

ORGANIC GEOCHEMISTRY OF SEDIMENTS ON  
THE FLANKS OF TANNER AND CORTES BANKS  
OFFSHORE FROM SOUTHERN CALIFORNIA

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U.S. Geological Survey

OPEN FILE REPORT

82-829

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## ABSTRACT

Holocene sediment, composed mainly of foram tests, occurs on the flanks of the Tanner and Cortes Banks, offshore southern California. The organic matter in this sediment differs in content and composition from the organic matter in nearby basins. Two sources of hydrocarbons are indicated: terrestrial plants and biodegraded or immature petroleum.

Introduction

To obtain preliminary information on the organic geochemistry of Holocene sediment on the flanks of the Tanner and Cortes Banks in the southern California Borderland, nine samples of surface sediment have been examined. The sediment is fine grained and composed mainly of Foraminifera tests. In this work the following parameters were measured: total carbon, organic carbon, carbonate carbon, extractable organic material (bitumen), hydrocarbons, and nitrogen, sulfur, and oxygen (NSO) containing organic substances. Analysis of the data obtained show that the organic matter in this sediment differs in content and in composition from the organic material in sediment in nearby basins. Although the ultimate objective of this kind of study is to define the origin and fate of the organic matter contained within these sediments, the data collected for this report are not sufficient to allow any definite conclusions. However, the distribution of saturated hydrocarbons indicates that there are at least two sources of hydrocarbons. First, hydrocarbons commonly found in basinal sediments and usually attributed to terrestrial plant origin, are present. Second, there is a complex mixture of hydrocarbons whose chromatographic record resembles biodegraded or immature petroleum.

The information in this report was obtained in 1975 for the Proceedings of the Workshop on Standard Reference Materials for Offshore Drilling - Petroleum, and was to be published in a National Bureau of Standards Special Publication. This publication was never issued. Therefore, we have elected to report our original results here.

### Procedures

Grab samples, box cores, and dart cores were obtained during a two week cruise in May, 1975, from the R/V VELERO. Subsamples were taken for organic geochemistry at twenty stations. These samples were collected to avoid sediment which had touched the surfaces of the grab and box core devices. The samples were frozen immediately in wide-mouth glass jars which previously were cleaned and rinsed with organic solvents. Dart cores were frozen in their liners. Of the original twenty samples, nine were selected for this work. Samples from the grab and box cores were thawed and from 300 to 400 gm of wet sediment were removed and placed in aluminum soil containers. These samples were then refrozen and placed in glass desiccators which were attached to a freeze-drying apparatus. Freeze drying was completed (indicated when there was no further weight loss) in three days. About 125 gm of sediment was removed from the dart core taken at station 416. This sample was sent frozen to the Branch of Oil and Gas Resources, Denver, Colorado, where it was processed independently.

The following procedure was applied to the remaining eight samples recovered from grab and box cores. About 100 gm of dried sediment were placed in an all glass, coarse frit thimble and were extracted overnight by Soxhlet extraction with about 300 ml of methylene chloride. Sulfur was removed by activated copper strips placed in the boiling extract. The extract was

evaporated to about 50 ml and 10 percent of the extract was used to obtain the weight of extractable organic material (bitumen). The remaining extract was evaporated to near dryness, and n-hexane was exchanged for methylene chloride. The extract, dissolved in 5 ml of n-hexane was applied to a chromatographic column composed of 9 gm of silica gel activated at 150°C and prepared in n-hexane. This column was eluted with 10 additional ml of n-hexane followed by 15 ml of benzene and 15 ml of methanol. The n-hexane, benzene, and methanol fractions were each collected. Mainly hydrocarbons were eluted with n-hexane and benzene. Organic compounds containing nitrogen, sulfur, and oxygen were in the methanol fraction. Weights were obtained on each of these fractions.

Gas chromatographic analyses of the fraction eluting with n-hexane provides a measure of the complexity of the saturated hydrocarbons present. This fraction was analyzed on a Perkin Elmer model 3920 gas chromatograph equipped with a 50' x 0.02" SCOT column coated with SE 30. The column temperature was raised during the course of analysis at 8°/min from 80° to 230°C and held at 230°C until the analysis was complete. Helium pressure was maintained at 12 psi.

In addition to samples taken for extraction, aliquots of dried sediment were also removed for carbon determinations. Two independent assessments were made of total carbon by dry combustion utilizing the Pregl and Leco methods. Organic carbon values were obtained by wet oxidation (methods developed by Rinehart Laboratories, Arvada, Colorado). Inorganic carbon was determined by difference between total and organic carbon values.

### Results and Discussion

The results of this work are summarized on Tables 1 and 2 and Figures 1-

3. Table 1 lists the nine samples analyzed and provides a brief description of each. Table 2 summarizes the analytical measurements. Figure 1 is a sample location map. Figure 2 shows chromatograms of the saturated hydrocarbons in eight samples. A chromatogram for the saturated hydrocarbons in the sample analyzed in Denver is shown in Figure 3.

All of these samples came from the surface of slopes adjacent to the tops of the Tanner and Cortes Banks. All samples, except one, were removed from sediments below the 200 m depth contour. The age of the samples is Holocene. The dried sediment is all light olive gray, silty, very fine grained sand composed mainly of the tests of planktonic foraminifera. Although uniform in color, the sediment shows some variety in composition of detrital particles. The olive color, which seems to be mostly associated with silty particles, is due to the presence of glauconite.

Because of the dominance of foraminifera in all of these samples the calcium carbonate content is high, ranging from 25 to 67 percent and averaging 53 percent. These values were calculated from the carbonate-carbon determinations. The calcium carbonate content of these samples generally exceeds that of sediments in nearby basins (12-39 percent)(Emery, 1960, p. 220). The average calcium carbonate of 53 percent compares well with the average content found on bank tops (56 percent) but exceeds the average value reported for basin slopes (19 percent)(Emery, 1960, p. 181). Apparently the foraminifers partially dissolve during deposition. Those tests which eventually reach the basins will have dissolved more than the tests reaching the slopes adjacent to the bank tops because of the difference in residence times in the water column. Thus, more calcium carbonate will be deposited adjacent to the bank tops than in the basins.

In contrast to the calcium carbonate content, the organic carbon in these

sediments is less than that found in nearby basin sediment. For example, the organic carbon contents of the sediments studied here range from 0.66 to 2.5 percent and averaged 1.6 percent while in the nearby basin sediment these values range from 2.7 to 6.9 percent (Emery, 1960, p. 220). The average organic carbon content of the bank tops, basin slopes and basin floors have been reported by Emery (1960, p. 181) to be 0.47, 1.6, and 4.1 percent, respectively. The samples examined here have average organic carbon contents equal to the average for sediments on basin slopes. Thus the eight samples studied have carbonate contents comparable to those found in sediment on basin tops and organic carbon contents comparable to those found in sediment on the basin slopes. The observed relationships between the organic carbon content of these eight samples and the content of basin sediment can be explained by the more rapid winnowing and oxidation of organic matter on the slopes next to the tops of the banks than of the organic matter in the basins themselves.

The extractable organic material (bitumen) in the eight samples ranges from 62 to 264 ppm (average 141 ppm). These concentrations are much lower than found in nearby basin sediment. Emery (1960, p. 285) showed that near surface sediment from Tanner and San Clemente Basins had extractable organic contents of 1440 and 650 ppm, respectively. The content of hydrocarbons in the eight samples is generally low, ranging from 11 to 66 ppm (average 31 ppm). Again compared with the hydrocarbons in Tanner Basin (167 ppm) and San Clemente Basin (43 ppm) the amounts found in sediments near the bank tops are less than in the nearby basins. Also the content of NSO compounds in sediments near the bank tops is less than that found in nearby basin sediments.

The distributional patterns of the saturated hydrocarbons as provided by gas chromatographic analyses are shown in Figure 2a and 2b. The following

discussion applied to the eight samples processed in Menlo Park. The chromatographic results obtained in Denver will be considered separately. The region of the chromatograms between peaks designated 17 and 26 reflects the presence of an unresolved, complex mixture of hydrocarbons. This mixture is present in all samples except that in Sample 308 the amount of this material is very small. The presence of this kind of unresolved, complex mixture in sediments has been commonly attributed to biodegraded (Farrington and Quinn, 1973; Blumer and Sass, 1972), or to immature petroleum (Hunt, 1979). Similar chromatographic patterns have been obtained from weathered tar balls (Butler and Harris, 1975). No clearly defined biological source of this complex mixture is yet known. Additional work is required to define accurately the processes responsible for these unresolvable mixtures.

Besides the complex mixture, the chromatograms indicate that n-alkanes ranging from C<sub>17</sub> to C<sub>33</sub> are also present in all samples. The chromatographic patterns can be arranged into two groups. Chromatograms for samples 25, 266, 339, and 412 (Group I) (Figure 2a) have the following characteristics in common:

(1) The pattern resulting from the unresolved complex mixture is the dominant feature present. The feature reaches a maximum in the region of the C<sub>21</sub> to C<sub>23</sub> n-alkanes.

(2) n-alkanes from C<sub>17</sub> to C<sub>24</sub> are distributed such that neither even nor odd carbon numbered molecules predominate. This kind of distribution of n-alkanes is common in petroleum and other organic matter which has undergone extensive diagenesis.

(3) From C<sub>25</sub> to C<sub>33</sub> the n-alkanes with odd numbers of carbon atoms are distinctly dominant.

Chromatograms for samples 66, 308, 402, and 438 (Group II) (Figure 2b)

differ in some aspects from those in Group I:

(1) The chromatographic pattern for the complex mixture is less pronounced and reaches a maximum in the region of the  $C_{23}$  to  $C_{25}$  n-alkanes.

(2) n-alkanes for the entire molecular weight range detected from  $C_{17}$  to  $C_{33}$  have a distribution which is characterized by a dominance of the odd-carbon numbered species.

This dominance of odd-carbon-numbered n-alkanes is characteristic of hydrocarbons from biological sources (Clark and Blumer, 1967). Studies of hydrocarbons in sediments from San Nicolas Basin also show that odd-carbon-numbered n-alkanes are predominant (Mitterer and Hoering, 1968). In fact, the n-alkanes in most modern marine sediments and older sediment which has not undergone extensive diagenesis, have this characteristic pattern.

The gas chromatogram of the saturated hydrocarbons from Sample 416 is shown in Figure 3. The distributional pattern of hydrocarbons shown does not fit well into either of the two groupings of patterns described previously. Sample 416 was processed by the Branch of Oil and Gas Resources at Denver as a part of an independent but related study. Differences in procedures and instrumentation between work done in Denver and Menlo Park hinder the making of direct comparison of chromatograms. Sample 416 contains mainly an unresolved complex mixture of hydrocarbons somewhat similar to the mixtures found in samples of Group I. Peaks attributable to n-alkanes are superimposed on the unresolved major peak, but these n-alkanes do not show a dominance of odd-carbon-numbered molecules even in the range from  $C_{25}$  to  $C_{33}$  as do the n-alkanes in all other samples. Rather the apparent distribution of n-alkanes is similar to what is found in petroleum and other ancient, altered sedimentary organic matter. The saturated hydrocarbons in Sample 416 may represent petroleum contamination.



In summary, the hydrocarbons in the samples examined for this report may come from at least two sources. The odd-carbon-numbered n-alkanes may represent the contribution from modern biological materials from terrestrial plant sources or from reworked older sediments in which the n-alkanes still maintain a dominance of odd-carbon-numbered molecules. The unresolved complex mixture of hydrocarbons could represent additions to the sediments of biodegraded or immature petroleum from natural seepage or from spills.

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Table 1. Sample Description

| <u>No.</u> | <u>Type</u> | <u>Uncorrected<br/>depth of<br/>water (m)</u> | <u>Latitude &amp;<br/>Longitude</u> | <u>Location Description</u>  | <u>Sediment Description</u>   |
|------------|-------------|---|-------------------------------------|--|---|
| 25         | Box core    | 410   | 32°42.16'N<br>119°18.39'W           | About midway between north end of Tanner Bank and north end of Cortes Bank | Light olive gray (5Y 5/2) silty, very fine-grained foraminiferal sand with occasional spicules.                                     |
| 66         | Box core    | 330   | 32°46.60'N<br>119°11.47'W           | North of north end of Tanner Bank  | Light olive gray (5Y 5/2) silty, very fine-grained, foraminiferal and detrital mineral sand   |
| 266        | Grab        | 230   | 32°37.31'N<br>119°15.32'W           | North of north part of Tanner Bank   | Light olive gray (5Y 5/2) very silty, very fine-grained foraminiferal sand  |
| 308        | Grab        | 210   | 32°33.08'N<br>119°10.74'W           | North of middle part of Tanner Bank  | Light olive gray (5Y 5/2) silty, very fine-grained foraminiferal sand   |
| 339        | Grab        | 190   | 32°35.24'N<br>119°06.82'W           | Between the south end of Tanner Bank and middle part of Cortes Bank        | Light olive gray (5Y 5/2) silty, very fine-grained, foraminiferal and detrital mineral sand   |
| 402        | Grab        | 250   | 32°29.59'N<br>119°03.92'W           | North of southern part of Cortes Bank                                      | Light olive gray (5Y 5/2) silty, very fine-grained foraminiferal and detrital mineral sand with about 5% fine-grained shell debris  |
| 412        | Grab        | 230   | 32°24.94'N<br>119°07.48'W           | South flank of southern part of Cortes Bank                                | Light olive gray (5Y 5/2) silty, very fine-grained foraminiferal and detrital mineral sand with about 5% fine-grained shell debris  |
| 416*       | Dart core   | 303   | 32°23.23'N<br>119°05.61'W           | South flank of southern part of Cortes Bank                                | Light olive gray (5Y 5/2) silty, very fine-grained foraminiferal and detrital mineral sand with about 5% fine-grained shell debris  |
| 438        | Grab        | 365   | 32°29.44'N<br>119°17.86'W           | South flank of northern part of Cortes Bank                                | Light olive gray (5Y 5/2) silty, very fine-grained foraminiferal and detrital mineral sand with about 10% fine-grained shell debris |

\* Sample analyzed by Branch of Oil and Gas Resources, Denver, Colorado

Table 2.--Summary of Organic Geochemical Data

| Sample Number | Total Carbon % |         | Organic Carbon % | Carbonate Carbon % | CaCO <sub>3</sub> % | Extractable                    |  | Hydrocarbons ppm | NSO Compounds ppm |
|---------------|----------------|---------|------------------|--------------------|---------------------|--------------------------------|--|------------------|-------------------|
|               | (Leco)         | (Pregl) |                  |                    |                     | Organic Material ppm (Bitumen) |  |                  |                   |
| 25            | 9.5            | 9.5     | 2.2              | 7.3                | 61                  | 117                            |  | 23               | 111               |
| 66            | 7.2            | 7.6     | 1.6              | 6.0                | 50                  | 156                            |  | 45               | 115               |
| 266           | 10.2           | 10.5    | 2.5              | 8.0                | 67                  | 264                            |  | 50               | 175               |
| 308           | 9.7            | 9.8     | 2.0              | 7.8                | 65                  | 196                            |  | 66               | 143               |
| 339           | 3.9            | 3.7     | 0.66             | 3.0                | 25                  | 62                             |  | 11               | 50                |
| 402           | 9.2            | 9.5     | 1.6              | 7.9                | 66                  | 159                            |  | 28               | 123               |
| 412           | 5.8            | 5.4     | 0.92             | 4.5                | 38                  | 71                             |  | 12               | 39                |
| 438           | 7.7            | 7.9     | 1.3              | 6.6                | 55                  | 103                            |  | 11               | 93                |

Sample analyzed by Branch of Oil and Gas Resources, Denver, Colorado, by independent procedures\*. Values presented have not been averaged with the data for the other eight samples.

|     |     |   |     |     |    |     |  |    |   |
|-----|-----|---|-----|-----|----|-----|--|----|---|
| 416 | 5.3 | - | 1.0 | 4.3 | 35 | 229 |  | 58 | - |
|-----|-----|---|-----|-----|----|-----|--|----|---|

% and ppm - on the basis of dried sediment

\* Letter dated August 1, 1971, from G. Claypool, Branch of Oil and Gas Resources, to K. Kvenvolden and J. Taylor

## FIGURES

Figure 1. Map of sampling sites. Depths are in meters.

Figure 2. Gas chromatograms of saturated hydrocarbons in samples from the flanks of Tanner and Cortes Banks. Peaks attributed to n-alkanes are designated by their respective carbon numbers. The dashed line is the approximate baseline and is caused by the continuous bleed of liquid phase from the chromatographic column. The chromatographic response of the hydrocarbons is measured between the baseline and the chromatographic curve.

2a. Group I samples--25, 266, 339, 412.

2b. Group II samples--66, 308, 402, 438.

Figure 3. Gas chromatogram of saturated hydrocarbons in Sample 416.

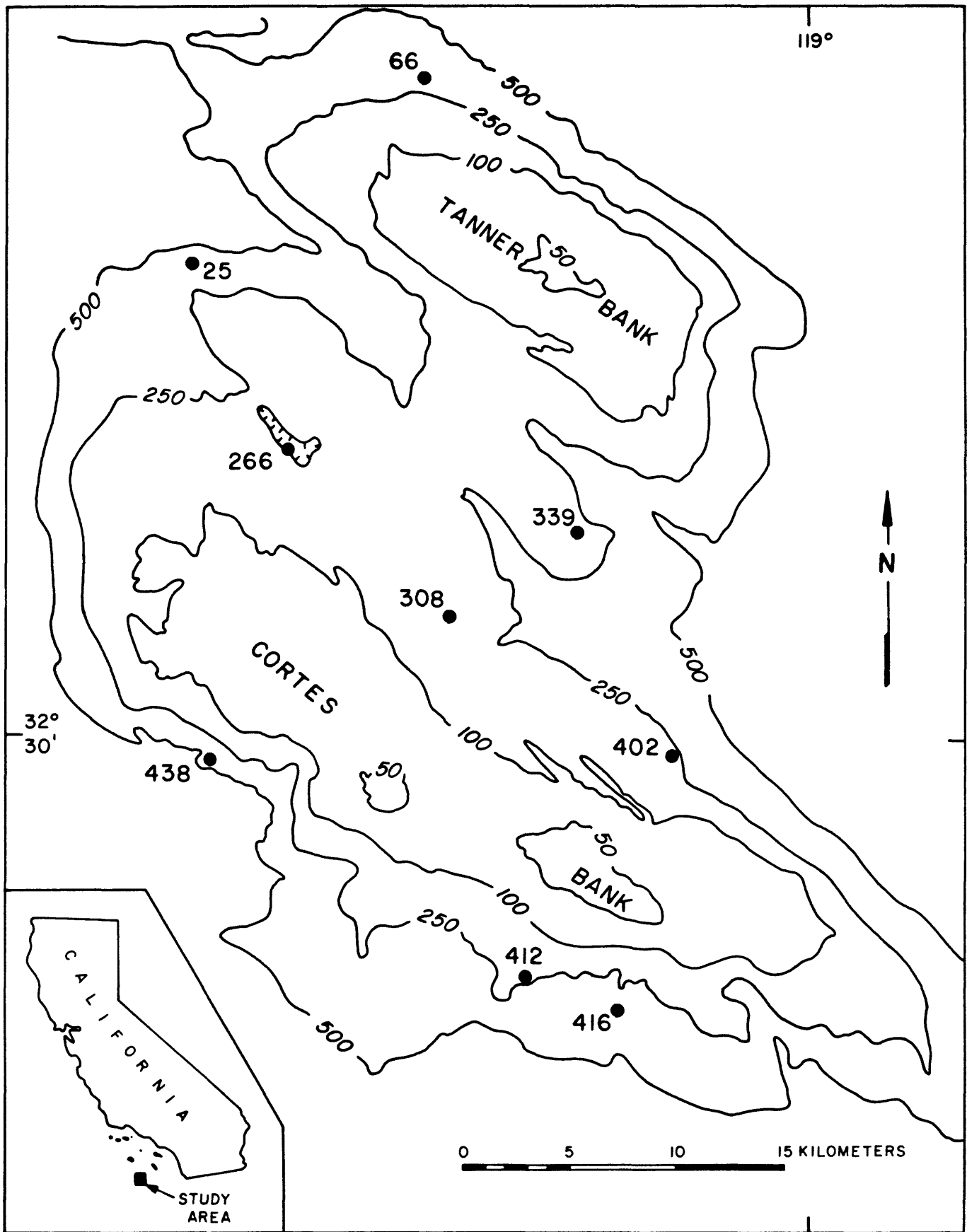


Figure 1

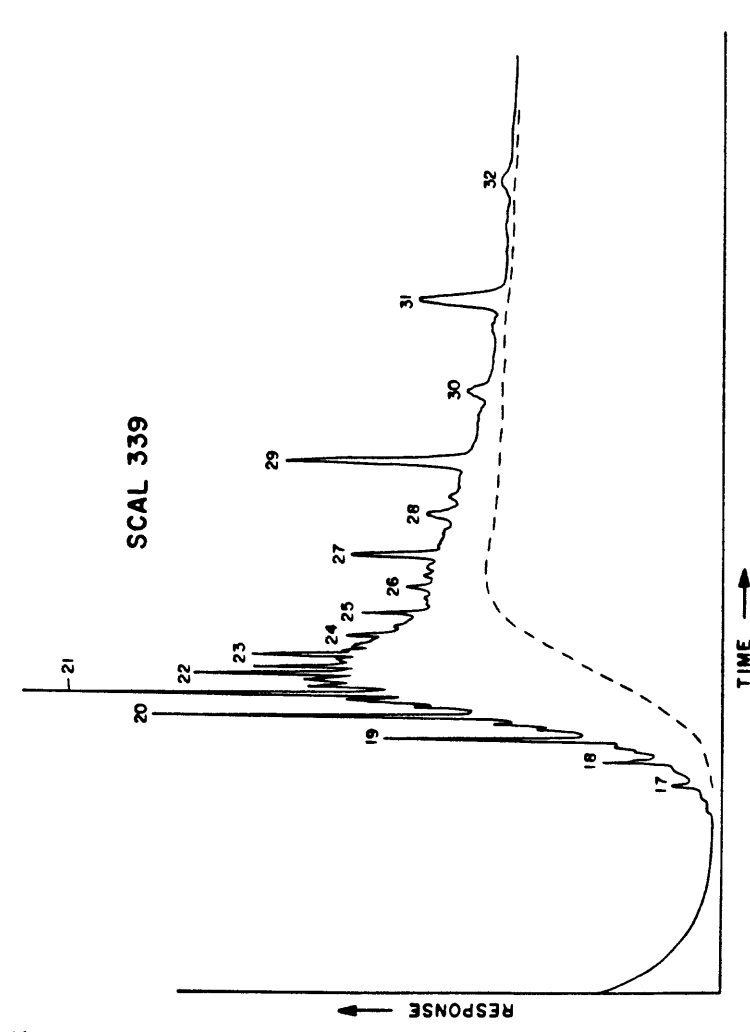
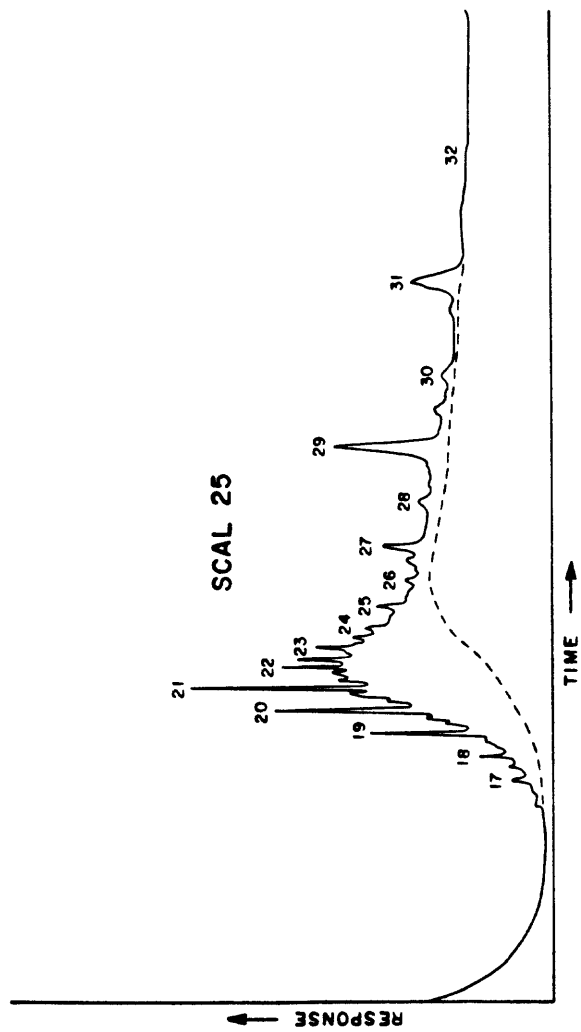
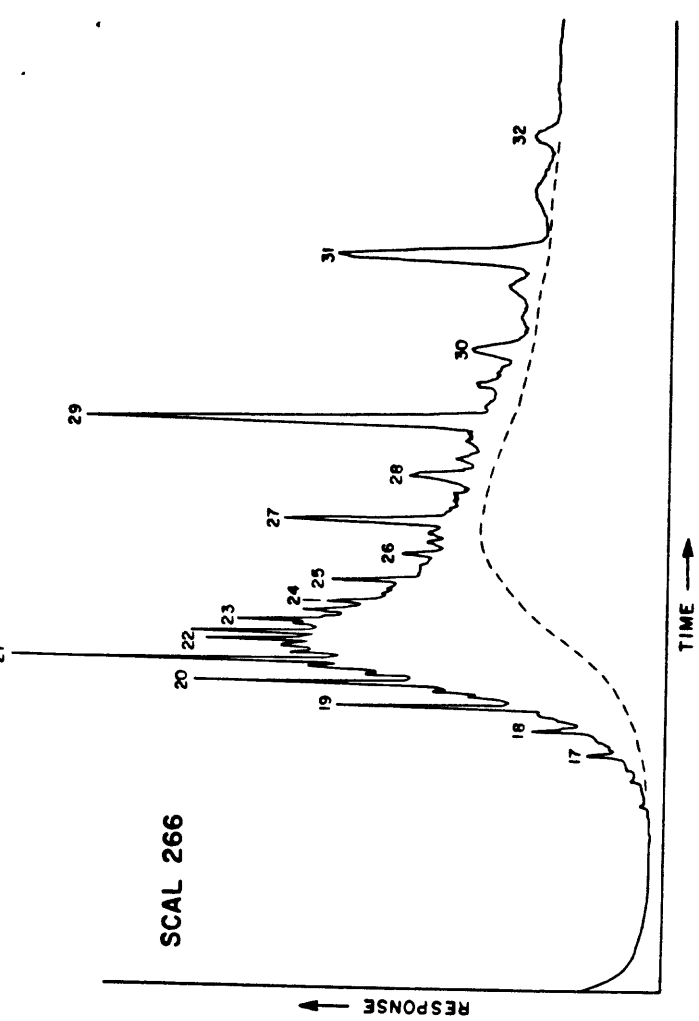


Figure 2a



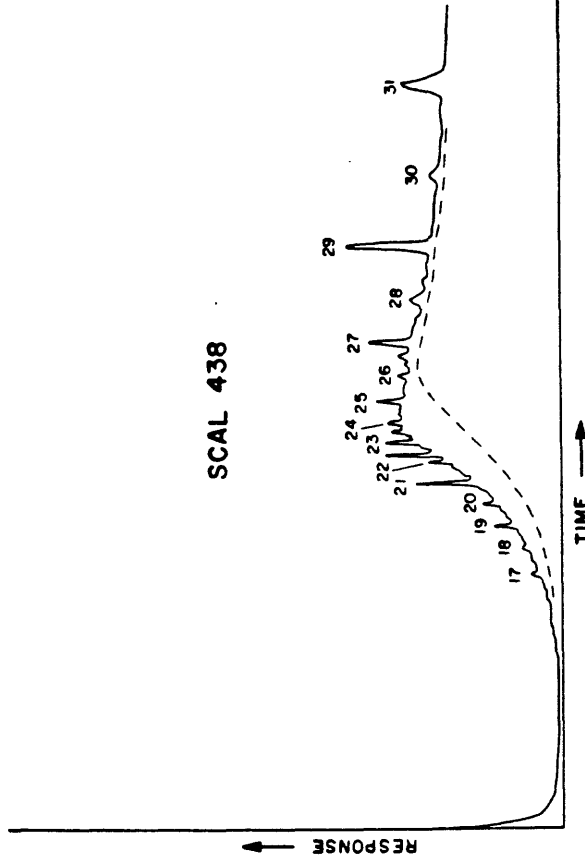
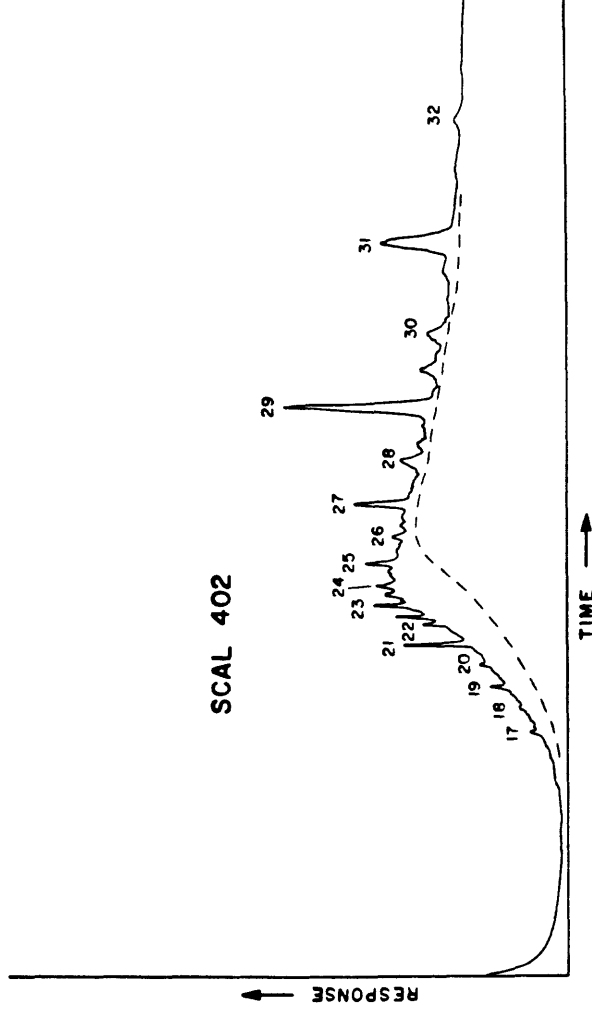
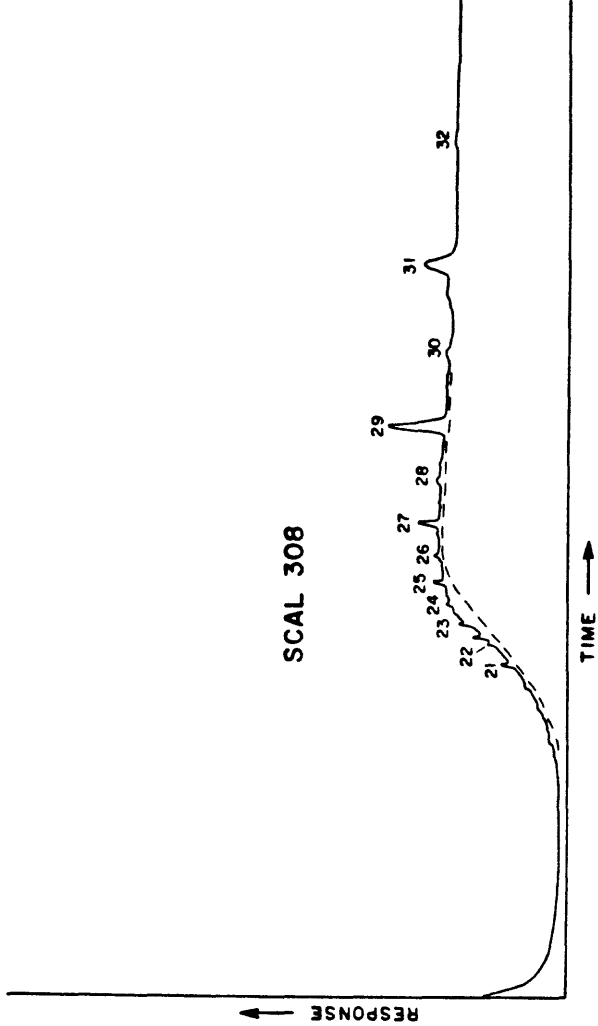
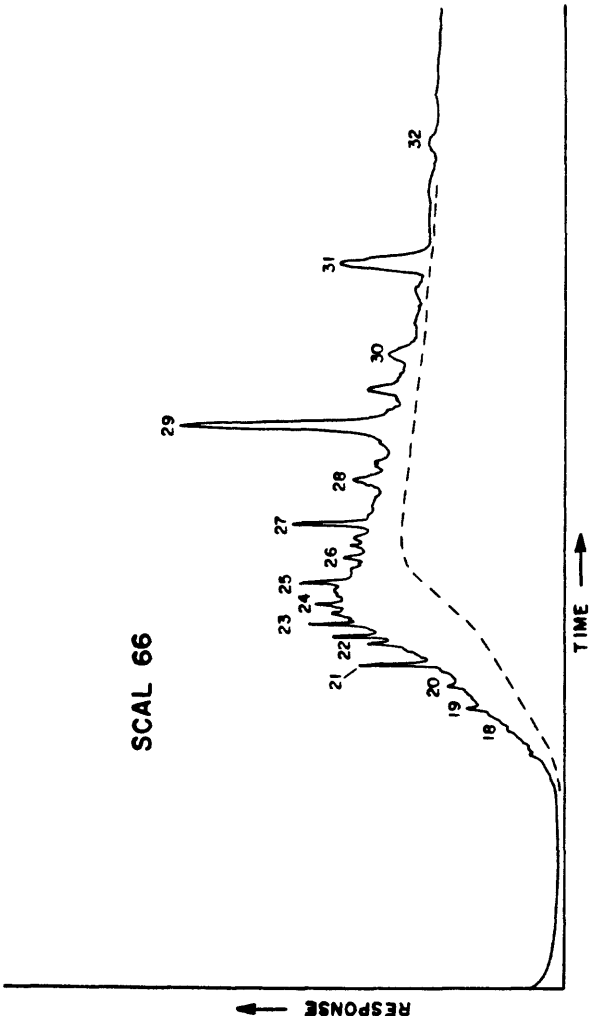


Figure 2b

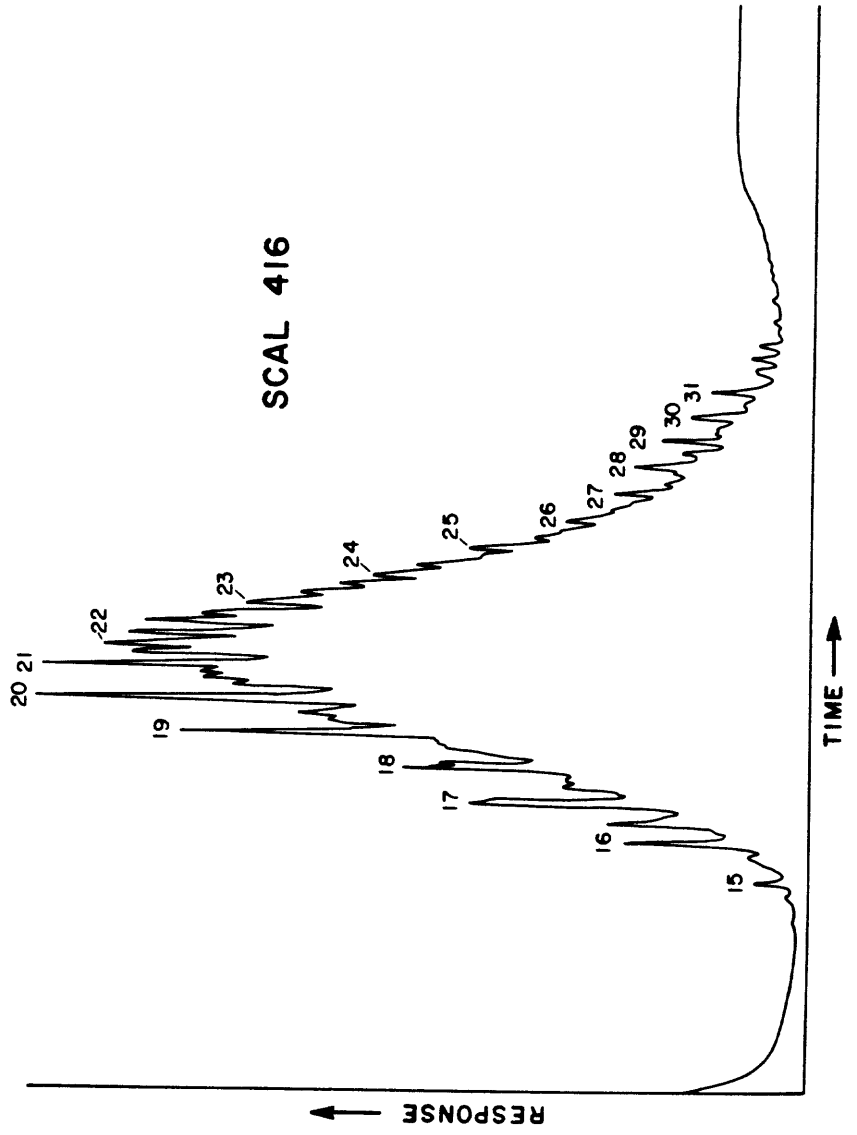


Figure 3