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36. GEOCHEMISTRY OF LABILE ORGANIC MATTER IN SEDIMENTS AND INTERSTITIAL WATER RECOVERED FROM SITES 651 AND 653, ODP LEG 107 IN THE TYRRHENIAN SEA[1]

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ABSTRACT

Sediment and interstitial water from Sites 651 and 653 (ODP Leg 107) were investigated by organic geochemical methods to characterize labile organic compound classes (amino compounds and carbohydrates) and to evaluate their progressive diagenetic and thermal degradation in deep-sea sediments.

Downhole distribution of dissolved organic carbon (DOC) appears related to redox zones associated with bacterial activity and of diagenetic recrystallization of biogenic tests and not so much to organic matter concentrations in ambient sediments. DOC ranges from 250 to 8300 μmol/L (3–100.1 ppm). Amino acids contribute 10%–0.3% of DOC; carbohydrates range from 78 to 5 μmol/L.

Rate of degradation of amino acids by thermal effects and/or bacterial activity at both sites (significantly different in sedimentation rates: average 41 cm/1000 yr in the top 300 m at Site 651, average 3.9 cm/1000 yr in the Pliocene/Quaternary sequence at Site 653 to 220 mbsf) is more dependent on exposure time rather than on the depth within the sediment column. Variability in neutral, acidic, and basic amino acid fractions of total amino acids (with a range of 1.1–0.02 μmol/g sediment; up to 2.5% of organic carbon) varies with carbonate content and by differences in thermal stability of amino acids.

Distribution patterns of monosaccharides are interpreted to result from differences in organic matter sources, sedimentation rates, and the degree of organic matter decomposition prior to and subsequent to burial. Total particulate carbohydrates range from 1.82 to 0.21 μmol/g sediment and contribute about 8% to the sedimentary organic matter. Investigation of trace metals in the interstitial waters did not show any correlation of either DOC, amino compounds, or carbohydrates.

INTRODUCTION AND GEOLOGICAL BACKGROUND

Leg 107 of the Ocean Drilling Program drilled a transect of seven sites across the Tyrrhenian sub-basin of the Mediterranean Sea (Fig. 1). The transect was designed to (1) clarify the age of back-arc spreading behind the subduction zone of the Calabrian arc by recovering basaltic basement rocks in the Marsili and Vavilov basins; and (2) to study the association of back-arc evolution with the timing and mechanism of passive margin evolution on the eastern continental margin of Sardinia.

Results of drilling on Leg 107 document the history of tectonic movement and the evolution that led to the present configuration of the back arc and the passive margin (Kastens, Mascle, et al., 1987). Aspects of regional geology and Mediterranean geological history with respect to the late Miocene salinity crisis are discussed in numerous articles in the present volume.

Of particular interest among the sites drilled during Leg 107 are Site 651 in the Vavilov Basin, which is floored by basalt, and Site 653 on the Sardinian margin. At the former site, chemically altered sediments were recovered at the contact with a complex basement unit. Strata from Holes 653A and 653B include a largely undisturbed and complete pelagic section of Messinian to Pleistocene age.

We extended the scope of shipboard analyses presented in the site chapters (Kastens, Mascle, et al., 1987) by studying samples from these two sites in greater detail. In addition to interstitial water properties determined onboard the *JOIDES Resolution*, we measured organic constituents (organic carbon, carbohydrates, amino compounds) in pore waters and in the respective squeezed sediment cakes. Trace metals were determined in the pore waters of Holes 651A and 653A and B in order to evaluate (1) possible interactions of dissolved organic and inorganic constituents, and (2) possible hydrothermal influence on pore water composition at Site 651.

The investigation of interstitial water chemistry in relation to the composition of the pelagic sediments in the Tyrrhenian Sea had two objectives. The first objective was to trace the composition and quantity of labile organic constituents through successive stages of organic matter remineralization and sediment diagenesis. Profiles of dissolved organic matter concentrations and compositional differences are useful in following bacterial or other diagenetic processes that convert particulate to dissolved organic matter. Recrystallization of biogenic hard parts of microorganisms, for example, should result in different compositions relative to bacterial degradation of organic matter.

The second area of investigation concerns possible hydrothermal influences on the composition of interstitial waters and the range of organic constituents in sediment and pore water. Sediment overlying young basaltic ocean floor at Site 651, where there is a high geothermal gradient of about 150°C/km, would be expected to show thermal effects on organic matter, whereas sediment from Site 653 (geothermal gradient approximately 80°C/km) should show predominantly biogenic effects. An investigation of carbohydrates and amino compounds in the pore water and in the sediment would resolve differences of thermal history and input characteristics for the two sites.

A brief description of the sedimentological facies and sediment type for each of the two sites has been excerpted from Kastens, Mascle, et al. (1987) as background for our geochemical studies.

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[1] Kastens, K.A., Mascle, J., et al., 1990. *Proc. ODP, Sci. Results*, 107: College Station, TX (Ocean Drilling Program).

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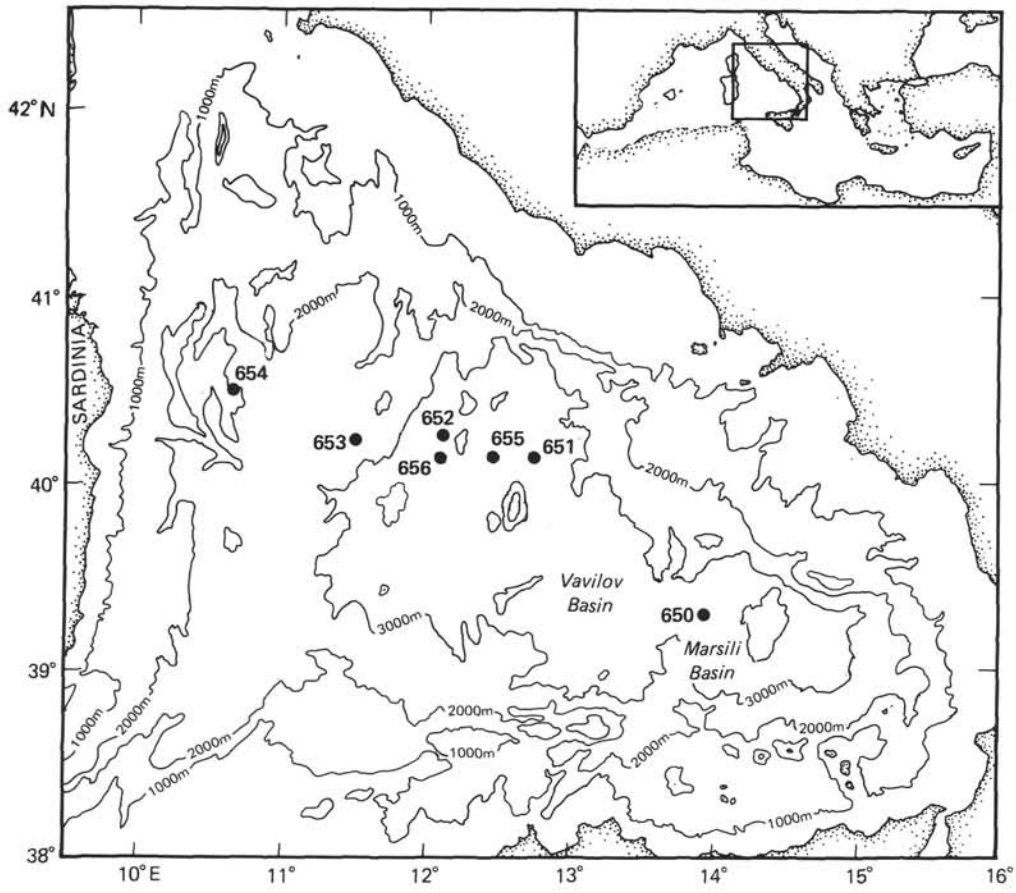

Figure 1. Location map of sites drilled during ODP Leg 107.

Site 651

Site 651 is located on the abyssal plain of Vavilov Basin in 3578 m water. The basaltic oceanic crust here is late Pliocene in age, and heat flow measurements showed a high gradient of 14.6°C/100 m. Two sedimentary units and a basement unit were recognized at Site 651: sedimentary Unit I (0–136 mbsf) is comprised of volcanogenic sediment with variable contributions of marly nannofossil-rich mud. The unit is of late Pleistocene age, and the sediments accumulated at rates of about 70 cm/1000 yr. Average $CaCO_3$ content is 17.7% ± 8.2% and ranges from 1.9% to 42.2%.

Sedimentary Unit II (136–387.6 mbsf) consists of marly nannofossil chalks and oozes, volcanic ash, calcareous siltstone, mudstones, and claystones. Dolostones and metalliferous claystones and dolostones (Mn-Fe-enriched) are prominent in Subunit IIb (347.8–387.6 mbsf) at the contact of Unit II with the basaltic basement. In the upper part of Unit II, 11 individual organic-carbon-rich sapropels and sapropelic layers were found in Cores 651A-18R, −27R, −28R, and −34R to −37R. The maximum value for C_{org} of 4.16% by weight was encountered in Sample 651A-36R-1, 54–56 cm. Carbonate content in Subunit IIa averages 21.7% ± 17.7% $CaCO_3$ and ranges from 0.2% to 69.6%. In Subunit IIb, in the altered and in places brightly colored dolostones, $CaCO_3$ averages 47.2% ± 13% and ranges from 12.4% to 64.9%. Basement is comprised of a complex assemblage of serpentinized peridotite, basalts, basaltic breccia, dolerites, metasediments, and metadolerites.

Site 653

Site 653 was drilled close to DSDP Site 132 on the eastern rim of the Cornaglia Basin in 2817 m water depth. The geothermal gradient at this site decreases with depth and has a mean value of 80°C/km in the top 200 m. Two major sedimentary Units were recognized in the 264.3 m penetrated. Unit I (0–220 mbsf in Hole 653A and 0–216 mbsf in Hole 653B) was deposited in an open marine hemipelagic to pelagic sedimentary environment. Sediments are composed of gray and brown nannofossil oozes, foraminiferal nannofossil oozes and minor mud, which accumulated at an average rate of 4 cm/1000 yr over the Pliocene/Pleistocene. Carbonate content varies widely due to the abundance of clastic sand and muds, as well as volcaniclastic constituents. Average $CaCO_3$ in Subunit Ia of Hole 653B (0–86 mbsf) is 39.7% ± 10.3%, while Subunit Ib (86–209.1 mbsf) averages 60.6 ± 5.7% $CaCO_3$ with less clastic dilution. Fourteen discrete sapropel and sapropelic intervals were encountered in Subunit Ia of Hole 653B while they appear to be absent in Subunit Ib. The highest number of sapropels was found in Cores 653B-7H and -8H between 55 and 65 mbsf (Emeis et al., this volume). The maximum concentration of organic carbon of 4.2 wt% was encountered in Sample 653B-7H-4, 29–31 cm. Subunit Ic marks the transition from subaerial deposits of Messinian sediments in sedimentary Unit II to the marine sediments of Unit I and consists of calcareous marine sediments (nannofossil oozes and marls), which are colored red and yellow by migrating iron from the underlying lithologic Unit II (220–240.7 mbsf in Hole 653A and 216–264 mbsf in Hole 653B). Average $CaCO_3$ content in Subunit Ic is 52.2% ± 7.2% with a relatively narrow range of 41.9%–60.4%.

Unit II represents sedimentation in a restricted marine evaporitic and subaerial environment during the Messinian desiccation of the Tyrrhenian Sea. Dark gray gypsum-bearing sand, laminated gypsum, and dark gray to olive gray and red dolomitic nannofossil mud with lenticular gypsum characterize the

upper Messinian section. Occurrence of brightly colored red and yellow bands of iron-rich precipitates increases downsection. Carbonate content averages 15.7% ± 7.1% $CaCO_3$ and ranges from 8.1% to 24.1%. Correlation of Messinian sediment within the few meters distance of Holes 653A and 653B proved to be difficult, a fact which suggests considerable lateral facies variabiltiy within the Messinian depositional environment.

SAMPLES AND METHODS

Samples investigated here are listed in Tables 1 and 2 along with a brief description of sediment facies. Samples of interstitial waters were obtained by standard shipboard techniques (Gieskes and Peretsman, 1986). Two 5-mL aliquots of each sample were sealed in pre-combusted glass ampoules and immediately frozen. Trace elements were determined by graphite furnace atomic absorption spectroscopy on one sample aliquot.

Dissolved organic carbon in the interstitial waters was determined by an instrument that employs UV oxidation coupled to an infrared detector for detection of CO_2. The sample was acidified and purged prior to DOC oxidation to expel inorganic CO_2 (Mueller and Bandaranayake, 1983). Dissolved amino compounds were measured following hydrolysis of 1–3 mL sample in 6N HCl under argon for 23 hr at 110°C. Analyses were performed on a Biotronic Amino Acid Analyzer and quantified against standards. Particulate amino compounds in squeezed cakes were measured after hydrolysis of 50–150 mg dried and crushed subsamples under the same conditions.

Concentrations of carbohydrate monomers were measured after acid hydrolysis of 50–100 mg freeze-dried and ground sediment or 1–3 mL interstitial water. Hydrolysis was carried out with 2N HCl at 100°C for 3.5 hr under argon atmosphere in precombusted glass ampoules. The samples were analyzed and compared to standards on a Biotronik Sugar Analyzer by liquid chromatography (Mopper, 1977; Mopper et al., 1978) after hydrolysates had been desalted by electrodialysis. Details of all organic geochemical methods are given in Michaelis and Ittekkot (1982). At present, we have no data to decide whether artifacts are introduced during sampling and interstitial water squeezing in the case of the dissolved fractions. Comparison of *in-situ* filtrated water and water obtained from squeezing (Seifert et al., unpubl. data) suggests that the squeezing method is advantageous because of frequent seawater dilution in the *in-situ* samples. Considering the rather dramatic changes in pressure, temperature, and oxygen content of the environment, we cannot exclude the possibility that DOC changes considerably in quality and quantity. Differences in the samples are obvious, however, and possible sampling artifacts are presumed to be significantly less important than differences in *in-situ* conditions.

RESULTS AND DISCUSSION

Dissolved Organic Carbon

DOC values from 367 to 3,292 μmol/L were detected in pore waters from Hole 651A (Table 3), whereas the values for Holes 653A and 653B are in the range of 258–8,340 μmol/L (Table 4). The range of DOC concentrations agrees reasonably well with results from other deep-sea and nearshore sediments, although the results appear to be on the low side due to low sedimentary organic carbon concentrations in the pelagic and hemipelagic sediments of the Tyrrhenian Sea (e.g., Emeis and Mycke, this volume). For example, Michaelis et al. (1982) reported concentrations from 2,580 to 17,000 μmol/L from organic-rich sediments of the Gulf of Mexico; Emeis et al. (1987) found values from 4,000 to 12,000 μmol/L DOC from interstitial waters of the northwest Atlantic Ocean. Interstitial waters from nearshore sediment of the Atlantic Ocean investigated by Henrichs and Farrington (1987) ranged from 1,000 to 9,160 μmol/L DOC.

Profiles of DOC concentrations show distinct downhole changes (Fig. 2) which cannot be attributed to obvious lithological differences. In both sections organic-rich sapropel layers were found, which are concentrated between 55 and 65 mbsf in Hole 653A, and between 310 and 350 mbsf in Hole 651A. None of these potential sources of dissolved organic matter appear to influence the distribution of DOC, however, and thus the observed variability in DOC concentrations with depth may result from DOC production or loss that is related more to diagenetic changes than to abundance of sedimentary organic matter and lithology.

One of the diagenetic zones that control DOC production or loss is, e.g., related to decrease in interstitial sulfate, which coincides with DOC minima at both sites (i.e., Sample 651A-7R-2, 140–150 cm; 653B-7H-5, 140–150 cm; Table 3, 4). This coincidence may result from high microbial activity and consumption of dissolved organic matter in this zone. Also the high amino

Table 1. Samples and lithofacies of Hole 651A.

Sample	Depth (mbsf)	Description	$CaCO_3$	C_{org}
1R-3, 140–150	4.4	Calcareous-rich silty mud	22.7	n.d.
3R-1, 54–67	10.8	Calcareous mud	27.2	n.d.
4R-3, 54–67	23.3	Gray clayey nanno-rich mud	18.5	n.d.
7R-2, 140–150	52.4	Pumice	1.9	0.00
12R-1, 50–55	97.9	Clayey-bearing carbonaceous mudstone	42.2	0.00
14R-3, 25–29	120.0	Ash-bearing marly calcareous ooze	19.7	n.d.
17R-1, 25–28	146.0	Silty mud	21.0	n.d.
18R-5, 140–150	162.3	Marly nannofossil chalk	34.1	1.30
23R-1, 140–150	204.6	Clayey mudstone	6.1	n.d.
26R-1, 140–150	233.7	Clayey mudstone	4.4	0.11
34R-1, 140–150	310.7*	Marly nannofossil chalk	33.9	0.22
37R-2, 20–27	339.9	Calcareous claystone	47.0	n.d.
37R-4, 20–27	342.9*	Foraminifer-nannofossil chalk	34.4	n.d.
39R-2, 68–74	359.7	Metalliferous dolostone	45.1	n.d.
39R-3, 127–133	361.8*	Metalliferous dolostone	45.1	n.d.
39R-4, 69–75	362.7	Metalliferous dolostone	49.9	n.d.
40R-2, 55–60	369.3	Metalliferous dolostone	49.3	0.00
40R-3, 39–44	370.6	Metalliferous dolostone	n.d.	n.d.
40R-4, 55–60	372.3	Metalliferous dolostone	50.4	n.d.
41R-2, 14–20	378.4	Dolostone	13.0	n.d
41R-4, 14–20	381.4	Dolostone	60.9	0.0

* = Near sapropels; n.d. = not determined because high inorganic carbon content resulted in error with calculating organic carbon by difference.

Table 2. Samples and lithofacies of Holes 653A and 653B.

Sample	Depth (mbsf)	Description	$CaCO_3$	C_{org}
A 1H-2, 140–150	2.9	Nannofossil ooze	36.6	n.d.
B 1H-4, 39–46	4.9	Marly nannofossil ooze	23.5	1.12
B 2H-5, 131–137	13.5	Nannofossil ooze	65.2	0.13
B 3H-4, 143–149	22.0	Nannofossil ooze	53.8	0.17
B 4H-3, 142–149	31.5	Foraminifer-nannofossil ooze	20.9	0.26
B 5H-5, 142–148	44.0*	Foraminifer-nannofossil ooze	49.3	0.61
A 6H-5, 140–150	49.0*	Marly nannofossil ooze	38.7	n.d.
B 6H-4, 140–148	51.9*	Foraminifer-nannofossil ooze	59.0	0.00
B 6H-5, 58–66	52.6*	Foraminifer-nannofossil ooze	58.7	0.57
B 7H-3, 143–149	59.4*	Marly foram-nannofossil ooze	46.8	0.57
B 7H-5, 140–150	62.8*	Foraminifer-nannofossil ooze with ash and sapropel layer	36.3	0.25
B 8H-2, 50–56	66.9	Foraminifer-nannofossil ooze	38.4	0.65
B 9X-2, 120–126	77.1	Marly foram-nannofossil ooze	55.1	0.69
A11H-5, 140–150	96.4	Foraminifer-rich nannofossil ooze	56.4	n.d.
B12X-3, 142–148	107.0	Foraminifer-rich nannofossil ooze	67.3	0.00
B13X-4, 142–148	118.0	Foraminifer-nannofossil ooze	60.1	n.d.
B14X-2, 104–110	124.1	Foraminifer nannofossil ooze	54.3	n.d.
B16X-3, 140–148	144.9	Foraminifer nannofossil ooze	57.1	0.03
B17X-3, 140–148	154.4	Foraminifer-nannofossil ooze	57.7	0.15
B18X-4, 142–150	165.5	Foraminifer-nannofossil ooze	61.0	0.29
B19X-4, 115–121	174.1	Foraminifer-nannofossil ooze	59.2	n.d.
B20X-3, 141–148	182.4	Foraminifer-nannofossil ooze	56.2	n.d.
B21X-3, 141–148	191.4	Foraminifer-nannofossil ooze	68.4	n.d.
B22X-3, 80–86	201.0	Foraminifer-nannofossil ooze	56.1	n.d.
B23X-3, 80–86	210.5	Foraminifer-nannofossil ooze	46.8	n.d.

A = Hole 653A, B = Hole 653B; * = Near sapropels; n.d. = not determined because high inorganic carbon content resulted in error with calculating organic carbon by difference.

acid content in the interstitial water is accompanied by high β-alanine (β-Ala) and γ-amino- butyric acid (γ-ABA) percentages in the amino acid fraction of the sediment in Hole 653A; the implications of these observations will be discussed below.

Amino compounds

Amino acids in pore waters range from 1.41 to 13.5 μmol/L, which amounts to 9.6% and 0.3%, respectively, of the DOC (Tables 5 and 6). Data for amino acids and amino sugars in sediment samples are listed for Sites 651 and 653 in Tables 7 and 8, respectively. The amino sugar contents varies from 0 to 145 nmol/g at Site 651 and from 24.2 to 256 nmol/g at Site 653.

The vertical distributions of total hydrolyzable amino acids for Holes 651A and 653B are depicted in Figures 3 and 4. Both profiles show a general decrease with depth with only minor variability in the Pliocene samples. The neutral amino acids are dominant in samples of Hole 651A (Fig. 3). In the lower Pleistocene and upper Pliocene samples acidic amino acids are more abundant than are basic amino acids. In the predominantly dolomitic sediment at 357.5 mbsf, the percentage of basic amino acids increases compared to the acidic fraction. This increase could be attributable to the loss of acidic amino acids during recrystallization of biogenic carbonate tests, or to a lower contribution of basic amino acids, which are preferentially adsorbed on clay minerals, in the carbonate-rich dolomitic sediments. Because acidic amino acids are more stable under high temperature conditions than are basic amino acids in unaltered calcite shell materials (Vallentyne, 1969), the loss of acidic compounds must be preceeded by the liberation from recrystallization of hard parts prior to thermal degradation. Ornithine, a basic amino acid, together with neutral-amino acids glycine and alanine are highest in the samples from the dolomitized interval (Table 7). Ornithine is the most stable amino acid in studies on the thermal stability of amino components in humic acid (Khan and Sowden, 1971). Amino sugars (AS), which are the least thermally stable amino compound, are absent in the deepest part of Hole 651 (Table 7).

Of the neutral, acidic, and basic amino acids at Site 653 (Fig. 4), the neutral compounds show an increasing dominance with depth. In general, the acidic amino acids are more abundant than the basic amino acids in all samples below 20 mbsf. Exceptions are Samples 653B-8H-2 and 653B-4H-3 which are distinguished by low carbonate contents. Acidic amino acids are known to be major constituents of the organic matrix in calcified skeletons (Weiner et al., 1983; Degens, 1976; Schroeder, 1975; King and Hare, 1972) and are also easily adsorbed onto carbonate particles (Carter and Mitterer, 1978). On the other hand, they are less apt to be incorporated into the lattice of clay minerals than are basic amino acids (Hedges and Hare, 1987). Therefore it seems feasible that the early diagenetic decomposition of amino acids leads to a relative enrichment of acidic relative to basic amino acids in carbonate-rich sediments whereas the acidic amino acids decrease relative to basic amino acids in clay-rich sediments. Laboratory decomposition experiments under conditions of high pressure and temperature on Okhotsk Sea sediments support this suggestion (Maita et al., 1982).

Several studies on amino acids in core samples show a downhole increase of the nonprotein amino acids γ-amino butyric acid (γ-ABA) and β-alanine (β-Ala) relative to the total amino acid fraction (e.g., Whelan, 1977). Both components are common in sediment samples (Aizenshtat et al., 1973; Hare, 1973). γ-ABA and β-Ala are thought to be biological decarboxylation products of other amino acids such as glycine (Gly) and aspartic acid (Asp) (Aizenshtat et al., 1973; Vallentyne, 1964), whereas

Table 3. Results of interstitial water analyses, Hole 651A.

Sample	Depth (mbsf)	pH	Alk	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	Sal	Ca/Mg	SiO_2	K^+	Sr	Mn	Fe	DOC
1R-3, 140–150	4.4	7.54	3.59	11.46	59.90	28.21	663	39.5	0.19	—	—	—	—	—	—
3R-1, 54–67	10.8	7.84	5.01	9.76	26.69	13.64	574	37.0	0.37	668	26.5	156	16.0	0.9	766
4R-3, 54–67	23.3	7.78	6.34	18.25	40.34	20.55	493	40.0	0.45	367	27.3	184	0.1	6.6	808
7R-2, 140–150	52.4	8.19	2.49	2.94	25.18	13.12	612	39.0	0.12	189	17.1	114	17.0	0.5	367
12R-1, 50–55	97.9	—	—	48.65	11.23	20.93	621	40.0	4.33	—	—	—	—	—	—
14R-3, 25–29	120.0	7.09	1.47	30.67	13.48	23.98	584	39.5	3.76	257	21.7	579	57.6	5.2	1658
18R-5, 140–150	162.3	7.59	1.99	23.33	22.48	18.62	594	39.0	1.05	473	18.9	563	21.0	—	1392
23R-1, 40–150	204.6	7.65	1.68	24.64	15.78	19.74	559	39.0	1.56	689	17.1	346	36.5	0.6	1833
26R-1, 30–150	233.7	7.48	2.07	19.49	41.39	28.81	582	39.2	0.47	333	13.2	188	41.2	0.8	—
34R-1, 140–150	310.7	7.50	2.53	6.67	15.58	11.04	587	39.0	0.43	402	12.3	132	41.1	0.5	3292
37R-4, 20–27	342.9	—	—	27.81	47.69	34.09	574	36.0	0.58	284	11.3	162	23.9	0.3	2450
39R-3, 127–135	361.8	7.50	2.03	30.73	50.55	31.78	576	39.0	0.61	387	9.9	113	7.3	0.4	
39R-4, 69–75	362.7	—	—	19.41	40.79	24.94	564	36.0	0.48	—	—	—	—	—	—
40R-2, 55–60	369.3	—	—	19.66	41.39	25.76	522	32.5	0.47	—	—	—	—	—	—
40R-3, 39–44	370.6	—	—	25.93	41.89	27.62	535	34.0	0.62	—	—	—	—	—	—
41R-2, 14–20	378.4	7.59	2.03	13.11	39.89	26.35	509	32.0	0.33	177	8.6	95	7.1	3.3	2450
41R-4, 14–20	381.4	—	—	14.32	41.99	27.61	543	35.0	0.35	—	—	—	—	—	—

Alkalinity, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, K^+ in mmol/L; salinity in ‰; SiO_2, Sr, Mn, Fe, and DOC in μmol/L. — = not determined.

Table 4. Interstitial water analyses, Site 653, Leg 107.

Sample	Depth	pH	Alk	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	Sal	Ca/Mg	SiO_2	K^+	Sr	Mn	Fe	DOC
1H-2, 40–150	2.9	7.68	2.99	6.9	51.1	24.6	606	37.5	0.13	363	14.6	110	61.2	0.5	350
2H-5, 140–150	13.5	7.51	3.73	9.3	50.7	26.3	524	36.0	0.18	—	—	—	—	—	
3H-4, 143–149	22.0	—	—	8.5	54.0	24.6	581	39.0	0.16	132	13.4	167	22.6	0.7	2700
4H-3, 42–149	31.5	—	—	7.0	47.2	21.5	600	38.0	0.15	32	13.5	196	7.7	0.3	1383
5H-5, 142–148	44.0	—	—	15.6	60.5	25.3	608	39.5	0.26	162	12.7	232	14.7	0.6	—
6H-5, 40–150	49.0	7.49	2.80	18.4	66.5	30.5	550	38.0	0.28	323	12.9	219	20.3	3.0	—
6H-4, 140–148	51.9	—	—	7.7	35.7	26.8	613	38.5	0.21	228	10.7	239	21.1	18.2	—
7H-5, 140–150	62.8	7.38	3.25	15.3	59.7	17.6	623	40.0	0.26	425	12.5	260	28.6	4.3	258
8H-2, 50–56	66.9	—	—	12.2	57.8	28.0	589	40.0	0.21	178	13.8	289	27.3	2.9	658
11H-5, 40–150	96.4	7.11	2.66	18.9	53.3	24.0	634	40.0	0.36	294	13.3	338	27.1	6.6	—
12X-3, 42–148	107.0	—	—	21.1	63.6	34.2	665	42.0	0.33	217	13.4	378	12.7	0.5	1280
13X-4, 142–149	118.0	—	—	22.3	61.9	33.5	654	42.5	0.36	65	9.8	199	8.3	0.4	1542
14X-2, 104–110	124.1	—	—	21.8	59.7	34.1	630	44.5	0.37	226	9.6	403	13.7	0.9	8340
16X-3, 140–148	144.9	—	—	26.9	61.9	34.5	621	45.0	0.43	259	12.9	415	13.5	20.0	6150
17X-3, 140–148	154.4	—	—	25.4	64.5	37.3	636	42.0	0.39	247	9.6	374	7.5	0.5	2800
18X-4, 142–150	165.5	—	—	28.6	67.5	40.5	683	44.0	0.42	98	9.9	396	13.6	1.6	2450
21X-3, 141–148	191.4	—	—	36.3	67.7	43.3	690	44.0	0.54	36	13.5	441	22.6	13.2	883
22X-3, 80–86	201.0	—	—	29.8	72.2	36.8	681	46.0	0.41	166	12.8	426	25.1	0.3	—
23X-3, 80–86	210.5	—	—	28.2	75.1	31.7	695	45.0	0.38	291	12.4	417	57.9	1.1	733

Alkalinity, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, K^+, in mmol/L; salinity in ‰; SiO_2, Sr, Mn, Fe, and DOC in μmol/L; — = not determined.

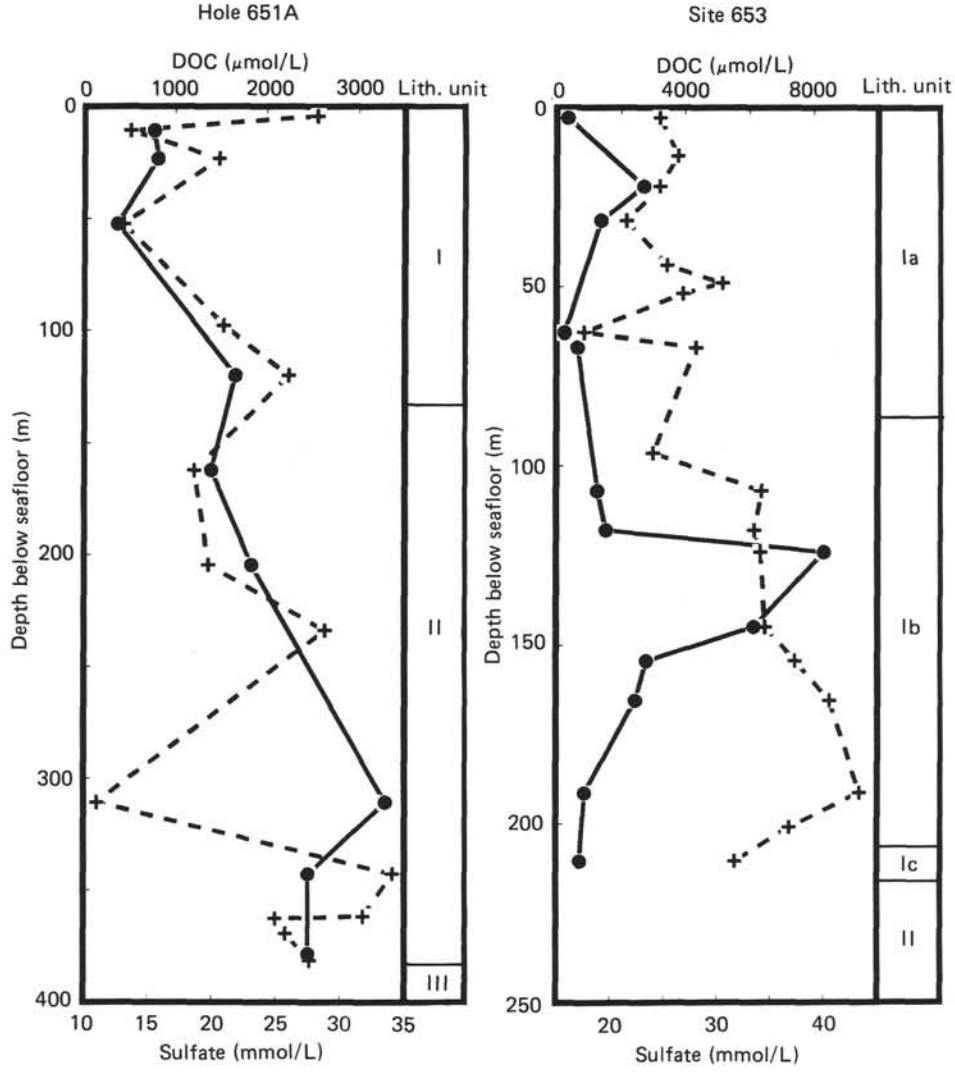

Figure 2. Downhole variations in dissolved organic carbon (DOC, solid lines) and sulfate (broken lines) at Hole 651A and Site 653, respectively. Note the different depth scales.

Table 5. Amino acids (AA) in interstitial waters, Hole 651A.

Sample	34R-1	40R-2	41R-2
Asp	5.2	8.9	5.2
Thr	9.2	2.5	1.3
Ser	6.7	12.8	5.8
Glu	23.5	10.3	0.0
Gly	16.9	25.3	10.6
Ala	3.1	14.2	0.0
Val	3.8	5.0	26.1
Ile	2.6	1.5	2.4
Leu	3.2	3.3	3.4
Tyr	1.5	0.0	0.0
Phe	1.7	0.0	1.4
βAla	2.8	0.0	3.8
γABA	1.2	5.1	4.8
Orn	8.0	7.7	24.0
Lys	4.6	3.6	7.1
His	4.4	0.0	1.7
Arg	1.5	0.0	2.6
Total AA (μmol/L)	13.52	1.41	1.64
Depth (mbsf)	310.7	369.3	381.4
DOC (mg/L)	39.5	n.d.	29.4
AA/DOC (%)	1.8	n.d.	0.31

Individual amino acids are given in mol%

Table 6. Amino acids (AA) in interstitial waters, Site 653.

Hole	653A	653B	653B	653B	653B	653B	653B
Sample	1H-2	7H-5	8H-2	12X-3	16X-3	17X-3	22X-3
Asp	7.8	8.3	7.6	8.3	7.9	7.7	6.8
Thr	4.2	5.1	3.2	3.5	3.7	4.1	5.2
Ser	13.9	24.8	18.1	11.4	17.2	20.3	14.8
Glu	10.1	16.3	17.3	24.2	17.2	12.3	11.9
Gly	23.1	12.9	16.9	13.6	14.6	15.5	12.5
Ala	8.1	4.2	9.6	4.2	9.1	7.7	11.5
Val	3.8	2.3	3.7	4.4	4.8	3.2	3.7
Ile	2.2	2.6	2.3	2.7	2.4	2.3	2.8
Leu	3.1	2.8	3.1	3.5	3.2	3.0	2.8
Tyr	1.8	3.2	1.0	1.5	0.0	0.0	2.1
Phe	1.6	3.1	1.8	1.6	1.9	1.8	2.2
γABA	0.5	0.0	0.0	0.5	0.0	0.0	0.0
Orn	11.7	9.1	9.7	12.4	10.3	11.7	15.8
Lys	3.6	1.9	2.6	2.9	4.0	3.1	3.9
His	4.5	2.6	2.9	4.0	3.2	3.7	3.9
Arg	0.0	1.0	0.3	1.4	0.6	3.6	0.0
Total AA (μmol/L)	8.34	1.6	11.37	12.88	15.02	2.6	5.21
Depth (mbsf)	2.9	62.8	6.9	107.0	144.9	154.4	201.0
DOC (mg/L)	4.2	3.1	7.9	15.4	73.8	33.6	n.d.
AA/DOC	9.56	2.64	2.39	4.45	1.01	0.38	n.d.

Individual amino acids are given in mol%

Table 7. Amino acids (AA) and amino sugars (AS) in sediment, Hole 651A.

Hole	653A	653B	653B	653B	653B	653B	653B	653A	653B	653B	653B	653B	653B	653B
Sample	3R-1	4R-3	12R-1	17R-3	18R-5	23R-1	37R-2	37R-4	39R-2	39R-3	40R-2	40R-4	41R-2	41R-4
Asp	12.1	13.0	8.0	7.7	7.2	8.1	6.6	5.8	8.5	9.4	2.0	8.6	4.5	5.1
Thr	2.9	3.6	1.2	2.0	1.2	4.3	3.3	1.0	5.4	8.3	0.0	2.8	0.7	0.4
Ser	2.0	2.5	1.6	1.0	1.5	4.5	6.9	2.2	15.8	10.7	12.2	7.0	1.4	15.6
Glu	3.7	8.1	5.2	4.7	4.5	12.5	14.9	13.8	3.7	6.9	4.0	11.5	4.3	6.6
Gly	8.7	11.2	9.5	1.5	10.3	13.6	16.9	24.4	16.5	19.1	58.9*	17.4	60.8*	39.8*
Ala	6.1	8.0	5.9	15.0	6.6	9.3	15.1	7.4	6.9	6.1		7.0		
Val	4.4	6.2	3.2	5.7	4.7	4.4	6.2	5.8	3.6	5.6	2.1	3.5	2.7	5.2
Met	0.2	0.4	1.6	0.0	0.7	0.0	0.0	13.3	0.0	0.0	0.0	0.0	0.0	0.0
Ile	1.4	3.2	1.3	3.4	1.7	2.7	2.1	2.1	3.0	2.6	2.7	0.9	2.9	2.6
Leu	4.1	4.9	2.1	6.7	4.0	5.0	3.8	3.3	3.8	4.2	5.9	3.4	5.3	4.1
Tyr	0.2	1.0	0.4	0.6	0.3	0.0	1.0	0.6	1.3	3.8	0.0	0.0	0.0	0.0
Phe	1.6	2.3	1.0	2.1	1.2	1.6	2.0	1.4	1.1	3.3	0.0	0.0	0.0	0.0
βAla	17.8	9.7	14.2	12.8	16.2	7.8	2.3	5.8	3.0	0.0	0.0	4.0	0.0	0.0
γABA	17.6	11.7	27.3	22.8	28.0	13.4	2.4	6.0	2.0	3.1	6.8	5.3	1.4	1.5
Orn	1.9	1.8	2.8	2.2	2.7	5.0	3.1	2.1	12.4	5.3	0.8	18.8	10.6	13.8
Lys	6.5	5.9	5.1	7.3	5.3	4.8	2.7	2.6	4.7	5.3	0.0	6.0	0.0	0.0
His	2.7	1.7	5.2	2.5	2.9	0.0	9.2	2.5	5.0	0.0	0.0	0.0	2.4	2.9
Arg	6.1	4.9	3.2	2.1	0.7	2.8	1.4	0.0	3.8	6.4	4.7	3.9	3.0	2.4
Total AA (μmol/g)	0.58	0.97	0.46	0.21	0.41	0.09	0.16	0.08	0.09	0.07	0.02	0.04	0.04	0.04
$GlcNH_2$	48.2	92.8	47.0	33.1	47.9	4.7	24.2	3.1	10.2	0.0	0.0	0.0	0.0	0.0
$GalNH_2$	29.8	52.1	17.5	11.1	9.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total AS (nmol/g)	78.0	144.9	64.5	44.2	57.3	4.7	24.2	3.1	10.2	0.0	0.0	0.0	0.0	0.0
Depth (mbsf)	10.8	23.3	97.9	149.0	162.2	204.6	339.9	342.9	359.7	361.8	369.3	372.3	378.4	381.4
AA/C_{org} (%)	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
AS/C_{org} (%)	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

* Gly + Ala.

Table 8. Amino acids (AA) and amino sugars (AS) in sediment, Site 653.

Sample	1H-4	2H-5	3H-4	4H-3	5H-5	6H-4	6H-5	7H-3	8H-2	9X-2	12X-3	13X-4	14X-2	16X-3	17X-3	18X-4	19X-4	20X-3	21X-3	22X-3	23X-3
Asp	8.3	7.3	11.1	5.1	14.4	11.9	12.4	11.0	6.0	17.4	13.6	11.1	14.8	12.1	13.6	11.0	10.5	10.3	11.8	9.4	8.7
Thr	2.5	1.1	1.7	1.9	2.5	1.3	1.6	1.1	1.1	1.9	2.1	1.1	0.6	0.0	3.0	2.7	0.6	0.8	3.9	4.0	2.7
Ser	3.1	2.7	2.0	5.1	4.5	4.9	4.5	1.5	4.7	1.2	6.4	5.0	0.4	2.2	5.9	6.7	3.9	8.3	4.6	12.5	8.7
Glu	5.3	4.0	4.0	4.8	9.4	8.8	8.9	9.2	4.3	13.6	11.8	9.4	9.0	15.9	15.4	14.5	13.9	13.6	18.3	11.1	9.5
Gly	5.0	6.0	2.6	5.3	12.0	9.4	10.0	5.4	7.1	12.4	11.7	9.4	8.6	13.9	10.3	12.3	10.8	15.9	11.4	13.3	8.0
Ala	7.8	4.4	6.2	7.3	9.3	7.8	9.1	8.3	4.6	7.5	9.9	5.9	11.7	10.1	11.0	12.8	11.9	11.4	13.3	11.4	20.2
Val	3.5	2.8	3.4	3.0	5.3	4.7	5.2	4.2	3.6	7.4	5.8	6.8	7.0	8.3	5.0	7.4	6.2	8.6	8.1	6.3	6.0
Met	1.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	0.7	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.0
Ile	1.6	1.1	1.1	1.3	2.3	2.3	2.2	1.2	2.1	2.2	1.7	3.4	2.3	1.8	2.0	2.1	1.9	2.5	2.7	2.6	1.7
Leu	2.4	2.4	3.2	2.8	3.4	3.2	3.5	2.3	3.1	4.6	3.5	3.5	4.8	4.2	4.5	3.9	4.3	3.6	5.2	4.8	4.1
Tyr	0.5	0.3	0.2	0.7	0.6	1.9	0.9	1.1	0.0	0.8	3.4	1.1	0.0	0.0	1.5	0.9	0.7	0.6	0.9	2.3	0.4
Phe	0.9	0.7	1.3	1.5	1.9	1.6	1.5	1.8	1.5	1.5	2.1	1.6	0.8	0.0	2.3	1.4	1.4	1.1	1.0	2.7	2.5
βAla	17.9	16.5	17.0	15.4	8.1	9.4	9.9	13.8	13.8	8.5	5.1	8.6	12.2	8.3	7.7	5.4	7.3	3.6	5.4	3.0	7.8
γABA	26.5	33.2	35.8	33.2	13.8	16.2	17.4	30.5	29.6	13.4	8.7	15.3	18.9	7.4	7.9	5.5	10.8	4.7	5.1	2.9	5.7
Orn	2.6	4.5	0.9	4.3	3.8	5.2	4.5	2.1	11.2	2.2	5.2	6.8	1.6	3.1	2.6	4.8	4.2	7.5	2.1	7.3	6.7
Lys	4.0	0.8	4.5	4.2	3.5	3.8	4.5	4.5	4.2	4.2	5.9	3.5	4.5	6.0	4.5	4.7	6.2	4.5	3.5	3.9	4.7
His	2.2	3.0	1.9	1.6	2.8	6.1	1.6	0.9	1.1	1.3	3.0	1.1	1.0	6.6	2.1	3.8	4.6	3.0	0.8	1.8	2.5
Arg	5.0	9.1	2.9	2.3	0.0	1.4	2.1	1.0	1.5	0.0	0.0	4.6	1.4	0.0	0.8	0.0	0.9	0.0	2.1	0.1	0.0
Total AA (μmol/g)	1.06	0.65	0.45	0.7	0.46	0.3	0.27	0.33	0.24	0.31	0.17	0.12	0.19	0.2	0.21	0.17	0.16	0.1	0.12	0.23	0.09
$GlcNH_2$	170.0	74.1	16.1	23.0	45.2	35.1	37.3	25.6	177.4	25.3	25.3	124.9	26.3	30.7	17.1	4.2	13.9	21.7	9.0	28.1	21.6
$GalNH_2$	85.7	32.9	4.3	5.4	11.8	6.8	10.1	6.3	10.9	0.0	1.0	5.2	3.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total AS (nmol/g)	255.7	107.0	20.4	28.4	57.0	41.9	47.4	31.9	188.3	25.3	26.3	130.1	29.5	30.7	17.1	4.2	13.9	21.7	9.0	28.1	21.6
Depth (mbsf)	4.9	13.4	22.0	31.5	44.0	51.9	52.6	59.4	66.9	77.1	107.0	118.0	124.1	144.9	154.4	165.5	174.2	182.4	191.4	201.0	210.5
AA/C_{org} (%)	0.55	2.47	1.3	1.35	0.38	n.d.	0.25	0.29	0.19	0.22	n.d.	n.d.	n.d.	n.d.	0.72	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
AS/C_{org} (%)	0.14	0.49	0.08	0.07	0.06	n.d.	0.05	0.03	0.18	0.02	n.d.	n.d.	n.d.	n.d.	0.07	0.01	n.d.	n.d.	n.d.	n.d.	n.d.

Individual amino acids are given in mol%; $GlcNH_2$ = glucoseamine, $GalNH_2$ = galactoseamine, AA/C_{org} = percentage of amino acids of organic carbon, AS/C_{org} = percentage of amino sugars of organic carbon.

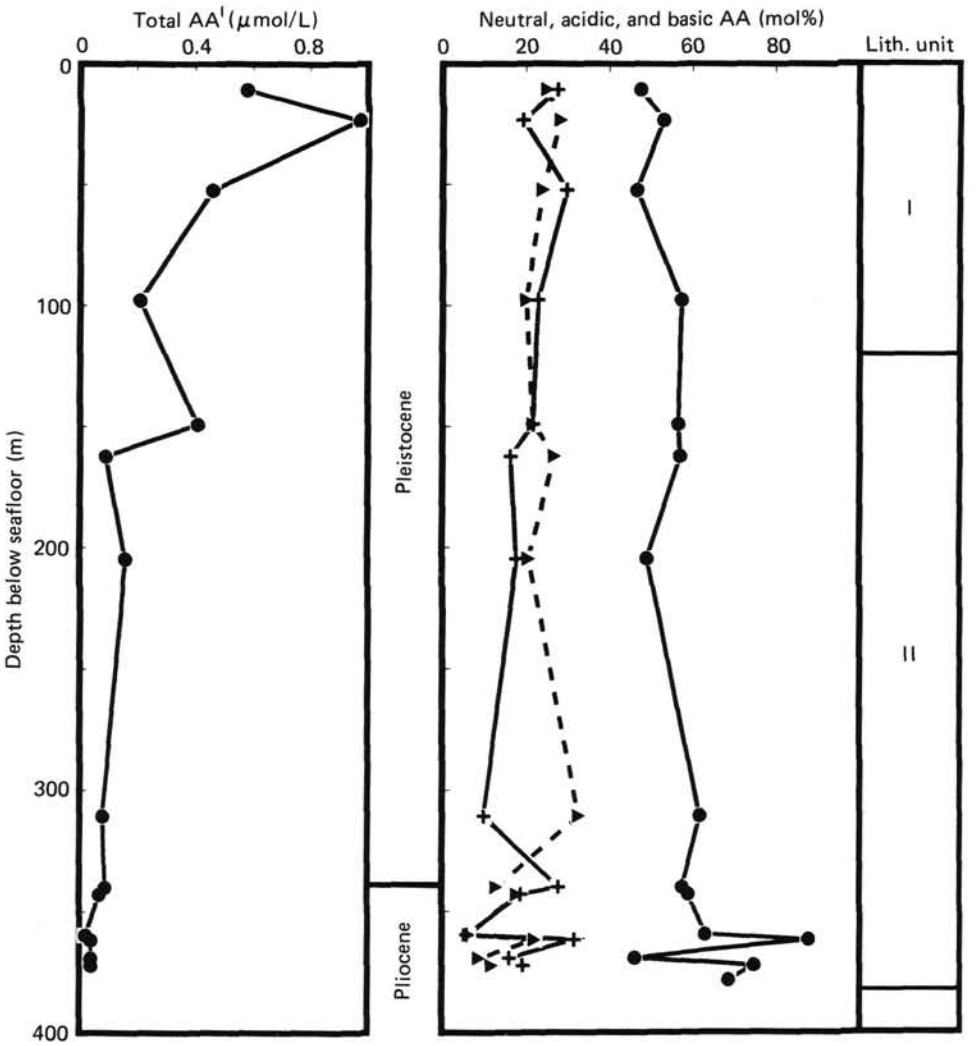

Figure 3. Downhole variability in the total amount of amino acids (AA) in sediments of Hole 651A (left). The contributions of neutral (dots, solid line), acidic (triangles, broken line), and basic amino acids (pluses, solid line) are depicted to the right. Neutral amino acids are threonine, serine, glycine, alanine, valine, isoleucine, and leucine. Acidic amino acids are aspartic and glutamic acid, and basic amino acids are arginine, histidine, lysine, and ornithine.

γ-ABA can also result from chemical diagenesis of glutamic acid (Glu) (Itihara, 1973; Schroeder, 1975).

The Glu/β-ABA and Asp/β-Ala ratios for sediment samples from Sites 651 and 653 are shown in Figures 5 and 6, respectively. β-Ala could only be detected in one sample below 360 mbsf at Site 651A. Quaternary samples display similar curves for these ratios at both sites, and the Glu/γ-ABA and Asp/β Ala ratios are low. We believe that these results may be an indication of high microbial activity in the young sediments, because degradation of primary amino compounds increases the abundance of these degradation products. Near the Pliocene/Pleistocene boundary (Samples 653B-9X-2 and 651A-37R-2) both ratios increase; this increase may indicate that amino acids bound to the organic matrix of biogenic calcite comprise a major partion of the total amino acid fraction, which is only 0.31 and 0.16 μmol/g of sediment (less than 0.02 of organic carbon; Table 8). Amino acid spectra of foraminifers are found to be dominated by aspartic acid, glycine, and glutamic acid (King and Hare, 1972), and no γ-ABA and β-Ala was detected in cleaned shell material from deep-sea sediments as old as 40.000 yr (Schroeder, 1975). According to these observations, the acidic amino acids embedded in the protein matrix of calcitic shell material are not degraded to γ-Ala or β-ABA during early diagenesis, but instead are protected from bacterial or thermal degradation, until recrystallization of the carbonate tests sets them free.

Ornithine also represents another nonprotein amino acid, which may originate from either abiotic and microbial degradation of arginine (Degens, 1970) or from constituents of bacterial cell walls (Goossens et al., 1986; Kandler, 1979, 1981). In contrast to the results from Site 653, high percentages of ornithine are found in the dolomitic Pliocene strata of Hole 651A. This finding may be ascribed to higher thermal stability of ornithine compared to other amino acids (Khan and Sowden, 1971). Low concentrations of γ-Aba and β-Ala were found in the dissolved amino acids of interstitial waters, whereas ornithine was abundant in all analyzed samples (Table 3).

Carbohydrates

Concentrations of carbohydrates in sediment are given in Tables 9 and 10 for samples from Site 651 and Site 653, and sugar values for pore waters are summarized in Table 11. Total amounts of sugars in sediments range from 0.21 to 1.82 μmol/g, and in pore water from 5.01 to 78.42 μmol/L.

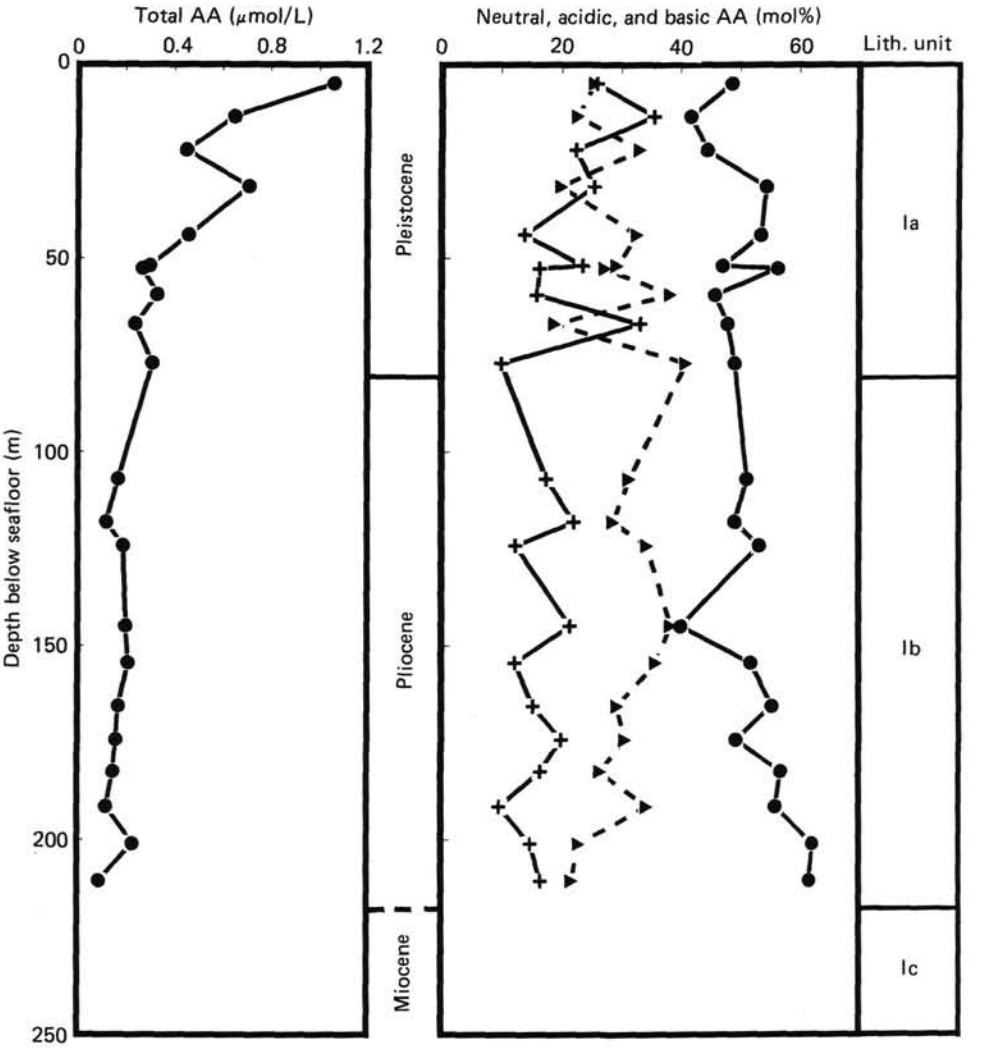

Figure 4. Downhole variability in the total amount of amino acids (AA) in sediments of Site 653 (left). The contributions of neutral (dots, solid line), acidic (triangles, broken line), and basic amino acids (pluses, solid line) are depicted to the right. Neutral amino acids are threonine, serine, glycine, alanine, valine, isoleucine, and leucine. Acidic amino acids are aspartic and glutamic acid, and basic amino acids are arginine, histidine, lysine, and ornithine.

The downhole distribution pattern of total sugars in sediment samples from Site 653 (Fig. 7) resembles that of total amino acids. Sample 653B-20X-3 (182.4 mbsf) is an exception because sugar contents are higher than in other Pliocene samples. Figure 7 also gives the variations in the galactose/fructose ratio. Galactose, together with mannose, rhamnose and xylose, is abundant in fresh plankton (Cowie and Hedges, 1984; Hecky et al., 1973; Degens and Mopper, 1975) and is, with mannose and glucose, the main sugar in bacterial cell walls (Kandler and König, 1978). Galactose is also a component of the heteropolysaccharides of land plants. Fructose has been found to be a major constituent in the sugar fraction of old sediments (Michaelis et al., 1986; Mopper et al., 1978; Emeis et al., 1987). Analyses of recent sediments from a variety of environments revealed low fructose contents, however, and these studies suggest high stability of fructose relative to other carbohydrates (Mopper, 1977; Bartsch, 1987). A preferential association of fructose with polyvalent metals, particularly with transition metals, has been described by Charley et al. (1963) and Barker et al. (1974). Degens and Mopper (1976) proposed this association as a stabilizing mechanism that preserves both metals and fructose. An enrichment of this sugar was also found in the humic matter of river water by Seifert and Ittekkot (1985), who believe that the incorporation of fructose in macromolecules and chelates protects this sugar against early diagenetic transformation in the geological environment. A feasible source of fructose is the abiotic epimerization of glucose in weakly alkaline solutions (Mopper et al., 1980). Laboratory experiments in seawater at a pH of 8.1 showed that this epimerization is significant especially at temperatures exceeding early diagenetic levels.

The galactose/fructose ratio can thus be used as an indicator of the relative freshness of the organic matter. Sediments that contain only weakly degraded organic material will have high galactose/fructose ratios, while those containing organic material exposed to biotic or thermal degradation processes for longer periods of time have low ratios. Furthermore, the galactose/fructose ratio should decrease with time as a function of differential degradation and as an effect of higher stability of fructose as compared to galactose and other carbohydrate monomers.

The galactose/fructose ratios for samples from Core 651A are listed in Table 9. The ratio decreases with depth, and a minimum in Sample 18R-5 coincides with a low carbonate value. As shown in Figure 7, the curve of the galactose/fructose ratios for

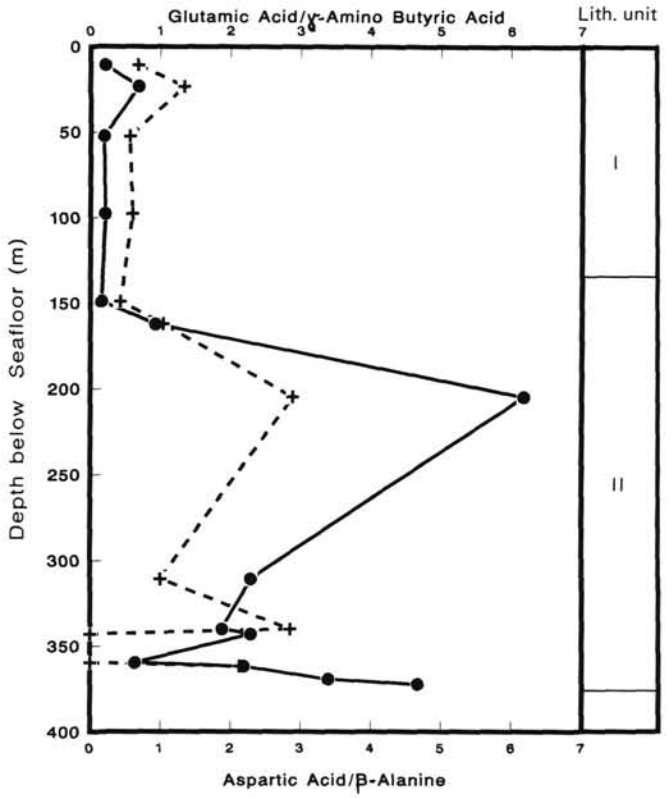

Figure 5. Depth plots of the ratios of glutamic acid to γ-amino butyric acid (dots, solid line) and aspartic acid to β-alanine (pluses, broken line), which are two indicators for microbial degradation in sediments of Hole 651A. Low values show advanced degradation, while high values may denote organic matter of terrestrial origin. See text for explanation.

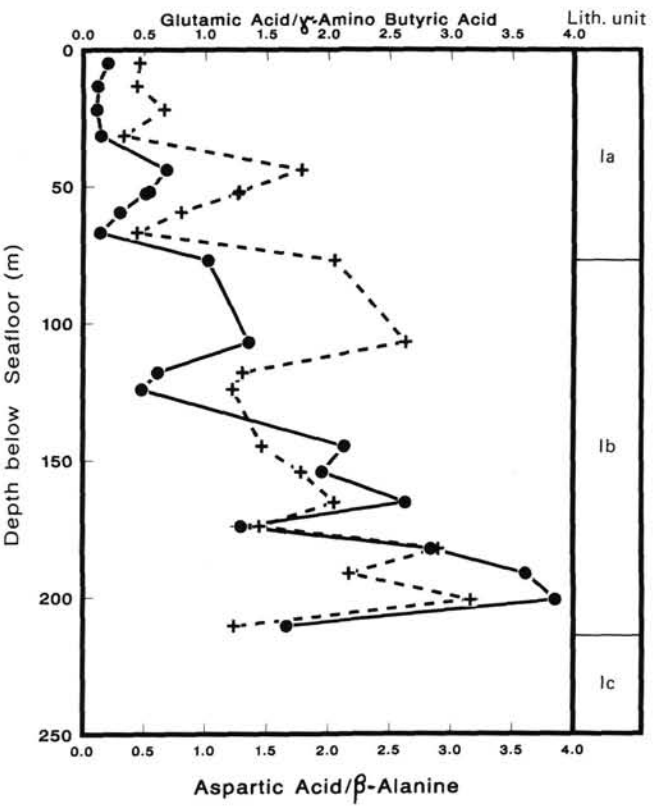

Figure 6. Depth plots of the ratios of glutamic acid to γ-amino butyric acid (dots, solid line) and aspartic acid to β-alanine (pluses, broken line), which are two indicators for microbial degradation in sediments of Site 653. Low values show advanced degradation, while high values may denote organic matter of terrestrial origin. See text for explanation.

Hole 653B is in good agreement with the distribution of total carbohydrates: samples high in organic carbon have higher ratios, because they contain more labile galactose when compared to samples low in organic carbon. Exceptions are the Samples 653B-4H-3 and -8H-2, which are characterized by a low carbonate content. In these samples the organic material may derive from terrigenous sources and may have been exposed to intensive decomposition prior to deposition. The differences among the other samples are presumably caused by factors such as variations in the quantity and quality of primary production and by different sedimentation rates, which affect the duration and degree of bacterial decomposition.

An increase in the dominance of fructose and glucose with depth in the carbohydrates of interstitial waters is observed at both sites. Previous studies of carbohydrates in interstitial waters from DSDP Leg 93 revealed similar trends (Emeis et al., 1987). Glucose and fructose are found to be the major sugars in subsoil waters (Spitzy, 1982) and in the free dissolved fraction of seawater (Mopper et al., 1980; Ittekkot et al., 1981). These observations underscore their relative stability and comparatively long residence time in both particulate and dissolved form. The fructose concentrations in the dissolved carbohydrate fraction are higher in Hole 651A than in Hole 653B. Whereas the fructose maximum in Sample 653B-6H-4 may be correlative with a high value for dissolved iron (Table 4), we are not able to explain the observed trends in dissolved carbohydrates with the available data. It appears that metal stabilization does not play any significant role in preserving dissolved sugars, as will be briefly discussed below.

Analyses of selected minor and trace constituents in the interstitial waters of Sites 651 and 653 are listed in Tables 3 and 4.

Table 9. Carbohydrates in sediment, Hole 651A.

Sample	3R-1	12R-1	17R-3	18R-5	40R-2
Rha	5.9	3.9	5.5	3.2	0.0
Man	11.3	5.5	6.6	1.5	4.1
Fru	4.6	19.4	20.9	50.2	31.5
Ara	20.5	11.4	13.0	2.9	1.3
Fuc	10.1	5.5	5.6	1.8	1.0
Gal	17.7	13.1	11.8	0.7	5.0
Xyl	11.5	6.8	7.6	1.0	0.5
Glc	18.5	34.5	29.1	38.8	56.6
Total (μmol/g)	0.98	0.56	0.91	1.42	0.23
Depth (mbsf)	10.8	97.9	149.0	162.2	369.3
Gal/Fru	3.88	0.68	0.56	0.01	0.16

Individual sugars are given in mol%.

We had hoped to find indications of unusual trace metal abundances, in particular of manganese and iron. We expected to see effects of halmyrolysis of volcanic ash and of alteration of the relatively young basalts at Site 651, and we had expected to verify correlations of dissolved metals with chelating agents in DOC. Even though the abundances vary widely for both elements, we failed to recognize any meaningful trend in the data. This result may be attributable to some extent to inadequacies in sample preparation (squeezing at laboratory temperatures and under oxygen on less than clean benches) and to the effects of complexing agents (such as DOC and certain carbohydrates) on

Table 10. Carbohydrates in sediment, Site 653.

Sample	1H-4	2H-5	3H-4	4H-3	5H-5	6H-4	6H-5	8H-2	9X-2	16X-3	18X-4	20X-3	23X-3
Rha	7.3	3.0	5.7	3.1	4.2	4.4	4.9	3.9	4.5	0.0	1.3	9.8	11.9
Rib	7.9	0.0	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Man	9.0	10.4	15.1	10.5	18.1	13.7	22.7	15.0	20.4	7.2	4.6	15.3	4.7
Fru	5.6	6.5	7.2	22.6	3.1	17.4	3.7	10.2	3.8	23.3	18.0	4.4	14.6
Ara	13.2	14.9	15.2	17.8	16.6	1.4	12.7	17.4	14.0	11.9	9.3	6.4	14.1
Fuc	8.8	5.0	7.2	11.6	12.8	10.1	12.3	11.9	13.5	17.9	12.6	10.6	8.1
Gal	18.2	16.5	14.6	10.6	18.4	11.1	14.1	11.7	11.9	12.0	5.9	18.2	1.3
Xyl	9.7	10.6	11.1	5.6	11.4	9.3	11.9	9.2	9.1	4.1	4.6	9.4	1.0
Glc	20.4	33.1	20.9	18.3	15.5	32.6	17.7	20.7	22.9	23.6	43.8	25.9	44.3
Total (μmol/g)	1.82	1.5	0.53	1.44	0.56	0.3	0.69	0.52	0.65	0.32	0.44	1.24	0.21
Depth (mbsf)	4.9	13.4	22.0	31.5	44.0	51.9	52.6	66.9	77.1	144.9	165.5	182.4	210.5
CHO/C_{org} (%)	1.1	8.0	2.1	4.4	0.6	n.d.	0.8	0.6	0.7	n.d.	1.1	n.d.	n.d.

Individual sugars are given in mol%

Table 11. Carbohydrates in interstitial water, Sites 651 and 653.

Hole	653B	653B	653B	653B	651A	651A	651A
Sample	3H-4	5H-5	8H-2	13X-4	3R-1	7R-2	18R-5
Rha	9.4	5.1	7.6	2.4	0.0	0.0	0.0
Man	14.8	11.0	12.7	1.9	3.1	0.7	0.5
Fru	2.0	9.2	17.2	13.1	39.9	47.2	52.8
Ara	7.1	5.7	13.9	0.0	2.3	3.7	0.3
Fuc	7.1	6.8	7.2	0.0	7.2	3.4	2.3
Gal	13.7	11.2	4.9	7.9	5.9	4.6	0.8
Xyl	6.0	3.9	10.2	1.5	2.5	0.8	0.6
Glc	40.0	47.2	26.4	73.2	39.1	39.6	42.7
Total (μmol/L)	5.01	7.76	17.08	7.5	24.8	25.38	78.42
Depth (mbsf)	22.0	44.0	66.9	118.0	10.8	52.4	162.2

Individual sugars are given in mol%

metal solubility. These organic substances, as was pointed out above, are liberated during various stages of sediment and organic matter diagenesis, and are pronounced near organic-rich horizons. The available data preclude speculation on the mechanisms of organic matter/metal interactions, however, and we are not at all certain whether the high metal concentrations in some samples are related to dissolved organic matter.

CONCLUSIONS

Downhole distribution of labile organic components in sediments (amino acids and sugars, and carbohydrates) seems to be affected by differences in source materials and their resistance to microbial degradation, by sedimentation rate, and by thermal maturity, rather than by organic matter abundances in the sediment. Comparison of distributions of these compound classes from Sites 651 and 653, where sedimentation rates differ by a factor of two, and which have different thermal histories, shows that increased heat flow at Site 651 resulted in preferential depletion of amino sugars. A concomitant relative enrichment of thermally stable amino acids, such as ornithine, glycine, and alanine was noticed and suggests that recrystallization of carbonate tests liberated acidic amino acids from proteinaceous matrices. These unstable compounds were subsequently destroyed.

Amino acid distribution corroborate the fact that the spatial range for microbial degradation of organic matter is dependent on sedimentation rates:

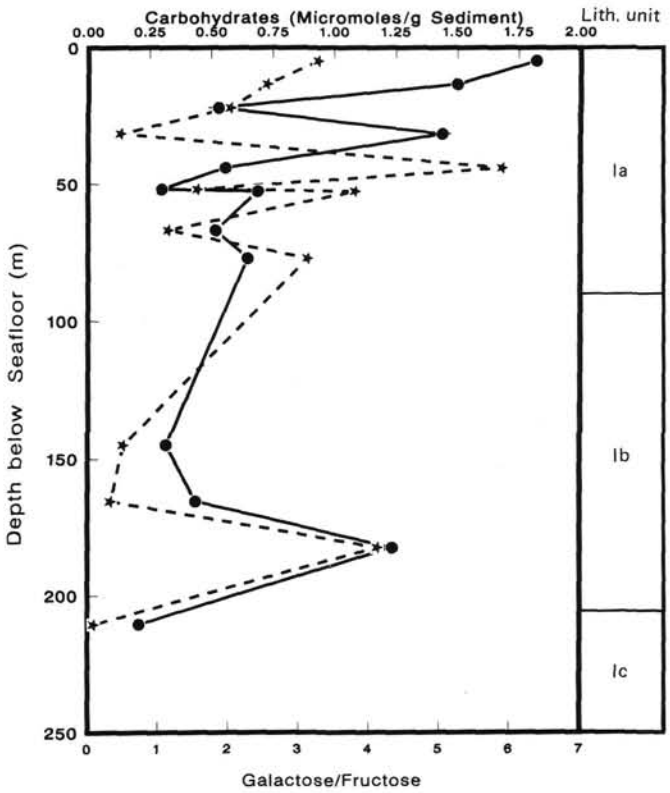

Figure 7. Total carbohydrates in sediment of Site 653 (dots, solid line) in relation to sediment depth, organic carbon content of the sediment, and the ratio of galactose/fructose (stars, broken line). It apppears that the state of degradation decreases as the amount of buried organic matter increases. This observation implies that bacterial degradation does not proceed to completion even though sulfate and labile organic matter is present.

Site 651 has sedimentation rates roughly 10 times those of Site 653 (roughly 40 cm/100 yr vs. 4 cm/1000 yr), and the zone of amino acid depletion is expanded at Site 651. Depth within the sediment column does not appear to have an effect on the rate of degradation. Ratios of glutamic acid to γ-amino butyric acid and of aspartic acid to β-alanine appear to be useful in tracing ongoing bacterial degradation of sedimentary organic matter even at sediment depths of a few hundred meters.

Carbohydrate distribution appears to be related to source of organic matter and time. Stable sugars such as fructose increase in their molar contributions relative to more labile sugars such as galactose. The ratio of labile versus stable sugars may be a valuable tool for estimating the state of organic matter degradation in sedimentary sections. It is interesting to note that bacterial decomposition of relatively labile components does not proceed to the point of depletion, even though oxygen donors (sulfate) and labile organic matter (here: galactose) are still present.

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