Depth profiles of amino acids in porewater of sediments from the Norwegian - Greenland sea

Amino acid
Porewater
Oxic sediment
Norwegian-Greenland Sea

Acide aminé
Eau interstitielle
Sédiment pélagique
Mer de Norvège et de Groenland

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ABSTRACT

Dissolved free amino acids (DFAA) and dissolved combined amino acids (DCAA) were determined in the porewater of sediment cores from the Norwegian-Greenland Sea (water depth from 1000 to 3300 m). Concentrations in the sediment column were generally found to decrease with depth. The amino acid composition of DFAA and DCAA was remarkably constant. The relative contributions of acidic amino acids decrease with depth, however. Composition patterns for samples for water depth 1000-2000 m and for deep-sea samples (water depth > 3000 m) show characteristic differences. Some secondary concentration maxima several centimeters below the sediment-water interface are found, probably related to the bioturbation activity of benthic macrofauna.

RÉSUMÉ

Acides aminés dans l'eau interstitielle des sédiments de la mer de Norvège et de Groenland

Les acides aminés dissous libres (DFAA) et les acides aminés dissous combinés (DCAA) ont été déterminés dans l'eau interstitielle des sédiments de la mer de Norvège et de Groenland (profondeur d'eau entre 1000 et 3300 m). Leurs concentrations dans la colonne sédimentaire décroissent avec la profondeur. La composition des DFAA et DCAA reste remarquablement constante pour la plupart des acides aminés sauf la contribution des acides aminés acidiques, qui décroît avec la profondeur. La composition en acides aminés des sédiments (profondeur d'eau entre 1000 et 2000 m) et des sédiments profonds (profondeur d'eau > 3000 m) diffèrent de manière caractéristique. Quelques maxima secondaires de concentration ont été trouvés à plusieurs centimètres au-dessous de l'interface eau-sédiment, influencés probablement par l'activité de la macrofaune benthique.

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INTRODUCTION

Amino acids in marine sediments have been analyzed quite frequently in order to study the diagenesis of organic matter (Dungworth *et al.*, 1977; Maita *et al.*, 1982; Gonzalez *et al.*, 1983). Individual compounds such as amino acids are more informative for the understanding of diagenetic processes than broader parameters such as total organic carbon (TOC). Amino acids constitute an important fraction of labile organic nitrogen, and must be expected to be closely linked to early diagenesis mediated by biological processes.

In the sediment, diagenetic processes mainly take place in the porewater, since chemical reactions are likely to occur in the liquid phase or at solid-liquid boundaries. In order to model the oxidation of organic matter, porewater depth profiles of various (inorganic) oxidants and oxidation products have been analyzed (Froehlich *et al.*, 1979; Bender

and Heggie, 1984). Organic compounds, including amino acids, also have been measured in porewaters.

Investigations of amino acids in porewater have been undertaken mainly in coastal waters (Henrichs and Farrington, 1987; Burdige and Martens, 1990), estuaries (Jørgensen *et al.*, 1980), and some special environments such as salt marsh soils (Gardner and Hanson, 1979), mangrove forests (Stanley *et al.*, 1987), and fjords (Jørgensen *et al.*, 1981). There are only few data available on amino acids in porewater of deep-sea sediments. Data have been reported for two samples of the Peruvian upwelling zone at water depths of 1428 and 5300 m (Henrichs *et al.*, 1984), and for a sample taken at 4200 m water depth east of the Gulf of Maine (Henrichs and Farrington, 1979). In these anoxic sediments, concentrations of total dissolved free amino acids (DFAA) varied between 3 and 50 µmol* l^{-1}, glutamic acid, glycine and alanine being the most abundant. Also, non-protein amino acids such as ß- glutaric acid and ß-alanine were detected in some of the subsamples. ODP-samples from the Panama Basin (water depth approx. 3400 m) were analyzed for amino acids by Kawahata and Ishizuka (1993). In these anoxic sediments they found concentrations of 0.18-2.1 µmol*g^{-1}, 0.87- 6.9 µmol*l^{-1}, and 0.92-9.2 µmol*l^{-1} for sediment, porewater DFAA, and porewater dissolved combined amino acids (DCAA), respectively (obviously due to a typing error they use mmol instead of µmol in their text, but figure captions are in µmol). The composition pattern of amino acids is rather similar to that of the Peruvian-samples, dominated more or less by the same amino acids and also containing non-protein amino acids.

It has been shown that even in deep-sea sediments biologically mediated diagenetic activity is triggered by seasonal variations in the supply of sedimentary matter (Smith and Baldwin, 1984). In oxic and suboxic sediments, the seasonal variation in the activity of benthic macrofauna (also influencing microbial activity) can possibly be reflected in depth profiles of porewater constituents.

In an attempt to detect general features and relations in oxic and suboxic sediments from greater water depths, concentrations of free and combined amino acids in porewater were measured in numerous cores from samples in a well defined larger region of the ocean in the present study. Sampling was done in the research area of the German Joint Research Program SFB 313 in the Norwegian-Greenland Sea, an area dominated by sediments which are oxic or suboxic at the surface. Disturbances of the normally rather smooth profiles in certain sediment depth and apparently seasonal variations in concentrations are discussed and related to benthic activity.

Experimental

Samples were collected from the Norwegian-Greenland Sea during cruises 128, 137 and 142 of R.V. "Poseidon" in June 1986, February 1987 and November 1987, respectively, and during cruise no. 2 of R.V. "Meteor" in June/July 1986. Figure 1 shows the sample locations, Table 1 lists the sample stations. At two sites (H and Z), samples were taken repeatedly in hours and also at intervals of several months to study the influence of different annual seasons on amino acid composition. Site Z is located on the Voering Plateau at 1430 m water depth and was repeatedly sampled during the program. Site H is on the continental ridge at about 1000 m water depth, where the sediment record possibly includes contributions from lateral advection. Water depths at the sampling stations ranged from 950 m on the Norwegian continental slope to 3300 m in the Lofoten Basin.

Sediment samples were taken using a box-corer (50×50 cm surface area, Wuttke Comp., FRG). Subsamples were taken with polyacrylic tubes (10 cm in diameter). The cores (30-40 cm in length) were cut into

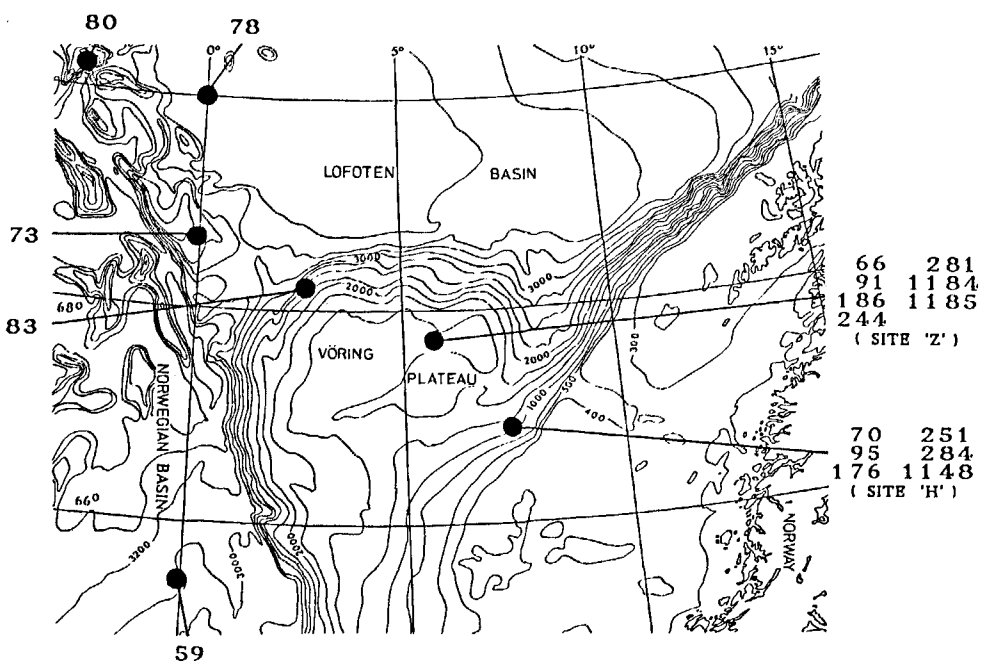

Figure 1

Map of the research area in the Norwegian-Greenland Sea. Sampling sites are indicated by station numbers. Numbers 59 to 95 refer to cruise 2 of R.V. Meteor, numbers 176 and 186, 244 to 284, and 1148 to 1185 refer to cruises 137, 128, and 142, respectively, of R.V. Poseidon.

slices of 0.5 to 2 cm thickness from which the porewater was squeezed. A device was used that allowed for simultaneous squeezing of 12 to 18 samples and on-line filtration of the porewater through 0.4 µm membrane filters. The pressure applied (nitrogen gas) did not exceed 1.5 bar. The device for porewater recovery is described elsewhere and proved to be comparable to centrifugation (Mintrop, 1990). The whole procedure was carried out at close to *in situ* temperature (1-2°C).

Aliquots of the porewater were taken for hydrolysis to determine dissolved combined amino acids (DCAA). The remaining sample was deep-frozen after poisoning by addition of $HgCl_2$ (1 µg per cm^3). The squeezed sediment "cakes" were also stored frozen.

Hydrolysis was carried out on board ship. Concentrated hydrochloric acid (suprapur, Merck, FRG) was added to the porewater sample to give a final concentration of 6 mol*l^{-1}. Ampoules were sealed under nitrogen gas and heated to 110°C for 24 hours. The method for HPLC-analysis of amino acids is described elsewhere (Mintrop, 1990; Wenck *et al.*, 1991). Briefly, amino acids in the porewater samples were treated with o-phthaldialdehyde in an alkaline borate or citrate buffer to obtain derivatives which were separated on a C-18 reversed-phase column and detected and quantified fluorimetrically. The hydrolysates were treated in the same manner as the porewater samples after they had been dried in a vacuum centrifuge (Speedvac, USA) and taken up with ultrapure water. The sediment samples were freeze dried, weighted into ampoules and hydrochloric acid (diluted to 6 mol*l^{-1} with ultrapure water) was added. Hydrolysis was carried out in the same fashion as for porewater samples and the residual sediment was removed by centrifugation before drying. The whole procedure was controlled by analysis of blanks and standards (Amino acid hydrolysates # AA 2161, AA 6282, AA 6407 from SIGMA, USA).

Table 1

List of sample positions, date of sampling and water depth.

Station	Depth (m)	Position	Site	Date
244	1429	67°39'N 5°48'E	Z	26 May 86
281			Z	04 Jun 86
66			Z	24 Jun 86
91			Z	30 Jun 86
186			Z	14 Feb 87
1184			Z	06 Nov 87
1185			Z	06 Nov 87
251	970	67°0'N 7°45'E	H	25 May 86
284			H	04 Jun 86
70			H	25 Jun 86
95			H	01 Jul 86
176			H	09 Feb 87
1148			H	31 Oct 87
59	3062	65°31'N 0°7'W	-	22 Jun 86
61	1245	67°43'N 5°55'E	-	23 Jun 86
73	2251	68°42'N 0°14'W	-	26 Jun 86
78	3294	70°0'N 0°4'W	-	27 Jun 86
80	2133	70°16'N 3°22'W	-	28 Jun 86
83	2390	68°14'N 2°33'E	-	30 Jun 86
89	1289	67°47'N 6°0'E	-	30 Jun 86
185	601	67°16'N 8°43'E	-	13 Feb 87
256	1246	67°5'N 7°30'E	-	28 May 86
258	1250	67°44'N 5°56'E	-	29 May 86
276	1700	68°0'N 2°40'E	-	01 Jun 86
1161	1286	67°47'N 6°6'E	-	01 Nov 87
1197	1700	68°1'N 2°41'E	-	07 Nov 87
1217	2179	72°34'N 10°28'W	-	07 Nov 87

RESULTS

Depth profiles of amino acid concentrations

Dissolved combined amino acids (DCAA)

A general feature in all cores is the mostly exponential decrease of DCAA concentrations calculated as the difference of total hydrolyzable (THAA) and dissolved free amino acids (DFAA) with depth. Figures 2*a* and 2*b* show the values from a number of cores obtained at sites Z and H, respectively. The sum of concentrations of DCAA in porewater ranged from 75 to 15 µmol*l^{-1} at the sediment-water interface and from 20 to 4 µmol*l^{-1} below 20 cm sediment depth. In several cores, subsurface maxima were observed at depths between 6 and 12 centimeters [*c.f.* st. 186, 1184 (site Z) and 95, 176 (site H)]. Excluding the secondary maxima, the general shape of the concentration profiles of DCAA remains more or less constant throughout the season. Slightly elevated DCAA concentrations were found at site Z at the end of June and high values in the top centimeter at site H at the beginning of July. It is reported that fresh material (recognized by high chlorophyll content) had reached the sediment surface of site H but was not found at site Z at the time of sampling (Gerlach *et al.*, 1987).

Dissolved free amino acids (DFAA)

Like the DCAA, DFAA concentrations generally show an exponential decrease with depth. Figures 3*a* and 3*b* show the values from cores obtained at stations Z and H, respec-

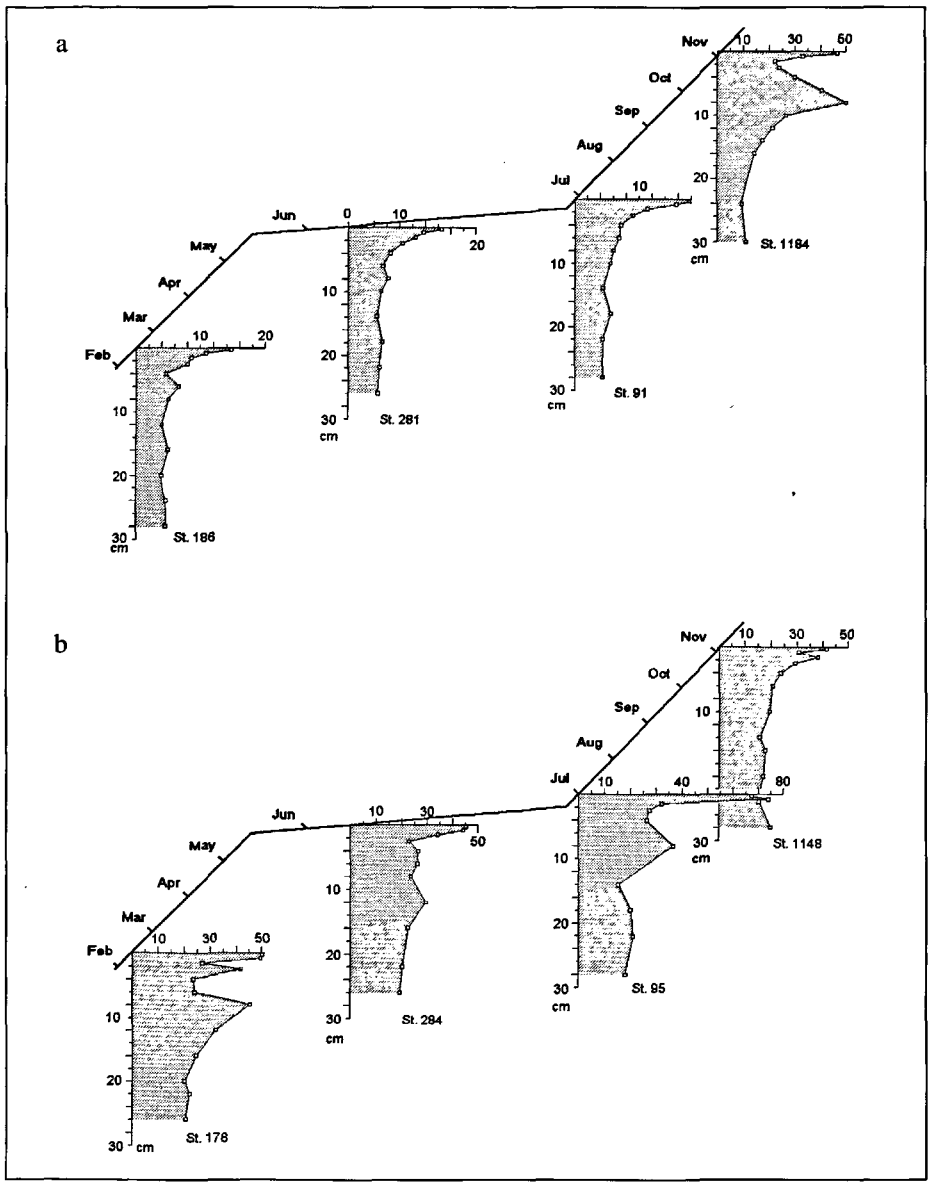

Figure 2

Depth profiles of the sum of DCAA concentrations at different seasons; site Z (a) and site H (b). Concentrations are given in µmol·l^{-1} (Note different scale for st. 1184).

tively, and Figure 3*c* shows the profiles from several further stations (see Fig. 1 for locations). Concentrations range from 6 to 11 µmol*l^{-1} and from 1 to 6 µmol*l^{-1} at the surface and at 20 cm sediment depth, respectively. Some samples show secondary concentration maxima (up to 20 µmol*l^{-1}) of DFAA in deeper sediment layers similar to the situation for DCAA (*cf.* st. 73, 80, 91, 176, 244, 281, 284, 1148, 1184, 1185). Regarding the season of sampling, the May and June depth profiles look rather similar for each site (st. 244, 281, 66, 91 and 251, 284, 70), whereas the surface concentrations at st. 95 (site H) are elevated. Values at site Z (st. 186) in February are very low and approach those found for the deepest samples (> 3000 m, st. 59 and 78). The October/November profiles show concentration maxima in the 4-8 cm range. This is considered to be significant, taking into account that the sample st. 1184 was recovered with the box-corer and sample st. 1185 by means of a gravity corer at the same nominal position on the same day and that both samples show similar profiles.

Composition of the amino acid fractions

DCAA composition

The spectrum of DCAA is practically constant along the depth profiles (Fig. 4). The only change was a slight decrease in the relative contribution of the acidic amino acids, aspartic (asp) and glutamic acid (glu). Representative examples, st. 281 and st. 1148, are shown in Figure 4 but the other profiles were similar and are not presented here. There was no evidence of any influence of the date of recovery on amino acid composition. Table 2 shows the compositions for the two sites H and Z.

DFAA composition

The spectrum of individual amino acids for DFAA indicates only minor variation along the sediment column as was also observed for DCAA (*see* above). Figure 5 shows st. 1185 (*a*) and st. 95 (*b*) as examples. Only the acidic amino acids asp and glu decrease significantly with depth

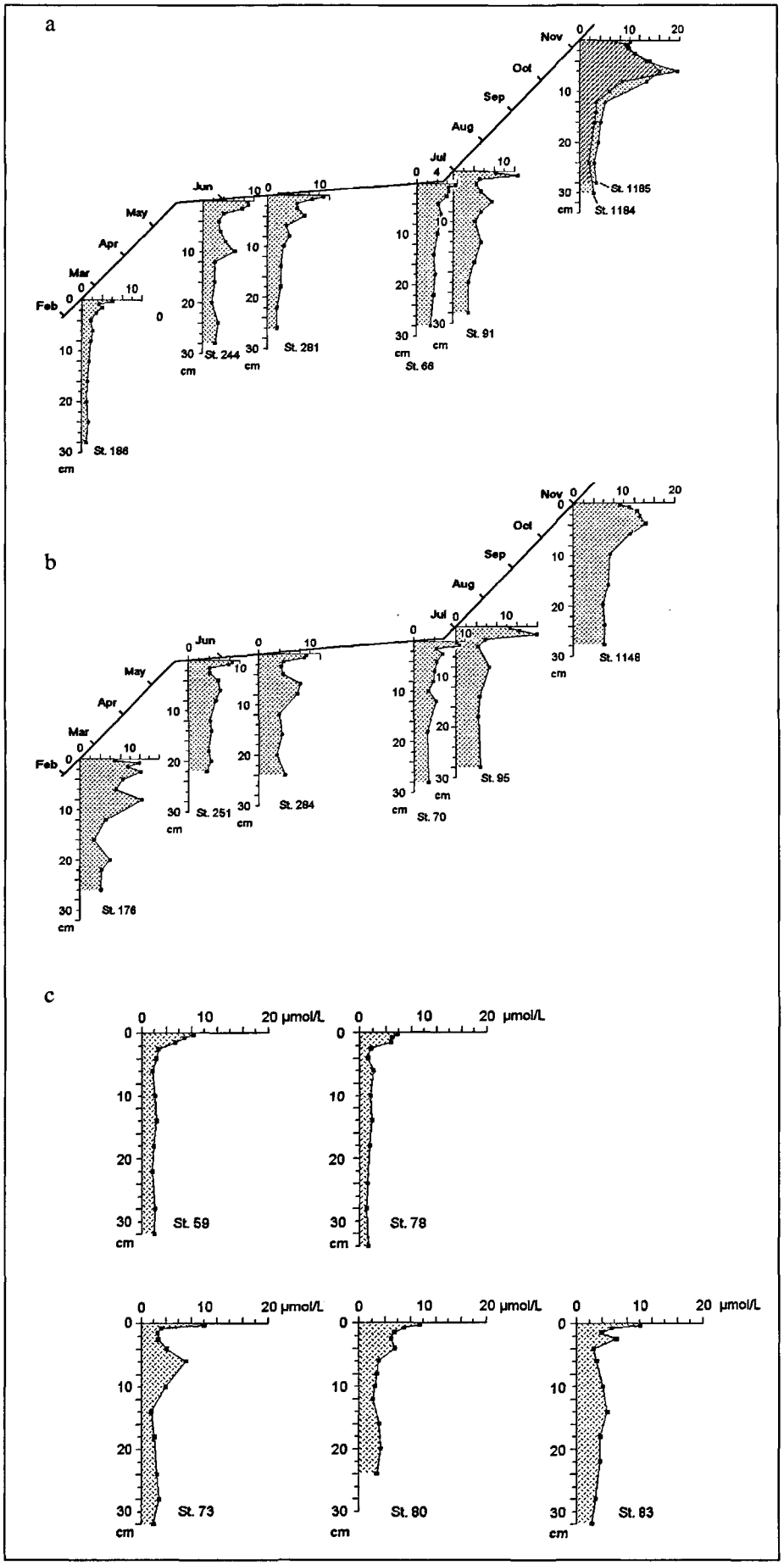

Figure 3

Depth profiles of the sum of amino acid concentrations in DFAA at site Z (a), at site H (b) and five further stations (c, see Fig. 1 for positions). Concentrations are given in µmol·l^{-1}.

Table 2

Molar percentages of individual amino acids in DCAA and DFAA. Mean values of all depth intervals from 4 cores each of sites Z and H (sampled at different seasons; sites Z: st. 91, 186, 281, 1184; site H: st. 95, 176, 284, 1148) and mean values and relative standard deviation for all depth intervals (n = 94) from these 8 cores. For DFAA also the mean values and relative standard deviation of the depth intervals from a total of 28 cores (n = 323) are presented (see Fig.1 and Table 1 for locations.)

	DCAA[1], molar comp. (%)			DFAA[2], molar comp. (%)			
Aminoacid	**Site Z**	**Site H**	**Sites Z + H**	**Site Z**	**Site H**	**Sites Z + H**	**all stations**
asp	9.3	9.8	9.5 ±2.2	6.7	8.4	7.5 ±1.3	8.3 ±1.9
glu	14.5	14.6	14.5 ±2.3	11.5	12.9	12.2 ±3.1	13.4 ±5.5
ser	10.6	11.8	11.2 ±1.5	15.3	14.8	15.0 ±3.8	14.1 ±4.4
his	1.0	1.3	1.2 ±0.5	1.5	1.8	1.6 ±0.6	1.5 ±0.9
gly	22.4	20.72	1.5 ±2.0	13.3	12.11	2.7 ±2.6	15.2 ±4.4
thr	4.4	5.9	5.2 ±1.2	3.8	4.3	4.1 ±0.6	3.8 ±0.7
ala	10.4	11.6	11.1 ±1.7	12.5	9.2	10.8 ±3.6	11.4 ±3.9
arg	3.7	3.5	3.6 ±0.7	4.8	3.7	4.3 ±1.2	3.8 ±1.5
tyr	2.9	2.4	2.6 ±1.3	3.3	3.1	3.2 ±0.9	3.0 ±1.0
val	4.4	6.1	5.3 ±1.9	5.5	6.8	6.2 ±1.3	6.2 ±2.0
met	1.7	0.5	1.1 ±0.8	0.8	1.0	0.9 ±0.3	0.8 ±0.4
ile	3.7	2.9	3.3 ±0.7	5.9	6.3	6.1 ±0.6	5.8 ±2.0
phe	3.1	2.6	2.8 ±0.6	6.0	6.6	6.3 ±2.0	4.8 ±2.1
leu	5.4	5.2	5.3 ±0.8	5.5	6.4	6.0 ±1.3	5.6 ±1.5
lys	2.4	1.0	1.7 ±0.8	3.6	2.6	3.1 ±1.4	2.4 ±1.4

[1] The values for asp and glu typically decrease from ca. 15 % at the sediment top to ca. 8 % at 30 cm sediment depth (asp), anf from ca. 17 % to ca. 12 % (glu) respectively.

[2] The values for asp and glu typically decrease from ca. 12 % at the sediment top to ca. 5 % at 30 cm sediment depth (asp), and from ca. 16 % to ca. 5 % (glu), respectively.

in most of the samples. Also the molar contribution (in %) for any given amino acid is similar in DFAA and DCAA fractions (Table 2). The two sites with water depths exceeding 3000 m (Figure 5, *c,d*) are quite different, however, in respect of the depth profiles for some amino acids, especially glu. Figure 6 presents a scatter plot of the relative contribution (mol %) for three selected amino acids [asp, glu, glycin (gly)]. Data for samples collected at 28 stations during different seasons have been combined (the mean values for each depth horizon are connected by the solid line). For purposes of comparison, values for the two deepest stations (59 and 78) are marked by filled squares in Figure 6 and the averages are connected by a hatched line. Obviously, they show a different depth profile for asp and especially glu, but not for gly (6c) and the other amino acids, which are not shown here. The molar percentage for asp at these two stations is somewhat higher than for the other stations, and is accompanied by a steeper gradient in the upper two centimeters. Glu values are significantly higher at greater sediment depth, with a relative decrease towards the surface in the upper two centimeters.

DISCUSSION

Amino acids in sediment and porewater

Despite physico-chemical alterations of sediment organic matter occurring on time scales measured in hundreds of thousands of years, which will not be considered here (race-

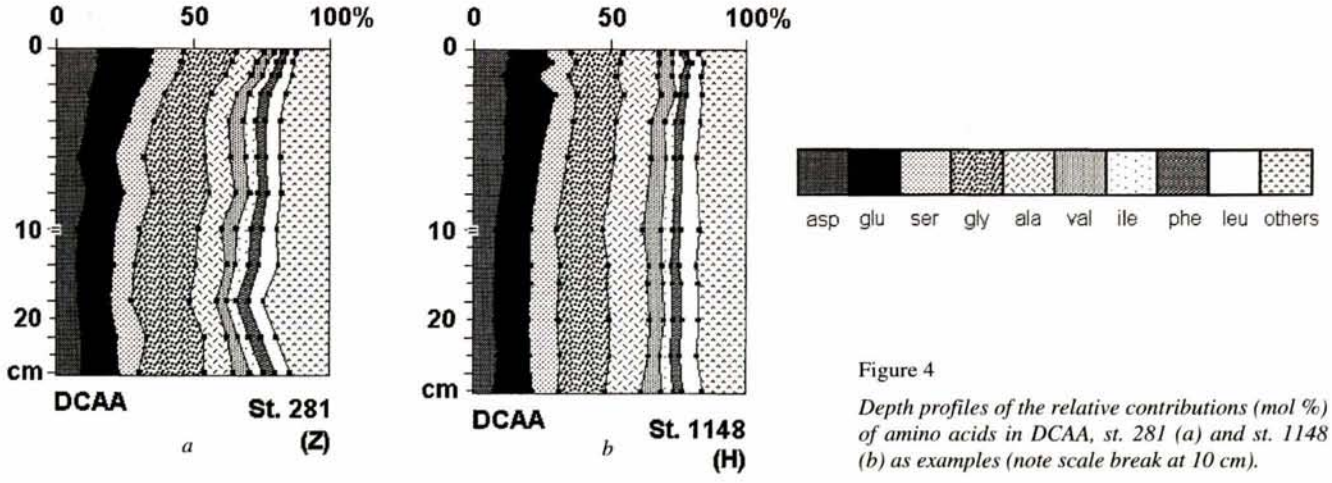

Figure 4

Depth profiles of the relative contributions (mol %) of amino acids in DCAA, st. 281 (a) and st. 1148 (b) as examples (note scale break at 10 cm).

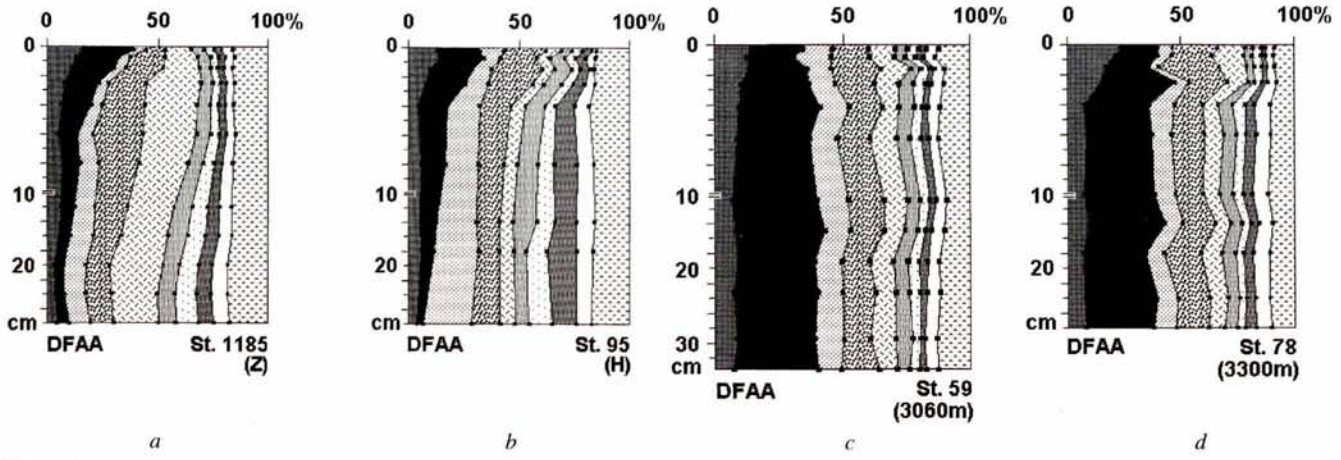

Figure 5

Depth profiles of the relative contributions of amino acids (mol %) in DFAA, st. 1185 (a), st. 95 (b), st. 59 (c) ans st. 78 (d) as examples (note scale break at 10 cm).

mization of amino acids, formation of kerogens, etc.), the chemical reactions in sediments are predominantly biologically mediated. In these processes, microorganisms (mainly bacteria) play a key role. This holds true for all types of sediments, whereas in cases where the sediment is not completely anoxic, the activity of benthic macrofauna can significantly contribute to the reactions in deep-sea sediments: (i) sediment particles and adhering microorganisms are mixed by bioturbation activity; (ii) some animals construct burrows and tube systems, thereby creating specific microhabitats for bacteria (Aller, 1984); (iii) water (together with dissolved nutrients and oxygen) is exchanged vertically between different sediment horizons by bioirrigation (pumping) (Emerson *et al.*, 1984). Although it cannot be generally claimed that numbers and activities of bacteria are higher in oxic than in anoxic sediments, the diversity of bacterial metabolism certainly is greater in the former type.

The amino acid concentrations in porewater at the sediment surface exceed those in the overlying seawater by one or two orders of magnitude (Mintrop, 1990). Thus a net diffusive flux from the sediment into the sea water must take place. The liberation of dissolved amino acids from organic matter in the sediment must compensate for (i) the diffusive transport of DFAA and DCAA into the water column; (ii) loss by mineralization of amino acids into inorganic nitrogen compounds; and (iii) the incorporation into biomass.

We still have very limited knowledge about the different pathways of particulate organic nitrogen remineralization and the specific role that the two fractions of dissolved amino acids (DFAA and DCAA) play in this context. As pointed out by Jørgensen *et al.* (1980), amino acids in porewater may have numerous sources and sinks. These include excretion and incorporation by living organisms, release from the intracellular pool of bacteria, microbial uptake, utilization and exudation by algae, physicochemical adsorption and abiotic chemical transformation (dehydration, racemization, etc.). Therefore, amino acids can be recycled several times before they finally end up as inorganic nitrogen or macromolecular humic substances.

For these reasons, the calculation of fluxes from amino acid concentrations requires further information that is at present unavailable. Calculations from concentrations of inorganic ions which are considered as educts and products of diagenesis (and by this, a distinct diagenetic pathway is defined), and from their sediment diffusion coefficients cannot be applied here. The reason is that amino acids and especially DCAA (for which we do not even know the molecular size, since this fraction is only operationally defined) do not behave like inorganic ions. Amino acids by their physicochemical properties are more likely to be affected by sorption including chemical binding to organic films due to lipophilic interaction. The bioturbation of the sediment by macrofauna has to be considered for our samples. This adds another complicating factor, since this activity is normally included in the calculations by defining an effective diffusion coefficient, which is unknown for amino acids.

Seasonality of porewater concentrations

Measuring the concentration of amino acids in porewater only permits comparison of the relative magnitude of the "pool" of a class of organic substances in various depth horizons and, possibly, the seasonal variation of its size, without providing information about "reactivity", *i.e.* availability to biological processes, or about turnover rates.

Nevertheless, regarding the concentrations measured, a seasonal variation becomes obvious, indicating that either the "filling" or "draining" rate (or both) of the "pool" varies seasonally. The winter values of site Z for all depth horizons are rather low (st. 186). The fact that the corresponding sample from site H does not show these low values may be due to effects such as downslope transport and mixing of fresh material during winter storms, what has been observed for this location (Blaume, 1992), with consequent enhancement of macrofaunal and/or microbial activity.

Summer values are considerably higher, though, unfortunately, we do not have samples of the main sedimentation period, except at st. 95, where new material has already arrived at the sediment surface. In late autumn (st. 1184/1185), rather high concentrations were encountered. We believe that these higher values represent the remains of enhanced productivity triggered by the main autumn sedimentation, which occurs in this area in July/August

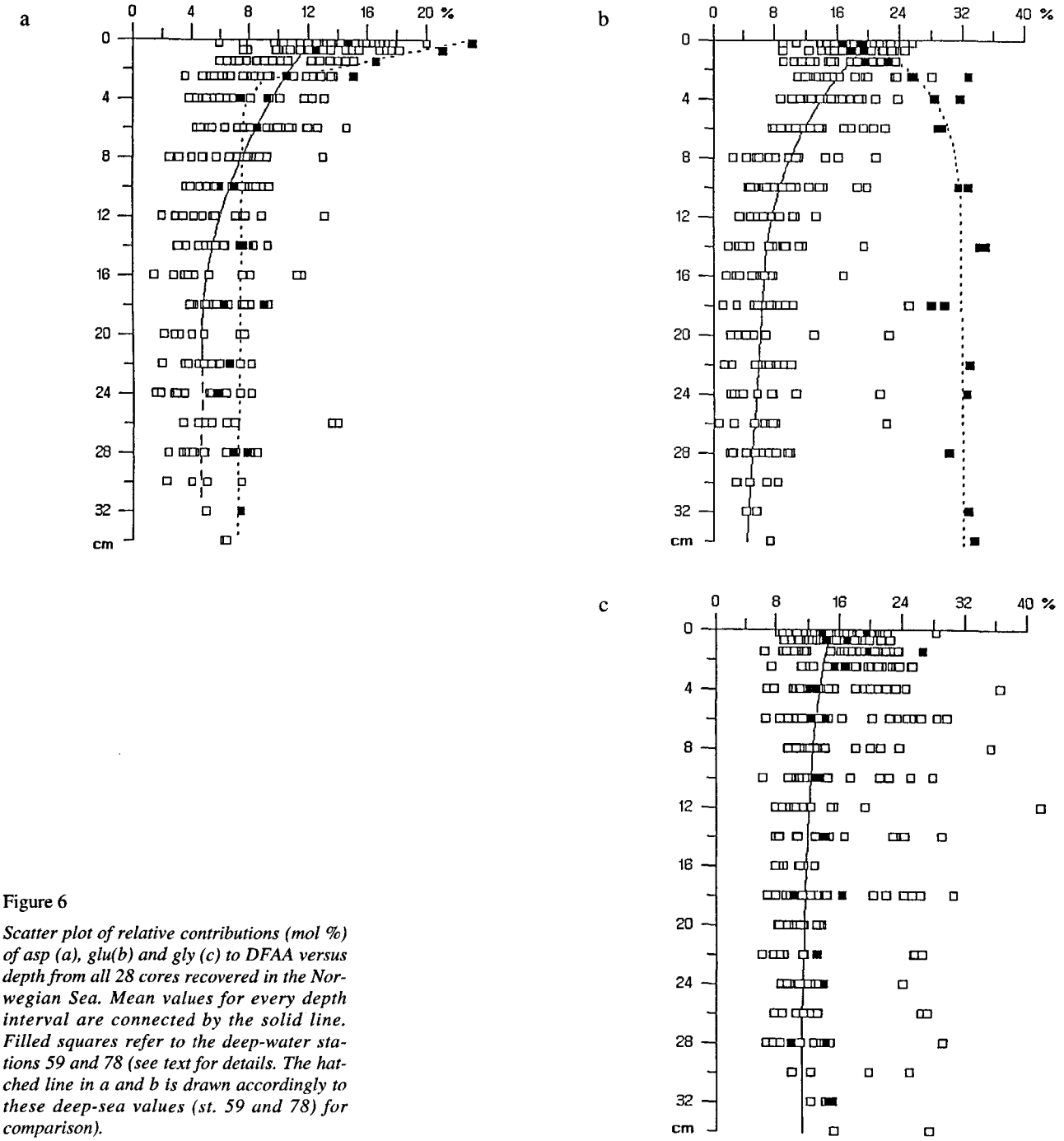

Figure 6

Scatter plot of relative contributions (mol %) of asp (a), glu(b) and gly (c) to DFAA versus depth from all 28 cores recovered in the Norwegian Sea. Mean values for every depth interval are connected by the solid line. Filled squares refer to the deep-water stations 59 and 78 (see text for details. The hatched line in a and b is drawn accordingly to these deep-sea values (st. 59 and 78) for comparison).

(Bathmann *et al.*, 1990). While the concentration over the entire sediment column is slowly approaching winter values, the activity of macrofauna keeps the concentrations high at the depth horizon they frequent.

Secondary maxima

Similar secondary concentration maxima to those mentioned above were also reported by Burdige and Martens (1990) from their samples. These samples, however, were completely anoxic and the authors related the maxima they found to the transition zone from sulphate reduction to methanogenesis. The sediments we analyzed, however, were oxic or suboxic at least in the upper 30 cm, *i.e.* concentrations of nitrate in the porewater never approached zero values. The depth zones where the secondary maxima occurred (6-12 cm) are more likely to be linked to the bioturbation depth and could also be related to the depth, where macrofauna are reported to build large horizontal burrow structures.

Molar composition

Due to the method applied (OPA-derivatization), the presented total concentrations (100 %) are constituted by the 15 amino acids listed in the table. Smaller but unknown contributions to natural total concentrations originate from secondary amino acids (not measurable by this

method), from cystine/cystein (low fluorescence yield of the derivative), and from tryptophane. The latter is known to undergo partial decomposition upon hydrolysis. Some minor peaks in the chromatograms, representing as yet unidentified amino acids and probably small di- or tripeptides [which are reported to elute within the amino acid elution range under these conditions (Schneider *et al.*, 1984)] are not included in the calculations. We believe that for these reasons the total amount of amino acids could be higher by as much as 15 to 20 % than the values presented here.

The composition of the whole sediment was constant along the cores, showing very small standard deviation between cores from the same site. Also the composition of particulate matter, collected in a sediment trap at 750 m depth just above site Z over a period of 16 months (Bathmann *et al.*, 1990) showed remarkably constant amino acid composition (but different from the sediment) though accompanied by huge variation in flux (Mintrop, 1990, *see* also Table 3 and Fig. 7). Nevertheless, the uniform composition of amino acids in the porewater was unexpected. Obviously, no specific processes exist in the sediments we analyzed, which affect exclusively the concentration of one or a specific group of amino acids. All amino acids seem to be processed at a nearly uniform rate. Only the acidic amino acids asp and glu show decreasing relative contributions with depth. Since it is unlikely that a single diagenetic process would affect all amino acids in the same way, it is more likely that the composition results from many different reaction pathways created by a variety of different macro- and microorganisms living in the sediment. The pattern that we found differs significantly from that observed in the porewater of anoxic sediments, where glutamic acid plays a dominant role. This has been reviewed by Stanley *et al.*, (1987) who compared amino acid patterns of several anoxic sediments ranging from mangrove forests and coastal sediments to deep sea samples. On the other hand, our findings show similarities with an oxic coastal sample from the Limfjord, Danmark, investigated by Jørgensen *et al.*, 1981 (Rønbjerg sample).

Table 3

Molar percentages of individual amino acids in THAA of whole sediment at site Z (st. 186, 281, 1184). For comparison, mean molar percentages of sediment trap material collected over a period of 16 month in a trap above site Z (at 750 m depth) are also given.

amino acid	sediment (molar comp.) (%) mean	std. dev. (n=37)	trap material (molar comp.) (%) mean	std. dev. (n=26)
asp	14.91	± 1.71	10.61	± 0.85
glu	9.17	± 1.05	9.94	± 1.23
ser	9.26	± 2.10	8.87	± 2.00
his	0.81	±0.53	2.25	± 0.88
gly	17.21	± 4.06	10.84	± 1.60
thr	7.65	± 1.14	6.50	± 0.69
ala	13.21	± 2.21	9.43	± 0.96
arg	5.50	± 1.65	4.99	± 0.83
tyr	1.27	± 0.85	4.49	± 0.94
val	6.40	± 1.07	7.88	± 0.63
met	1.46	± 0.82	1.76	± 0.95
ile	2.94	± 0.69	6.23	± 0.95
phe	2.54	± 0.73	4.52	± 0.68
leu	4.67	± 0.89	7.40	± 0.79
lys	3.00	± 1.10	4.30	± 1.71

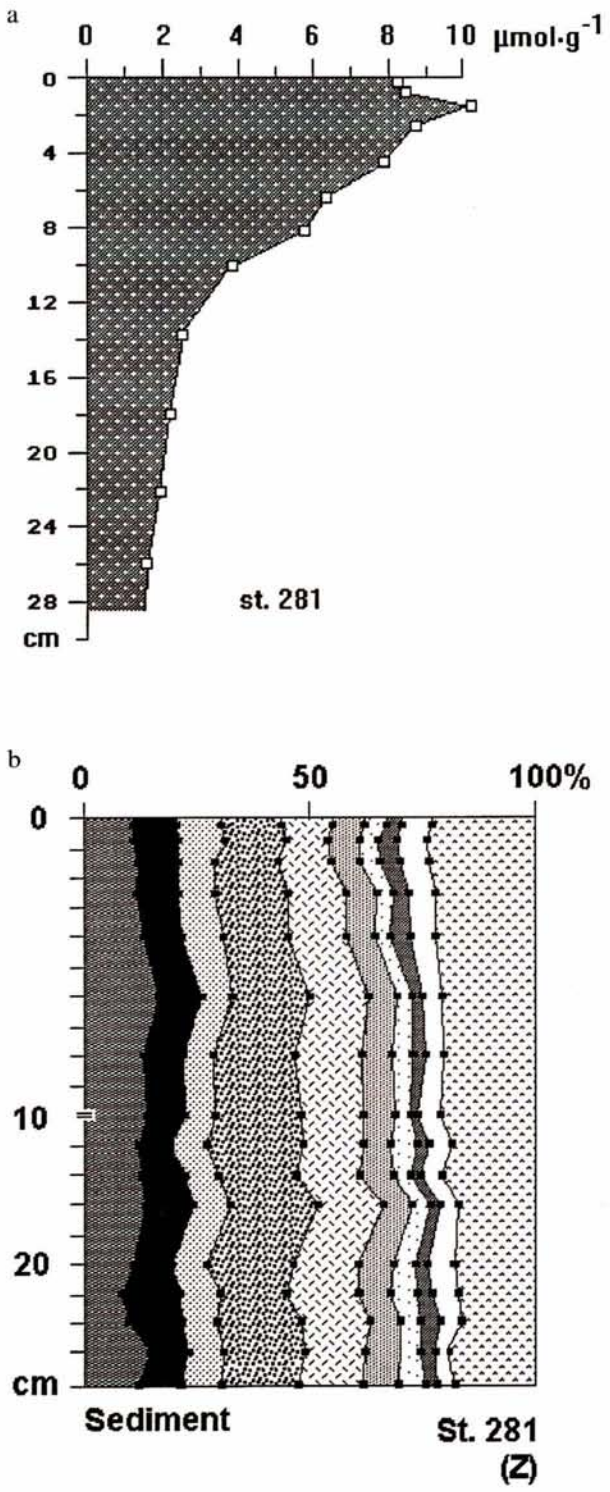

Figure 7 (a) (b)

Depth profile of amino acid concentrations and molar composition in whole sediment at site Z.

Deep-sea samples

In our deepest samples (water depth > 3000 m), the bioturbation activity is one order of magnitude lower (Mintrop, 1990) and restricted to the upper 1 or 2 centimeters This is where we found relatively high contributions of glutamic acid below this horizon, a major component reported from (non-bioturbated) anoxic sediments.

We believe that the depth profiles of amino acid concentrations can be interpreted as a reflection of diagenetic activity, decreasing from the sediment surface; and that they also confirm the seasonal variation of benthic activity found in this sediment (Graf, 1989; Linke, 1989). Additional support, regarding the secondary maxima found, arises from the fact, that bioturbation in this sediment reaches down to a depth of about 6 to 12 centimeters and horizontal burrow structures are often encountered in these layers (Romero-Wetzel, 1989). As could be shown for sediments from the same region, microbial biomass and activity associated with tubes and burrows of macrofauna are greatly enhanced over the bulk sediment. It can be expected that major transformations of organic material occur in these microenvironments created by bioturbation (Köster *et al.*, 1991).

We therefore establish the hypothesis that the diversity of microorganisms, supported by existence and activity of benthic macrofauna, is responsible for a more or less uniform decay of all amino acids, whereas predominance of specific bacteria, encountered in poorly habitated and anoxic sediments, leads to enhanced contributions of individual amino acids to DFAA. This theory should be investigated in further studies.

CONCLUSION

Depth profiles of amino acids dissolved in porewater are linked to microbial activity and obviously reflect its local and seasonal variation. The multiple metabolic processes of organisms seem to be reflected in the relatively constant composition of the pool of amino acids. The specific bioturbation activity of macrofauna is responsible for variations in the depth profiles and relatively high activity in subsurface depth horizons. Seasonal variations in the supply of particulate matter triggers the activity in deep sea sediments and this obviously influences the concentrations of DFAA in porewater. Future investigations can focus on detailed issues. Since only microliter quantities of porewater are required for amino acid determinations, the content of distinct burrow tubes can now be analyzed, and comparisons can be made between sediments with different dominant benthic fauna species. The composition of the amino acid fraction in relation to oxic/anoxic conditions and to the degree of bioturbation should be followed in deep sea sediments to obtain a better understanding of the role amino acids play in early diagenesis of organic matter.

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