Survival of Amino Acids in Marine Sediments

Proteinaceous material is carried into marine sediments upon the death and burial of aquatic organisms. The fate of this material has been a subject of conjecture, most investigators believing that it is rapidly decomposed (*1*). Studies of the thermal stability of an amino acid have recently shown that these compounds may survive intact for a long time at ordinary temperatures (*2*). In addition, protective mechanisms may play a part in preserving protein from early microbiological decomposition in terrestrial and marine muds. Recent work (*3*) has demonstrated the formation of complexes of protein with lignins and with clays, which are resistant to attack by microorganisms. Traces of proteins or peptides have been detected in fossil clams from the Pleistocene (*4*), and amino acids have been found in invertebrate and vertebrate fossils as old as the Ordovician (*2*).

In the present work, the amino acid content was determined for a typical recent shallow-water, marine deposit and for a similar sediment laid down during the Oligocene, approximately 30 million years ago. The recent sample was collected by coring on the inner continental shelf of the Gulf of Mexico and represents a narrow sedimentary layer at a depth of approximately 120 cm; this is below the zone of major bacterial activity (*5*). The age of the sediment is probably not more than a few thousand years. The ancient, or Oligocene, sample comprised a section of a marine shale core that was cut from the lower Anahuac formation in Fort Bend County, Tex., at a depth of 5000 ft.

Table 1. Comparison of a Recent and an Oligocene marine mud.

Content	Recent	Oligocene
Carbonate carbon (%)	0.71	1.49
Organic carbon (%)	0.53	0.27
Organic nitrogen (%)	0.044	0.032
Amino acids (μ mole/g)*	3.0	0.51
Principal amino acids in order of decreasing abundance†		
Identification certain	valine +++	alanine +++
	leucines +++	glutamic acid ++
	alanine ++	glycine +
	glutamic acid ++	proline +
	aspartic acid ++	leucines +
	glycine ++	aspartic acid < +
	proline ++	
	tyrosine ++	
	phenylalanine +	
Identification tentative	arginine ++	valine +

* For an amino acid mixture, 1 μmole/g is approximately 0.01 percent.

† Order of abundance: +++, high; ++, medium; +, low.

Immediately upon collection, both sediment samples were frozen in dry ice. In the case of the shale sample, the outer portion of the core was removed by turning on a lathe while the core was still frozen; the center was then crushed, suspended in distilled water, and milled to yield a thin slurry. On freeze-drying, both the recent and ancient samples were reduced to a powder with a flourlike texture.

The two samples were hydrolyzed, and the solutions were freed of salts electrolytically and by passage through Dowex 50 cation-exchange resin. Amino acids in the salt-free concentrates were resolved by one- and two-dimensional paper chromatography, using t-butanol-water-formic acid and phenol-water-ammonia as irrigation liquids. Positive identifications of individual amino acids were obtained by comparison of R_f values, using pure amino acids for reference, and by means of specific color reagents—for example, ninhydrin, isatin, 1,2-naphthoquinone-4-sulfonic acid and 1-nitroso-2-naphthol.

Data in Table 1 show that the modern and ancient marine samples selected for study are quite similar with respect to concentrations of carbonate carbon, organic carbon, and nitrogen. In contrast, the concentrations of free or combined amino acids are less in the Oligocene sample by a factor of 6.

Despite the difference in concentration, the arrays of amino acids in the two samples, modern and ancient, are strikingly similar, with the exception of the absence of tyrosine, phenylalanine, and arginine in the latter. Tyrosine, containing a chemically reactive phenolic group, would not be expected to be as stable as the other amino acids under earth conditions. Phenylalanine and arginine, likewise, are among the less stable of these acids.

Hitherto the detection of amino acids in ancient material has been limited to fossil shells or bones. Little or nothing is known about finely grained marine sediments. Although shell fragments were not eliminated from the samples, amino acids were also obtained on alkaline hydrolysis, where the shell structure was not disintegrated. Using Abelson's values for ancient shells (*4*), it would appear that more than 80 percent of the amino acids are associated with the noncalcareous portion of the Oligocene sample. Thus the amino acids of living organisms, in addition to those in large fragments of bone and shell, also may survive for long periods of time.

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On the Presence of Free Sugars in Filtered Lake Water

It has almost universally been assumed that simple organic nutrients do not constitute more than a minute fraction of the "dissolved" organic matter of lake and ocean water. The main evidence for this assumption is the fact that fresh-water and marine bacteria, when they are cultured in the laboratory, are capable of utilizing extremely small concentrations of organic nutrients (*1*). The only low molecular weight organic compounds that have been demonstrated to occur in filtered lake water are the vitamins thiamin (*2*), niacin (*3*), and biotin (*3*), each of which is present in concentrations less than 1 mg/m³. There is also evidence that free amino acids may be present in lake water (*4*), but the concentrations and identities of the amino

Table 1. Concentrations of free sugars in samples of filtered lake water and filtered controls (double-distilled water). Trace (*t*) is less than 0.5 mg/m³.

Sample	Date	Depth (m)	Vol. of sample (lit)	Sucrose (mg/m³)	Glucose (mg/m³)
L. Opinicon	1/6/55	2	20	5	2
Little Round L.	1/8/55	1	4	2	1
Little Round L.	1/8/55	9	4	4	2
Little Round L.	1/8/55	14	4	10	5
Control			4	t	0
Control			2	1.5	0
Control			2	0	0