39. ORGANIC GEOCHEMISTRY OF INTERSTITIAL WATERS, SITES 474 AND 479, LEG 641

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INTRODUCTION

Studies of the nature and amount of dissolved organic matter (DOM) in pore-water solutions have been confined mostly to recent sediments (Henrichs and Farrington, 1979; Krom and Sholkovitz, 1977; Nissenbaum et al., 1972). The analyses of organic constituents in interstitial waters have not been extended to sediment depths of more than 15 meters (Starikova, 1970). Large fluctuations in organic contents of near-bottom interstitial fluids suggest that organic compounds may provide insight into the chemical and biological processes occurring in the sedimentary column. Gradients in inorganic ion concentrations have been used as indicators of diagenesis of organic matter in deep sediments and interstitial waters. Shishkina (1978) attributed the occurrence of iodine and Cl/Br ratios that deviated from the value of seawater to the breakdown of organic matter and the liberation of bromide during mineralization. Sulfate depletion and maxima in ammonia concentrations were interpreted to be a consequence of sulfate reduction reactions in pore fluids, even at depths of more than 400 meters (Miller et al., 1979; Manheim and Schug, 1978). The purpose of this chapter is to study organic carbon compounds dissolved in interstitial waters of deep sediments at Sites 474 and 479.

METHOD

Twenty-four interstitial water samples and nine sediment samples from Holes 474, 474A, and 479 were studied. The concentrations and types of dissolved organic carbon (DOC), amino acids, and carbohydrates in pore fluids were determined. Organic carbon, organic nitrogen, amino acid, and carbohydrate analyses were carried out on the sediment samples.

Dissolved organic carbon. Determinations of the organic carbon content of pore waters were performed with an Erba Science total carbon monitor TCM 400/P, which operates on the principle of high temperature wet oxidation. A 10-ml sample was mixed with a 2% solution of nitric acid and was stripped by nitrogen, producing peaks for inorganic and volatile organic carbon. An aliquot of the residual liquid was introduced into a catalytic oxidation furnace at 940°C. The resulting CO₂ was reduced and detected in an FID as residual organic carbon. The accuracy of this method was determined by comparing our Sargasso seawater results with those obtained by MacKinnon (1978). Five replicate analyses were made on each pore-water sample after a hundredfold dilution of the original sample with double-distilled, deionized water. The values were corrected for the distilled water blank.

Amino acids. Amino acids in pore fluids were analyzed after the evaporation of 1-ml sample to dryness, the addition of 1 ml of 6N

HCl, and hydrolysis at 110°C for 22 hr. The hydrolysate was desalted on Bio Rad AG 50W resin and introduced into a modified automatic amino acid analyser (Biotronik). Separation was achieved by ion exchange chromatography using DC-6A resins (Durrum) and o-phthalaldehyde as fluorescence reagent.

For amino acid analyses of sediments, 100 mg of dry sample was hydrolyzed with 2 ml of 6N HCl at 110° C for 22 hr. The extract was filtered through glass fiber filters, evaporated, and the residue taken up in a sodium citrate buffer (pH = 1.8). An aliquot of this was then injected into the amino acid analyzer.

Carbohydrates. Carbohydrates were analyzed on a modified Biotronik carbohydrate analyzer (Mopper, 1978) operating at a nanomole sensitivity. All naturally occurring reducing monosaccharides could be detected.

To determine total sugars in interstitial waters, an aliquot of 0.5 ml of pore water was mixed with 2 ml of 2N HCl in a sterilized glass ampule; it was then sealed under argon and hydrolyzed for 3.5 hr. at 100°C. The hydrolyzed mixture was desalted by electrodialysis, and its sugar content was analyzed.

The sediment samples were dried, and 1 g of each was introduced with 2 ml of concentrated H_2SO_4 into a sterilized glass ampule to react for 2 hr.; the ampule was kept at 5°C. The acid was then diluted to 1.8N, and the ampule was sealed under argon and hydrolyzed for 4 hr. at 100°C. The filtered hydrolysate was electrodialyzed before analysis.

RESULTS

Analysis data for interstitial water are presented in Tables 1 and 2 and in Figures 1 and 2. Data on sediment analyses are given in Table 3 and Figure 3. For sugars and amino acids, only total amounts are reported. A more detailed discussion of the concentration and distribution of individual carbohydrates and amino acids will be given elsewhere (Michaelis et al., unpublished).

Table 1. Interstitial water data, Leg 64, Site 474.

Core/Section (depth in m)	DOC (mg/l)	TAA (µmol/l)	Amino Acid Carbon (% DOC)	TC (µmol/l)	Carbohydrate Carbon (% DOC)
474					
2-1, 10.9	37	58.8	7.57	43.2	8.08
3-2, 21.9	87	n.d.	n.d.	51.5	4.15
5-2, 40.9	124	44.3	1.81	64.3	3.60
7-3, 60.0	39	73.4	10.49	27.2	4.79
474A					
1-2, 173.9	87	38.3	2.71	31.5	2.51
4-4, 205,4	79	60.3	3.99	15.8	1.35
7-2, 230.9	51	25.2	2.37	23.4	3.18
10-1, 257.9	102	15.0	0.83	16.3	1.07
13-3, 289.4	70	10.1	0.72	85.2	8.66
16-4, 319.4	47	8.5	0.81	8.3	1.15
19-1, 343.3	43	35.2	4.40	9.1	1.47
23-3, 384.4	31	4.1	0.58	12.1	2.68
40-4, 546.2	204	41.3	1.13	17.2	0.58

Note: TAA = total amino acids; n.d. = not determined.

¹ Curray, J. R., Moore, D. G., et al., *Init. Repts. DSDP*, 64: Washington (U.S. Govt. Printing Office).

Table 2. Interstitial water data, Leg 64, Site 479.

Core/Section (depth in m)	DOC (mg/l)	TAA (µmol/l)	Amino Acid Carbon (% DOC)	TC (µmol/l)	Carbohydrate Carbon (% DOC)
1-1, 1.4	49	38.8	3.98	14.9	2.10
3-1, 20.4	100	59.3	2.77	16.5	1.14
5-3, 42.1	73	156.3	9.73	n.d.	n.d.
7-5, 64.4	52	63.4	6.00	21.2	2.81
9-2, 78.9	54	52.9	6.24	27.4	3.52
11-2, 97.5	41	100.3	11.24	22.5	3.73
17-5, 159.4	188	56.7	1.53	10.4	0.36
21-4, 195.9	48	23.8	2.50	9.5	1.27
24-4, 224.4	68	11.8	0.85	20.4	1.93
27-4, 252.9	20	25.3	6.45	9.8	3.20
39-4, 366.9	41	38.9	4.78	25.8	4.27

Note: TAA = total amino acids; n.d. = not determined.

DISCUSSION

Site 474

During the deep-sea drilling operation at Site 474. beyond the continental slope, Pliocene through Pleistocene sediments were recovered. Units I through V, consisting mostly of diatomaceous mud with mud turbidites, show large variations of DOC in their interstitial waters. Dissolved organic carbon varies between 31 and 204 mg/l. A maximum concentration of 204 mg/l was measured in a pore-fluid sample from section 474A-40-4 at a sub-bottom depth of 546 meters. This sample was taken from a layer of silty clay between two dolerite sills. Total carbohydrates (TC) make up 0.5 to 8.6% of the organic carbon dissolved in interstitial waters. The carbohydrate concentration shows no regular trend with depth. Section 474A-13-3 (289.4 m sub-bottom) contains the highest amount of dissolved carbohydrates (85.2 mol/1; 8.7% DOC).

Significant changes within the top 100 meters (i.e., within Units I and II) seem to be caused by input variations. Profiles of DOC and dissolved carbohydrates show similar gradients. Nearly 5% carbohydrate carbon of the total DOC is observed. Microbial and abiotic alterations at greater sediment depths may lead to different trends in DOC and TC.

As expected, the more labile amino acids exhibit rather smooth concentration profiles. Their distributions are relatively homogeneous throughout the sediment column. The variations of amino acid carbon of the total DOC in the uppermost 50 meters cannot be interpreted easily. Where carbohydrates and amino acids show minimum concentrations and DOC remains constant (e.g., at a depth of about 150 m; Unit III), diagenetic changes in pore fluids are to be expected.

Interestingly, in Holes 474 and 474A there is a maximum concentration of carbohydrates at 289 meters (Unit IV). The DOC remains constant, whereas carbohydrate carbon increases to 8.7%. This has occurred because the compounds were probably shielded from diagenetic alteration. A possible mechanism is metal complexation, which hinders microbial attack and diagenetic decay. Metal-complexed amino acids and carbohydrates especially have been found in sediments deposited under oxic conditions. In these cases, the stabilized metal-complexed amino acids and carbohydrates can account for 65% of the total amount (Degens and Mopper, 1979). The concentration maximum in this horizon is not smoothed by diffusion but, rather, is confined to the depth range of 30 to 50 meters.

The high DOC value in pore fluids from 546 meters (a silty clay between two dolerite sills) suggests a reducing sedimentary environment with a high contribution of organic matter at the early stages of ocean-floor development. High thermal stress and the physical isolation of this thin unit by two dolerite sills have decreased the amount of simple organic compounds, such as sugars and amino acids. Their common percentage of DOC decreases to 1.7%. The high DOC content in this sample may be caused by organic matter of high molecular weight.

Site 479

Sediment

The profile of organic carbon follows the succession of three lithostratigraphic units. Late Pleistocene sediments, to a depth of 200 meters, show carbon contents of 18 to 35 mg/g sediment. The unit from 200 to 350 meters, with C_{org} contents of 5 to 10 mg/g sediment, is succeeded by the laminated mudstones of Unit III, which contain more than 35 mg/g sediment organic carbon.

Carbohydrates and amino acids make up only 1.5% of the sediment in the upper section and show a nearly constant decrease with increase in depth. At 400 meters they comprise only 0.2%. The nearly linear decrease of carbohydrates and amino acids with depth seems to be generated diagenetically and is independent of the bulk organic matter of the sediment. Definite alterations of these highly reactive compounds occur in the upper 50 meters of the sediment column. In samples below 50 meters, their contents are already 1%, and abiotic decay reactions become predominant.

Interstitial Waters

Dissolved organic carbon values of Hole 479 pore fluids are in the same range as those in Holes 474 and 474A. The DOC maximum at the early/late Pleistocene boundary can be correlated across both sites.

Most striking is the discrepancy between the DOC profile and the organic carbon content of the sediment. The results suggest two different carbon pools, which have been separated at a very early stage of sedimentation. An exchange between organic matter in the sediment and DOC in pore fluids seems to be very limited, because even in greater depths the two profiles do not approach each other. We believe that the significant changes of DOC with depth argue against a widespread vertical diffusion of organic compounds. Correlation of the two maxima in Holes 479, 474 and 474A at the early/late Pleistocene boundary lends further support to this argument.

The carbohydrate content in the interstitial waters of Hole 479 is very constant and shows little fluctuation. Amino acid concentrations are highly variable in the upper 100 meters but reach a constant level below 200



Figure 1. Interstitial water data, Site 474 (DOC = dissolved organic carbon; TC = total carbohydrates; TAA = total amino acids).

935



Figure 2. Interstitial water analyses, Site 479 (DOC = dissolved organic carbon; TC = total carbohydrates; TAA = total amino acids).

Core/Section	Organic Carbon	TAA	Amino Acid Carbon	TC	Carbohydrate Carbon
(depth in m)	(ing/g)	(//mol/g)	(** OC)	(//moi/g)	(% OC)
474A					
7-2, 230.6	6.8	532.6	0.42	683.1	0.68
28-2, 430.2	8.6	93.4	0.06	71.4	0.05
32-2, 468.2	10.7	154.2	0.07	20.0	0.01
479					
3-2, 21.7	18.2	4880.5	1.50	3751.6	1.41
7-5, 64.3	34.5	1261.4	0.21	3365.0	0.67
15-5, 140.1	24.5	2285.3	0.52	1498.5	0.42
22-5, 206.7	6.2	234.1	0.22	360.5	0.39
37-5, 349.4	10.0	290.6	0.17	49.5	0.03
43-1, 400.2	35.9	677.0	0.11	39.3	0.01

Table 3. Organic carbon contents, Sites 474 and 479.

Note: TAA = total amino acids.

meters. The percentage of the amino acid carbon of the total DOC shows variations that may be correlated with dolomitic layers caused by adsorption. Small concentrations of amino acids and carbohydrates at a correspondingly high level of DOC suggest that the efficiency of polymerization to DOC of high molecular weight is very high. The amino acids and carbohydrates have probably existed as easily consumable compounds that were not metal complexed. High micro-organism populations and reducing conditions in the water column are the probable environment. Gieskes (1975) and Einsele (1977) focus on the question of compaction flow versus diffusion of dissolved species in a sedimentary diagenetic environment. From the limited data in this chapter it appears that diffusional flux is insignificant—at least at rates of sedimentation on the order of 160 to 200 m/m.y. At lower rates of sedimentation, one might envision a diffusional flux. We will address ourselves more specifically to this subject in Michaelis et al. (unpublished), and present a full documentation of the amino acid and sugar data.

As a final note we would like to emphasize that we started with those organic substances that can be dissolved in aqueous media. The chemical behavior of such nonpolar molecules as higher-weight hydrocarbons (>C-5) has not been investigated because of limited samples. We intend to pursue this question during subsequent legs.

CONCLUSION

These first organic geochemical analyses of interstitial water samples indicate a fruitful line of investigation. Interstitial solutions show significant compositional changes of DOC with depth.

Carbohydrate and amino acid percentages of DOC are, in general, negatively correlated with DOC. High concentrations of DOC, combined with low amino acid



Figure 3. Variations of organic carbon (OC), Site 479.

and carbohydrate concentrations, could be a result of reducing sedimentary conditions. Low DOC values and high amounts of carbohydrates and amino acids may indicate an oxic paleoenvironment.

The concentration of dissolved organic matter in pore fluids far exceeds the DOC content of seawater, and its variations are nearly independent of the carbon content of the sediment. The results of our study suggest that a considerable amount of dissolved organic matter in the interstitial waters probably belongs to a soluble macromolecular fraction. This is reminiscent of dissolved organic matter in the deep sea. We propose that the mechanisms forming these substances are melanoidin (Gagosian and Stuermer, 1977) and polyphenolic condensation (Degens, 1970) reactions. Analyses of artificial melanoidins have shown that the recovery of the reactants (amino acids and sugars) is very incomplete (Nissenbaum, personal communication). The general distribution pattern of sugars and amino acids can also be a result of reduced recovery of these substances during acid hydrolysis of interstitial waters.

A correlation of carbohydrates, amino acids, and DOC in pore fluids across a number of deep-sea drilling sites can lead to a better understanding of the paleoenvironment and its relation to the tectonic development of this area during sedimentation. Furthermore, temperature effects are readily discernable.

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REFERENCES

- Degens, E. T., 1970. Molecular nature of nitrogenous compounds in sea water and recent sediments. In Hood, D. W. (Ed.), Organic Matter in Natural Waters: University of Alaska Institute of Marine Science, Publication 1: Anchorage (University of Alaska Institute of Marine Science), 77-106.
- Degens, E. T., and Mopper, K., 1979. Early diagenesis of sugars and amino acids in sediments. *In* Larsen, A. G., and Chillingar, G. V. (Eds.), *Diagenesis in Sediments and Sedimentary Rocks:* Amsterdam (Elsevier), pp. 143-205.
- Einsele, G., 1977. Range, velocity, and material flux of compaction flow in growing sedimentary sequences. Sedimentology, 24:639-655.
- Gagosian, R. B., and Stuermer, D. H., 1977. The cycling of biogenic compounds and their diagenetically transformed products in seawater. *Mar. Chem.*, 5:605-632.
- Gieskes, J. M., 1975. Chemistry of interstitial waters of marine sediments. Earth Planet. Sci. Lett., 3:433-453.
- Henrichs, S. M., and Farrington, J. W., 1979. Amino acids in interstitial waters of marine sediments. *Nature*, 279:319-322.
- Krom, M. D., and Sholkowitz, E. R., 1977. Nature and reactions of dissolved organic matter in the interstitial waters of marine sediments. *Geochim. Cosmochim.* 9 (a, 41:1565-1573.
- MacKinnon, M. D., 1978. A dry oxidation method for the analysis of the TOC in seawater. Mar. Chem., 7:17-37.
- Manheim, F. T., and Schug, D. M., 1978. Interstitial waters of Black Sea cores. In Ross, D. A., Neprochnov, Y. P., et al., Init. Repts. DSDP, 42, Pt. 2: Washington (U.S. Govt. Printing Office), 637–651.
- Michaelis, W., Mycke, B., Vogt, J., et al., unpublished. Organic carbon in deep interstitial waters.
- Miller, R. S., Lawrence, J. R., and Gieskes, J. M., 1979. Interstitial water studies, Sites 386 and 387, Leg 43. *In* Tucholke, B. E., Vogt, P. R., et al., *Init. Repts. DSDP*, 43: Washington (U.S. Govt. Printing Office), 669–674.
- Mopper, K., 1978. Sugars in borate medium. Anal. Biochem., 85: 528-532.
- Nissenbaum, A., Baedecker, M. J., and Kaplan, I. R., 1972. Studies on dissolved organic matter from interstitial water of a reducing marine fjord. *In Gaertner*, H. R. v., and Wehner, H. (Eds.), *Ad*vances in Organic Geochemistry 1971: Oxford (Pergamon), pp. 427-440.
- Shiskina, O. V., 1978. Distribution of bromine, Cl/Br relationships, and iodine in interstitial water of the Black Sea, based on DSDP Leg 42B. In Ross, D. A., Neprochnov, Y. P., et al., Init. Repts. DSDP, 42, Pt. 2: Washington (U.S. Govt. Printing Office), 631-635.
- Starikova, N. D., 1970. Vertical distribution patterns of dissolved organic carbon in sea water and interstitial solutions. Oceanology, 10:796-807.