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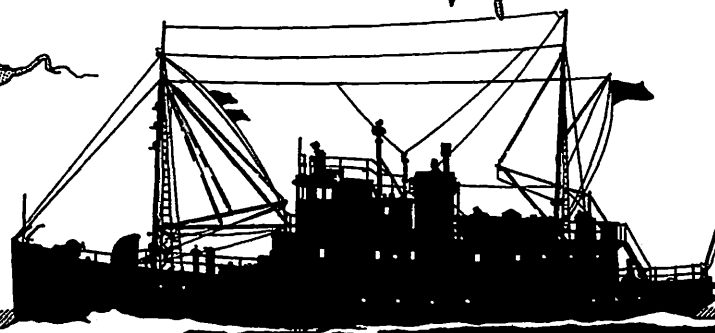
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Technical Report No. 71

MARINE SEDIMENTS OF PRINCE OF WALES STRAIT AND AMUNDSEN GULF, WEST CANADIAN
ARCTIC, by Richard G. Bader and Vernon J. Henry. (pp. 35 - 52)

Technical Report No. 72

SPRING CHANGES IN PHYTOPLANKTON ABUNDANCE IN A DEEP ESTUARY, HOOD CANAL,
WASHINGTON, by John P. Barlow. (pp. 53 - 67)

Technical Report No. 73

SOME CONSIDERATIONS OF OXYGEN UTILIZATION RATES IN PUGET SOUND, by
Clifford A. Barnes and Eugene E. Collias. (pp. 68 - 80)

Technical Report No. 74

NOTES CONCERNING THE HALOCLINE IN THE NORTHEASTERN PACIFIC OCEAN,
by Richard H. Fleming. (pp. 158 - 173)

Technical Report No. 75

CONTROL OF SEDIMENTATION AND BOTTOM CONFIGURATION BY CONVECTION CURRENTS,
LAKE WASHINGTON, WASHINGTON, by Howard R. Gould and Thomas F. Budinger.
(pp. 183 - 198)

Technical Report No. 76

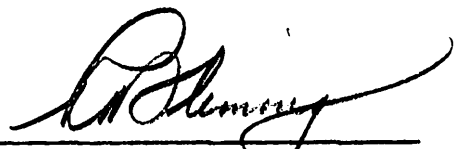
THE OCCURRENCE OF PIGMENTS IN MARINE SEDIMENTS, by Taivo Laevastu.
(pp. 325 - 334)

Technical Report No. 77

DIURNAL STUDY OF PHYTOPLANKTON PIGMENTS, AN IN SITU STUDY IN EAST SOUND,
WASHINGTON, by Charles S. Yentsch and Robert F. Scagel. (pp. 567 - 583)

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THE OCCURRENCE OF PIGMENTS IN MARINE SEDIMENTS¹

By

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ABSTRACT

Qualitative and quantitative studies of pigments in marine sediments, using chromatographic and spectrophotometric methods, showed the presence of degradation products of chlorophylls; some of their optical properties are given. It is concluded that pigments decompose rapidly in aerated, coarse-grained sediment whereas in deeper layers of the same sediment, under anaerobic conditions, decomposition is slow. It is suggested that the decreasing amount of pigment with increasing depth of sediment can be used as a criterion for determining the past environmental conditions of deposition.

INTRODUCTION

According to Neaverson (1940), it is probably chlorophyll which gives the greenish color to some marine sediments; he noted that visible chlorophyll grains in marine sediments became brownish in color upon oxidation and decomposition.

Investigations of Motovskij Bay by Gorschkova (1938) showed that organic substance in shallow water sediment was richer in chlorophyll than that from deep water sediment; quantitative determinations by him gave the following results: organic carbon in shallow water 1-2%, in deep water 1.3-2.8%; chlorophyll in shallow water 0.0014-0.0037%, in deep water 0.0008-0.0023%. Klenova and Jastrebova (1938), who found 0.6-3.74 mg chlorophyll

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in 100 g fine fraction of sediment from the Caspian Sea, stated that chlorophylls are best preserved in anaerobic conditions.

Jastrebova (1938) recorded the presence of chlorophyll in old burning shales from the Upper Jura. From chlorophyll determinations in sediments from the Barents Sea and from laboratory experiments on conditions of preservation of chlorophylls in sediments, Jastrebova concluded that chlorophylls are well preserved by fine muds but are quickly oxidized in sandy sediments. A correlation was found between the amount of fine grain-size fraction and the amount of chlorophyll present in surface sediment. The mean value of chlorophyll in surface sediment from the Barents Sea was 0.75 mg in 100 g dry sediment; from the Kola Fjord it was 0.5–5.7 mg in 100 g sediment without fraction greater than 1.0 mm. Furthermore, Jastrebova suggested that the amount of chlorophyll in the sediment surface and its relation to organic substance gives a measure for the rate of ventilation of surface sediment and that the rate of progressive decrease of chlorophylls in sediment can be used as a measure to determine the rate of sedimentation.

Fox and Anderson (1941), in a spectrographic study of pigments in sediment, found no chlorophylls, but they did find several green compounds which they believed to be decomposition products of chlorophylls. Vallentyne (1955, 1957) concluded that the green pigments occurring in sediments are sedimentary chlorophyll degradation products (SCDP) rather than chlorophylls, and that undoubtedly the green lipoidal substances of sediments were formed from plant chlorophylls. Vallentyne (1957) has provided a short summary of previous works on pigments found in sediments. Orr and Grady (1957) found 4 to 100 ppm of chlorophyll derivatives, calculated as pheophytin α , in surface sediment samples from marine basins off southern California, and Gillbricht (1952) reported that the amount of chlorophyll in dead detritus in sea water was four times that in living plankton.

In the present study an attempt has been made to give a quantitative picture of the pigments present in sediments of the San Juan Archipelago. The nature of pigments and some of their optical properties as well as their condition of preservation in relation to sediment depth have been investigated.

METHODS

Separation and identification of various pigment components was made chromatographically with combined absorption columns after the procedures given by Strain (1945) and by Zechmeister and Chohnoky (1941). In the separation process, the following absorbents were used: (a) powdered sugar for chlorophyll *a* and *b*; (b) magnesium carbonate for protochlorophylls; (c) calcium carbonate for xanthophylls; (d) dialuminium trioxyd for carotenes. Ethanol, methanol, acetone, petroleum ether and benzene were used as solvents and chromatogram developers.

Since pigments oxidize rapidly when in contact with air, the sediment samples were taken from the cores as quickly as possible and kept in tightly-packed, air-tight tubes. The sediment was then dried in vacuum over a diluted sulphuric acid that gave a vapor pressure corresponding to 60 % saturation pressure at 20° C (laboratory conditions).

The method developed by Richards with Thompson (1952) for simultaneous quantitative determination of different chlorophylls and carotenoids in marine plankton was followed to a great extent in the quantitative investigations. 0.5–1 g air-dried sediment was leached for 18 hours with a given amount (5–10 ml) of 90 % acetone; the suspension was shaken several times during this period. The samples were then centrifuged and the optical densities of the resulting acetone solution were measured with a Beckman DU Spectrophotometer.

By chromatographic separations, chlorophylls were found in only trace amounts in the surface layers of sediment. The pigment compounds were assumed to be mainly the hydration and oxidation products of chlorophylls, but the specific absorption coefficients of these hydration products are not known. The quantities of pigment have therefore been reported in pigment units (PU), following Richards with Thompson's computation. In most cases, only the equivalent *a* component has been computed. Assuming that the specific absorption coefficient of the green pigments found in sediment is close to the specific absorption coefficients of chlorophylls, one PU approximates one μg pigment.

Estimation of organic carbon in sediments was made by Shollenberg's method with Allison's (1935) modification. This method is

also described and used by el Wakeel and Riley (1957) for determination of organic carbon in marine muds.

STUDY MATERIAL

Short sediment cores were collected with a gravity corer from different environmental conditions in the San Juan Archipelago. Two of these (Cores 1 and 2) were taken from East Sound where water layers are fairly stable during most of the year. Organic production is also greater there than in any other locality of the area and the water has a low dissolved oxygen content close to the bottom. The sediments are rich in organic matter because little decomposition of organic matter takes place on sediment surface. The color of these sediments is greenish-black to greenish-grey and they often smell of hydrogen sulfide.

Cores 3-9, taken from other localities of the San Juan Archipelago where the bottom water has a high dissolved oxygen content, varied greatly from place to place, according to the depth of water and the strength of tidal currents near the bottom. These cores consisted of coarse sand, small amounts of organic matter and calcareous shell fragments.

Nature and Optical Properties of Pigments in Sediments. The pigments were easily soluble in 90 % acetone, and the resulting solution was brownish-green. They were also easily soluble in ethanol and methanol, but with a less intense and much greener color than that from acetone. The pigments were only slightly soluble in benzene, which gave a pale brownish-green solution. Petroleum ether had practically no effect on the pigments and the solution was colored only a light bluish-green.

Except for indications of traces in the uppermost layers of the sediment, no chlorophylls were found by chromatographic separation, a finding which corresponds with results of Fox and Anderson (1941). One of the most common pigments found by these authors had the wavelength of maximum absorbency in petroleum ether at 669 m μ . According to Orr and Grady (1957), pheophytin *a* gives absorption maxima in chloroform at 668 m μ . The absorption spectra of the 90 % acetone solutions of the sediments are given in Fig. 1.

In general, these absorption spectra are somewhat similar to those found in plankton extracts (Richards, 1952). However, they

also show some characteristics similar to the absorption spectra of pheophytin *a* (Orr and Grady, 1957). In this study the wavelength of maximum absorbency of pigments from a sediment surface layer was about $667\text{ m}\mu$, which possibly indicates the presence of chlorophyll, found in traces by chromatographic separation of these sedi-

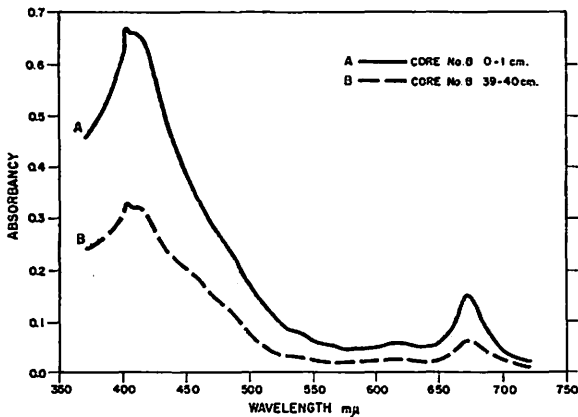


Figure 1. Absorption spectra of 90% acetone solutions of sediments.

ments. In more oxidized sediments and especially in layers at depth, the wavelength of maximum absorbency is $670\text{--}672\text{ m}\mu$. The other peak of maximum absorbency of $608\text{ m}\mu$ shows the same tendency to move towards the longer wavelength in more oxidized sediments.

Peaks of 480 and $510\text{ m}\mu$ indicate the presence of carotenoids, but these peaks are also present to some extent in pheophytin *a*. Because of the great similarity of optical properties of chlorophyll *a* and its degradation products, it is assumed that the chlorophylls found by Russian workers represent in reality the same degradation products as those found by Fox and Anderson (1941), Vallentyne (1955), Orr and Grady (1957) and in the present work.

Quantitative Occurrence of Pigments in Sediments. Using the formulae of Richards with Thompson (1952), only the chlorophyll *a* component was calculated; in Table I this is represented as pigment in pigment units (PU). Cores 1 and 2, taken from anaerobic conditions in East Sound, had a high content of both organic carbon and pigments which did not become less with depth. This probably indicates that no decomposition of organic matter takes place in

TABLE I. ORGANIC CARBON AND GREEN PIGMENTS IN THE SEDIMENTS FROM SAN JUAN ARCHIPELAGO

Core No.	Locality, Character of Sediment, and Depth of Water	Sediment Depth (cm)	Organic Carbon (%)	Pigments in P.U. in 1 g Dry Sediment
1	East Sound Greenish black mud; smells of H ₂ S Depth 22 m	0.5- 2	3.16	115
		4- 6	3.28	125
		9-11	3.12	130
		14-16	3.14	110
		19-21	3.28	135
		22-24.5	3.01	130
2	As above Depth 27 m	0.5-2		105
		4- 6	3.30	65
		9-11		95
		14-16	2.84	100
		19-21	3.11	75
		23-24.5	2.90	100
3	Composite sample, S. Juan Channel Dark gray sandy mud Depth 50-100 m	0- 5	1.76	31
4	George Pt., Shaw Is. Black sandy mud Depth ca. 120 m	0- 1	2.22	19
		9-10	1.81	12
		15-16	1.38	10
5	George Pt., Shaw Is. Dark gray sand and shells Depth ca. 120 m	0- 1	2.12	17
		13-14	0.87	3
6	NE of Brown Island Gray sand and shells Depth 50 m	0- 1	1.60	15
		10-11	0.74	4
7	Lopez Sound Fine sandy mud Depth 42 m	0- 1	1.52	61
		4- 5	1.66	22
		9-10	1.10	10.5
		14-15	2.50	19.5
		19-20	2.41	18.5
		24-25	2.49	18.0
		29-30	2.48	19.0
		34-35	2.59	17.5

TABLE I (continued).

Core No.	Locality, Character of Sediment, and Depth of Water	Sediment Depth (cm)	Organic Carbon (%)	Pigments in P.U. in 1 g Dry Sediment
8	Off Friday Harbor Gray sandy mud Depth 17 m	0- 1	0.91	16.5
		4- 5	0.75	10.5
		9-10	0.98	8
		14-15	1.40	5.5
		19-20	1.19	4.5
		24-25	1.36	6.5
		29-30	1.40	8
		34-35	1.03	7.5
9	Off Friday Harbor Coarse gray sandy mud with shells Depth 34 m	0- 1	1.06	21
		4- 5	1.12	14
		9-10	1.08	10.5
		14-15	0.91	6
		19-20	0.90	3

the sediment in this anaerobic environment. Core 1, from shallow water, had more pigments per unit amount of organic matter than Core 2. This also indicates that the degeneration of organic matter takes place essentially while sinking in the water, before it reaches the anaerobic bottom. The mean pigment content of 1 g organic matter was about 2 mg or 0.2 %, assuming that 1 PU equals 1 μ g pigment.

A combined sample of surface sediment (designated as Core 3) from San Juan Channel showed 3.2 % organic matter (org C \times 1.8), in which only 0.1 % pigment was present. By comparison, the chlorophyll content of dry plankton has been estimated as 2.9 % by Riley (1946). Cores 4 through 9 showed varying amounts of organic carbon and pigments, the amount of pigment in relation to organic matter apparently being dependent on the texture of the sediment. The pigments decreased rather rapidly in the uppermost 10-15 cm, but showed little decomposition (Fig. 2) and reducing conditions in the deeper sediment layers. The above findings also show that pigments cannot be used either as an indicator for the amount of organic matter in the sediments or as a measure for the rate of sedimentation.

However, the amount of pigment in relation to the amount of organic matter and the decrease in the amount of pigment with

depth of sediment can be used as criteria for determining conditions of deposition and decomposition of sediments. In coarse sediment and in places where the water above the sediments is high in dissolved oxygen, decomposition of pigments is rather rapid. On the other hand, in deep water, pigments decompose to a great extent

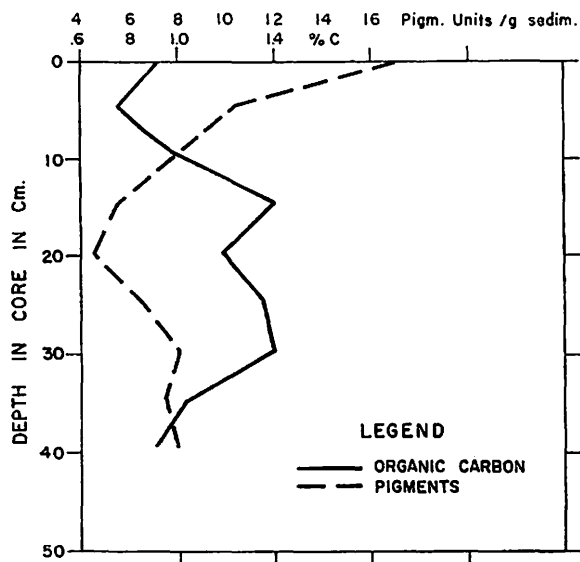


Figure 2. Distribution of pigments and organic carbon at different depths of sediment in Core 8.

in the water mass before reaching the sediment, hence the amount of pigment and organic matter is less in deep water sediments than in shallow water sediments by the same basic organic production in the water mass above the sediment. Therefore, consolidated sediments containing pigments must have been deposited in relatively shallow and badly aerated or euxinic waters.

There are enough pigments in shallow water sediments to give them the characteristic greenish or bluish color. Upon oxidation (f. i., ignition) of these sediments, the brownish or reddish-brown color is attributed to higher amounts of iron and manganese oxides.

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SUMMARY

1. The absorption spectrum of pigments from sediments in 90% acetone solution is given in Fig. 1. The peaks of maximum absorption shift toward the greater wavelengths with advancing oxidation and decomposition of pigments.

2. In coarse and well-aerated sediments the pigments decompose rapidly. In fine sediments, and especially in sediments from anaerobic conditions, the pigments are relatively stable.

3. Although the amount of pigment and its decrease within the depth of sediment cannot be used as an indication of the amount of organic matter or as a measure of the rate of deposition, it may be used as a criterion for the environment of deposition.

4. The green pigments are the coloring compounds of shallow water sediments.

5. The organic matter in the sediment surface in San Juan Archipelago contains 0.1–0.2% pigments.

6. Below 10–15 cm of the sediment surface, reducing conditions prevailed in most coastal sediments.

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