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MOLECULAR COMPOSITION OF NITROGENEOUS COMPOUNDS IN SEA WATER AND RECENT MARINE SEDIMENTS

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ABSTRACT

Data and concepts on the molecular composition of nitrogeneous organic matter in sea water and sediments are presented. Proteins and protein-derived metabolites, such as urea and amino acids, account for the bulk of the dissolved organic matter in the sea; the low C/N ratio with a mean of 2.5 to 3.0 supports this inference. These compounds, however, do not occur in the free state primarily, but they are combined, e.g., in clathrate-type complexes. The particulate organic matter in surface waters is largely represented by living organisms and in deep waters by intact or partially degraded biogenic material.

Detritus and dissolved organic matter supplied to the sediments are used for de novo synthesis of proteins by micro-organisms and burrowing animals. Polymerization may also be achieved via epitaxial growth on mineral surfaces. In oxidizing environments, nitrogenous compounds are diagenetically degraded rather rapidly unless they are protected by minerals such as organic clay derivatives or shell carbonates. In contrast, strongly reducing environments do favor the preservation of organic matter as a consequence of low biological acitvity. The latter circumstances may even lead to a redistribution and separation of distinct organic molecules via natural chromatography.

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INTRODUCTION

The distribution of organic carbon and nitrogen in sea water is known in detail and certain trends are established. In general, the dissolved organic carbon decreases from a high of about 1 mg/l in surface waters to values in the range of 0.4 to 0.6 mg/l in waters below the 200 meter mark (Duursma, 1961, 1965; Holm-Hansen et al., 1966; Menzel, 1967; Menzel and Ryther, 1968). Seasonal variations are only observed in surface waters. Skopintsev et al. (1966), by using a different analytical method, obtain carbon concentrations three times as high.

Relative to the dissolved organic carbon, the particulate organic carbon content is lower by a factor of five to ten in surface waters, and by a factor of fifty to one hundred in deep waters.

The C/N ratios of dissolved organic matter may fluctuate strongly in surface waters; they are particularly high in warm water environments with values up to 20 to 30 (Duursma, 1961). At lower temperatures the C/N ratios are more in accordance with those observed in deep waters (C/N = $\sim$3). In contrast, the C/N ratio of planktonic material is in the order of 5 to 6 (Fleming, 1940; Holm-Hansen et al., 1966), and that of the particulate organic matter in the sea about 8 to 12 (Menzel and Ryther, 1968). The ratios for the particulate organic matter actually represent upper limits because carbonate detritus is frequently present on filters combusted for organic carbon determinations.

In Recent marine sediments, the amount of organic matter falls in the range of 0.1 to 3% (Emery, 1960; Degens, 1967). A number of parameters control the variation in total yield, i.e., organic productivity, rate of deposition, mineral composition, activities of micro-organisms and burrowing animals, and Eh/pH relationships. The C/N values

are in the order of 8 to 12 and commonly increase with depth of burial. For ancient sediments the C/N values are most frequently around 20 to 30.

In comparison to the detailed knowledge on the carbon and nitrogen content in oceans and sediments, information on their molecular structure is limited. As a matter of fact, only a small number of organic molecules, and which account for less than 10% of the total organic matter, have so far been identified (Duursma, 1965; Degens, 1967).

The present work is an attempt to understand the molecular nature of the nitrogenous fraction of the bulk organic matter. On the basis of the C/N ratios, it seems that nitrogen-containing biochemicals represent a rather substantial portion of the total organic matter.

DATA PRESENTATION

Problem analysis

The amount of free amino acids, sugars, fatty acids, and phenols in sea waters and sediments is rather small; they represent less than 10% of the total organic matter (Fig. 1). The question thus arises, what is the molecular nature of the remaining 90%?

As an approach to solve this problem we make the heuristic statement that:

(1) all organic matter in the ocean is biogenic, and

(2) the bulk is principally derived from phytoplankton.

The possibility that terrigeneous material may also add to the organic carbon pool in the sea should be ignored at this point.

In following this concept, the systematics of our data presentation is:

(1) plankton,

(2) particulate organic matter,

(3) dissolved organic matter, and

(4) sediments.

Plankton

The bulk of the nitrogen in organisms is tied up in the form of proteinaceous materials. Other biochemicals, such as nucleic acids, are quantitatively only of minor significance at least as far as nitrogen balance estimates are concerned. Inasmuch as the identification of individual proteins and peptides is beset by too many analytical problems, the presentation will be limited to the amino acid spectrum of the total proteinaceous material.

The amino acid content in plankton collected off the coast of Peru and Ecuador along the downstream course of the Humboldt Current is rather uniform (Table 1). This is noteworthy, because samples No. 2, 14, and 16 are predominantly phytoplankton (90%); in contrast, there is a predominantly zooplankton population in samples No. 4, 9, and 11. The remainder of the samples represent mixtures of various amounts of phyto- and zooplankton. It is implied that except for total yield which is higher for the zooplankton, there are no substantial changes occurring in the distribution of amino acids in the food chain phytoplankton-zooplankton. The high abundance of acidic and basic amino acids is emphasized.

To study the effect of water temperature and of respiration in prolonged darkness, the neritic diatom, Skeletonema costatum (WHOI clone "Skel"), the estuarine clone "3H" of the diatom, Cyclotella nana, and the green flagellate, Dunaliella tertiolecta (clone "Dun") were grown in enriched sea water following a procedure outlined by Guillard and Ryther (1962). The cultures were subsequently left in darkness for up to 19 days (Table 2).

Two major trends become apparent:

(1) a gain in proteins with increase of water temperature, and

(2) a decrease in protein content with length of respiration.

The respiration effect implies that the organisms preferentially lose proteins when left in darkenss. By taking the Dunaliella values of Hellebust and Terborgh (1968) showing a respiration loss in carbon by 50 to 60% in 20 days, it becomes evident that at the intitial stages of respiration (Table 2) proteins are lost more rapidly than either the carbohydrates or lipids (unpublished results). This metabolic characteristic will naturally influence the molecular pattern of the dissolved organic matter in the sea inasmuch as proteinaceous breakdown products are (a) rather complex in nature (e.g., urea, amino acids, phenolic compounds, quinones, indoles, and others), and (b) constantly discharged into the sea water.

Particulate organic matter

Most of the particulate organic matter in surface waters is living plankton, and on first sight the amino acid composition seems to support this inference (Table 3A).

Yet, the presence of ornithine, citrulline, and that of urea and some of the amino butyric acids suggests that degradation already has started. Values for urea range from: not detactable to 5 µg/l; α - and γ -amino butyric acids are present in trace amounts. The identification of urea is of special significance in view of the fact that urea is gradually decomposed upon acid hydrolysis. In turn, its presence even after 6N HCl hydrolysis for 22 hours must mean that initially, that is, before hydrolysis, larger quantities were present which must have been condensed in some fashion. This phenomenon would also account for the high yield in ammonia, since neither glutamine, asparagine, or the hexosamines are abundant enough to explain this feature.

The depth relationships are of special significance. Aside of the decreasing trend in total yield, systematic changes in serine, glycine, alanine and the basic amino acids can be observed.

Dissolved organic matter

a) free : The distribution of free amino acids is surprisingly uniform throughout most of the water column (Table 3B and 3C); exceptions are surface waters which exhibit a certain spread in numbers. Most marked is the high abundance of glycine, serine, and ornithine. The virtual absence of arginine should be considered in conjunction with the high concentration of ornithine and urea; most of the samples have a urea content between 2 and 20 µg/l. These three amino aompounds (+aspartic acid and citrulline) are biochemically connected via the so-called urea cycle. Attention should also be called to the glycine-serine relationship; both amino acids are biochemically

interrelated and constitute together with urea and ornithine two of the more prominent nitrogenous metabolic waste materials. Glucosamine is present in quantities of a few µg/l.

b) combined : The bulk of the amino acids in the dissolved organic matter occurs in the form of higher molecular weight compounds with molecular weights between 400 and 10,000. This characteristic is furthermore substantiated by the fact that acid hydrolysis of filtered sea water which has passed 0.4 micron filters, will release amino acids in concentrations far above those reported for the free constituents (Table 3C). In some ways the amino acid spectrum bears certain relationship to the particulate organic matter, while in others it is more like the free amino acid pattern. However, the rather small amount of acidic amino acids represents a native feature. The high abundance of ammonia in connection with the presence of urea is a remarkable coincidence. The relationships in total yield between the particulate and dissolved organic matter are summarized in Figure 2.

Sediments

a) free:

The amino acids dissolved in interstitial waters or which can be extracted with water or ammonium acetate from the sediment material are generally termed "free." They occur in reasonable qunatities in recent sediments; in oxidizing environments the amount and nature of the free amino acids appears to be closely related to the level of microbial activity. Namely, in sediments where the level of microbial activity is low, the amino acid concentration is in the order of 0.01 to 1 µg/g, whereas well

populated sediments may contain up to 200 µg/g. In contrast, the free amino acid content is extremely high in reducing sediments particularly if micro-organisms are absent or the activities are low. Under such circumstances a rather remarkable feature emerges, i.e., the separation of amino acids along a vertical sediment profile (Fig. 3). This phenomenon can best be explained by natural chromatography along clay mineral surfaces in the course of diagenesis and compaction.

b) combined:

The amino acid distribution from representative cores from the Indian Ocean (Table 4A) and Atlantic (Table 4B) indicates that the total yield in amino acids of various stations is within the same range, although the total concentration of combustible organic matter may vary by a factor of 2 to 3. Within a certain range, the amino acid content drops from a few hundred µg/g present in the upper 2 meters of burial to about 100 µg/g at a depth greater than 5 meters. In Pacific sediments of the Experimental Mohole (Rittenberg et al., 1963), the amount of amino acids decrease nearly exponentially from about 325 µg/g near the surface to 15 µg/g at 170 meter depth; the whole section covers about 25 million years of earth history.

The presence of hydroxyproline is of biochemical interest, since this amino acid is tied up in collagen-type proteins. The presence of β-alanine is a consequence of the microbial utilization of aspartic acid in the early stages of diagenesis. Ornithine is principally derived from arginine with the simultaneous production of urea; most of the urea, however, has been destroyed during acid hydrolysis; yet fair amounts can still

be recognized. Small quantities of α - and γ -amino butyric acids can be recovered. They are principally derived from threonine and glutamic acid, respectively. Traces of allo-isoleucine and $\alpha - \varepsilon$ diaminopimelic acid are present in all samples investigated.

c) shell material:

Deep sea carbonate ooze contains large quantities of foraminiferal tests. These contain proteins which once have served as templates for the epitaxial growth of the shell carbonates. Inasmuch as these proteins are intimately associated with the carbonate phase, they will be protected from microbial degradation and thus survive the initial stages of diagenesis. There is only little difference in the distribution of amino acids in samples taken at different time intervals over the last 8,000 years (Table 5A). Eventually, however, these proteins will become hydrolyzed and will release their hydrolyzation products to the interstitial waters.

Contributions from shell proteins to the nitrogenous fraction of sediments can be rather substantial should organisms highly enriched in mineralized tissues become part of the sediment deposit (Table 5B).

DISCUSSION

In surface waters, the bulk of the particulate organic matter is represented by living plankton. Upon death of the organisms, the vast majority of the biochemical molecules will be utilized again by organisms and consequently are recycled as a kind of "continuous food chain" within the upper 200 meters of the water column.

The small fraction of the organic debris that eventually escapes into deeper waters and gradually settles to the bottom of the sea still contains unaltered biochemical compounds; in addition, condensation products from metabolic waste materials or decaying tripton are incorporated in the deep sea particulate matter.

Based on Tables 3A and 3B, and data on carbon content in deep waters (e.g., Menzel, 1967; Menzel and Ryther, 1968), more than 50% of the particulate organic matter is proteinaceous in nature. Aside of intact peptides, so-called heteropolycondensates contain nitrogenous compounds. The molecular nature of heteropolycondensates is quite variable and is determined by the amount and type of the associated organic molecules. The high abundance of aromatic compounds, however, suggests that either depside or chlathrate structures are involved. The latter kind of arrangement is particularly favorable because mixtures of polar and neutral compounds can be accommodated within the same structural framework (Fig. 4). The high abundance of oxygen functions (e.g., hydroxyl, carboxyl, and carbonyl functions) is noteworthy. They will enhance the structural stabilization and also promote the formation of metal ion co-ordination polyhedra (Degens and Matheja, 1967). The last phenomenon will lead to a reorganization of the sturctural order (Fig. 5).

Studies on the extracellular products released by planktonic organisms are a lively concern among biologists (e.g., Fogg, 1966; Hellebust, 1965; Webb and Johannes, 1968). Aside of glycollate which is excreted by most photosynthesizing organisms, nitrogenous substances represent the most dominant metabolic waste materials. The reason that even intact peptides or amino acids are released still represents an unsolved problem (Wangersky, 1965). Experiments have shown (Stewart, 1963) that up to 45% of the nitrogen fixed by

some organisms is excreted. In view of these figures and the low C/N ratio, nitrogenous compounds probably account for a substantial portion of the dissolved organic matter in the sea.

The way these excretionary products are stabilized in the sea is not yet completely understood. The chief reason for this lack of knowledge has to do with the complexity of the individual products and reactions involved. Much confusion has also been generated due to the arbitrary separation of particulate and dissolved organic matter into distinct classes of compounds. Chemically speaking, such a classification has little information content with regard to the elucidation of the molecular nature of the organic compounds in the sea. The so-called dissolved organic matter is composed of more than 90% of material that has a molecular weight (MW) greater than 400. The bulk of the organic compounds with MW> 400 falls in the 3,000 to 5,000 MW-range as ascertained by molecular sieve techniques. Hydrolyzation of this material will release substantial amounts of monomers; yet, some high molecular weight products are still intact after this treatment.

The generally low C/N ratios of dissolved organic matter, the presence of urea even after hydrolysis, the high abundance of amino acids and aromatic compounds in connection with the high yields in oxygen, suggest that oxygen and nitrogen are used in the structural stabilization of the high-molecular weight fraction. Peptides do account for some of the materials. Urea may easily react with aldehydes and produce long-chain polymers; alternatively, its oxygen may be used for co-ordinative purposes. The molecular structure of urea (Lenné, 1954; Fig. 6) easily renders itself for such molecular work assignments.

The presence of urea represents a rather unique physiological phenomenon. This compound was long considered an exclusive metabolic product of higher organized animals, whereas ammonia excretion was believed to exist among the invertebrates. It is now known that urea also occurs in plants (McKee, 1962). Arginase, which splits arginine to urea and ornithine, has indeed been observed in marine algae (Smith and Young, 1955). Ornithine hereby acts catalytically in the synthesis of urea from added ammonia, and the high abundance of arginine and aspartic acid (or asparagine) in marine plankton makes physiological sense. These molecules are simply used as a convenient nitrogen storage reservoir but also function as active metabolites.

Aside of arrangements involving peptides or urea condensates, oxygen may also be organized in the form of chlathrates (Fig. 4). Thus phenols, quinones, amino acids, amines, sugars, fatty acids, alcohols, and their respective polymers may coexist within the same polymer by virtue of their oxygen functions. Further molecular stabilization can be achieved by metal ions involving metal ion co-ordination polyhedra (Fig. 5).

Interactions of the dissolved organic matter with inorganic detritus, in particular with clay minerals will lead to polymerizations of organic matter by epitaxial growth (Degens and Matheja, 1967). Although these reactions may already proceed in the sea, on large scale they only take place in the sediments in response to the activities of micro-organisms and burrowing animals. The metabolic waste materials hereby generated can become an integral part of mineral structures, for example, in organic clay derivatives (e.g., Weiss, 1969), or they may become adsorbed on mineral surfaces. Silicate surfaces are known to act as an effective polymerization agent for organic

monomers, but they also exhibit catalytic functions (Degens and Matheja, 1967). In consequence, metabolites can be condensed or chemically altered by means of organic-inorganic interactions in the sediment strata. Given sufficient time, the heterogeneous condensation products formed in the initial stages of diagenesis will be eventually reduced either to aromatic condensates resembling graphite, or to light paraffinic hydrocarbons -- in particular, methane. Carbon dioxide, ammonia, and water are simultaneously released; the ammonia may subsequently proxy for cations in clay minerals or become adsorbed.

In the chapter on "Problem Analysis" the heuristic statement was made that the organic matter in the sea is principally generated by phytoplankton. Stable carbon isotopes of the particulate organic matter in the sea show δC^{13} values which are in agreement with this statement. Namely, the particulate matter in cold surface water has δC^{13} values of around -25 permil (Sackett et al., 1965) while the particulate matter in tropical regions has values of around -15 permil. The reason for this difference is related to photosynthetic processes (Deuser et al., 1968). The zooplankton simply inherits this isotope pattern and even the δC^{13} of the organic matter in Recent marine sediments is a true reflection of the carbon isotope distribution in the local plankton population. In contrast, the dissolved organic matter is depleted in C^{13} by 5 to 10 permil relative to the average plankton crop (Deuser, 1968). Several explanations can be offered to account for this phenomenon:

(1) lipid materials are the main constituents,

(2) terrigenous organic matter is the chief contributor, and

(3) metabolic waste is isotopically light relative to its biochemical precursor.

The first suggestion can be dismissed. Organic solvent extractable compounds represent at most 5% of the total dissolved organic matter; furthermore, the nitrogen content is too high. There is also little evidence in support of the second alternative. Seasonal fluctuations in total yield are a consequence of plankton bloom and in no way are related to continental runoff. The third suggestion appears to be the most likely one. It is known that the degradation of organic matter may introduce isotope fractionation. Abelson and Hoering (1961) for instance have shown that decarboxylation of amino acids will introduce isotope fractionation in the sense that the CO_2 released can be enriched by 20 permil in C^{13} relative to the remainder of the molecule. In addition, internal variations among the amino acids cover a range of about 17 permil. It is this type of mechanism that may have caused the depletion in C^{13} in the dissolved organic matter. Controlled experiments with algal cultures are intended to test this supposition.

Indirect support for this inference can be obtained by following the carbon isotope distribution of organic matter in the course of diagenesis. Ancient marine sediments have a δC^{13} between -25 and -28 permil (Fig. 6), whereas most Recent marine sediments have a δC^{13} in the range of -19 to -21 permil (Table 4). Thus, as far as the isotope distribution is concerned, the organic matter in the sea follows the same trend as the organic matter in the sediment, i.e., the alteration products are lighter by several permil relative to the starting material. This relationship also proves that the particulate organic matter in the sea is the main contributor of the organic matter in the sediments. The dissolved organic matter, even though it is more abundant by one to two orders of magnitude, appears to be only a secondary carbon source for the sediments.

SUMMARY

The organic matter in the sea is largely composed of nitrogenous compounds. Aside of intact peptides and proteins, so-called "heteropolycondensates" are present. A chlathrate-type molecular structure is suggested for these condensates. In this way, neutral and polar organic molecules can coexist within the same molecular framework. Free compounds, i.e., monomers, such as amino acids, fatty acids, and sugars amount to less than 10 per cent of the total organic matter.

The bulk of the organic matter can be considered as metabolites which are principally derived from the planktonic and microbial populations living in the sea. Terrigenous contributions to the organic matter in the oceans are negligible except within the immediate area of river discharge (estuarine environment).

Sediments derive their organic carbon principally from the particulate organic matter in the sea. Contributions from the dissolved organic matter are only of secondary importance. In the course of diagenesis, nitrogenous organic matter is preferentially eliminated as ascertained by the gradual increase in C/N ratios with geologic time.

Table 1

DISTRIBUTION OF AMINO ACIDS IN PLANKTON*
(in residues per 1000)

Sample No.	Stn No.	Water temperature (°C)	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ILEU	LEU	DOPA	TYR	PHE	LYS	HIS	ARG	Total * (% dry weight)	Hexosamine (% dry weight)	δC13 ** ‰
1	Off Callao	17.9	115	57	61	138	48	159	105	11	53	29	35	76	1	26	34	25	13	13	31	0.79	-21.2
2	Off Callao	16.8	120	61	69	121	51	138	106	3	49	22	33	72	4	25	29	71	7	18	14	0.54	-19.8
3	Off Callao	16.6	113	101	58	134	52	113	99	3	44	19	19	67	2	28	31	64	8	29	30	2.98	-18.0
4	590	22.8	96	54	55	119	36	121	98	32	59	31	40	72	-	30	31	61	13	49	48	3.22	-19.9
5	591	19.7	100	57	52	113	53	120	86	15	53	23	37	66	-	26	29	72	17	82	35	1.81	-16.5
6	593	20.5	91	55	48	115	51	131	91	15	59	22	39	67	-	30	38	65	18	74	43	2.40	-18.6
7	595	24.1	109	55	60	134	54	132	104	13	58	23	38	76	-	33	32	45	9	36	36	2.36	-18.1
8	597	18.3	96	58	51	123	60	144	99	21	50	21	39	69	-	27	28	66	6	34	41	2.83	-17.4
9	599	19.7	96	50	60	134	41	144	107	2	57	22	39	73	-	38	32	70	19	36	48	2.14	-20.3
10	601	21.1	96	52	60	122	40	139	103	6	60	22	41	72	-	28	32	62	21	37	43	2.59	-19.5
11	603	21.0	119	58	42	115	37	140	88	2	61	22	44	70	-	31	25	67	20	39	46	2.65	-18.3
12	606	24.6	90	52	49	119	36	151	108	22	56	20	36	69	-	35	24	64	16	51	39	2.09	-19.9
13	607	24.2	110	49	40	139	31	135	93	3	61	23	44	76	-	32	29	68	21	37	39	1.94	-19.7
14	609	20.6	95	55	57	118	35	145	98	32	56	21	38	69	-	35	24	63	22	43	18	0.80	-20.2
15	610	25.7	95	59	56	117	35	161	87	35	55	19	37	65	-	33	23	64	5	55	30	0.86	-19.7
16	611	25.8	107	57	49	122	46	148	106	17	54	21	26	68	-	24	15	58	30	43	18	1.00	-20.4
17	612	25.0	105	57	61	123	34	123	106	4	52	20	36	73	-	34	17	72	23	59	29	2.57	-20.6
18	614	21.9	100	35	36	118	33	164	91	24	59	25	42	73	-	29	15	79	24	51	25	2.13	-20.1
		mean	100	50	53	121	43	140	99	14	56	23	38	71	-	31	34	63	16	45	35	2.15	-19.3

* Total protein fraction

** C^{13}/C^{12} ratio of total organic carbon relative to PDB (see: Craig, 1957)

*(after Degens et al., 1968)

Table 2

DISTRIBUTION OF AMINO ACIDS IN PLANKTON
(in residues per 1000)

Species	Temp (°C)	Resp (days)	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ILEU	LEU	TYR	PHE	LYS	HIS	ARG	TOTAL PROTEINS (% Dry Weight)	GLUCOSAMINE (% Dry Weight)	δC^{13} (‰)
	8	0	143	56	71	133	59	130	131	6	58	9	39	82	20	44	10	1	6	11.3	0.018	-21.0
	8	6	153	53	68	140	42	118	115	14	61	10	39	66	19	47	24	4	27	8.0	0.006	
Skeletonema costatum ("Skel")	18	0	127	56	75	133	58	103	126	12	51	13	34	73	20	36	43	9	31	17.9	0.027	-18.9
	18	6	148	55	69	127	45	125	123	14	60	14	37	79	17	40	27	10	9	15.2	0.015	
	18	19	140	59	66	119	30	143	119	8	65	10	49	94	21	43	14	7	15	9.3	0.089	
	27.5	0	127	66	76	125	45	122	117	3	64	19	45	88	20	45	21	8	10	22.4	0.033	-17.0
Cyclotella nana ("3H")	20	0	129	60	60	110	50	117	121	4	68	18	47	88	24	50	26	10	20	16.7	0.010	-17.0 *
	30	0	121	61	72	129	23	126	117	18	65	17	49	97	14	51	24	4	13	18.8	0.016	-12.8
Dunaliella tertiolecta ("Dun")	20	0	124	55	67	134	45	129	134	5	49	11	26	89	17	39	32	8	36	19.6	0.027	-16.2 **
	20	5	109	56	60	111	48	103	136	6	46	17	25	102	13	38	62	11	55	6.0	0.025	-20.9
	20	12	107	55	59	110	46	108	136	6	45	17	23	108	13	38	64	13	52	6.1	0.016	-21.8
	20	19	101	60	58	107	50	111	95	6	45	28	26	86	14	28	63	33	87	6.3	0.009	-21.7

* at 10°C δC^{13} = -18.8

** after 1 day respiration δC^{13} = -18.8

Table 3a

AMINO ACID COMPOSITION OF PARTICULATE ORGANIC MATTER
(in residues per 1000)

CHAIN 48
SARGASSO SEA
STATION 650

Sample No.	Depth (Meter)	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ILEU	LEU	TYR	PHE	LYS	HIS	ARG	ORN	TOTAL µg/l
1	1	110	51	130	150	18	100	65	47	40	14	37	72	23	32	44	18	44	11	27.5
2	100	89	63	120	130	33	100	67	22	35	8	34	70	26	34	67	33	63	7	26.9
3	200	71	77	110	130	28	69	39	16	42	6	38	62	29	63	88	n.d.	100	24	7.6
4	800	61	26	110	190	31	140	28	24	39	8	37	71	31	33	120	16	31	n.d.	5.3
5	1000	75	39	67	160	31	130	32	31	29	10	41	65	38	35	92	28	89	17	11.2
6	2500	76	73	80	130	19	110	28	11	33	9	31	58	22	25	150	6	120	21	10.8
	MEAN	80	55	103	148	27	108	43	25	36	9	36	66	28	37	94	20	75	16	14.8
										STATION 649										
7	Surface	95	61	100	130	35	81	58	52	45	8	37	69	19	34	95	8	46	23	83.0
8	1	94	81	110	130	29	78	57	31	42	14	36	73	22	34	91	1	81	n.d.	38.4
9	200	85	49	60	150	42	86	49	10	53	8	7	52	8	9	140	52	120	23	16.3
10	400	81	39	69	130	30	88	47	46	52	14	34	69	28	35	120	9	120	tr.	15.9
11	800	80	44	75	150	26	120	33	30	35	11	36	75	30	39	91	9	110	10	18.6
12	1400	13	51	89	140	13	120	36	44	37	8	48	63	14	31	110	20	120	38	14.5
13	2500	71	44	77	140	35	110	37	15	39	11	31	62	25	66	88	2	130	12	10.3
14	5000	←								visually estimated										→ ~5-10
	MEAN	74	53	83	139	30	98	45	33	43	11	33	66	21	35	106	14	104	15	25.1

Table 3b

AMINO ACID COMPOSITION OF PACIFIC WATER SAMPLES
(in residues per 1000)

Experimental Mohole Drilling Site

Sample No.	Depth meters	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	LEU	TYR	PHE	LYS	HIS	ARG	ORN	Total µg/liter
									Particulate Matter										
1	0	32	37	207	63	46	195	148	-	43	11	82	7	20	23	11	13	62	20.6
2	2000	21	51	297	9	51	279	135	-	18	7	48	12	28	2	9	3	30	5.9
3	3000	11	38	396	9	38	254	118	-	29	5	62	1	11	1	5	-	22	6.4
									Free										
4	0	38	76	295	27	-	164	107	-	23	-	38	22	22	21	22	-	145	45.9
5	2000	40	65	290	32	-	145	153	-	44	-	27	23	25	18	20	-	118	10.5
6	3000	82	45	277	18	-	217	79	-	23	-	41	18	20	29	17	-	134	87.5

(after Rittenberg et al., 1963)

Table 3c

AMINO ACID ANALYSIS OF BUZZARDS BAY SURFACE SAMPLES
(in residues per 1000)

Sample No.	APS	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ILEU	LEU	TYR	PHE	LYS	HIS	ARG	ORN	Total µg/liter
											Particulate Matter								
1	78	53	79	135	41	121	93	14	59	15	37	69	25	29	71	17	60	2	179
2	35	25	25	97	95	112	94	13	17	22	44	77	42	53	125	31	90	4	144
3	64	50	74	121	42	112	86	8	23	3	36	69	34	37	84	32	95	33	198
4	68	46	68	121	51	112	87	9	50	13	28	64	27	35	87	31	96	6	213
5	92	67	108	159	15	124	95	14	60	1	27	60	7	15	64	23	62	5	172
6	75	43	84	114	18	124	71	10	49	15	31	58	26	31	115	41	97	2	221
7	83	54	93	135	17	139	87	12	54	15	37	74	26	38	75	12	45	4	178
mean	78	48	76	126	40	121	88	11	45	12	34	67	27	34	89	27	78	8	186
											Total Dissolved								
8	24	35	64	21	30	94	113	8	50	12	44	67	26	32	89	137	54	108	401
9	19	22	123	13	66	243	120	30	26	24	48	82	19	30	43	48	14	29	185
10	20	33	86	15	50	242	123	34	27	11	51	86	20	32	77	11	49	30	187
11	15	36	102	14	78	216	101	22	23	1	51	75	8	35	87	34	46	34	129
12	16	43	74	17	78	113	100	5	17	3	11	72	28	47	110	55	100	111	240
13	17	44	91	17	55	205	96	11	24	8	65	87	8	12	89	33	82	60	209
14	16	37	103	13	102	217	87	6	29	33	50	58	3	13	57	53	54	67	197
15	17	42	70	20	68	178	65	13	18	9	59	84	3	51	100	64	77	60	199
mean	18	39	89	16	66	189	100	16	27	13	47	76	14	31	81	54	60	62	218
											Free								
16	153	33	155	53	9	393	69	3	21		21	18	3	4	43	10		12	56
17	65	27	145	145	19	365	110	4	45		11	11	3	4	6	10		30	72
18	77	43	101	91	10	267	82	3	64		12	20	13	11	45	49		109	77
19	51	16	86	50	9	309	64	12	56		8	8	3	4	122	10		191	50
20	53	45	160	69	35	285	60	11	50		38	19	24	29	38	28		56	58
21	62	24	126	27	9	350	182	26	50		15	17	14	15	58	10		14	38
22	92	35	116	66	9	393	89	27	87		9	8	3	4	23	16		20	69
23	94	31	129	50	19	271	71	33	53		16	12	9	9	85	41		83	66
mean	81	32	127	69	15	329	91	15	53		16	14	9	10	52	22		64	61

(after Siegel and Degens, 1966)

Table 4a

DISTRIBUTION OF AMINO ACIDS IN INDIAN OCEAN SEDIMENTS*
(in residues per 1000)

PISTON CORE 17
(Lat. 24°02'N, Long. 58°59'E; Depth 3341 m)

SAMPLE NO.	DEPTH cm	OH-PRO	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ISO	LEU	TYR	PHE	β-ALA	ORN	LYS	HIS	ARG	TOTAL μg/g	GLUCOSAMINE μg/g	GALACTOSAMINE μg/g	C %	$\delta^{13}C$ ‰
1	50-55	22	51	32	68	82	79	278	129	4	76	12	38	52	13	17	-	24	18	5	-	341	18	11	0.1	-20.2
2	150-155	59	40	68	85	51	77	257	120	2	58	12	17	52	12	18	37	4	32	15	-	309	13	13	0.1	n.d.
3	250-255	tr.	53	56	105	67	75	271	120	24	56	12	36	52	12	16	-	4	34	8	-	163	6	1	0.6	-20.4
4	360-365	tr.	77	162	71	97	51	202	143	2	45	7	29	68	7	9	20	8	59	13	2	249	18	17	1.2	n.d.
5	453-458	tr.	32	74	54	44	79	222	116	13	78	6	41	52	11	18	24	21	83	15	19	200	10	6	0.9	-20.7
6	575-580	tr.	86	51	66	89	81	243	128	9	83	7	46	66	11	14	-	12	44	8	-	120	5	3	0.9	-20.8
7	830-835	tr.	20	82	59	55	84	260	135	4	83	6	42	54	10	15	29	6	46	8	-	97	5	4	0.5	-20.3

PISTON CORE 18
(Lat. 20°35'N, Long. 63°53'E; Depth 3338 m)

8	4-10	15	34	61	85	85	61	265	136	8	27	4	15	28	2	4	58	24	49	12	2	705	14	3	0.9	-18.9
9	50-55	40	66	62	99	58	64	204	122	60	87	6	31	40	3	14	tr.	32	37	9	1	381	25	24	1.3	-19.9
10	100-105	12	76	68	98	65	64	208	127	21	72	8	32	40	3	12	17	16	92	17	-	598	15	10	1.0	n.d.
11	150-155	13	32	64	66	79	72	203	124	10	76	6	29	54	6	21	54	26	55	12	1	609	40	23	1.0	n.d.
12	200-205	7	74	67	57	68	84	235	137	3	78	6	34	45	5	12	41	13	42	3	1	294	22	18	1.0	-19.3
13	250-255	29	60	67	79	61	64	183	106	7	75	4	34	46	5	12	53	19	52	20	5	321	40	24	0.8	n.d.
14	300-305	28	73	65	35	59	56	207	121	7	76	2	29	39	2	9	61	45	65	12	1	319	41	29	0.8	n.d.
15	350-355	23	93	67	54	72	67	230	126	2	82	3	37	48	2	8	41	31	64	5	1	226	32	17	0.8	n.d.
16	400-405	tr.	93	62	43	75	81	177	115	9	73	3	45	60	8	21	37	31	56	7	1	846	20	46	2.0	n.d.
17	650-655	tr.	128	73	60	86	71	171	116	3	77	4	37	60	4	18	24	18	62	5	1	229	41	27	0.9	n.d.
18	750-755	tr.	108	65	50	67	54	218	131	3	71	4	31	45	5	11	64	27	59	8	6	170	5	3	0.7	-19.2
19	950-955	22	81	67	62	59	75	171	113	7	70	6	27	46	6	17	58	41	84	10	-	162	25	19	0.8	-20.3
20	975-980	tr.	104	58	42	59	68	227	143	5	86	2	38	51	2	9	56	10	21	38	-	116	13	18	1.1	n.d.

PISTON CORE 19
(Lat. 16°14'N, Long. 54°45'E; Depth 2929 m)

21	0-5	tr.	151	60	64	57	76	290	46	6	54	9	30	43	6	33	33	32	49	1	7	836	68	84	1.0	-19.3
22	50-55	20	86	69	52	72	85	196	101	4	66	13	29	56	17	28	26	20	32	17	-	675	36	26	1.1	-19.7
23	150-155	18	142	53	65	86	114	199	102	13	76	3	11	39	10	33	-	23	25	5	-	443	1	1	1.7	n.d.
24	450-455	tr.	83	44	53	36	67	274	155	7	103	4	49	54	11	16	-	17	12	4	-	71	1	1	2.9	n.d.
25	575-580	tr.	91	99	49	47	3	172	79	8	115	2	71	78	1	6	22	27	126	10	35	122	24	12	1.5	-19.6

*(after Degens and Hunt 1960)

Table 4b

DISTRIBUTION OF AMINO ACIDS IN ATLANTIC SEDIMENTS*
(in residues per 1000)

WOODS HOLE - BERMUDA TRANSECT

SAMPLE NO.	WATER DEPTH m	OH-PRO	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ISO	LEU	TYR	PHE	β-ALA	ORN	LYS	HIS	ARG	TOTAL μg/g	GLUCOSAMINE μg/g	GALACTOSAMINE μg/g	C %	N %	$\delta^{13}C$ ‰
1A	20	-	138	69	86	101	53	179	93	5	59	13	41	52	26	22	22	2	34	6	17	2962	66	74	n.a.	0.245	-20.9
2	200	29	155	70	58	70	30	171	72	1	44	6	23	30	33	26	7	1	129	4	36	511	17	14	0.37	0.022	-19.9
3	500	10	75	66	100	76	53	192	86	6	61	12	40	50	13	22	21	37	60	23	7	1624	86	57	0.42	0.077	-20.1
4	2000	9	82	59	80	64	41	227	95	2	54	6	24	29	2	7	9	73	118	18	1	878	56	57	0.59	0.135	-22.3
5	3800	33	55	66	95	65	45	218	101	5	61	5	25	36	5	9	63	44	37	28	2	1028	48	83	0.44	0.066	-20.4
6	4800	15	56	72	103	63	45	253	104	7	64	6	27	33	3	8	66	16	43	11	3	708	38	42	n.d.	0.061	-20.4
7	3800	54	120	69	106	74	33	225	115	9	67	1	23	29	1	9	n.d.	30	14	19	2	719	7	12	n.d.	0.077	-20.6
8	4700	34	43	99	64	42	46	265	129	8	80	7	29	31	1	8	25	24	23	41	1	388	8	21	0.23	0.049	n.d.
9	4700	32	118	72	62	80	29	223	115	11	62	1	21	23	1	43	25	20	23	10	2	340	7	7	n.d.	0.044	n.d.
10	5000	29	75	86	101	59	49	236	129	3	68	2	27	34	2	2	27	28	27	15	2	490	14	24	n.d.	0.050	-19.7
11	5000	24	65	93	64	30	40	266	154	14	58	9	24	28	1	4	2	27	32	4	1	232	14	13	n.d.	0.054	-19.7
12	5000	24	16	93	95	30	42	256	150	24	79	5	25	31	2	7	36	20	47	17	1	351	23	25	0.28	0.056	-20.1
13	2100	18	114	67	82	66	5	229	90	1	53	43	30	42	15	20	23	14	17	2	26	2162	53	39	0.15	0.035	-24.7
14AA	1200	-	48	54	41	41	47	254	116	1	58	29	12	51	26	24	3	-	50	3	81	351	3	3	n.d.	0.037	-21.6

A Woods Hole
AA Bermuda

*(after Degens et al., 1968)

Table 5a

AMINO ACID DISTRIBUTION IN FORAMINIFERA OF THE RED SEA
(in residues per 1000)

SAMPLE NO.	CORE	DEPTH cm	OH-PRO	ASP	THR	SER	GLU	PRO	GLY	ALA	CYS	VAL	MET	ISO	LEU	TYR	PHE	LYS	HIS	ARG	TOTAL µg/g	GLUCOSAMINE µg/g	C^{14} - AGE
1a*	154P	0-10	42	269	37	42	138	35	167	78	5	63	3	30	35	1.3	5	17	15	28	397	7.9	RECENT
1b**			72	253	33	30	130	64	157	73	6	59	3	28	32	1.5	5	16	13	25	371	6.6	
2a*	118K	0-5	47	256	21	21	125	37	160	97	3	74	3	33	52	0.7	11	16	15	25	208	2.4	~3000
2b**			50	243	20	20	119	42	162	95	4	80	4	32	51	0.8	11	17	15	26	186	2.3	
3*	118K	45-50	99	243	24	50	111	67	128	62	3	62	6	30	35	0.7	7	14	15	23	198	1.3	~5000
4*	118K	70-75	64	265	36	36	134	57	144	67	5	59	2	27	32	0.6	9	18	17	27	210	0.8	~6000
5*	118K	100-105	22	363	28	30	127	46	142	73	2	75	4	0	39	1.1	12	15	12	411	313	5.8	~7000
6*	118K	125-130	37	296	51	47	122	21	151	93	3	65	2	25	27	0.9	9	15	14	23	247	2.2	~8000

* decalcified prior to hydrolysis

** hydrolysis of total sample

CHAIN CRUISE 61

Table 5b

AMINO ACID DISTRIBUTION IN SHELL MATERIALS *
(in residues per 1000)

	$CaCO_3$					SiO_2	
	Pelecypoda (51)	Gastropoda (40)	Cephalopoda (4)	Echinoidea (4)	Bryozoa (3)	Sponges (3)	Diatoms (1)
OH-Pro	-	0.01 (0-0.1)	-	1 (0-36)	0.1 (0-7)	-	-
Asp	136 (77-240)	114 (69-185)	98 (75-128)	88 (78-98)	117 (110-136)	123 (109-142)	132
Thr	28 (18-44)	46 (28-76)	34 (18-64)	48 (42-55)	59 (53-66)	47 (30-74)	82
Ser	66 (43-102)	85 (58-124)	95 (62-146)	81 (77-86)	77 (60-98)	102 (58-173)	116
Glu	50 (35-72)	87 (52-145)	65 (42-128)	109 (106-112)	102 (93-112)	83 (67-102)	109
Pro	52 (28-98)	61 (36-102)	55 (15-205)	78 (66-92)	50 (36-67)	64 (49-85)	28
Gly	271 (185-398)	153 (99-238)	153 (89-262)	171 (121-241)	148 (127-172)	134 (99-179)	115
Ala	66 (43-101)	89 (52-153)	126 (74-216)	85 (79-91)	92 (89-95)	94 (79-112)	105
Cys	14 (6-33)	9 (4-23)	7 (0-65)	1 (0.5-2)	13 (4-39)	5 (4-8)	15
Val	33 (22-49)	48 (34-69)	36 (20-64)	38 (31-45)	48 (38-60)	62 (55-69)	60
Met	18 (8-39)	14 (6-31)	8 (5-13)	21 (18-25)	16 (14-18)	8 (3-19)	26
I-Leu	20 (13-31)	31 (20-46)	21 (17-26)	26 (21-32)	31 (25-39)	40 (27-59)	43
Leu	34 (26-44)	71 (51-100)	44 (29-67)	58 (47-70)	59 (46-76)	70 (67-73)	91
Tyr	11 (2-61)	11 (5-24)	23 (15-75)	20 (16-25)	23 (21-25)	24 (16-35)	21
Phe	30 (19-48)	24 (14-43)	30 (20-45)	25 (19-32)	28 (24-33)	24 (12-48)	32
OH-Lys	0.03 (0-0.6)	0.03 (0-0.2)	-	0.6 (0-11)	0.4 (0-8)	-	-
Lys	22 (13-38)	26 (17-41)	20 (5-83)	45 (35-57)	49 (40-61)	40 (22-72)	5
His	4 (1-14)	3 (1-16)	5 (0-35)	16 (13-20)	17 (10-30)	12 (7-23)	16
Arg	24 (6-96)	22 (9-52)	23 (10-56)	69 (60-80)	50 (41-60)	30 (21-42)	2
Total ** (µg/g)	3334	1415	21180	7813	43437	5852	90057
Proteins ** / Hexosamines	143.97	108.30	1.37	33.36	21.23	10.98	0.53

* Geometric mean
** Arithmetic mean
Numbers in parentheses are 1 σ ranges

(after Degens et al., 1967)

Figure 1

Distribution of free constituents in sea water. The individual samples have been grouped into systematic classes of compounds and have been plotted in the form of cumulative frequency diagrams to summarize the information in a comprehensive form. The diamond-shaped figures represent the 2 sigma range. The data are presented in µg C/l to allow a direct comparison to the total dissolved organic matter which is generally reported in mg C/l.

Figure 2

Distribution of free, combined, and particulate amino acids in representative sea water samples. The diamond-shaped figures cover the 2 sigma range.

Figure 3

Separation of amino acids along a vertical sediment profile of Santa Barbara Basin sediments off the coast of California. Data are presented in residues per 1000. A zippeton pattern was used when the amount of amino acids exceeded 100 residues per 1000. On top of the figure the free ammonia content is shown; it gradually decreases from a high of about 270 µg/g at a depth of 4 meters to about 50 µg/g at the sediment/sea water interface (Degens, 1967).

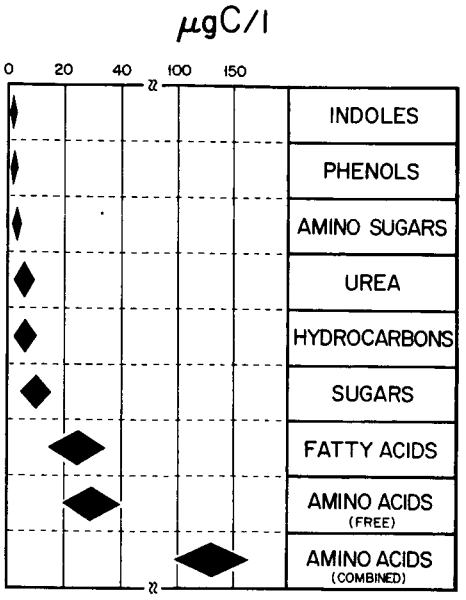

Figure 1

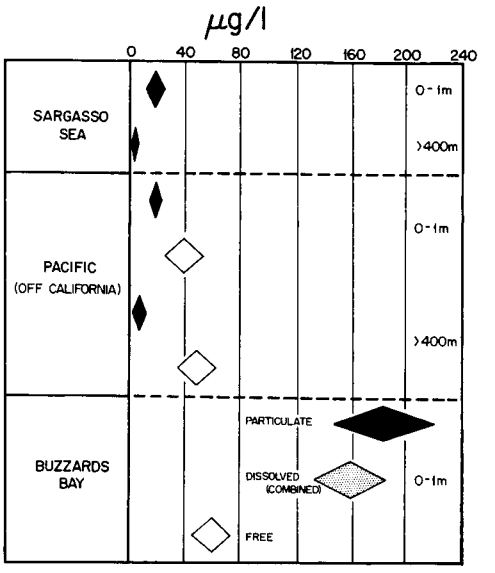

Figure 2

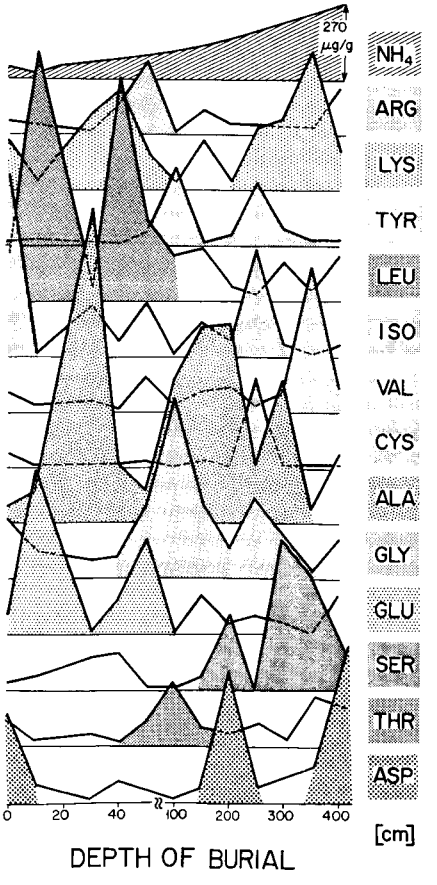

Figure 3

Figure 4

Structure of quinol (Fig. 4a). As a consqquence of electron-donator-acceptor (EDA) interactions, polar OH-groups are combined to hexagonal ring structures. The structural organization in a hypothetical chlathrate segment (Fig. 4b) illustrates the participation of OH-groups of sugars and amino acids, as well as the incorporation of peptides via the carbonyl group. The large interspace permits the incorporation of chain polymers and hydrophobic molecules. Metals may also be introduced into the structure (Degens and Matheja, 1967).

Figure 5

Metal ion co-ordination polyhedron. In this presentation, two carboxyl- and two carbonyl groups are shown, resulting in an octahedral co-ordination for the central metal ion. An increase in the number of polyhedra introduces a structural reorganization of the biochemical molecules. Other oxygen functions may equally well participate in the co-ordination of metals and thus introduce an increase in the biocrystallographical order of the organic molecules involved (Degens and Matheja, 1967). Some of the transition elements in sea water may be part of such structures and represent one of the factors limiting the primary production in upwelling waters in certain parts of the oceans (Barber and Ryther, 1968).

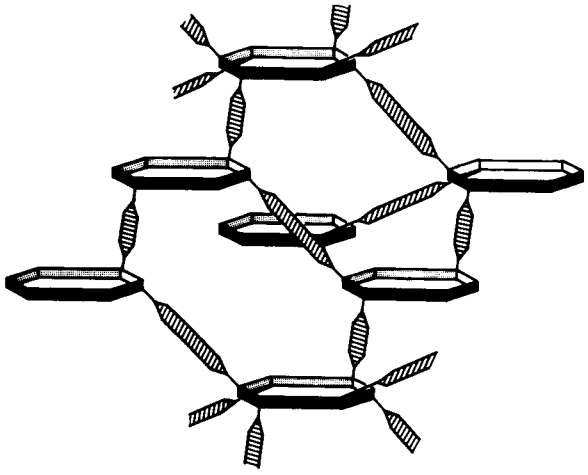

Figure 4a

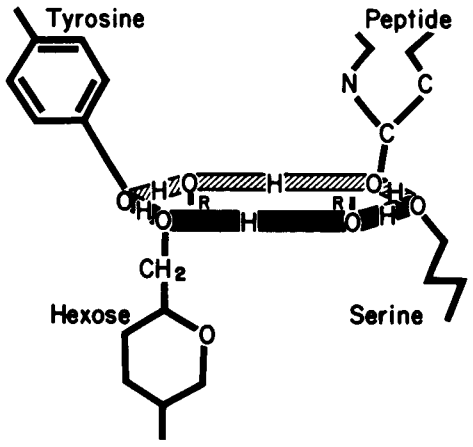

Figure 4b

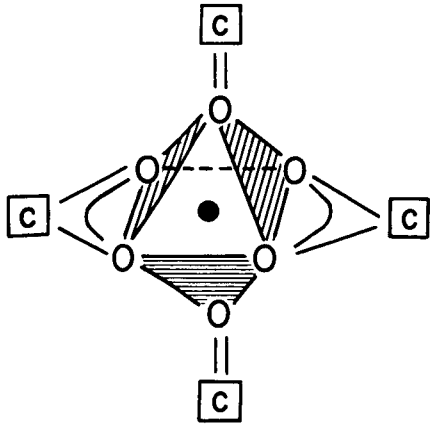

Figure 5

Figure 6

The unit cell of urea in adduct compounds is hexagonal and six urea molecules make up a unit cell (Schlenk, 1949; Smith, 1952; Lenne, 1954). Stability is achieved by hydrogen bonding between adjacent urea molecules and van der Waals forces between the individual urea molecules and between urea and the adduct compound located within the channel or tube formed by the urea molecules. Such a complex is structurally similar to chlathrate compounds. The formation of cage structures in general requires strong interactions between neighboring extended groups of atoms or molecules of the same type resulting in large enough stable configurations for the inclusion of elements or molecules of different type. Urea adduct compounds resemble chlathrates in that long-chain molecules force urea into configurations different from that of the normal urea structure which is tetragonal. The significance of oxygen in structural reorganizations of this type is apparent. Metal ions may even use this oxygen for co-ordinative purposes and thus increase the structural order of the participating molecules.

Figure 7

Stable carbon isotope distribution in plankton, sea water, and marine sediments. The lipid fraction of plankton is generally depleted in C^{13} by 5 to 10 permil relative to the total plankton sample. Similar depletions are observed for the dissolved organic matter relative to the particulate organic matter in the sea. Diagenetic processes also lower the C^{13} content of the organic matter to about the same extent (Degens, 1969). The diamond-shaped figures represent the 2 sigma range.

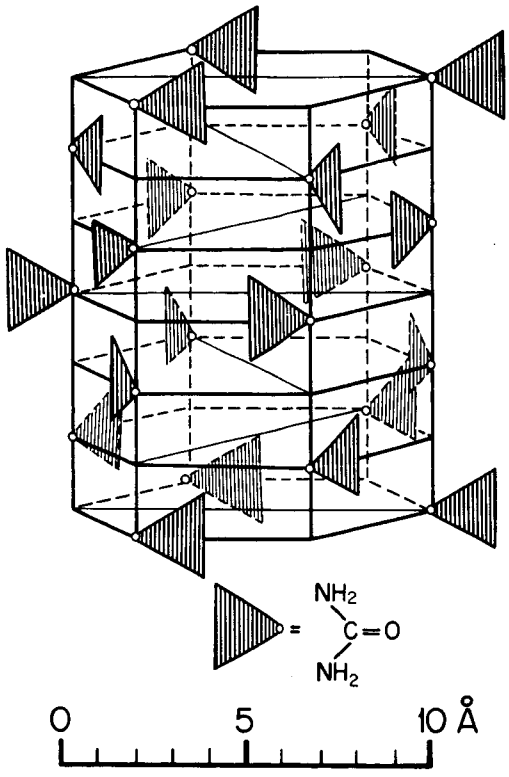

Figure 6

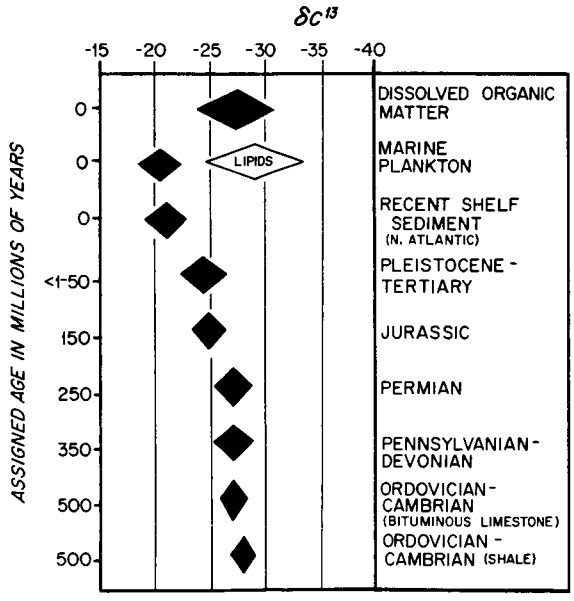

Figure 7

APPENDIX

Non-protein nitrogen sources, in particular urea and biuret, are presently widely used in ruminant rations. A full account on the important advances in ruminant nutrition with respect of the role of the rumen flora and fauna as synthesizers of protein from urea has been prepared in a book entitled "Urea as a Protein Supplement" edited by M. H. Briggs, Pergamon Press, 1967, 466 pp. In the context of our work on the organic matter in the sea, these studies in the field of animal husbandry are quite revealing, because in both instances urea has a key biochemical function.

At present, urea feeding in the United States amounts to about 200,000 tons per year, and the proportion of urea protein to all protein supplied by high protein feeds to cattle is rapidly rising from 9.4% in 1956 to 13.6% in 1963. It has been shown that urea can substitute for up to 40% of the protein ration without ill effects on the animals; however, the carbohydrate and true protein diet has to be nutritionally adjusted to the individual group of animals. Sulfur containing amino acids can be biosynthesized from sulfate; the remaining 10 essential amino acids are generated by the microbial population maintained in the rumen and which produce proteins of high biological value. Inorganic ions are rather influential in the urea turnover. Two-valent ions, for example, Mn, Mg, Ca, and Sr, stimulate urease activity, whereas Na, K, and Co have an inhibiting effect. This would suggest that urease produced by rumen bacteria is a metal-activated enzyme. The ability of the rumen microflora to synthesize B-vitamins in large quantities is striking, and urea rations even stimulate the production of B-vitamins. Dietary deficiencies of B-vitamins can thus be compensated for.

In summary, many factors influence the ability of the rumen microflora to utilize urea as a source for the biosynthesis of proteins. Analogously, the organic matter in sea water which contains large quantites of urea can only be used biologically should the right

proportions of biochemicals and appropriate metal ions be available. Much can be learned by the marine biologist from the series of articles in this -- on first sight -- unrelated field of science, "Ruminant Physiology." On the other hand, the fact that the dissolved organic matter in the sea is by far the largest organic carbon and nitrogen reservoir at the earth surface may perhaps stimulate research on its eventual biological utilization by domestic animals.

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