be stable with respect to decarboxylation for roughly 10^7 years. Extrapolation to high temperatures, however, indicates that alanine would decarboxylate rapidly at the Earth's sub-surface temperatures.

The non-protein amino acids β-alanine and γ-aminobutyric acid occur in sediments (Schroeder & Bada 1976), but are not present in biogenic carbonates (Schroeder 1977). Although these amino acids could be produced from the β- and γ-decarboxylation of aspartic and glutamic acids, this diagenetic reaction has not been observed in heated solutions of aspartic acid (Bada & Miller 1970). It is generally thought that β-alanine and γ-aminobutyric acid are produced during the biological degradation of aspartic and glutamic acids. β-alanine and γ-aminobutyric acid apparently are very stable with respect to both chemical and biological destruction because they are the only abundant amino acids present in abyssal marine clay sediments (Schroeder & Bada 1976).

Aspartic acid decomposes by reversible deamination producing fumaric acid and ammonia and the half-life for this reaction at neutral pH is 10^5 years at 25 °C (Bada & Miller 1968). In the absence of ammonia, aspartic acid is completely decomposed to fumaric acid, but when ammonia is present an equilibrium mixture of aspartic and fumaric acids is produced. Asparagine and glutamine undergo rapid irreversible deamidation yielding aspartic and glutamic acids and ammonia. This reaction has a half-life at 37 °C and neutral pH of a few days to years in peptides (Robinson & Rudd 1974) and its occurrence in living mammals is thought to play an important role in determining the *in vivo* lifetime of proteins (see Harding 1985). It is unlikely that asparagine and glutamine persist in natural systems on the Earth's surface for any appreciable length of time. Arginine decomposes by a reaction that yields urea and the non-protein amino acid ornithine (Murray *et al.* 1965). This is also a rapid geochemical reaction and has been observed in fossils 10^4 to 10^5 years old (Hare & Mitterer 1967; Galatik *et al.* 1988).

Serine and threonine decompose by dehydration, reversible aldol cleavage and decarboxylation, although the latter reaction is considerably slower than the other two (Bada *et al.* 1978; Bada & Man 1980). Dehydration yields racemic alanine from serine and racemic α-aminobutyric acid, an amino acid not found in proteins, from threonine. These reactions are rapid, and occur in living mammals (Masters 1985) and in the oceans (Bada & Hoopes 1979; Bada *et al.* 1982) and carbonate sediments (Bada *et al.* 1978; Bada & Man 1980). Reversible aldol cleavage yields glycine and the corresponding aldehydes of serine and threonine. Studies of deep ocean carbonate sediments have shown that aldol cleavage is slower than dehydration (Bada *et al.* 1978). Because the serine and threonine decomposition reactions are rapid on the geological time scale, the presence of these amino acids in ancient biogenic materials provides an indication that recent secondary amino acid contamination is present.

At high temperatures, the decomposition of all amino acids is rapid, and this instability greatly limits the possibility that amino acids are present in subsurface deposits on the Earth (Miller & Bada 1988). In fact, the contact of amino acids with hydrothermal solutions during sediment and ocean recycling is likely to be the major geochemical destruction pathway of amino acids on the Earth. This is supported by the observation that no detectable amino acids are present in 319 °C hydrothermal oceanic vent waters (Haberstroh & Karl 1989).

Shock (1990) has recently suggested that at high temperatures the stability of amino acids is determined not by their kinetic instability but by 'metastable' thermodynamic equilibrium. For example, Shock proposed that the following equilibrium governs the stability of alanine at 250 °C:

$$4 \text{ alanine} = \text{leucine} + 3 \text{ glycine}. \quad (2)$$

According to this equilibrium, 'metastable' concentrations of alanine, leucine and glycine would exist even at high, kinetically unfavourable, temperatures. To investigate this possibility, we heated alanine at 240 °C and pH 7 (figure 2). The main decomposition product was confirmed to be ethylamine, and the half-life for decarboxylation at 240 °C was 8 h, consistent with previous determinations (see figure 1). According to the equilibrium constant estimated by Shock for reaction (2), the solution heated for 25 h should have contained glycine at 0.006 M and leucine at 0.002 M. However, neither glycine or leucine was observed (detection limit in our analyses was very much less than 10^{-6} M). These results clearly show that the stability of alanine and other amino acids at high temperatures is not determined by 'metastable' equilibrium. At high temperatures amino acids are rapidly and irreversibly decomposed.

(*c*) *Racemization*

It has been known for over a century that the L-amino acids in living organisms are prone to racemization, a reaction in which a pure amino acid enantiomer is converted into a racemic mixture (see Bada (1985*b*) for review). In aqueous solution, the racemization reactions of free amino acids follow reversible first-order kinetics, whereas in proteins more complex kinetics are often observed because of complications associated with hydrolysis. The mechanism of the racemization reaction involves the abstraction of the amino acid α-hydrogen leading to the formation of a planar carbanion intermediate. This mechanism predicts that amino acids with R-groups that are electron-withdrawing should have the fastest racemization rates, and this is observed in several systems on the Earth. Amino acid racemization takes place rapidly under natural conditions, and the reaction has been detected both in living mammals and in fossil organisms. A summary of the racemization rates of the amino acids in various systems on the Earth is given in table 3.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

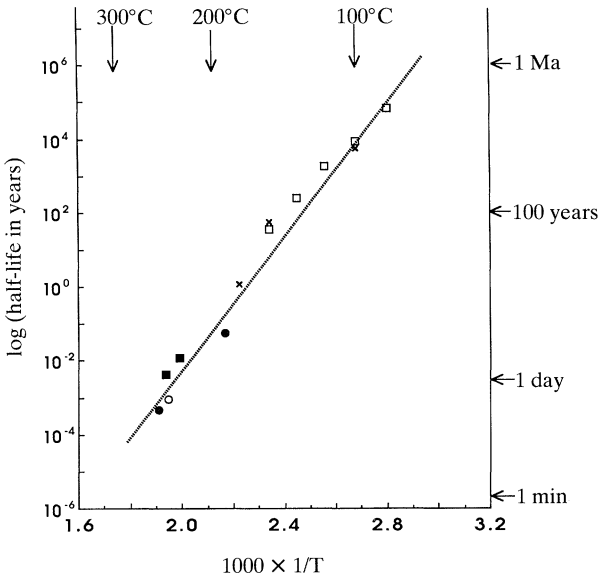


Figure 1. The half-life for the decarboxylation of alanine as a function of temperature (°K) at neutral pH. Closed circles, Abelson (1954, 1956). Abelson mainly published the data in graphical form making it difficult to retrieve the actual rate constants. The points shown are only those cases where percentage decomposition data for specified heating times and temperatures were given; open squares, Conway & Libby (1958) in aqueous solution; bold crosses, Conway & Libby (1958) dry; closed squares, Vallentyne (1964); and open circle, this report (see figure 2).

Table 3. *Amino acid racemization half-lifes*[a] *in years, except as indicated (from Bada 1985a)*

	half-life	
	aspartic acid	isoleucine
aqueous solution, pH 7–8		
free amino acids		
250 °C	19 s	2 min
100 °C	30 d	300 d
proteins		
100 °C	1–3 d	—
in vivo		
mammalian teeth	350	—
Holocene and Pleistocene fossils		
bones and teeth		
Egypt and Sudan	3500	—
East Africa	$0.5–20 \times 10^4$	1.3×10^5
southern California coastal	3×10^4	1.3×10^5
shells		
southern Florida	—	6×10^4
southern California	—	10^5
Canadian Arctic	—	3×10^5
deep-ocean sediments		
siliceous	—	2×10^6
carbonates	10^5	—

[a] One half-life is the time required to reach a D:L ratio of 0.33.

The racemization rates of amino acids are considerably faster than their rates of decomposition. Thus, even though the biosphere contains chiral amino acids, the amino acids in the other reservoirs contain both the D- and L-enantiomers. The presence of partly racemized amino acids may reduce the rate of biological amino acid utilization and this may account for the presence of the large quantities of amino acids in reservoirs outside of the biosphere.

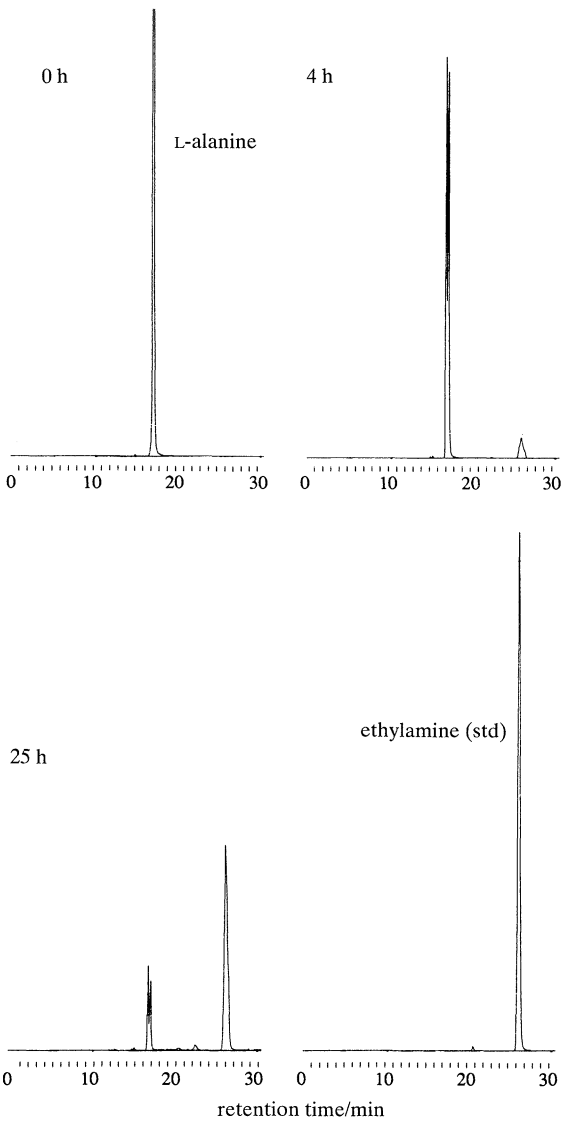


Figure 2. Decomposition of L-alanine (starting concentration = 0.2 M) in phosphate buffer (pH = 7.0) at 240 °C. HPLC analyses were done by using the procedure of Zhao & Bada (1989). After 4 h, L-alanine is completely racemized as indicated by the two peaks corresponding to the D- and L-enantiomers. The extent of decomposition is 35% after 4 h and 97% after 25 h. No detectable amounts ($\ll 10^{-6}$ M) of glycine (retention time = 14.8 min) or leucine (retention time = 26.0 min) were found.

At high temperatures, the rates of racemization are extremely fast. Extrapolation of the racemization rates of alanine determined between 90° and 140 °C (Bada 1971) give a half-life of only 1 min at 240 °C. Figure 2 shows that there is complete racemization of alanine after 4 h at 240 °C. The rapid racemization of amino acids at high temperatures could be one of the limiting factors that determine the maximum temperature at which life can exist.

The racemization of L-isoleucine at the β-carbon, which yields the non-protein amino acids L-alloisoleucine and D-isoleucine, is of particular interest because it is considerably slower than any of the other

amino acid racemization reactions (Bada *et al.* 1986). Studies indicate that the racemization of isoleucine at the β-carbon has a half-life of roughly 10 Ma in surface fossils, and 100 Ma in deep ocean sediments. The presence of the β-racemization products of L-isoleucine provides an excellent indicator of the degree of preservation of ancient amino acids in natural systems on the Earth.

(*d*) *Condensation reactions*

Amino acids, and the free amino group in small peptides and proteins, undergo condensation with sugars, a reaction commonly known as the browning or Maillard reaction (see Ledl & Schleicher (1990) for review). This reaction has been extensively investigated because it occurs during the preparation of some foods and in the tissues of living mammals, and the reaction products may alter the properties of the affected proteins. The products of the Maillard reaction include high molecular mass components (several thousand daltons), collectively known as melanoidins, which have characteristics similar to humic acids. Humic acids make up a large fraction of sedimentary organic carbon and are a major amino acid-containing component on the surface of the Earth. It has been often suggested that the Maillard reaction is the source of humic acids on the Earth (Maillard 1913; Hoering 1973; Hedges 1978). However, this process can only be one aspect of humic acid formation because amino acids are not a dominant humic acid component. There are concerns as to whether this reaction could take place in the oceans and other natural waters and in fossils because of the low concentrations of amino acids and sugars present.

An important point is that this condensation process provides a geochemical pathway for making polymeric amino acid components. The major difference between the amino acids in this geopolymer and those in proteins is that the carbon–nitrogen bond may be more stable than in the peptide bond, especially when an aminoketose produced by the Amadori rearrangement is the major product. Thus, whereas proteins are rapidly hydrolysed to free amino acids and small peptides, the amino acids bound in Maillard reaction products, which may include humic acids, are likely to be more resistant to hydrolysis and are thus preserved over long geological time periods.

(*e*) *Applications: age determination of biogenic materials*

In the last two decades the geochronological applications of one of the principal diagenetic reactions, racemization, have been extensively investigated. The main limitation of the amino acid racemization (AAR) dating method is that, because it is based on a chemical reaction, the extent of racemization in a fossil is a function not only of time, but is also dependent on variables such as temperature, humidity, extent of protein hydrolysis, the type of fossil matrix and the presence of secondary amino acid contaminants.

Probably the most successful application has been the AAR racemization dating of fossil biogenic carbonates, even though the kinetics of racemization in the carbonate matrix do not follow the expected reversible first-order kinetics. The protein components originally present in biogenic carbonates are rapidly hydrolysed to small peptide fragments and free amino acids, and these are retained by the carbonate matrix. Racemization in these various components is responsible for the complex kinetics that are observed. Various models have been presented to explain the racemization kinetics in carbonates (Wehmiller 1982; Mitterer & Kriausakul 1989), and from these relations the extent of racemization can be used to provide reliable relative age estimates. When these models can be calibrated by specimens with ages determined by independent dating techniques, absolute ages can be calculated. AAR dating of carbonate fossils has an upper dating limit of 10^5 to 10^6 years, and is particularly useful in dating carbonate fossils that are difficult or impossible to date by other methods. Racemization in ostrich egg shell appears to obey reversible first kinetics to a greater extent than does the reaction in other types of biogenic carbonates (Brooks *et al.* 1990). It has been suggested that ostrich shell found in archaeological deposits in Africa can be accurately dated back to 10^5 years by the AAR technique. By using the extent of racemization of isoleucine at the β-carbon, it may be possible to extend the range of applicability of the racemization technique of carbonate fossils into the greater than 10^7 year time range.

The AAR dating of fossil bone material has proven to be more problematic than for biogenic carbonates because the main protein initially present in the bone matrix, collagen, is prone to hydrolysis and the liberated peptides and free amino acids are not retained by the bone matrix (Bada 1985*a*, 1987). The amino acid content of bone decreases rapidly on a timescale of 10^3 to 10^4 years. Because bones are an open system with regard to amino acid migration, secondary amino acids can easily become incorporated into the bone matrix. Although amino acids have been detected in the bones of extinct animals, such as dinosaurs, these are mainly contaminates and not original components. The rapid degradation of collagen not only hampers the AAR dating of fossil bones but also causes severe problems in their radiocarbon dating (Bada 1990). Minor protein components of modern bone, such as those associated with the biomineralization process, may be much more resistant to hydrolysis and are thus preserved for longer periods than collagen (Masters 1987). These proteins may be the most useful components for both the AAR and radiocarbon dating of fossil bones.

Teeth, especially the enamel component, have been found to be an excellent material for the AAR dating of mammalian fossils (see Bada 1985*a*, 1987). Although the amino acid content of modern enamel is less than that of bone, the tooth enamel amino acids are retained for much longer time periods, are less prone to secondary contamination, and the racemization reaction follows the expected reversible first-order kinetic relation. Thus, the hydrolysis and contamination problems associated with the racemization dating of bones, and the kinetic complications encountered with carbonates, are less serious with tooth enamel. The best

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

demonstration of the application of the AAR-based technique for dating fossil tooth enamel has been obtained from the famous palaeoanthropological site of Olduvai Gorge in Tanzania, East Africa. In the oldest Olduvai deposit, which is 3.5×10^6 years old, the amino acids were found to be nearly completely racemized. This indicates that even over periods of millions of years the amino acids in enamel are preserved and minimally affected by the secondary amino acid contamination. By calibrating the rate of racemization in tooth enamel using samples from well dated stratigraphic levels, racemization ages for other deposits at Olduvai are obtained that are consistent with other independent age estimates.

One intriguing aspect of the amino acid racemization reaction is that it has been found to take place in living mammals, especially humans (see Bada (1984) for review). In proteins which are synthesized early in life, and which are not actively involved in metabolic processes, D-aspartic acid has been found to accumulate with increasing human age. There is a systematic increase of D-aspartic acid in tooth enamel and dentin, in some brain proteins and in the nucleus of the ocular lens during the human lifetime. The accumulation rate is $\sim 0.1\,\%$ per year, so in aged individuals significant amounts of D-aspartic acid are present in the affected tissues. Because most mammals in general do not live as long as humans, there is less D-aspartic acid in their tissues and as a result the extent of racemization is more difficult to accurately measure. Only aspartic acid is prone to *in vivo* racemization, which is consistent with the observations that it has the fastest racemization rate of the various biological amino acids when bound in proteins.

In vivo aspartic acid racemization in teeth can be used to assess the biological age of living mammals. Although this method may have limited use in ageing living humans because of well-documented birth records, for other long-lived mammals racemization offers an excellent way of establishing longevity. For example, aspartic acid racemization has been used to determine the age of narwhals, reclusive Arctic cetaceans for which little biological age information is available (Bada *et al.* 1983). Because mammalian body temperature is not maintained after death, the racemization process is effectively quenched, and provided there has been no *post mortem* racemization due to a long burial time or a warm burial environment, aspartic acid racemization in teeth can be used to estimate the age at death of humans in both forensic and anthropological cases (see Gillard *et al.* (1990) and references therein).

3. METEORITIC AMINO ACIDS

(*a*) *Unique composition and synthesis*

Although it has been known since the mid-19th century that some meteorites contain organic carbon, there was considerable controversy about whether amino acids were actually present. Although amino acids had been isolated from meteorites, these were generally thought to be mainly terrestrial contaminants (Hayes 1967). This controversy was resolved in 1969 when a carbonaceous meteorite fell in Murchison, Australia. This provided a pristine meteorite sample at a time when analytical techniques and criteria had just been developed to distinguish terrestrial amino acid contamination in Apollo Mission lunar samples. Amino acid analyses of the Murchison meteorite using these techniques showed that it contained a unique suite of amino acids (Kvenvolden *et al.* 1970, 1971). When the amino acids contained a chiral carbon, a racemic mixture was present. The dominant amino acids (see table 2) included some which only rarely occur in terrestrial organisms, and others that had never before been detected on the Earth either in organisms or as the diagenetic products of terrestrial amino acids. These results provided the first demonstration that amino acids existed elsewhere in the Solar System other than on the Earth.

It was soon shown that the distribution of amino acids in Murchison was very similar to the mixture produced in the Miller abiotic amino acid synthesis experiment (Wolman *et al.* 1972). Miller first demonstrated in 1953 that amino acids could be easily synthesized from simple starting components such as H_2, CH_4, NH_3, and liquid H_2O using an electrical discharge as a source of energy (see Miller 1987 for review). The amino acids are formed by the Strecker synthesis:

$$\text{aldehydes} + NH_3 + HCN = \text{amino acids}. \qquad (3)$$

The aldehydes and HCN were produced in the gas phase, and the amino acid synthesis was found to take place in aqueous solution. The similarity of the Murchison amino acid composition with that produced in the Miller experiment suggested that the meteoritic amino acids were formed by a similar Strecker pathway during the aqueous alteration phase of carbonaceous chondrites. Evidence supporting this mechanism was provided by the detection of α-hydroxyl carboxylic acids in the Murchison meteorite (Peltzer & Bada 1978; Peltzer *et al.* 1984). These compounds are produced by the cyanohydrin synthesis, a pathway similar to reaction (3), in which water replaces ammonia in the reaction.

One interesting characteristic of the Murchison amino acids is the predominance of α-alkyl-substituted amino acids. In contrast to the protein amino acids in which the presence of an α-hydrogen makes these amino acids highly susceptible to racemization, the α-alkyl group should prevent racemization. To show this, we investigated the racemization of valine and α-methyl-valine at 200 °C; the results are summarized in table 4. Whereas valine was completely racemized in 23 h at this temperature, the chirality of α-methyl-valine was unchanged. After 23 h, 97 % of the α-methyl-valine had decomposed. This implies that α-alkyl amino acids would decompose before any significant racemization took place. The presence of racemic α-alkyl amino acids in Murchison indicates that these amino acids where synthesized as racemic mixtures, and that there have been no natural processes that resolved (enrichment in one enantiomer) these racemic amino acids over the 4.5 billion year history of the meteorite.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

Table 4. *Chiral stability*[a] *of valine and α-methyl-valine in water at 200 °C*

heating time	D:L-Val	D:L-α-methyl-Val
0 h	0.27	0.26
23 h	0.96[b]	0.23[c]

[a] Enantiomeric ratios determined by using the method of Zhao & Bada (1989). The starting mixture of amino acids was generously provided by Professor Edwin Vedejs, Department of Chemistry, University of Wisconsin, Madison, U.S.A.
[b] Eighty-four per cent decomposition.
[c] Ninety-seven per cent decomposition.

(*b*) *Occurrence on the Earth*

The non-protein amino acids in the Murchison meteorite are either exceedingly rare, or have not been detected, in terrestrial organisms. In addition, they are not known to be formed by diagenetic processes from the protein amino acids and their decomposition products. Nevertheless, there may be trace amounts of the unique extraterrestrial amino acids found in the Murchison meteorite on the Earth.

Extraterrestrial matter in the form of micrometeorites and cosmic dust is continuously collected by the Earth. The flux of extraterrestrial organic carbon that is not heated to high pyrolytic temperatures during atmospheric passage, is estimated to be 3×10^8 g per year (Anders 1989). This organic carbon may contain roughly 1% of extraterrestrial amino acids if it has a composition similar to carbonaceous chondrites (Cronin *et al.* 1988). If the Earth's oceans were the main repository of the extraterrestrial organic matter, then the annual flux of extraterrestrial amino acids into the oceans would be 3×10^6 g and their accumulation rate in the oceans (volume = 10^{21} litres) would be 3×10^{-15} g l^{-1} per year. The maximum accumulation time if there is no biological utilization or removal by geochemical processes would be 10^7 years because the entire oceans circulate through the hydrothermal vents on this timescale, and during this exposure to high temperatures, amino acids would be completely destroyed (Miller & Bada 1983; Haberstroh & Karl 1989). Thus the maximum concentration of extraterrestrial amino acids in the present oceans would be 10^{-8} g l^{-1} or around 0.1 nM (10^{-10} M). This concentration is several orders of magnitude less than the concentration of total dissolved free protein amino acids in the oceans (Wing *et al.* 1990). With the highly sensitive amino acid analytical methods that are now available, however, this concentration of extraterrestrial amino acids in the oceans should be detectable.

There have been no investigations of extraterrestrial amino acids in the oceans, so at the present time it is not possible to ascertain whether there is indeed any accumulation of the unique extraterrestrial amino acids found in carbonaceous meteorites. The estimated maximum concentration of 0.1 nM for extraterrestrial amino acids in the oceans undoubtedly represents a best case scenario. Many factors such as their slow biological utilization, their conversion into compounds usable by organisms and their removal by physical processes probably reduce this maximum concentration to vanishingly low values in the present oceans.

Throughout the Earth's history, large asteroids and comets have impacted its surface. The present frequency is estimated to be one large bolide (> 10 km in diameter) impact every 10^8 years, but during the first billion years after the formation of the Earth this frequency was higher by several orders of magnitude (Shoemaker 1983). In fact it has been suggested that the frequent impact of objects 10–100 km in diameter on the early Earth would have pyrolysed any organics present and frustrated the origin and evolution of primitive organisms (Sleep *et al.* 1989). However, impact delivery of organics to the surface of the primitive Earth has been proposed as a significant source of the raw material necessary for the origin of life (Anders 1989; Chyba *et al.* 1990). Even though a rich mixture of organic molecules could have been synthesized if the early Earth had a reducing atmosphere (Miller 1987), this has been discounted because the required reduced gases may have been present in only trace amounts (Levine 1982; Kasting 1982; Kasting *et al.* 1983). Currently, considerable controversy exists about the source of the organic compounds necessary for the origin of life on Earth.

Evidence that organics have been added to the Earth's surface has recently been provided by the discovery (Zhao & Bada 1989) that extraterrestrial amino acids are associated with the Cretaceous–Tertiary (K/T) boundary, a period 65 Ma before present (BP) which represents one of the more extensive mass extinctions in the history of life on Earth. Compelling geochemical and physical evidence has been reported since 1980, when it was first found that K/T boundary sediments contained an excess of the rare crustal element iridium (Ir), that an asteroid or comet about 10 km in diameter collided with the Earth (see Alvarez & Asaro (1990) for summary). This collision may have caused the demise of a large cross-section of Cretaceous organisms ranging from marine plankton to dinosaurs.

The proposed bolide impact at the K/T boundary presented the opportunity to directly test the hypothesis of the impact delivery of organics to the Earth. Analyses of K/T boundary sediments from Stevns Klint, Denmark, showed that they contained α-aminoisobutyric acid and racemic isovaline (Zhao & Bada 1989), two of the most abundant non-protein amino acids in the Murchison meteorite (see table 2). These two amino acids were not found in sediments metres above and below the K/T boundary, nor were they found in any other sedimentary samples. Even though isovaline has been detected in some rare fungal peptides, it occurs as either the L- or D-enantiomer, and because of the α-methyl group, chiral isovaline is prevented from undergoing racemization. The presence of racemic isovaline in the K/T boundary sediments provides convincing evidence that this amino acid is extraterrestrial in origin.

One puzzling aspect of the extraterrestrial amino acids in the Stevns Klint K/T boundary sediments is how these compounds survived bolide impact, an event in which most of the impactor material was vaporized

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

by the high temperatures generated during the impact process. In addition, the extraterrestrial amino acids were not found in the same layer as the Ir signal, but rather in layers several cm above and below. Some possible explanations are: (i) the original amino acid signal has been disturbed by absorption–diffusion processes; (ii) the impact event was not instantaneous but rather took place over a certain time interval and consisted of several small bolides, some of which did not completely disintegrate upon impact, thus preserving some of the fragile organics; (iii) a comet trapped in the inner solar system partly evaporated before collision and the Earth accreted this debris both before and after impact (Zahnle & Grinspoon 1990); (iv) there were effective abiotic organic syntheses during impact involving hot mineral grains and the gases released from the pyrolysis of the bolide organics; and (v) the stability of amino acids at high temperatures in the gas phase is much greater than that predicted from the decomposition rates determined in heated aqueous solutions.

The extraterrestrial amino acids in K/T boundary sediments can be used to evaluate the efficiency of impact delivery of organics to the Earth. The total extraterrestrial amino acid concentration in the Stevns Klint K/T boundary sediments was estimated to be 5×10^{-5} g cm^{-2} (Zhao & Bada 1989). If this was the surface density worldwide, and most of the amino acids dissolved in the oceans, then the oceanic concentration of extraterrestrial amino acids would be roughly 1 nM, slightly greater than that calculated if the flux of extraterrestrial organics in cosmic dust and small meteorites accumulated in the ocean over a period of 10^7 years. Thus, the K/T bolide delivered amino acids at a level similar to the long-term accumulation from micrometeorites and cosmic dust. The impact delivery process still seems rather inefficient. In order for the oceans of the primitive earth to be rich in amino acids, the impact frequency would have to be much higher, and the survivability of amino acids during each impact the same as that of the K/T boundary event. In contrast, abiotic synthesis on the early Earth with a reducing atmosphere could have generated an estimated amino acid concentration in the primitive oceans of 10^{-4} M (Stribing & Miller 1987).

4. ORIGIN OF PROTEIN AMINO ACIDS AND CHIRALITY

The compositional differences between protein and meteoritic amino acids raises the question about why the group of amino acids on which life is based was selected, a problem which has been discussed by Weber & Miller (1981). On the early Earth, it is unlikely that only the protein amino acids were present. Abiotic synthetic processes would have produced a mixture of amino acids similar to that found in carbonaceous meteorites (Miller 1987). Even if the amino acids necessary for the origin and evolution of life were provided for extraterrestrial sources such as bolide impact, the mixture of amino acids on the early Earth would have been much more complex than the group of twenty amino acids which now characterize living organisms. Distinctive features of the protein amino acids are that they have α-hydrogens, α-amino groups and diverse side-chains (R-groups). Meteoritic amino acids are dominated by those with hydrocarbon R-groups, no α-hydrogens and the amino group in a number of positions. The protein amino acids have R-groups with acid and basic functionalities (aspartic and glutamic acids, lysine, histidine, arginine, tyrosine and cysteine), ones with functionalities important for α-helix stabilization (alanine, leucine, phenylalanine, valine, tyrosine, tryptophan, cysteine, methionine, histidine, asparagine and glutamine) and destabilization (serine, threonine, isoleucine, glycine, aspartic and glutamic acids, lysine and arginine), and ones with nucleophilic and peptide bond orienting functionalities (serine, cysteine, histidine and proline). The selection of amino acids that could form peptide sequences with a diverse range of structural and binding properties could have provided early life with important functions such as replication and the synthesis of desirable molecules. The protein amino acids fit the requirement of having diverse functional and peptide structural properties whereas the non-protein meteoritic amino acids do not.

The origin of amino acid chirality presents a difficult problem. Chirality is important because proteins cannot fold into configurations such as the α-helix if the amino acids are racemic. There are no known effective abiotic processes for generating chiral amino acids, which suggests that on the early Earth, only racemic amino acids would have existed. Because of the problem of racemization, it is likely that only after biotic protein synthesis became an efficient process in the evolution of early life could the chirality of amino acids be maintained in proteins (Bada & Miller, 1987). Instead of amino acid chirality preceding the origin of life, it may have developed after life was well established, and possibly in close association with the origin of protein biosynthesis. As to why the protein amino acids consist of only the L-enantiomers, it is probably simply a matter of chance. Life based on D-amino acids would function just as effectively as the L-amino acid system on which life is now based. Independent D- and L-amino acids based systems operating simultaneously, however, would be redundant and require duplicate sets of mRNA and enzymes. During the course of evolution of early life on Earth this redundance was eliminated. One system of chiral amino acids eventually dominated, and it was the one based on L-amino acids.

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