Geochemical Studies on Recent Sediments—IV.
Chlorophyll Degradation Products in Surface Muds from
the Kagoshima Bay in Japan*

Yukio Sugimura**

Abstract: Sediments from the basin of Kagoshima Bay have been examined for acetone-soluble chlorophyll derivatives which are regarded as the source material of the major porphyrins in crude oils.
For quantitative estimation, the pigments in sediment extracts were calculated as pheophytin equivalent which is believed to be the most abundant of several similar one.
13 surface sediment samples were examined. Determination were made for pigment, nitrogen, and carbon. That the pigment ranges from 6 to 53 ppm based on dry sediment and varies from 580 to 2820 ppm based on organic matter.
Chlorophyll derivatives in basin sediments which compared with the pigment content of phytoplankton are preserved as much as 10% or less in the surface zone of mud.
This method appear preferable to the previous acetone-chloroform system of pigment extraction, because of the easy care of extraction procedure.

1. Introduction
The pioneering work of Treibs (1934, 1936) in the thirties established the presence of porphyrins in various natural fossil sources. Recently, Orr (1958) Valentyne (1955) and other workers have extended the studies of these lipids in recent marine or lacustrine sediments.
The gross aspects of present knowledge are briefly summarised as follows. 1. Porphyrins are widespread in fossil organic materials but are much more abundant in petroleum and oil shales than in coals. 2. The organic structure of the porphyrins suggests that they are derived from chlorophyll, hemin and structurally related compounds. Chlorophyll derivatives are more abundant than those of hemin. 3. Porphyrins are present in fossil fuels in the form of metal complexes, but the material containing metals are not those originally present in common plant and animal pigments. Instead of magnesium and iron which are originally present in these pigments, vanadium and nickel are the abundant metals.
Very little is known about these organic matters of their abundance and behavior in mud from various sedimentary environments. Therefore it was worthwhile to investigate this problem in the surface muds of Kagoshima Bay, which is located in southernmost of Kyushu Island, Japan.

2. Materials and Methods
Sediment samples. Marine sediment samples were collected in the bay of Kagoshima in basin areas. Water depth ranges from 80 to 200 meters for these basin sediments. Oxygen is saturated near the surface, and decreases with depths. In order to the rapid oxidation of easily oxidised organic matter falling through water, oxygen have been consumed near the basin floor. Samples were bottled upon collection and stored in dark until used for analysis. An aliquot was taken for moisture determination in order to report the analytical result on the basis of dry sediment. Kjeldahl-nitrogen and organic carbon was run on the dry samples as an index of the organic content of the sediment.
Pheophytin standard solution. Pheophytin solution was prepared by the method of Zscheile and Comer (1941).
Procedure. The wet sediment was placed

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in a porcelain mortar, and 10 milliliters of 90 per cent acetone was added. The sample was grinded well and the mixture transferred into 100 milliliter flask with stopper. The mortar was cleaned with a fresh portion of 5 milliliter of acetone and the wash solution was added to the flask.

The flask was kept overnight in a dark cold room. After extraction, the filtrate was transferred to 50 or 100 milliliter separatory funnel containing 10 milliliters of benzene. A few milliliters of acetone was used to rinse the flask and complete the transfer. The contents were mixed very vigorously for 1 to 2 minutes. After the layers were well separated, the acetone solution of lower layer was discarded and then benzene layer was washed twice with each 10 milliliter portions of distilled water. The benzene solution was drained into a 50 milliliter flask, and dried with anhydrous sodium sulphate.

The drying agent was removed by filtration through a 5A filter paper, and the filtrate drained into 20 milliliter volumetric flask. The flask, funnel, and drying agent were rinsed with small portion of benzene and the volume was adjusted to 20 milliliters. A portion of this solution was transferred to a 1 cm glass cell and the absorbance was determined in a Beckman type spectrophotometer. Generally only the spectra region from 600 to 700 millimicron was run. The major pigments have identical absorption maxima and the solution gives a fairly sharp maximum at about 665 millimicrons in benzene by our spectrometer, from which the pigments were calculated as phoeyphytin equivalence in micrograms per gram of dry sediment.

The procedure adopted represents a compromise between complete recovery and a reasonable time for analysis. Duplicate determinations generally agree to better than 5 per cent.

3. Results and Discussion

Location of deposits sampling is shown in Fig. 1. Surface sediment samples from basins of Kagoshima Bay have been found to range from 6 to 53 ppm of chlorophyll derivatives calculated as phycoeythyin equivalent.

Results from 13 different samples are presented in Table 1. The station 12 which shows minimum content of pigments (6 ppm), is located near the active volcano "Sakurajima", and with a depth of 65 m. The deposit

Fig. 1. Location of mud sampling of Kagoshima Bay.

is mainly composed of sand and the organic content is very poor. The other samples are almost composed of mud and muddy sand, and the content of organic matters is rather abundant, and the pigment content ranges from 21 to 53 ppm, and the mean value of pigment is 37.8 ppm. The pigment content of the St. 9 is 53 ppm, which is appreciably higher at the surface of any other basin sediment. But the organic and pigment content between sediments of outer part basin and inner part basin of Sakurajima is apparently different. At inner part basin, in order to runoff of surrounded areas, it is some what different from outer basins on the production, rate of sedimentation and decomposition in water column of organic matters.

The outer basin sediment ranges from 34 to 53 ppm, the median of 45 ppm of pigment content, and the inner basin sediment shows a range from 21 to 45 ppm, the median of 30 ppm of chlorophyll derivatives content. Organic carbon and total nitrogen are also grouping as described above.

These general trend in pigment content of the sediments can be understood qualitatively in terms of a balance between organic
production, decomposition, and dilution by inorganic sediment.

Chlorophyll decomposition is perhaps best indicated by expressing the lipid content in terms of total organic matters rather than total sediments. The total organic matter in sediments is not easily determined but may be approximated from the organic carbon or total nitrogen content. According to Trask, the total organic matter (marine humus) is about 1.74 times the organic carbon. Calculated from the total organic matter in this way, the parts of phytohemin equivalent per million parts of organic matter are included in Table 1. The abundance of pigment based on organic matter rather than total sediment should be independent of production and dilution by inorganic sediments, it is thus a measure of the relative rates of decomposition of chlorophyll derivatives and organic carbon.

The concentration of pigment in organic matter ranges from a maximum of 2820 ppm in station 19 sample to a minimum of 580 ppm in station 20 sample.

Some comparison can be made between the chlorophyll content of phytoplankton and the phytohemin content of organic matter in sediments.

From the available data (Brandt and Raben 1921, Harvey 1934, Riley 1938, Gillibricht 1952, Atkins and Jenkins 1953) it appears that the organic matter suspended in the surface sea water (living cells and detritus on an ash free dry weight basis) contains 2-10% of green pigments estimated as chlorophyll; the median of 6%, or 60,000 ppm is a reasonable value to assume until better data become available. The difference in molecular weight between chlorophyll and phytohemin can be neglected in view of the other approximations which must be made.

Comparison of the pigment content with 60,000 ppm in phytoplankton indicates a preservation of 2.4% of the chlorophyll in station 19 and 0.97% in station 20 if carbon and phytohemin took similar behavior. The carbon loss is believed to be at least 90% and therefore the chlorophyll derivatives deposited in the surface sediments of these basins represent only 0.25% and 0.097%, respectively, of that produced by phytoplankton.

Table 2 lists the ranges and averages of phytohemin content for basin floor samples expressed as (1) parts per million parts of dry sediment and (2) parts per million parts of organic matter. The former values (1) represent the net result of production, decomposition, and dilution by inorganic matters, but the latter (2), being based only on composition of the organic matter, should be

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth in m.</th>
<th>Remarks</th>
<th>Org. C (%)</th>
<th>Total N (%)</th>
<th>C/N</th>
<th>Ignition loss (%)</th>
<th>Pheophytin ppm based on dry sediment</th>
<th>org. matter</th>
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<tr>
<td>6</td>
<td>82</td>
<td>Mf</td>
<td>2.02</td>
<td>0.155</td>
<td>13.0</td>
<td>16.1</td>
<td>50</td>
<td>1440</td>
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<tr>
<td>7</td>
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<td>Mf</td>
<td>2.08</td>
<td>0.241</td>
<td>8.6</td>
<td>21.2</td>
<td>34</td>
<td>950</td>
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<tr>
<td>8</td>
<td>200</td>
<td>Mf</td>
<td>2.03</td>
<td>0.240</td>
<td>8.5</td>
<td>20.0</td>
<td>51</td>
<td>1450</td>
</tr>
<tr>
<td>9</td>
<td>170</td>
<td>Mf</td>
<td>2.42</td>
<td>0.296</td>
<td>8.2</td>
<td>22.7</td>
<td>53</td>
<td>1280</td>
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<tr>
<td>10</td>
<td>107</td>
<td>Ms, G</td>
<td>1.50</td>
<td>0.090</td>
<td>16.0</td>
<td>13.1</td>
<td>39</td>
<td>1510</td>
</tr>
<tr>
<td>12</td>
<td>70</td>
<td>Sm</td>
<td>0.36</td>
<td>0.063</td>
<td>5.7</td>
<td>5.79</td>
<td>6</td>
<td>970</td>
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<tr>
<td>13</td>
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<td>Mf</td>
<td>1.96</td>
<td>0.195</td>
<td>10</td>
<td>18.5</td>
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<tr>
<td>14</td>
<td>110</td>
<td>Mf</td>
<td>1.28</td>
<td>0.129</td>
<td>10</td>
<td>15.0</td>
<td>42</td>
<td>1900</td>
</tr>
<tr>
<td>18</td>
<td>150</td>
<td>Mf</td>
<td>1.43</td>
<td>0.177</td>
<td>8.1</td>
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<td>45</td>
<td>1820</td>
</tr>
<tr>
<td>19</td>
<td>135</td>
<td>M, G</td>
<td>0.70</td>
<td>0.109</td>
<td>6.4</td>
<td>10.0</td>
<td>34</td>
<td>2820</td>
</tr>
<tr>
<td>20</td>
<td>200</td>
<td>Mf</td>
<td>2.11</td>
<td>0.177</td>
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<td>Mf</td>
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<td>15.4</td>
<td>29</td>
<td>1450</td>
</tr>
<tr>
<td>22</td>
<td>135</td>
<td>M, G</td>
<td>1.18</td>
<td>0.106</td>
<td>11.1</td>
<td>10.7</td>
<td>21</td>
<td>1030</td>
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</tbody>
</table>
Table 2. Range and averages for pheophytin, carbon, and nitrogen in sediment samples of Kagoshima Bay.

<table>
<thead>
<tr>
<th>Sample Group</th>
<th>No. of Samples</th>
<th>Depth Range in m.</th>
<th>Org. C (%)</th>
<th>Total N (%)</th>
<th>C/N</th>
<th>Pheophytin ppm based on dry sediment</th>
<th>org. matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer basin</td>
<td>7</td>
<td>82-200</td>
<td>1.28-2.42</td>
<td>0.090-0.296</td>
<td>8.2-16</td>
<td>35-53</td>
<td>950-1900</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(1.89)*</td>
<td>(0.192)</td>
<td>(9.84)</td>
<td>(43.4)</td>
<td>(1367)</td>
</tr>
<tr>
<td>Inner basin</td>
<td>5</td>
<td>133-200</td>
<td>0.70-2.11</td>
<td>0.106-0.177</td>
<td>6.4-11.1</td>
<td>21-45</td>
<td>580-2820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(1.32)</td>
<td>(0.139)</td>
<td>(9.49)</td>
<td>(30.0)</td>
<td>(1540)</td>
</tr>
<tr>
<td>Sand</td>
<td>1</td>
<td>70</td>
<td>0.36</td>
<td>0.063</td>
<td>5.7</td>
<td>6</td>
<td>970</td>
</tr>
</tbody>
</table>

* Mean value showed in round brackets.

independent of production and dilution except as these factors may have secondary effects on decomposition.

Therefore, comparison of the two sets of values in the different basins should give some idea of the importance of production and dilution as compared with decomposition in determining the pigment abundance in basin sediments.

In view of relation between carbon and pheophytin content, shows good agreement in Fig. 2. However depth relation did not

![Fig. 2. Relation between organic carbon and pigment.](image)

Fig. 3. Typical absorption spectra of sediment extract (90% acetone).

---; St. 9, ---; St. 13, ---; St. 19.

derived from chlorophyll a (Aronoff 1950). This correspondence is shown by comparison of maxima with the curve for pheophytin a which is included in Fig. 4.

![Fig. 3. Typical absorption spectra of sediment extract.](image)

![Fig. 4. Absorption spectrum of pheophytin a in acetone.](image)
Much less is known about the mode of decomposition of chlorophyll derivatives under conditions in sea water and sediments. The biological decomposition of chlorophyll has been investigated from various standpoints, but the applicability of these studies to the marine environment is limited. In surface waters, enzymatic oxidation may occur in dead phytoplankton, but it is less probable in the sediments.

The results of this study may be generalized to conclude that most marine sedimentary environments around Japan contain sufficient content of chlorophyll derivatives to furnish the major porphyrins found in crude oils.

The content of pigment is comparable to that of the sediment of off California basin.

A more complete understanding of the effect of the sedimentary environment on chlorophyll preservation would be facilitated by data on sedimentation rates in this area. For a better understanding of the geochemical significance of porphyrins in the origin of petroleum, a careful investigation is needed to determine the exact chemical nature of the porphyrins in sediments.

4. Summaries

(1) Sediment samples of the basin floor of Kagoshima Bay contain substantial amounts of chlorophyll derivatives.

(2) According to the content of chlorophyll derivative based on organic matter, the ratio of decomposition of organic detritus settling through water column is estimated at least 95%.

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