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32. ORGANIC COMPOUNDS IN SEDIMENTS AND PORE WATERS OF SITES 723 AND 724[1]

R. Seifert[2] and W. Michaelis[2]

ABSTRACT

Total organic carbon, amino compounds, and carbohydrates were measured in pore waters and sediments of Pliocene to Pleistocene age from Sites 723 and 724 (ODP Leg 117) to evaluate (1) relationships between organic matter in the sediment and in the pore water, (2) the imprint of lithological variations on the abundance and contribution of organic substances, (3) degradation of amino compounds and carbohydrates with time and/or depth, and (4) the dependence of the ammonia concentration in the pore water on the degradation of amino compounds in the sediment.

Total organic carbon concentrations (TOC) of the investigated sediment samples range from 0.9% to 8.7%, and total nitrogen concentrations (TN) from 0.1% to 0.5%. Up to 4.9% of the TOC is contributed by hydrolyzable amino acids (THAA) which are present in amounts between 1.1 and 21.3 μmol/g dry sediment and decrease strongly downhole. Hydrolyzable carbohydrates (THCHO) were found in concentrations from 1.3 to 6.6 μmol/g sediment constituting between 0.1% and 2.0% of the TOC. Differences between the distribution patterns of monomers in Sites 723 and 724 indicate higher terrigenous influence for Site 724 and, furthermore, enhanced input of organic matter that is relatively resistant to microbial degradation. Lithologically distinct facies close to the Pliocene/Pleistocene boundary yield different organic matter compositions. Laminated horizons seem to correspond with enhanced amounts of biogenic siliceous material and minor microbiological degradation.

Total amounts of dissolved organic carbon (DOC) in pore waters vary between 11 and 131 mg/L. Concentrations of DOC as well as of dissolved amino compounds and carbohydrates appear to be related to microbial activity and/or associated redox zones and not so much to the abundance of organic matter in the sediments. Distributions of amino acids and monosaccharides in pore waters show a general enrichment in relatively stable components in comparison to those of the sediments. Nevertheless, the same trend appears between amino acids present in the sediments from Sites 723 and 724 as well as between amino acids in pore waters from these two sites, indicating a direct relation between the dissolved and the sedimentary organic fractions.

Different ammonia concentrations in the pore waters of Sites 723 and 724 seem to be related to enhanced release of ammonia from degradation of amino compounds in Site 723.

INTRODUCTION AND GEOLOGICAL BACKGROUND

Introduction

Since the first studies of amino acids and carbohydrates were performed on post-Quaternary marine sediments (Erdman et al., 1956; Degens et al., 1961; Rittenberg et al., 1963), these compounds have been used for the characterization of immature sedimentary organic matter by many authors (e.g., Hare, 1973; Klok et al., 1984; Cowie and Hedges, 1984; Steinberg et al., 1987; Burdige and Martens, 1988). However, only few investigations are concerned with amino compounds and carbohydrates in both, sediments and the corresponding interstitial waters (Michaelis et al., 1982; Henrichs et al., 1984; Henrichs and Farrington, 1987). Degradation pathways of amino acids have been studied over times ranging from thousands to millions of years (e.g., Bada and Man, 1980) and several hypotheses on the nature of the enrichment in sediments of the more stable organic fraction have been proposed (e.g., Degens and Mopper, 1976; Henrichs and Doyle, 1986). However, there is a paucity of information on degradation and stabilization processes below the upper 1 or 2 m of the sediment column.

Legs 112 and 117 were conducted on continental margins both characterized by high primary productivity but distinguished by different sedimentary environments. Sediments recovered during these campaigns provide a nearly undisturbed record for the past million years. In addition, organic matter concentrations in these sediments were generally high, offering an excellent opportunity to study diagenetic processes of organic matter in relation to different sedimentary environments.

We investigated pore waters and sediments from Sites 723 and 724 according to their content of organic constituents (organic carbon, amino compounds, carbohydrates). The sites differ by their sedimentation rates during Pleistocene and Pliocene time (180 m/m.y. and 80 m/m.y. for Site 723 and Site 724, respectively). In comparison to Site 723, sediments at Site 724 contain greater proportions of terrigenous material but lower contributions of organic matter. Main objectives of this study were to elucidate: (1) the relationship between organic matter in sediment and corresponding pore water, (2) the influence of lithological variations on the organic matter, and (3) the relationship between ammonia content of pore water and amino compounds in the sediment. A brief description of the location and lithology for both sites based on the site chapters (Prell, Niitsuma, et al., 1989) is given below.

Study Area

The western Arabian Sea (Fig. 1) is characterized by monsoon-driven upwelling with strong seasonal variability. This seasonality is caused by differences in pressure gradients between the Indian Ocean and the Asian continent. During winter when cooling over Asia develops a high pressure cell, northeasterly winds flow from Asia over the Arabian Sea. During summer heating, ascending air masses over Asia generate an intense low pressure cell centered over the Tibetan Plateau. The gradient between this low pressure cell and the high pressure zone over the southern Indian Ocean creates southwest winds of considerable force. These winds, blowing parallel to the coast of Somalia and

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[2] Institut für Biogeochemie und Meereschemie, Universität Hamburg, Bundesstrasse 55, D-2000 Hamburg 13, Federal Republic of Germany.

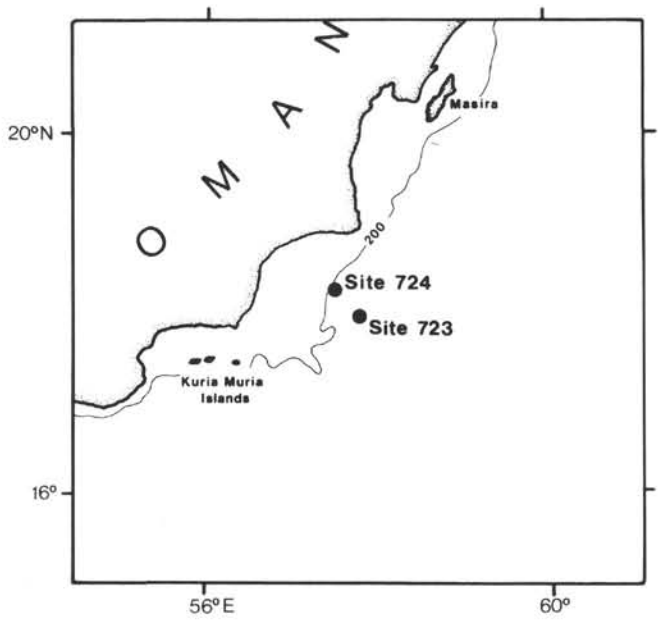

Figure 1. Location map for Sites 723 and 724.

Arabia, yield an offshore flow of warm surface water and thus cause deeper, nutrient-rich water to upwell along the coast (Prell and Streeter, 1982). The duration and extent of upwelling in the western Arabian Sea is determined by the speed and duration of the southwest monsoon. The sediment deposits off Arabia should therefore reveal a record of the monsoonal history as induced by the climatic and geomorphological changes since the Miocene.

The immediate goal of Leg 117 was to recover the sedimentary record deposited in the area of monsoonal upwelling in the western Arabian Sea since Miocene time. For this purpose eight sites were investigated on the continental margin of Oman. The sites are located in water depths ranging from 300 to 1450 m corresponding to the extent of a pronounced mid-water oxygen-minimum zone. The extent and intensity of this zone over the continental slope is substantially influenced by the advection of deep water (Wyrtki, 1973). Presently, the mid-water oxygen-minimum zone is present in water depths between 150 and 1400 m in the western Arabian Sea.

Site 723

Three holes were drilled on Site 723 at 18°03.079'N, 57°86.561'E (Holes 723A and 723B) and at 18°03.079'N, 57°86.5561'E (Hole 723C) (Fig. 1). These locations are on the continental margin of Oman close to the center of the slope basin in about 800 m water depth, the depth of the lowest oxygen concentrations found in the oxygen-minimum zone. The deepest hole, Hole 723A, penetrated 432.3 mbsf with a core recovery of 69%. Sediments obtained are of Pleistocene to late Pliocene age and reveal consistently high sedimentation rates of approximately 180 m/m.y. The sedimentary sequence is described as a single lithologic unit wherein three facies were identified.

Facies I dominates throughout the recovered section. It consists of foraminifer-bearing marly nannofossil ooze and calcareous clayey silt with an average biogenic carbonate content of 30%–50%. The terrigenous component comprises between 30% and 70% and is dominated by clay and silt-sized detrital calcite. Trace amounts of euhedral dolomite occur at all depths.

Facies II consists of dolomitic limestone in thin cemented layers. The composition of these layers is found to be similar to facies I. Facies II occurs in Holes 723A and 723B below 245 mbsf.

Facies III is characterized by light and dark laminae, 0.1–1 mm thick. The laminated intervals are usually less than 10 cm thick although one continuously laminated horizon about 2 m thick was observed. The light laminae consist of diatom ooze (diatomite) with trace amounts of radiolarians, silicoflagellates, and sponge spicules. Dark laminae are marly nannofossil ooze, similar in composition to facies I but often containing pellets or clay aggregates rich in organic material. The highest frequency of appearance of facies III is observed between 300 and 350 mbsf in the upper Pliocene although some laminated intervals occur in the lower Pleistocene. Facies III occurs in close association with facies II.

Site 724

Site 724 is located at 18°27.713'N, 57°47.147'E on the continental margin of Oman in the eastern part of the slope basin (Fig. 1). Water depth here is about 593 m, well within the oxygen minimum zone. Three holes were drilled at this site, penetrating up to 257.7 m of sediment, Recent to early Pliocene in age, with a mean recovery above 82%. The mean sedimentation rate is approximately 80 m/m.y. One lithological unit containing two facies was recognized at Site 724.

Facies I consists of calcareous clayey silt beds colored black, very dark grey, olive gray, and olive. The beds range from 5 to about 250 cm thickness and show predominantly burrow-mottled and gradational contacts. The approximate average composition of this facies is 30% clay, 25% detrital calcite, 10% quartz, and 22% nannofossils and foraminifers. The average carbonate content is about 50%.

Facies II consists of laminated diatomaceous clayey silt beds from 5 to 175 cm thick (average 62 cm) with dark olive grey, olive grey, and olive laminae less than 1 mm thick. The mean composition of this facies is dominated by diatoms (46%), followed by clay (33%), inorganic calcite (7%), and quartz and nannofossils (6% and 2%, respectively). The preservation of the lamination and in general high organic carbon values indicate a depositional environment with anoxic bottom water. Because of the enhanced silica content of facies II, this type of sediment might be an expression of high production of siliceous organisms in the overlying water column.

The sedimentary sequence of Site 724 is dominated by facies I while facies II occurs at late Pleistocene to early Pliocene times (Hole 724B in Core 23X, Hole 724C in Cores 15X, 19X, 20X, 22X, and 23X).

SAMPLES AND METHODS

Samples investigated here are listed in Tables 1 and 3 (Site 723) and Tables 2 and 4 (Site 724). Sampling of interstitial water was performed by standard shipboard techniques using a stainless steel press (Manheim and Sayles, 1974). All samples were poisoned with mercuric chloride and sealed in 5 mL pre-combusted glass ampoules immediately after sampling. Sediment samples were obtained from squeezed cakes corresponding to the respective pore water samples. Total organic carbon (TOC) and total nitrogen (TN) analyses were carried out with a Carlo Erba Elemental Analyzer Model 1104 with a thermal conductivity detector. The samples were pretreated with phosphoric acid to remove carbonate. Dissolved organic carbon (DOC) was measured with a Carlo Erba Total Carbon Monitor Model 400. The method is based on catalytic high temperature (880°C) combustion of the liquid sample. The released CO_2 is catalytically converted to methane and quantified by a flame ionization detector. Samples were acidified with nitric acid (2 wt%) and purged prior to DOC combustion to expel inorganic carbon. Amino compounds in squeezed cakes were measured after hydrolysis of

Table 1. Results of sediment analyses, Site 723.[a]

Core, section, interval (cm)	Depth (mbsf)	Age (ka)	TOC (%)	TN (%)	C/N (mol ratio)	THAA (μmol/g)	THAS (μmol/g)	THCHO (μmol/g)	THAA TOC (%)	THAS TOC (%)	THAA TN (%)	THA TN (%)	THCHO TOC (%)	THAA THAS	THCHO THAA	GlcN GalN
117-723A-																
1H-4, 145–150	5.9	33	2.41	0.15	18.7	22.25	2.25	6.41	4.93	0.56	26.13	2.10	1.84	9.90	0.29	1.36
3H-4, 145–150	23.4	130	1.29	0.06	25.1	5.38	0.80	2.70	2.27	0.37	15.65	1.87	1.43	6.74	0.51	1.36
6H-4, 145–150	52.3	291	3.81	0.18	24.7	7.64	2.17	6.59	1.08	0.34	7.26	1.68	1.20	3.53	0.86	1.63
9H-4, 145–150	81.3	486	3.46	0.18	22.4	3.69	1.20	2.33	0.59	0.21	3.43	0.93	0.47	3.08	0.63	1.60
13X-4, 145–150	120.0	718	3.75	0.24	18.2	2.86	1.38	3.75	0.43	0.32	2.04	0.81	0.70	2.07	1.31	2.45
17X-1, 145–150	154.3	901	2.71	0.17	18.6	2.55	0.97	2.50	0.51	0.20	2.58	0.79	0.64	2.64	0.98	1.67
20X-4, 145–150	187.7	1085	3.51	0.20	20.5	1.81	0.73	4.02	0.27	0.13	1.55	0.52	0.79	2.46	2.22	2.56
23X-1, 145–150	212.3	1215	3.86	0.23	19.6	2.91	1.19	2.49	0.40	0.18	2.14	0.72	0.45	2.45	0.86	2.41
26X-3, 120–125	244.0	1384	5.29	0.37	16.7	2.09	0.93	3.02	0.21	0.11	0.98	0.35	0.39	2.24	1.44	2.49
29X-6, 145–150	277.6	1562	4.91	0.33	17.4	2.41	0.85	2.84	0.27	0.10	1.27	0.36	0.40	2.83	1.18	2.80
32X-5, 145–150	304.9	1710	3.66	0.30	14.2	1.18	0.35	1.80	0.17	0.06	0.69	0.16	0.34	3.40	1.53	2.91
36X-5, 145–150	333.5	1871	4.17	0.31	15.8	1.68	0.55	2.37	0.21	0.08	0.98	0.25	0.39	3.07	1.41	2.72
39X-5, 145–150	362.4	2045	6.00	0.42	16.7	1.25	0.40	1.25	0.11	0.04	0.56	0.13	0.14	3.15	1.00	2.65
117-723B-																
42X-1, 145–150	382.0	2156	8.65	0.52	19.4	1.32	0.26	2.61	0.08	0.02	0.48	0.07	0.21	5.08	1.98	4.11

[a] Ages are calculated on biostratigraphical and magnetostratigraphical data from the shipboard party.

Table 2. Results of sediment analyses, Site 724.[a]

Core, section, interval (cm)	Depth (mbsf)	Age (ka)	TOC (%)	TN (%)	C/N (mol ratio)	THAA (μmol/g)	THAS (μmol/g)	THCHO (μmol/g)	THAA TOC (%)	THAS TOC (%)	THAA TN (%)	THA TN (%)	THCHO TOC (%)	THAA THAS	THCHO THAA	GlcN GalN
117-724C-																
1H-1, 145–150	1.5	20	1.24	0.06	24.2	7.39	0.67	3.29	3.30	0.33	23.9	1.57	1.86	11.0	0.45	1.35
117-724A-																
1H-3, 145–150	4.5	60	1.78	0.04	51.9	7.28	1.22	2.88	2.21	0.41	33.2	4.25	1.14	5.98	0.40	1.23
117-724C-																
2H-4, 145–150	8.8	119	1.99	0.06	38.7	4.60	0.90	2.73	1.18	0.27	12.6	2.10	0.94	5.10	0.59	1.24
3H-4, 145–150	18.2	241	1.38	0.07	23.0	3.87	0.88	1.69	1.52	0.38	9.87	1.76	0.50	4.41	0.44	1.71
117-724A-																
3H-4, 145–150	21.9	290	1.41	0.07	23.4	3.67	0.88	3.19	1.45	0.38	9.30	1.80	0.88	4.17	0.87	2.10
117-724C-																
4H-4, 145–150	27.7	366	2.40	0.11	25.4	6.85	1.96	6.07	1.58	0.50	10.7	2.50	1.74	3.49	0.89	1.81
5X-4, 145–150	37.2	492	1.44	0.06	28.0	2.65	0.67	4.17	1.03	0.28	7.53	1.58	1.99	3.93	1.57	1.89
117-724B-																
6X-3, 145–150	49.5	534	0.87	0.04	25.4	1.32	0.38	1.89	0.85	0.26	5.80	1.32	1.50	3.48	1.43	2.49
9X-4, 145–150	80.0	959	2.44	0.08	35.6	2.22	0.87	3.06	0.48	0.22	4.40	1.54	0.87	2.55	1.38	2.09
12X-5, 145–150	110.5	1212	2.44	0.09	33.5	1.96	0.92	3.07	0.44	0.23	3.91	1.52	0.86	2.12	1.57	2.22
16X-4, 145–150	147.7	1815	3.95	0.13	35.5	1.68	0.98	3.37	0.23	0.15	2.08	1.06	0.59	1.71	2.01	2.21
19X-4, 145–150	176.7	2252	3.53	0.13	31.7	1.54	0.78	4.34	0.25	0.13	2.20	0.85	0.85	1.96	2.82	1.77
23X-3, 145–150	213.9	2830	3.67	0.16	27.6	1.91	0.62	2.68	0.27	0.10	1.94	0.57	0.50	3.08	1.40	2.28
25X-4, 145–150	234.7	3163	2.42	0.13	21.7	1.06	0.31	1.74	0.25	0.08	1.35	0.33	0.50	3.44	1.64	1.99

[a] Ages are calculated on biostratigraphical and magnetostratigraphical data from the shipboard party.

50–150 mg dried and crushed subsample with 6N HCl under argon for 23 hr at 110°C. Analyses were performed on a Biotronik Amino Acid Analyzer and quantified against standards. Dissolved amino compounds were measured following hydrolysis of 1–2 mL dried sample in 6N HCl under the same conditions. The analytical error for total amounts was found to be smaller than ±6% for multiple preparation of aliquots of one sample. Repeated injections of one sample yielded differences in the mol% distribution of individual amino compounds below ±4%. Concentrations of carbohydrate monomers were measured after acid hydrolysis of 50–150 mg dried and ground sediment or 1–2 mL interstitial water. Hydrolysis was carried out with 2 N HCl at 100°C for 3.5 hr under argon in precombusted glass ampoules. The samples were analyzed on a Biotronik Sugar Analyzer by liquid chromatography (Mopper, 1977; 1978) and compared to standards. Hydrolysates were desalted by electrodialysis before analyses. Details of all organic geochemical methods used are given in Michaelis and Ittekkot (1982).

RESULTS

Sediments

TOC, TN, TOC/TN Ratios

Total organic carbon (TOC) values in Site 723 samples range from 1.3% to 8.7% and in Site 724 samples from 0.9% to 3.7% of dried sediment. The downhole increasing TOC concentrations in both sites (Tables 1 and 2) indicate a change in the sedimentary environment during Pliocene to Recent time for the studied area.

Table 3. Results of interstitial water analyses, Site 723.[a]

Core, section, interval (cm)	Depth (mbsf)	Age (ka)	DOC (mg/L)	$^{b}NH_4$ (mM)	$^{b}SO_4$ (mM)	DHAA (μM)	DHAS (μM)	DHCHO (μM)	DHAA DOC (%)	DHAS DOC (%)	DHCHO DOC (%)	DHAA DHAS	DHCHO DHAA	GlcN GalN	DHAA NH_4 (%)	DHAS NH_4 (%)
117-723A-																
1H-2, 145–150	3.0	16.7	21.6	1.20	20.6				8.35	1.86	4.55	5.90	0.35	1.27	2.54	0.38
1H-4, 145–150	6.0	33.4	16.0	1.22	23.2											
1H-5, 145–150	7.5	41.8	17.2	1.40	18.1	31.44	5.33	11.01								
117-723C-									6.82	1.39	23.52	6.14	2.37	1.67	2.78	0.37
									6.80	1.23	25.65	6.87	2.57	1.75	2.09	0.26
2H-2, 145–150	10.8	60.1	25.2	1.56	16.6	35.78	5.82	84.88	6.67	1.26	35.32	6.69	3.59	1.62	1.88	0.24
2H-5, 145–150	15.3	85.2	22.9	1.81	16.3	32.35	4.71	83.02								
3H-2, 145–150	20.5	114.1	23.1	2.04	11.8	32.32	4.83	116.11								
117-723A-									2.90	0.54		6.76		1.58	0.62	0.08
3H-4, 145–150	23.4	130.3	21.6	2.51	12.2	13.08	1.93									
117-723C-									12.80	0.77	20.32	20.72	1.09	1.46	2.37	0.01
									10.49	0.46		28.95		1.52	1.92	0.01
3H-5, 145–150	25.0	139.2	21.1	2.83	6.1	56.05	2.71	61.35								
4H-2, 145–150	30.1	167.6	28.1	3.89	13.0	62.81	2.17									
117-723A-									3.43	0.84		5.12		1.55	0.24	0.04
									1.90	0.68	3.55	3.61	1.27	1.54	0.11	0.03
6H-4, 145–150	52.3	291.2	33.8	12.17	0.0	24.08	4.71		1.95	0.62	3.67	4.02	1.25	1.55	0.11	0.02
9H-4, 145–150	81.3	486.5	52.1	20.46	0.0	21.15	5.86	26.91	2.02	0.34	2.99	7.68	0.98	1.19	0.08	0.01
13X-4, 145–150	120.0	718	62.4	28.29	0.0	25.79	6.42	32.22	0.85	0.19	5.01	6.02	3.70	1.29	0.04	0.01
17X-1, 145–150	154.3	901	60.7	35.25	0.0	26.49	3.45	25.86								
20X-4, 000–005	187.7	1085	72.2	37.04	0.0	13.70	2.28	50.63	1.20	0.09	3.69	16.70	2.07	1.68	0.04	0.00
23X-1, 145–150	212.3	1215	130.6	37.84	0.0				2.88	0.11	1.70	35.14	0.39	1.42	0.13	0.00
26X-3, 120–125	244.0	1384	61.3	39.62	0.6	15.88	0.95	32.81	1.70	0.05	0.93	47.46	0.42	1.04	0.10	0.00
29X-6, 145–150	277.6	1562	78.0	41.00	1.1	48.17	0.94	18.68	1.27	0.02	5.44	80.74	2.71	1.51	0.07	0.00
32X-5, 145–150	304.9	1710	100.0	40.04	0.4	35.94	0.76	15.04	2.14	0.02	4.48	117.56	1.35	2.23	0.13	0.00
36X-5, 145–150	333.5	1871	90.7	40.40	1.6	25.35	0.31	68.65								
39X-5, 145–150	362.4	2045	97.1	40.40	1.9	45.97	0.39	62.08								
117-723B-									2.42	0.00	7.52			1.99	0.15	0.00
42X-1, 145–150	382.0	2156	100.5	37.00	2.2	52.81	0.00	105.07								

[a] Ages are calculated on biostratigraphical and magnetostratigraphical data from the shipboard party.
[b] Results taken from site chapter (Prell, Niitsuma, et al., 1989).

Table 4. Results of interstitial water analyses, Site 724.[a]

Core, section, interval (cm)	Depth (mbsf)	Age (ka)	DOC (mg/L)	$^{b}NH_4$ (mM)	$^{b}SO_4$ (mM)	DHAA (μM/L)	DHAS (μM/L)	DHAA DOC (%)	DHAS DOC (%)	DHAA DHAS	GlcN GalN
117-724C-											
1H-1, 145–150	1.5	20	40.2	0.50	26.3	15.12	0.77	1.87	0.12	19.52	1.37
117-724A-											
1H-3, 145–150	4.5	60	29.0	1.02	19.4	26.23	1.68	4.87	0.35	15.63	1.95
117-724C-											
2H-4, 145–150	8.8	119	24.0	0.65	23.5	11.57	0.81	2.35	0.20	14.32	1.57
3H-4, 145–150	18.2	241	34.4	1.35	13.9	8.60	2.12	1.21	0.37	4.05	1.77
117-724A-											
3H-4, 145–150	21.9	290	19.5	0.76	22.1	8.71	1.00	2.17	0.31	8.74	1.57
117-724C-											
4H-4, 145–150	27.7	366	46.5	1.02	13.9	8.16	2.17	0.82	0.28	3.76	3.42
5X-4, 145–150	37.2	492	10.7	1.70	6.6	13.89	0.50	6.01	0.28	27.52	1.54
117-724B-											
6X-3, 145–150	49.5	534	21.7	2.37	0.9	15.42	0.76	3.13	0.21	20.29	1.98
9X-4, 145–150	80.0	959	32.9	7.61	0.7	12.33	2.11	1.86	0.39	5.84	1.61
12X-5, 145–150	110.5	1212	28.6	12.33	1.1	14.29	0.76	2.39	0.16	18.9	1.76
16X-4, 145–150	147.7	1815	48.3	15.04	1.8	13.02	0.76	1.28	0.10	17.06	1.26
19X-4, 145–150	176.7	2252	54.2	18.37	0.7	22.24	0.60	1.83	0.07	37.27	1.27
23X-3, 145–150	213.9	2830	79.2	19.29	1.5	8.13	0.37	0.52	0.03	22.28	1.55
25X-4, 145–150	234.7	3163	34.9	19.49	1.8						

[a] Ages are calculated on biostratigraphical and magnetostratigraphical data from the shipboard party.
[b] Results taken from site chapter (Prell, Niitsuma, et al., 1989).

Total nitrogen concentrations (TN) show a downhole pattern similar to the TOC. The amounts are in the range of 0.06%–0.52% of dry sediment for Site 723, whereas the values for Site 724 are in the range of 0.04%–0.16%. The lowest value in Site 723 is found in Sample 723A 3H-4, 145–150 cm, at 23.4 mbsf, while the maximum occurs at the deepest analyzed sample at 375.5 mbsf (723B 42X-1, 145–150 cm).

Atomic ratios of TOC/TN vary from 14.2 to 25.1 in Site 723 and from 21.7 to 51.9 in Site 724. Both sites reveal the highest TOC/TN ratios in the upper zone of the investigated sediment column. TOC/TN ratios in Site 723 are in general lower than in Site 724 which may be related to differences in the abundance of organic matter and in the ammonia content of interstitial waters as discussed below.

Total Hydrolyzable Amino Acids (THAA)

Sediment samples contained from 1.2 to 22.3 μmol THAA/g and from 1.1 to 7.4 μmol THAA/g in Sites 723 and 724, respectively (Tables 1 and 2). Amino acids account for 0.5%–26.1% of the TN and for 0.1%–4.9% of the TOC in Site 723. Between 1.4% and 33.2% of TN and 0.2% and 3.3% of TOC is contributed by amino acids in sediments from Site 724. The downhole decrease of the total amount of THAA as well as of their contribution to the TN and TOC mirrors the ongoing preferential degradation of amino acids with time. Downhole trends of the relative distributions are characterized by a decrease of acidic amino acids (i.e., aspartic acid and glutamic acid), threonine, serine, and arginine and by increasing contents of non-protein amino acids (i.e., β-alanine, γ-aminobutyric acid, and ornithine), lysine, and histidine (Tables 5 and 6). Figure 2 depicts the mean molar distributions of monomeric amino acids for Sites 723 and 724, respectively. Aspartic acid, glutamic acid, isoleucine, leucine, phenylalanine, and arginine are enriched in Site 724, whereas the THAA in Site 723 reveal enhanced contributions of non-protein amino acids, glycine, serine, alanine, histidine, and lysine.

Total Hydrolyzable Amino Sugars (THAS)

The conditions chosen to hydrolyze amino compounds are optimized for amino acids. Better yields of amino sugars are found by hydrolysis with 4 N HCl for 4 hr at 100°C (Belayouni and Trichet, 1980). Hydrolysis experiments with sediment samples reveal a loss of approximately 30% under the hydrolysis conditions used in this study (Mueller et al., 1986). The real concentrations of amino sugars are therefore probably about 1.4-fold higher than the values reported here. However, we have no indications for different stabilities of glucosamine (GlcN) and galactosamine (GalN) during hydrolysis

Concentrations of hexosamines are found in the range of 0.3–2.3 μmol/g (Site 723) and 0.3–2.0 μmol/g (Site 724) respectively (Tables 1 and 2). The contribution of THAS to the TOC varies between 0.02% and 0.56%. GlcN dominates over GalN in all samples (GlcN/GalN ratios between 1.2 and 4.1), and the GlcN/GalN ratio reveals a downhole decreasing trend.

Total Hydrolyzable Carbohydrates (THCHO)

Carbohydrates are present in sediments from Site 723 in concentrations between 1.3 and 6.6 μmol/g making up from 0.1% to 1.8% of the TOC (Table 1). Samples from Site 724 contain amounts of carbohydrates in the range of 1.7–6.1 μmol/g that is between 0.5% and 1.9% of the TOC (Table 2). The downhole decrease of THCHO is less pronounced compared to THAA, as shown by the increased THCHO/THAA ratios at greater depths, indicating relative higher carbohydrate stability. Obvious differences exist between the two sites with regard to the mean monomeric distribution of the sugars. Rhamnose and mannose are strongly enriched in Site 723 while fructose, ribose, and galactose contributions are higher in Site 724 (Fig. 3; Tables 7 and 8).

Pore Water

Dissolved Organic Carbon (DOC)

Dissolved organic carbon in the interstitial water samples from Site 723 was found in concentrations from 16 to 131 mg/L (Table 3). Pore waters above 30 mbsf are characterized by relatively low DOC values (< 25 mg/L), while below this depth the DOC concentrations increase reaching 131 mg/L at 212.3 mbsf (Sample 723A-23X-1, 145–150 cm). Pore waters of Site 724 revealed DOC values in the range of 11–79 mg/L (Table 4). The highest concentrations were found in the lower part (Samples 724B-16X-4, 145–150 cm to 724B-23X-3, 145–150 cm) of the hole where enhanced TOC values also occur. A pronounced DOC minimum showed up at 37.2 mbsf (Sample 724C-5X-4, 145–150 cm).

Hydrolyzable Amino Compounds (DHAA and DHAS)

Amino acids yield from 1% to 13% of the DOC in Site 723 and from 0.5% to 6.0% in Site 724 (Tables 3 and 4). High contributions of dissolved hydrolyzable amino acids (DHAA) appear in the upper 20 m and between 25 and 50 mbsf in both Sites (Fig. 4A). Total amounts of DHAA are in the range of 8–63 μM, revealing generally higher values in Site 723. The lack of correspondence between the downhole patterns of total amino acids in pore water and sediment makes unlikely a quantitatively relevant transfer of organic material from the sediment into the pore water during squeezing. As shown in Figure 5 (and Tables 9 and 10) glycine dominates the amino acid spectra of the pore waters in general. Hydroxy amino acids (i.e., threonine and serine), non-protein amino acids, and histidine are enriched in pore waters of Site 723 relative to pore waters of Site 724, which in turn show enhanced concentrations of acidic amino acids, isoleucine, leucine, phenylalanine, and arginine.

Dissolved hydrolyzable amino sugars (DHAS) are present in concentrations up to 6.4 μM and contribute from 0.0% to 1.9% (Site 723) and from 0.0% to 0.4% (Site 724) to the DOC.

Dissolved Hydrolyzable Carbohydrates (DHCHO)

Dissolved hydrolyzable sugars (DHCHO) in interstitial waters of Site 723 were found in concentrations from 15 to 116 μM, constituting between 1% and 35% of the DOC (Table 3). High contributions of DHCHO to the DOC appear in the upper 30 m of the sediment column where DOC values are low. Glucose and fructose dominate the monosaccharide spectra comprising in average about 63 mol% (Table 11). In general the relative distributions of the DHCHO exhibit large variations with no obvious downhole trend. No carbohydrate analyses were performed on interstitial waters from Site 724.

DISCUSSION

Organic Carbon Concentrations in Sediments and Pore Waters in Relation to Depth and Time

TOC concentrations scatter widely in the analyzed sediments revealing maximum values for samples of late Pliocene age, where laminated beds rich in organic matter occur in the sedimentary sequence of both sites (Tables 1 and 2). TOC contents thus appear to be mainly determined by the sedimentary environment and not by time- or depth-related degradation processes. DOC concentrations from 16 to 130 mg/L are in the range of results from other marine pore waters: Michaelis et al. (1982) found between 31 and 204 mg/L in pore waters from the Gulf of California; Emeis et al. (1987) reported values in the

Table 5. Amino acids and amino sugars in sediments, Site 723.

Core, section, interval (cm)	Cys (mol%)	Tau (mol%)	Asp (mol%)	Thr (mol%)	Ser (mol%)	Glu (mol%)	Gly (mol%)	Ala (mol%)	Val (mol%)	Met (mol%)	Ale (mol%)
117-723A-											
1H-4, 145–150	0.6	0.4	14.7	5.7	4.3	8.9	15.4	10.8	6.4	1.0	0.4
3H-4, 145–150	1.0	0.3	12.9	3.1	3.9	8.3	14.3	11.8	6.9	0.5	0.5
6H-4, 145–150	0.7	0.3	9.6	3.0	5.3	7.7	14.2	14.4	7.8	0.8	1.0
9H-4, 145–150	0.9	0.2	8.4	5.3	3.7	6.8	14.4	12.1	9.7	0.1	1.2
13X-4, 145–150	1.5	0.5	7.2	1.1	2.4	4.6	14.7	12.8	11.6	0.2	1.7
17X-1, 145–150	1.5	0.4	9.7	3.6	3.3	7.0	15.9	10.1	8.5	0.7	1.1
20X-4, 145–150	2.6	0.8	9.9	2.3	2.4	4.8	20.2	8.0	9.5	0.0	1.1
23X-1, 145–150	1.2	0.3	10.0	2.1	2.8	6.6	18.7	8.7	8.4	0.8	1.5
26X-3, 120–125	1.2	1.1	5.9	2.7	5.3	4.8	15.0	9.8	8.2	0.1	1.2
29X-6, 145–150	1.1	0.3	6.5	3.1	6.1	5.6	15.4	9.9	8.8	1.5	0.9
32X-5, 145–150	1.8	0.3	9.6	2.2	2.9	7.5	16.2	11.3	8.0	0.7	0.8
36X-5, 145–150	1.5	0.4	8.2	4.0	5.4	7.1	14.4	11.0	5.5	0.0	0.1
39X-5, 145–150	2.3	0.4	6.7	3.0	1.8	5.5	17.9	10.1	7.6	0.1	0.8
117-723B-											
42X-1, 145–150	2.1	1.0	7.0	0.5	1.2	6.8	15.7	9.6	5.8	0.1	0.5

Table 6. Amino acids and amino sugars in sediments, Site 724.

Core, section, interval (cm)	Cys (mol%)	Tau (mol%)	Asp (mol%)	Thr (mol%)	Ser (mol%)	Glu (mol%)	Gly (mol%)	Ala (mol%)	Val (mol%)	Met (mol%)	Ale (mol%)	Ile (mol%)
117-724C-												
1H-1, 145–150	0.4	0.2	18.1	6.3	3.4	7.9	12.3	8.8	5.7	0.9	0.2	3.9
117-724A-												
1H-3, 145–150	0.7	0.1	13.6	6.0	3.9	8.4	17.4	6.5	6.5	0.8	0.5	4.3
117-724C-												
2H-4, 145–150	0.8	0.2	20.7	3.4	2.2	8.7	11.2	9.6	6.6	0.8	0.5	4.2
3H-4, 145–150	0.9	0.4	13.5	4.3	3.2	6.9	17.4	5.9	8.3	1.1	0.7	4.9
117-724A-												
3H-4, 145–150	0.6	0.2	15.1	4.9	3.4	9.2	12.5	10.7	7.3	0.6	0.4	5.0
117-724C-												
4H-4, 145–150	0.6	0.3	11.7	4.0	3.1	7.7	13.8	11.0	10.5	0.7	0.4	5.7
5X-4, 145–150	0.7	0.2	14.8	2.4	4.1	9.1	13.1	10.5	8.1	0.8	0.7	5.5
117-724B-												
6X-3, 145–150	1.4	0.4	9.9	4.3	5.3	5.7	13.0	10.0	7.5	0.8	0.5	6.0
9X-4, 145–150	0.7	0.2	16.8	3.1	2.1	8.3	11.7	8.9	8.0	1.2	1.4	5.5
12X-5, 145–150	0.8	0.4	11.3	3.6	3.2	8.3	14.0	9.5	10.3	0.7	0.4	5.7
16X-4, 145–150	0.8	0.3	11.0	3.0	2.1	7.4	13.7	8.6	8.7	1.0	1.0	5.8
19X-4, 145–150	0.7	0.2	7.5	1.7	1.9	5.5	14.0	9.0	11.1	0.9	0.6	6.2
23X-3, 145–150	0.7	0.9	9.2	1.6	2.2	6.2	10.7	12.4	7.8	0.6	1.0	5.3
25X-4, 145–150	0.7	0.5	11.3	1.7	3.0	8.2	11.7	8.6	8.2	0.6	1.0	4.4

[a] HydL = hydroxylysine.
[b] MetH = methylhistidine.

range of 48–144 mg/L from interstitial waters from the North Atlantic Ocean. However, they are higher than concentrations of 6–49 mg/L found in pore waters of organic rich upwelling sediments from the Peru Margin (Seifert et al., 1990a). Even though high DOC values occur in the deeper part of Sites 723 and 724 where enhanced TOC values were found, we cannot discern a simple relationship between the amount of organic matter in the sediment and the DOC content of the corresponding pore water. These data suggest that the concentration of DOC in the pore water does not rely mainly on the abundance of organic matter in the respective sediment. We think it may be more likely related to microbial activity and associated redox zones.

Variation in the Abundance of Amino Compounds and Carbohydrates vs. Depth and Time

The amounts of amino compounds as well as their contribution to the TOC decrease strongly with time. Carbohydrates do not reveal a comparable trend, even though their contribution to the TOC is on the average lower in the deeper sections of the cores. The relatively high stability of carbohydrates in marine sediments below the upper 1.5 m was first reported by Rittenberg et al. (1963) and since then found in various marine cores (e.g., Michaelis et al., 1986; Seifert et al., 1990a, b). Another situation appears in the pore water: neither total amounts of amino acids nor of carbohydrates reveal any systematic trend

Table 5 (continued).

Ile (mol%)	Leu (mol%)	Tyr (mol%)	Phe (mol%)	β-Ala (mol%)	γ-ABA (mol%)	Orn (mol%)	Lys (mol%)	His (mol%)	Arg (mol%)	GlcN (μmol/g)	GalN (μmol/g)
3.7	6.0	2.0	3.9	0.8	1.1	1.0	6.0	1.8	5.1	1.29	0.95
4.8	7.8	1.7	4.6	1.3	2.0	1.1	6.5	2.3	4.2	0.46	0.34
4.8	7.6	1.9	4.2	1.3	2.6	0.9	6.3	2.2	3.6	1.34	0.82
5.7	8.6	2.0	4.8	1.9	1.8	1.5	6.2	2.4	2.3	0.74	0.46
7.0	10.0	2.0	4.9	2.1	1.2	1.4	8.3	2.9	2.2	0.98	0.40
4.9	7.4	2.6	4.1	2.5	1.9	1.6	7.5	3.5	2.2	0.61	0.36
4.7	6.8	1.5	3.5	3.5	2.8	2.0	9.0	2.4	2.2	0.53	0.21
4.4	7.0	2.0	3.4	3.0	5.5	1.4	6.9	3.3	1.9	0.84	0.35
4.2	6.4	2.2	3.5	3.5	7.0	3.4	9.8	3.5	1.2	0.66	0.27
5.4	7.8	2.5	4.1	3.1	1.9	2.3	6.9	4.9	1.8	0.63	0.22
3.9	5.9	2.3	3.5	3.1	3.9	1.5	7.6	4.9	2.2	0.26	0.09
4.5	6.2	1.7	3.1	3.3	3.3	4.5	9.5	3.4	2.6	0.40	0.15
4.1	5.2	1.5	2.5	5.3	3.5	2.5	10.6	5.6	3.1	0.29	0.11
4.6	7.0	2.6	3.7	4.7	2.8	3.9	11.2	6.7	2.6	0.21	0.05

Table 6 (continued).

Leu (mol%)	Tyr (mol%)	Phe (mol%)	β-Ala (mol%)	γ-ABA (mol%)	[a]HydL (mol%)	Orn (mol%)	Lys (mol%)	His (mol%)	[b]MetH (mol%)	Arg (mol%)	GlcN (μmol/g)	GalN (μmol/g)
6.2	1.4	3.8	1.1	0.8	0.3	0.5	5.6	1.4	2.2	8.3	0.39	0.29
7.0	1.2	3.7	1.1	1.5	0.4	0.9	8.1	0.9	0.4	6.1	0.67	0.55
6.5	1.7	3.8	1.6	1.9	0.4	1.6	7.6	0.8	0.9	4.2	0.50	0.40
7.9	1.2	3.8	1.5	2.0	0.3	1.3	8.4	0.8	0.0	5.4	0.55	0.32
8.0	2.0	4.2	1.1	0.7	0.3	0.5	6.2	0.6	1.3	5.2	0.60	0.28
8.4	2.0	4.5	1.4	0.8	0.3	1.4	6.8	0.8	0.0	4.3	1.33	0.64
8.6	1.9	4.4	0.9	0.6	0.3	1.0	6.3	0.6	2.6	2.8	0.44	0.23
11.8	1.6	4.5	1.3	1.3	0.5	0.4	6.5	0.9	2.3	3.9	0.27	0.11
8.4	2.1	4.5	1.7	1.9	0.3	2.0	7.0	0.6	1.3	2.3	0.59	0.28
8.8	1.4	4.3	2.3	1.7	0.3	1.0	6.9	0.7	1.5	2.8	0.64	0.29
8.9	2.4	4.7	2.5	2.4	0.4	2.6	8.3	0.7	0.0	3.7	0.68	0.31
9.2	1.8	4.6	3.2	2.2	0.6	2.0	8.5	4.5	0.0	4.3	0.50	0.28
8.4	1.6	4.2	4.3	9.3	0.0	2.9	5.9	0.4	2.8	0.7	0.44	0.19
7.2	2.1	8.3	6.7	4.5	0.0	1.0	5.3	3.7	0.0	1.4	0.20	0.10

with increasing age. However, the amino acid contribution to the DOC varies with depth. Figures 4A and B depict the portion of dissolved hydrolyzable amino acids (DHAA) in the DOC vs. depth and age. The curves yield quite different downhole patterns in Figure 4B whereas they coincide in Figure 4A: high values at about 5 m depth are followed by a relative minimum in the zone of the steepest sulfate decrease. The maximum occurs at 30–50 m depth concomitant with sulfate depletion and the initial increase of ammonia (Tables 3 and 4). These results indicate a microbial control of the DHAA concentration. Zones characterized by high microbial activity, indicated by the sharp decrease of sulfate in this case, yield low DHAA values, while the transition between sulfate reduction and methanogenesis is marked by high DHAA concentrations. In addition, the concentration pattern of DHAA suggests that microbial activity is more depth- than time-related.

Comparison of Amino Acids Contained in Interstitial Water and in the Sediment

As shown in Figures 2 and 5, there is a distinct difference between the amino acid distributions of sediment and pore water at both sites. Contributions of amino acids like glutamic acid, serine, glycine, and ornithine are high in the pore water. Valine, isoleucine, leucine, phenylalanine, and lysine represent much higher percentages of the amino acid fraction in the sediment in comparison to the interstitial water. Similar differences between these two fractions were observed in upwelling sediments from the Peru Margin (Seifert et al., 1990a). Several reasons are possible for the observed relative enrichment of distinct amino acids in the pore water: (1) different resistance of peptide bonds of the amino acid moieties against hydrolysis, (2) preferential adsorption of distinct compounds onto the solid phase, (3) selective

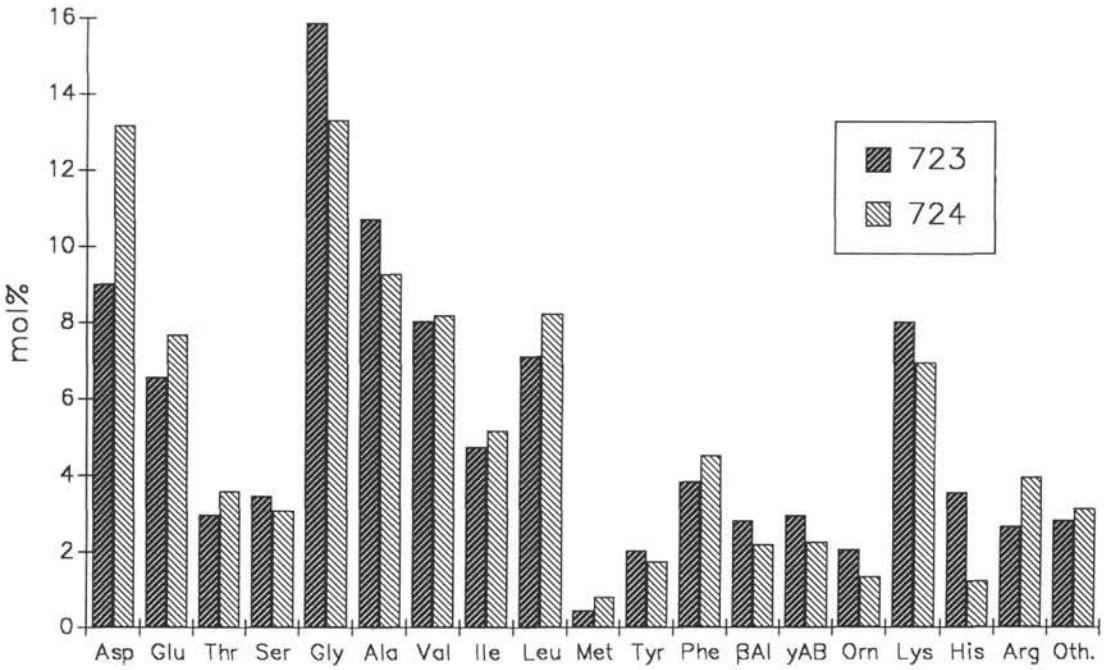

Figure 2. Average distribution of individual amino acid moieties in sediments of Sites 723 and 724. Asp = aspartic acid, Glu = glutamic acid, Thr = threonine, Ser = serine, Gly = glycine, Ala = alanine, Val = valine, Ile = isoleucine, Leu = leucine, Met = methionine, Tyr = tyrosine, Phe = phenylalanine, βAl = β-alanine, γAB = γ-aminobutyric acid, Orn = ornithine, Lys = lysine, His = histidine, Arg = arginine. Category "Others" (Oth.) includes cysteine, taurine, alloisoleucine, methylhistidine, and hydroxylysine.

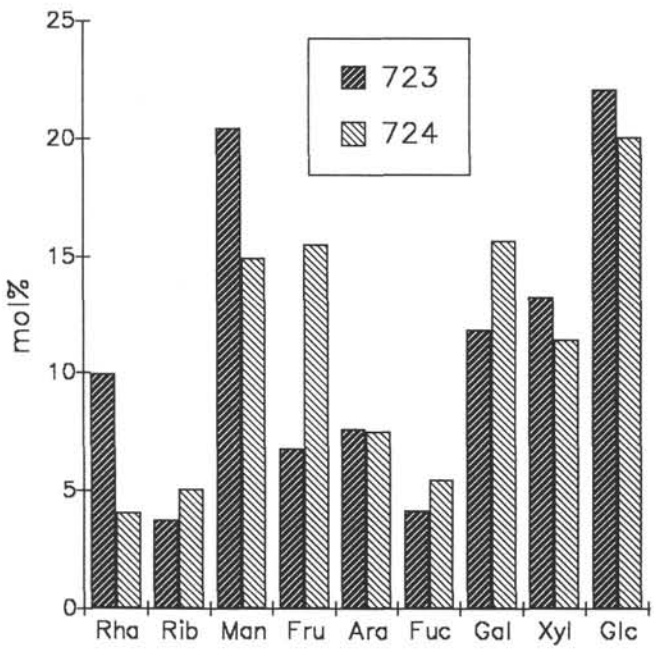

Figure 3. Average distribution of carbohydrate monomers in sediments of Sites 723 and 724. Rha = rhamnose, Rib = ribose, Man = mannose, Fru = fructose, Ara = arabinose, Fuc = fucose, Gal = galactose, Xyl = xylose, Glc = glucose.

uptake of amino acids into organic complexes, (4) chemical and biological production of amino acids during degradation, and (5) different solubility.

Relevant for the distribution of single amino acids is the difference in stability of the peptide bonds for the respective moieties. Peptide bonds adjacent to leucine, isoleucine, and valine are known to be more resistant to acid hydrolysis than are peptide linkages composed by other amino acid moieties (Bada and Man, 1980). This may be the reason of their generally low abundance in pore waters. Peptide linkages adjacent to acidic amino acids are most sensitive to acid hydrolysis (Bada and Man, 1980). This may play a crucial role for the strong decrease of acidic amino acids in the upper meters of the sediment, as observed also in several other studies (e.g., Maita et al., 1982; Burdige and Martens, 1988). The relative enrichment of glutamic acid against aspartic acid is probably caused by a higher stability of the former.

Several attempts have been made to elucidate the mechanism of selective adsorption of amino acids by minerals. Laboratory studies revealed preferential adsorption of free acidic amino acids as well as of macromolecular organic substances enriched in acidic amino acids on carbonate mineral surfaces (Jackson and Bischoff, 1971; Mueller and Suess, 1977; Carter, 1978; Carter and Mitterer, 1978). Results of Jackson and Bischoff (1971) indicate chemisorption of the β- and γ-carboxylate group instead of CO_3^{2-} ions in the crystal structure, resulting in a stable fixation of aspartic acid and glutamic acid.

Hedges and Hare (1987) studied the adsorption of 15 amino acids by H_2O_2-pretreated kaolinite and montmorillonite. They found basic amino acids to be in general preferentially adsorbed. Acidic amino acids were moderately adsorbed by kaolinite and hardly by montmorillonite. A small part of hydroxy and neutral amino acids was non-selectively removed from solution by mont-

Table 7. Carbohydrates in sediments, Site 723.

Core, section, interval (cm)	Rha (mol%)	Rib (mol%)	Man (mol%)	Fru (mol%)	Ara (mol%)	Fuc (mol%)	Gal (mol%)	Xyl (mol%)	Glc (mol%)
117-723A-									
1H-4, 145–150	8.7	4.5	17.6	4.2	8.8	8.4	15.7	12.1	20.0
3H-4, 145–150	12.1	8.1	17.3	5.7	8.6	5.3	11.7	13.4	18.0
6H-4, 145–150	12.2	8.6	15.2	8.8	7.6	6.5	13.3	7.4	20.5
9H-4, 145–150	10.4	3.0	13.5	3.8	6.4	6.1	18.1	12.7	26.0
13X-4, 145–150	12.4	1.7	21.9	4.1	5.1	7.6	17.7	11.8	17.7
17X-1, 145–150	16.0	4.4	13.5	4.5	9.0	4.2	14.8	13.3	20.3
20X-4, 145–150	8.3	3.6	24.7	9.3	7.6	5.0	10.2	13.0	18.3
23X-1, 145–150	9.8	3.4	20.0	16.2	8.8	10.0	7.8	11.3	12.5
26X-3, 120–125	15.3	5.3	18.9	2.9	6.4	2.9	11.8	14.5	22.0
29X-6, 145–150	6.3	1.6	31.5	7.2	6.4	0.0	9.5	12.9	24.5
32X-5, 145–150	5.6	2.0	23.6	13.4	8.2	0.0	8.2	15.2	23.8
36X-5, 145–150	3.4	1.0	30.1	5.7	6.7	0.0	8.8	14.5	29.7
39X-5, 145–150	14.7	4.5	11.1	2.6	9.8	2.4	7.5	18.0	29.4
117-723B-									
42X-1, 145–150	3.4	1.4	27.8	6.9	7.8	0.0	10.8	15.5	26.4

Table 8. Carbohydrates in sediments, Site 724.

Core, section, interval (cm)	Rha (mol%)	Rib (mol%)	Man (mol%)	Fru (mol%)	Ara (mol%)	Fuc (mol%)	Gal (mol%)	Xyl (mol%)	Glc (mol%)
117-724C-									
1H-1, 145–150	0.9	3.4	7.3	18.3	6.2	3.6	13.2	8.1	39.1
117-724A-									
1H-3, 145–150	1.7	1.6	6.6	49.6	5.2	0.8	5.7	5.8	23.0
117-724C-									
2H-4, 145–150	2.5	6.7	16.7	9.7	9.1	8.9	18.7	11.8	15.8
3H-4, 145–150	7.3	8.3	13.5	5.8	6.2	6.1	19.2	11.2	22.5
117-724A-									
3H-4, 145–150	4.7	4.2	19.0	9.4	7.2	6.3	18.8	13.0	17.3
117-724C-									
4H-4, 145–150	7.3	4.5	16.3	7.1	7.9	8.2	18.9	14.6	15.2
5X-4, 145–150	1.7	7.8	13.6	15.7	7.6	7.3	17.4	12.5	16.4
117-724B-									
6X-3, 145–150	2.2	6.3	15.6	9.1	7.3	7.9	20.6	12.2	18.8
9X-4, 145–150	4.0	7.8	8.9	27.0	6.0	5.1	11.5	9.0	20.7
12X-5, 145–150	4.6	4.2	11.7	17.6	6.3	6.8	17.3	14.3	17.3
16X-4, 145–150	7.0	2.7	23.9	6.2	7.3	5.7	16.7	14.5	16.0
19X-4, 145–150	5.8	3.5	22.3	10.2	8.0	4.3	15.4	11.9	17.5
23X-3, 145–150	6.3	5.2	19.6	12.5	12.5	2.7	14.0	10.9	16.2
25X-4, 145–150	1.2	4.8	14.9	19.5	8.6	2.9	12.6	10.3	25.3

morillonite. Kaolinite only weakly adsorbed hydroxy amino acids and glycine and not measurably other neutral amino acids. In contrast, Bader et al. (1960) described much higher adsorption of aspartic acid by montmorillonite than by kaolinite. This discrepancy may be related to the use of untreated minerals by Bader et al. (1960). However, adsorption on mineral surfaces should remove preferentially basic and acidic amino acids from the dissolved phase, whereby acidic amino acids have a greater affinity to carbonate minerals and basic amino acids to silicate minerals. In addition, organic material in the organic matrices of calcified and silicated skeletons as well as organic compounds intercalated (interlayer adsorbed) by montmorillonite are suggested to be protected against microbial attack (Schroeder, 1975; Theng, 1974). Thus adsorption may be a reason for the relative depletion of aspartic acid and basic amino acids in the dissolved phase (Tables 3 and 4; Figs. 2 and 5). The inverse behavior observed for the basic amino acid ornithine will be discussed below.

Investigations of Suess (1970; 1973) on the adsorption of organic compounds onto carbonates suggest that every available particle surface is covered by a monomeric organic layer. Steady state conditions adjusted within 2 hr for the adsorption of amino acids by clay minerals were found by Hedges and Hare (1987). Therefore the adsorption of organic molecules by mineral surfaces seems to be a very rapid process. Mineral surfaces of subrecent marine sediments rich in organic matter like discussed here are coated with organic material and no free active mineral surfaces may exist to remove organic matter from the dissolved phase. This indicates that amino acids produced in the sediment by degradation or microbial activity may be adsorbed

Table 9. Amino acids and amino sugars in interstitial waters, Site 723.

Core, section, interval (cm)	Cys (mol%)	Tau (mol%)	Asp (mol%)	Thr (mol%)	Ser (mol%)	Glu (mol%)	Gly (mol%)	Ala (mol%)	Val (mol%)	Met (mol%)	Ale (mol%)
117-723A-											
1H-5, 145–150	1.2	0.2	8.4	6.6	17.7	7.7	20.9	12.3	3.9	0.0	0.4
117-723C-											
2H-2, 145–150	1.1	0.1	8.2	5.7	12.9	13.0	17.9	12.3	3.4	0.4	0.5
2H-5, 145–150	0.9	0.0	7.0	4.9	12.9	15.8	17.3	14.2	5.2	0.6	0.2
3H-2, 145–150	0.9	0.0	7.2	5.1	12.9	13.6	19.3	14.2	3.6	0.2	0.2
117-723A-											
3H-4, 145–150	3.1	0.0	8.0	3.9	8.0	11.1	20.7	13.6	4.4	0.7	0.7
117-723C-											
3H-5, 145–150	1.3	0.3	6.5	4.2	16.9	8.7	17.7	12.3	4.8	0.8	0.7
4H-2, 145–150	0.0	0.0	7.7	4.3	18.4	12.5	19.6	10.6	3.8	0.5	0.0
117-723A-											
6H-4, 145–150	3.5	0.2	6.8	4.1	7.4	10.6	19.1	13.2	6.7	0.3	0.5
9H-4, 145–150	7.1	0.2	7.6	4.1	8.0	13.0	16.7	13.4	5.2	0.0	2.0
13X-4, 145–150	7.9	0.4	6.3	4.1	7.8	10.4	18.5	11.9	7.9	0.3	0.8
17X-1, 145–150	4.6	0.3	7.5	4.8	18.3	12.4	15.9	10.2	7.4	0.0	0.4
20X-4, 000–005	11.2	0.0	7.4	2.7	12.1	14.4	22.4	5.2	3.8	0.4	0.6
26X-3, 120–125	7.8	0.0	8.4	4.2	11.4	12.5	19.4	6.7	9.3	0.0	0.5
29X-6, 145–150	5.6	0.5	6.6	3.1	13.3	15.6	26.9	1.2	4.6	0.5	0.0
32X-5, 145–150	4.2	0.2	9.0	4.0	15.5	14.4	17.0	9.1	8.0	0.1	0.2
36X-5, 145–150	6.5	0.4	6.6	2.9	13.3	12.1	22.0	9.3	4.6	0.6	0.4
39X-5, 145–150	2.5	0.2	8.0	4.6	20.6	6.6	19.9	10.3	4.7	0.4	0.2
117-723B-											
42X-1, 145–150	3.6	0.7	7.1	4.8	22.8	6.0	17.5	9.0	4.1	0.3	0.2

to a minor degree and are therefore enriched in the dissolved phase.

Glycine is a decomposition product of threonine and serine by aldol-cleavage, alanine can originate from the dehydration of serine (Bada and Man, 1980). Ornithine is absent in living proteins and suggested to originate from degradation of arginine (Hare, 1969; Degens, 1970) or from constituents of bacterial cell walls (Goossens et al., 1986; Kandler, 1979; 1981). The continuous production of these three amino acids in the sediment may explain their enrichment in the dissolved phase.

Another factor assumed to be relevant for the selective stabilization of organic components is the formation of organic complexes. Adsorption of amino acids by organic matter may predominate that by minerals (Rosenfeld, 1979). High concentrations of amino acids are found in fulvic acids extracted from sediments and sea water (Nissenbaum and Kaplan, 1972; Gagosian and Stuermer, 1977). The formation of sugar-amino acid condensation products are suggested to occur in seawater or in marine sediments at weakly alkaline pH-conditions (Hedges, 1978). Sugar and amino acid rich complexes are thought to be precursors of melanoidins (Angrick and Rewicki, 1980). Laboratory experiments yield favorite incorporation of basic amino acids into melanoidins (Hedges, 1978; Rubinsztain et al., 1984). These processes may therefore reveal enhanced conservation in particular of basic amino acids and their depletion in the dissolved phase.

Despite the basic differences between the dissolved and the sedimentary fractions, a similar trend appears between the sites in each fraction. Most amino acids enriched in the sediments of Site 723 compared to the sediments of Site 724 reveal also higher percentages in the pore waters of Site 723 compared to pore waters of Site 724 (Tables 5, 6, 9, and 10; Figs. 2 and 5). This points to the existence of a direct relationship between the two fractions that is not apparent from the total concentrations of amino acids.

Comparison Between Site 724 and Site 723

Distribution patterns of amino compounds in sediments of Sites 723 and 724 reveal enrichment of acidic amino acids at Site 724 and higher contributions of non-protein amino acids at Site 723 (Fig. 2; Tables 5 and 6). Microbial degradation is suggested to enhance the concentrations of β-alanine, γ-aminobutyric acid, and ornithine. Ornithine was found in cell walls of various bacteria (Goossens et al., 1986; Kandler, 1979; 1981) and may also originate from microbial and abiotic degradation of arginine (Degens, 1970). β-Alanine and γ-aminobutyric acid are commonly thought to be microbial decarboxylation products of other amino acids like aspartic acid and glutamic acid, respectively (e.g., Vallentyne, 1964; Aizenshtat et al., 1973). According to Schroeder (1975) neither β-alanine nor γ-aminobutyric acid results from chemical degradation. Increasing contributions of these amino acids with depth as observed in sediment trap samples (Ittekkot et al., 1984a, b; Mueller et al., 1986) as well as with time in sediment cores (e.g., Aizenshtat et al., 1973; Hare, 1973; Seifert et al., 1990a, b), therefore indicate enrichment of microbially reworked organic matter.

Additional information can be obtained from the glutamic acid/γ-aminobutyric acid and aspartic acid/β-alanine ratios. Acidic amino acids are known to be preferentially associated with carbonate particles (Carter and Mitterer, 1978) and to be major constituents of the organic matrix in calcified skeletons (King and Hare, 1972; Degens, 1976; Weiner et al., 1983). Those acidic amino acids associated with the carbonate phase of the sediment are suggested to be protected against microbial attack (Schroeder, 1975). From the above discussion both sites reveal increasing portions of microbially reworked amino compounds

Table 9 (continued).

Ile (mol%)	Leu (mol%)	Tyr (mol%)	Phe (mol%)	β-Ala (mol%)	γ-ABA (mol%)	Orn (mol%)	Lys (mol%)	His (mol%)	Arg (mol%)	GlcN (μmol/g)	GalN (μmol/g)
2.1	3.3	1.7	1.6	1.3	0.1	6.2	3.1	0.0	1.4	2.98	2.35
1.7	2.4	1.7	1.4	1.2	2.7	4.5	1.9	6.5	0.6	3.65	2.18
2.0	2.4	1.7	1.4	1.0	1.6	3.4	1.6	5.4	0.3	2.99	1.71
1.7	2.6	1.7	1.5	1.0	1.9	3.0	4.0	4.6	0.8	2.99	1.84
2.0	3.1	1.6	1.6	2.7	0.9	3.8	4.0	5.4	0.7	1.19	0.75
2.4	3.6	1.9	1.7	0.9	0.4	6.8	4.1	3.3	0.8	1.60	1.10
1.8	2.8	1.4	1.1	0.7	1.0	6.4	3.5	3.1	0.9	1.31	0.86
1.7	3.2	1.2	1.1	3.0	1.7	4.4	5.6	5.1	0.5	2.86	1.84
2.3	2.9	0.8	1.1	2.1	5.9	3.7	2.2	0.0	1.7	3.55	2.31
1.5	2.3	0.8	0.6	2.4	2.0	3.5	5.4	4.7	0.5	3.90	2.52
1.3	2.2	0.9	1.7	1.6	1.8	4.7	3.6	0.0	0.5	1.88	1.57
1.6	2.8	0.8	0.9	2.2	2.8	4.2	3.3	0.0	1.1	1.28	0.96
1.3	2.2	0.8	0.9	2.6	2.2	5.1	3.8	0.0	0.8	0.59	0.35
2.1	3.7	1.4	1.9	0.9	2.7	3.7	3.9	0.0	1.8	0.80	0.57
2.1	3.3	1.2	1.4	0.9	0.8	5.2	2.7	0.0	0.6	0.39	0.37
1.7	2.8	1.4	1.3	1.3	1.0	10.2	0.5	0.0	0.9	0.19	0.13
1.9	3.1	1.7	1.2	0.8	1.1	10.2	0.3	0.0	1.5	0.27	0.12
2.1	3.2	2.0	1.8	0.5	0.5	12.3	0.5	0.0	1.1	0.00	0.00

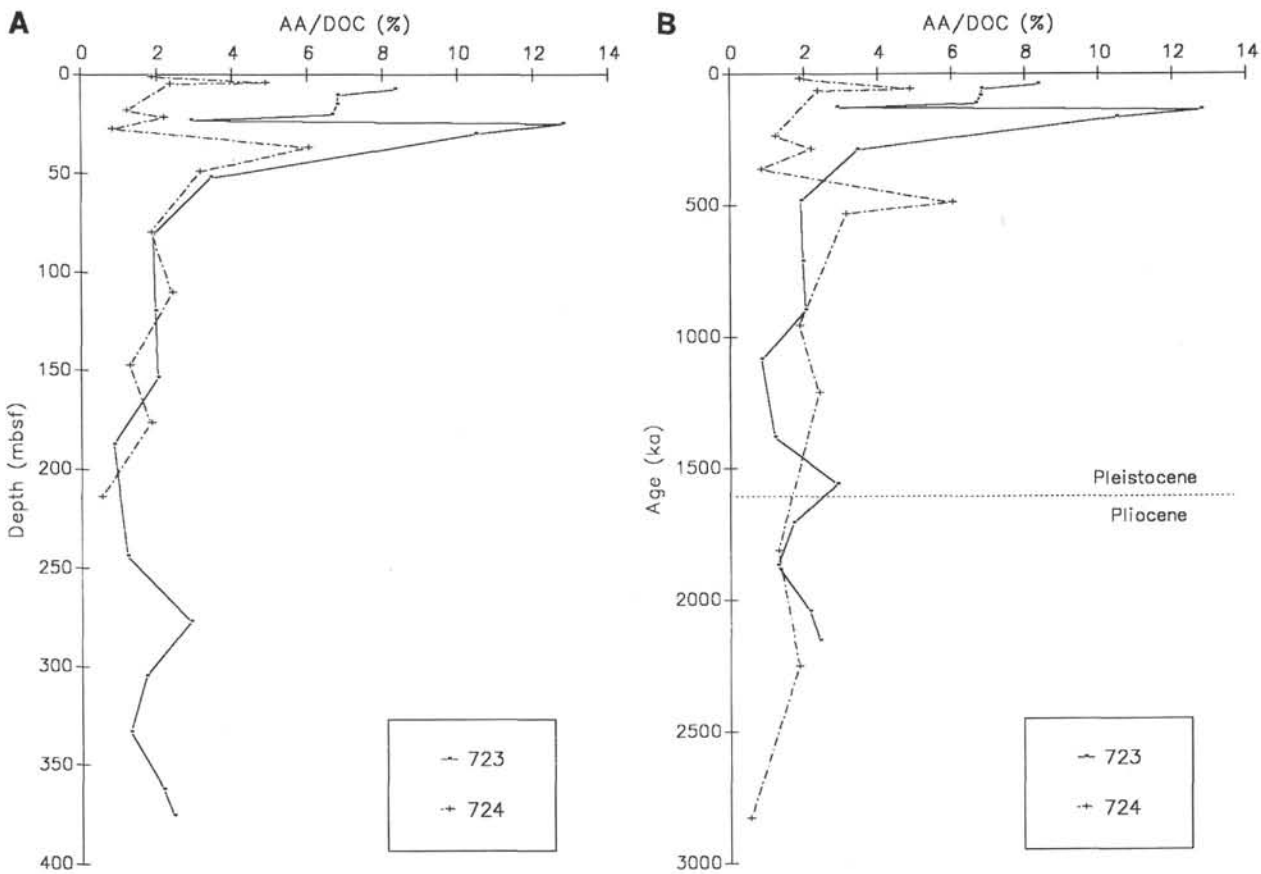

Figure 4. Contribution of dissolved hydrolyzable amino acids to the DOC (AA/DOC). **A.** Percent vs. depth. **B.** Percent vs. time.

Table 10. Amino acids and amino sugars in interstitial waters, Site 724.

Core, section, interval (cm)	Cys (mol%)	Tau (mol%)	Asp (mol%)	Thr (mol%)	Ser (mol%)	Glu (mol%)	Gly (mol%)	Ala (mol%)	Val (mol%)	Met (mol%)	Ale (mol%)	Ile (mol%)
117-724C-												
1H-1, 145–150	2.3	0.0	8.2	5.1	13.3	14.5	17.0	9.5	3.2	0.0	0.0	2.5
117-724A-												
1H-3, 145–150	0.8	0.0	9.4	6.5	7.5	14.7	13.9	9.3	5.6	0.3	0.1	4.1
117-724C-												
2H-4, 145–150	0.0	0.4	10.4	3.9	10.7	13.9	18.3	14.1	4.6	0.0	0.5	1.6
3H-4, 145–150	1.8	0.0	10.1	3.1	8.3	9.1	20.0	12.3	7.3	0.9	0.9	3.4
117-724A-												
3H-4, 145–150	1.4	0.0	9.5	4.0	12.4	16.8	19.5	7.3	4.4	1.6	0.0	2.4
117-724C-												
4H-4, 145–150	0.0	1.2	11.2	2.2	8.8	14.4	21.0	14.0	5.4	0.5	0.4	1.5
5X-4, 145–150	0.0	0.0	12.6	3.4	12.5	13.3	19.9	13.6	5.9	03	0.7	2.0
117-724B-												
6X-3, 145–150	1.9	0.0	7.8	3.7	9.2	7.4	38.1	0.0	10.8	0.0	0.0	1.2
9X-4, 145–150	0.9	0.1	10.5	3.2	7.9	8.8	22.2	7.8	5.8	1.8	3.6	3.4
12X-5, 145–150	5.5	0.0	7.6	4.4	8.0	9.7	23.8	7.6	8.2	0.4	0.6	2.2
16X-4, 145–150	5.0	0.4	7.5	3.4	12.0	15.5	18.2	11.2	4.7	0.0	0.8	2.3
19X-4, 145–150	3.9	0.4	4.9	2.6	16.2	9.7	26.7	9.7	3.4	0.0	0.5	1.8
23X-3, 145–150	7.2	0.9	6.5	2.4	7.9	12.9	13.6	12.1	7.2	0.0	0.6	2.5

down the sediment column as shown by increasing contributions of non-protein amino acids with depth (Tables 5 and 6). The average higher aspartic acid/β-alanine and glutamic acid/γ-aminobutyric acid ratios at Site 724 (6.0 and 3.4, respectively), compared to Site 723 (3.2 and 2.2, respectively) are an expression of enhanced concentrations of acidic amino acids in Site 724 (Fig. 2), probably due to higher carbonate contents.

Concerning the distribution of individual carbohydrates, rhamnose and mannose are strongly enriched in Site 723 whereas fructose, ribose, and galactose contributions are higher in Site 724 (Fig. 3). High fructose contributions are typical for the organic matter of marine sediments with enhanced terrigenous influence and/or severely diagenetically altered marine sediments (Mopper et al., 1978; Michaelis et al., 1986; Emeis et al., 1987; Seifert et al., 1990b). In recent sediments, ribose may originate from living microbiota (Klok et al., 1984; Cowie and Hedges, 1984). In older sediments as studied here, ribose appears to be associated to the carbonate. Organic-rich but carbonate-poor sediments of the Peru upwelling region from ODP Site 681 contained extremely low amounts of ribose (Seifert et al., 1990a). Therefore, we ascribe the enhanced contribution of fructose in Site 724 to higher terrigenous input and/or higher degradation of organic matter. The ribose content seems to be related to the abundance of carbonate as also revealed by comparison of lithological facies I with lithological facies III in Site 723 (see below).

Lithological Imprint on the Organic Content of the Sediment

All samples we received from Sites 724 and 723 belong to the lithological facies I, except for three from Site 723 which are taken from laminated intervals described as facies III (i.e., Samples 723A-29X-6, 145–150 cm, 723A-36X-5, 145–150 cm, and 723B-42X-1, 145–150 cm). For comparison of the two facies we excluded the latter sample for two reasons. First, it is the deepest sample investigated which makes it difficult to distinguish between time-related effects and those related to lithological variations. Second, this sample reveals unusual high TOC concentrations concomitant with extremely low amounts of amino compounds. However, the main contrast to the other samples from facies III is the low amount of amino sugars (no amino sugars could be detected in the pore water from Sample 723B-42X-1, 145–150 cm) and the high THAA/THAS and GlcN/GalN ratios (Table 1). Amino sugars are known to be less thermally stable than other amino compounds (e.g., Seifert et al., 1990b). The low amino sugar concentrations together with the downhole increase of ethane and propane observed by the shipboard party (Prell, Niitsuma, et al., 1989) may indicate enhanced thermal influence on the organic matter at depth at Site 723. Both other samples from facies III are associated upward and downward by samples belonging to facies I. In addition, the TOC values of the samples are approximately between those from the bordering samples. Both samples reveal enhanced contributions of amino compounds and carbohydrates to the TOC in comparison to the neighboring samples (Table 1).

Figure 6 depicts the mean amino acid distribution for facies I (Samples 723A-39X-5, 145–150 cm, 723A-32X-5, 145–150 cm, and 723A-26X-3, 145–150 cm) and facies III (Samples 723A-36X-5, 145–150 cm, and 723A-29X-6, 145–150 cm). There is no striking difference between the two distribution patterns, probably because the primary signal is diminished by degradation. However, the enhanced percentages of hydroxy amino acids (i.e., threonine and serine) in facies III indicate a higher contribution of biogenic siliceous material compared to facies I. Threonine and serine are known to be enriched in diatom cell walls and to be probably involved in biogenic silification (Hecky et al., 1973; Degens, 1976). Positive correlation of the concentrations of these amino acids with the amount of biogenic silica are reported from sediment trap studies (Ittekkot et al., 1984a, b; Mueller et al., 1986). The lower percentages of glycine, β-alanine, and γ-aminobutyric acid in facies III point to a minor contribution of microbially degraded organic material. Macko and Estep (1984) found that bacterial growth on glycine and glucosamine is slow compared to growth on other amino acids.

Table 10 (continued).

Leu (mol%)	Tyr (mol%)	Phe (mol%)	β-Ala (mol%)	γ-ABA (mol%)	HydL (mol%)	Orn (mol%)	Lys (mol%)	His (mol%)	MetH (mol%)	Arg (mol%)	GlcN (μmol/g)	GalN (μmol/g)
4.4	1.4	2.1	1.0	1.1	0.0	3.9	3.8	5.0	0.0	2.0	0.45	0.33
7.5	1.7	2.5	0.4	0.2	0.0	1.7	5.5	1.3	0.0	6.7	1.11	0.57
3.5	0.5	1.1	0.5	1.3	0.4	5.9	0.4	0.0	7.6	0.5	0.49	0.31
5.4	1.1	1.5	1.3	1.4	0.0	5.6	3.3	0.0	0.0	3.3	1.36	0.77
3.2	1.2	1.2	0.5	1.0	0.0	8.4	2.2	2.1	0.0	1.0	0.61	0.39
3.0	0.6	1.0	0.8	3.3	2.3	4.5	2.4	0.0	0.0	2.9	1.68	0.49
3.5	0.1	1.0	0.5	0.7	0.3	5.3	2.9	0.0	0.0	1.4	0.31	0.20
3.1	0.9	0.7	0.9	0.9	0.0	7.1	4.3	0.4	0.0	1.6	0.50	0.25
4.9	1.2	1.4	0.8	0.7	0.0	7.2	5.0	0.0	0.0	2.6	1.30	0.81
4.0	1.3	1.8	1.2	0.8	0.0	5.6	4.7	0.0	0.0	2.6	0.48	0.27
3.5	1.1	1.7	1.7	1.2	0.0	4.8	3.6	0.0	0.0	1.5	0.43	0.34
4.4	0.9	1.6	1.0	0.9	0.0	5.2	3.0	1.4	0.0	1.8	0.33	0.26
3.8	1.4	2.1	1.5	1.4	0.0	7.7	4.8	1.3	0.0	2.5	0.22	0.14

Table 11. Carbohydrates in interstitial waters, Site 723.

Core, section, interval (cm)	Rha (mol%)	Rib (mol%)	Man (mol%)	Fru (mol%)	Ara (mol%)	Fuc (mol%)	Gal (mol%)	Xyl (mol%)	Glc (mol%)
117-723A-									
1H-5, 145–150	5.9	5.4	10.8	24.1	0.0	0.0	6.4	2.3	45.1
117-723C-									
2H-2, 145–150	0.3	2.9	25.3	22.8	3.0	1.7	6.6	12.8	12.6
2H-5, 145–150	2.4	0.0	18.6	23.3	1.9	0.9	4.4	9.1	39.4
3H-2, 145–150	1.6	0.7	15.5	33.3	1.8	1.2	4.3	9.3	32.3
3H-5, 145–150	2.4	n.d.	n.d.	31.8	5.8	0.0	4.3	12.3	43.3
117-723A-									
9H-4, 145–150	7.0	14.2	11.4	8.4	4.4	7.5	12.1	9.0	26.0
13X-4, 145–150	9.7	4.4	10.1	16.9	0.9	2.2	7.1	3.7	44.9
17X-1, 145–150	9.4	10.0	12.9	15.9	0.0	0.0	16.4	5.2	30.2
20X-4, 000–005	5.0	3.1	5.2	37.5	0.0	0.0	3.6	2.6	43.1
26X-3, 120-125	5.3	23.1	18.1	9.0	0.0	0.0	6.4	2.4	35.7
29X-6, 145–150	5.3	6.7	14.4	23.9	0.0	0.0	3.9	2.8	43.0
32X-5, 145–150	4.9	0.0	22.6	18.8	0.0	0.0	8.6	4.8	40.3
36X-5, 145–150	0.0	0.0	4.2	54.4	0.0	0.0	1.0	2.0	38.4
39X-5, 145–150	1.8	0.0	22.8	19.9	3.0	0.0	5.8	14.1	32.6
117-723B-									
42X-1, 145–150	0.0	0.0	0.0	47.1	0.0	0.0	0.3	0.8	51.7

n.d. = not determined.

High concentrations of glycine and amino sugars are therefore expected in sedimentary organic material that underwent severe microbial decomposition. In addition, microbial degradation is suggested to enhance the concentrations of β-alanine and γ-aminobutyric acid as discussed above. The enhanced contribution of amino compounds and carbohydrates as well as the differences in the amino acid distributions support the interpretation of facies III type sediments as deposited under conditions of high productivity and pronounced oxygen depletion in the water column and/or at the sediment surface.

As shown in Figure 7, the main differences between the two facies with respect to the monosaccharide distribution are the enhanced mannose and the lower rhamnose, ribose, and arabinose contents in facies III. The difference in the ribose and arabinose content may be attributed to the enhanced carbonate content of facies I. The extremely high percentage of mannose is probably caused by the high contribution of degraded, microbially-derived organic material. Carbohydrates from cell walls of methanogenic bacteria are known to contain high contributions of mannose, galactose, and glucose (Kandler and König,

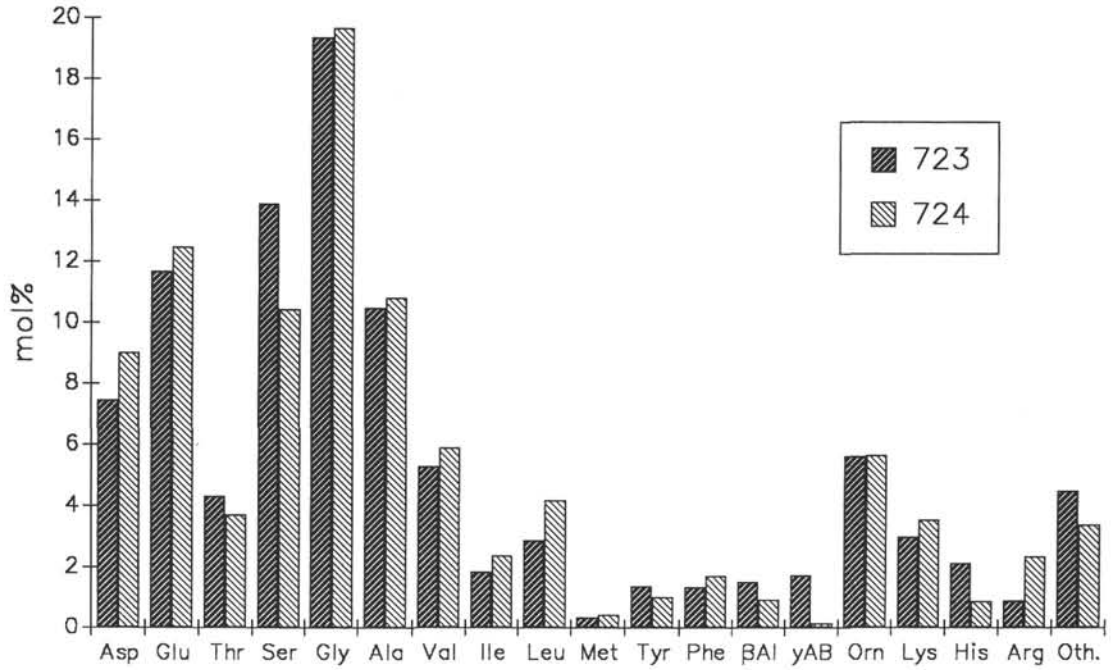

Figure 5. Average distribution of individual amino acid moieties in interstitial waters of Sites 723 and 724. Abbreviations as in Figure 2.

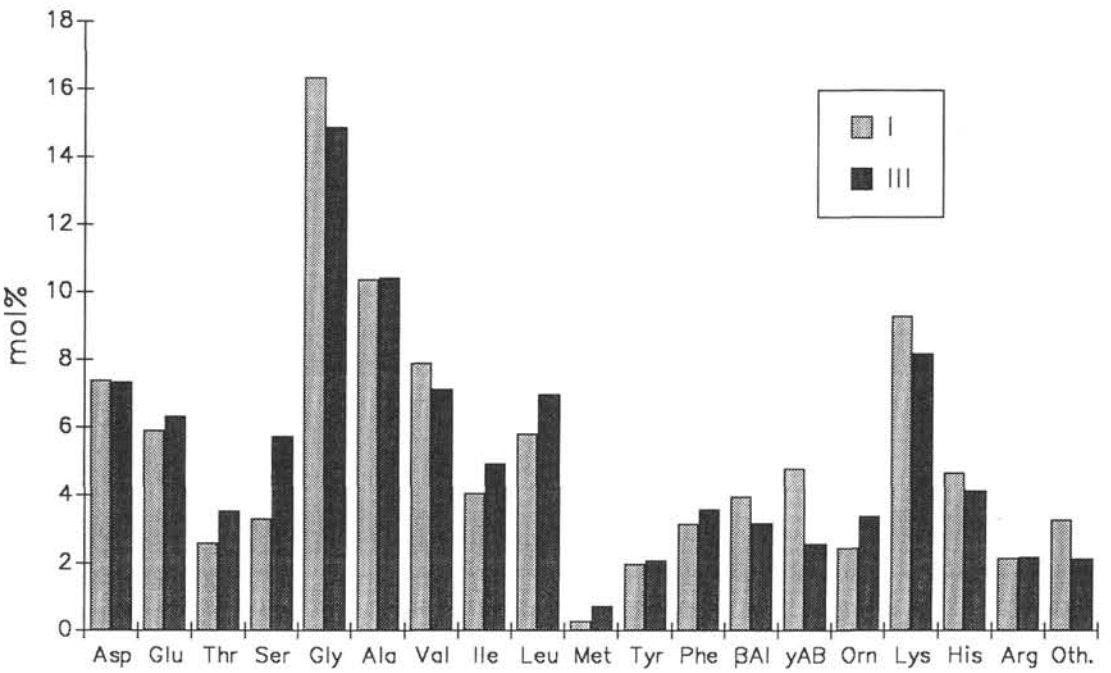

Figure 6. Average distribution of individual amino acids moieties in facies I (Samples 723A-39X-5, 145–150 cm, 723A-32X-5, 145–150 cm, and 723A-26X-3, 145–150 cm) and facies III (Samples 723A-36X-5, 145–150 cm, and 723A-29X-6, 145–150 cm), Site 723. Abbreviations as in Figure 3.

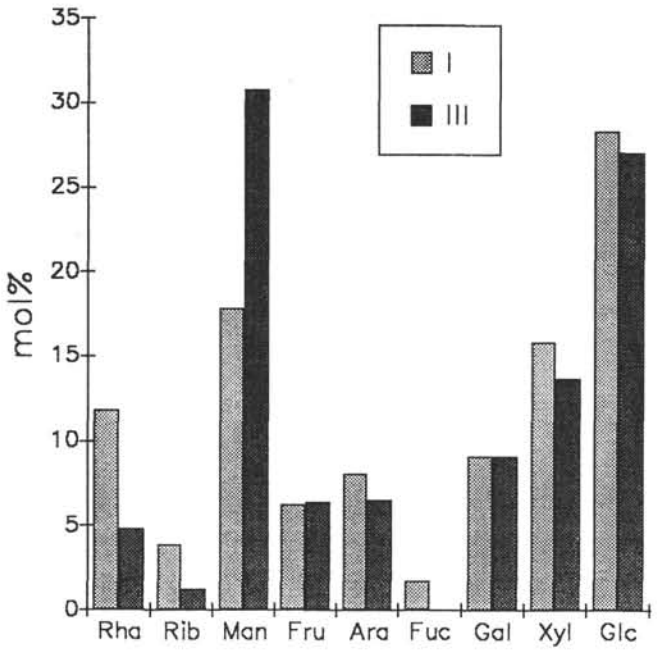

Figure 7. Average distribution of carbohydrate monomers in facies I (Samples 723A-39X-5, 145–150 cm, 723A-32X-5, 145–150 cm, and 723A-26X-3, 145–150 cm) and facies III (Samples 723A-36X-5, 145–150 cm, and 723A-29X-6, 145–150 cm), Site 723. Abbreviations as in Figure 3.

1978; Sprott et al., 1983). In addition, mannose was found to be relatively enriched in diagenetically altered marine sediments (Moers et al., 1989).

Possible Ammonia Production from Degradation of Sedimentary Amino Compounds

One striking difference between Sites 723 and 724 are the ammonia concentrations in the pore waters. Both sites reveal an increase of the ammonia content between 25 and 150 mbsf. The maximum NH_4^+ values in Site 724 are below 20 mM, while concentrations in Site 723 exceed 40 mM. To test whether these observations can be explained by the differences in the ammonia release from degradation of amino compounds, we tried to evaluate this release for both sites. Our calculations are based on the simplifying assumption that all samples have had identical contributions of amino compounds to the TOC at a certain depth. The potential ammonia release for each sample is then given by the difference between the calculated amount of nitrogen bound as amino compounds at a certain depth and the actual amount of amino compound nitrogen measured in that sample. The starting depth was chosen just above the strong increase of NH_4^+ in the pore water for each site respectively (Samples 723A-3H-4, 145–150 cm, and 724C-5X-4, 145–150 cm). The results are shown in Figure 8. All amounts are given per liter of pore water calculated using the physical properties of sediment measured by the shipboard party. Depicted are the calculated ammonia release by the degradation of amino compounds (N from THAC) and the NH_4^+ increase in the pore water (NH_4 in PW) applied to the above defined starting depth. It appears that the differences of the NH_4^+ concentrations between the sites are explicable by the respective degradation of amino compounds. In addition, it seems possible to refer the total NH_4^+ in the pore water to the degradation of amino acids and amino sugars, even when a considerable amount of NH_4^+ is adsorbed on sediment solids as indicated by the study of Mackin and Aller (1984).

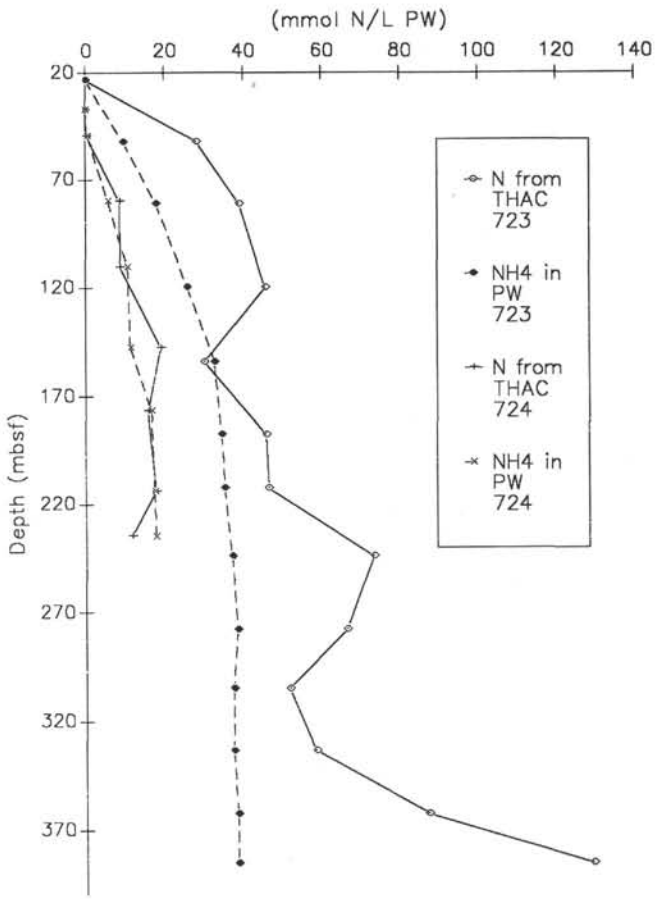

Figure 8. Calculated ammonia release by the degradation of amino compounds (N from THAC) and the NH_4^+ increase in the pore water (NH_4 in PW).

CONCLUSIONS

Total amounts of DOC and concentrations of dissolved amino compounds and carbohydrates seem to be not directly related to the TOC abundance in the sediment but more likely are related to zones of microbial activity.

Distributions of monomeric amino acids and monosaccharides reveal general differences between pore water and sediment. Amino acid distributions are assumed to be related to: (1) different stabilities against biological and chemical degradation, (2) enrichment of amino acids linked by peptide bonds relatively stable against acid hydrolysis in the sediment, (3) selective adsorption, (4) production of distinct compounds during degradation, and (5) different solubility.

Fructose and glucose are the dominant carbohydrates in the pore water as reported earlier for dissolved carbohydrates in seawater and interstitial water, as well as for very degraded sediments. Carbohydrates in the sediments yield average compositions with high contributions of glucose, mannose, galactose, and xylose. Rhamnose, ribose, arabinose, fucose, and fructose concentrations are above 4 mol%.

Comparison of the amino compounds and carbohydrates in Site 723 and Site 724 indicate a higher degree of degradation prior to fixation in the sediments of Site 724 which may be related to enhanced terrigenous influence. Microbial degradation products are more abundant in the organic matter of Site 723.

Lithologically distinct facies in Site 723 are characterized by differences in the organic matter contribution in samples older

than 1.2 m.y., even though the signal encoded in the investigated organic substances is presumed to be diminished by degradation. Laminated horizons yield enhanced contributions of amino compounds and carbohydrates to the TOC. Monomeric distributions indicate minor contributions of microbially degraded material combined with increased amounts of biogenic siliceous material in this lithological facies. Differences in carbonate content are mirrored in the carbohydrate spectra.

Calculations of the nitrogen release by degradation of amino compounds with depth at the sites show that variations in ammonia concentrations of pore water are probably caused by the degradation of amino compounds in the sediment.

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