

## Extractable and pyrolyzed hydrocarbons in shallow-water carbonate sediments, Florida Bay, Florida

R. M. MITTERER<sup>1</sup>, I. P. DZOU<sup>1</sup>, R. M. MIRANDA<sup>1</sup> and M. E. CAUGHEY<sup>2</sup>

<sup>1</sup>Department of Geosciences, University of Texas at Dallas, Richardson, TX 75083-0688, U.S.A.

<sup>2</sup>University of Texas Marine Science Institute, Port Aransas, TX, U.S.A.

**Abstract**—A three-dimensional organic geochemical survey conducted in Florida Bay, a subtropical carbonate environment with multiple sources of organic matter, illustrates the hydrocarbon source potential of shallow water carbonate sediments and the effect of multiple biochemical sources on the organic sedimentary imprint. Organic carbon (TOC) in the sediments averages about one per cent. Concentrations of extractable organic matter (EOM) and hydrocarbons are slightly higher, and of organic carbon slightly lower, in sediments of the marine-dominated part of the bay. Hydrocarbon distribution, which is a function of the type of organic matter, also varies across the bay. The C<sub>15+</sub> *n*-alkanes in sediments of the terrestrially-influenced portion exhibit a bimodal pattern, with maxima at C<sub>27</sub> or C<sub>29</sub> and C<sub>18</sub> and a marked odd/even carbon-number predominance in the C<sub>21</sub>–C<sub>31</sub> range. In contrast, C<sub>15+</sub> *n*-alkanes in sediments of the marine-dominated portion have maxima at C<sub>17</sub> or C<sub>18</sub> and C<sub>23</sub> or C<sub>24</sub>. TOC decreases, but EOM and hydrocarbon content increase, with depth in the sediment. Hydrous and anhydrous pyrolysis of bulk sediments and individual carbonates generates a new suite of *n*-alkanes with an even carbon-number predominance and a maximum at C<sub>22</sub>. Yields of EOM and hydrocarbons are comparable for both types of pyrolyzates and are 6 to 8 times greater than *in situ* EOM and hydrocarbons. Carbonate sediments deposited in low energy, shallow-water, environments have the potential to be good oil source rocks.

**Key words:** hydrocarbons, *n*-alkanes, pyrolysis, carbonates, organic carbon

### INTRODUCTION

Carbonate and clastic depositional environments differ not only in their sedimentary and mineralogical characteristics, but they may also exhibit significant differences in types of organic matter present, in processing of the organic matter by microorganisms, and in the early diagenetic reactions of the organic matter. Compared to clastic sediments, carbonates differ in their association with organic matter by containing an internal matrix that is largely proteinaceous in composition (Mitterer and Cunningham, 1985). Similarly, dissolved humic substances adsorbed to the surfaces of carbonate grains are also rich in hydrolyzable amino acids (Carter and Mitterer, 1978). Conversely, clastic sediments contain organic matter in the dissolved, adsorbed and particulate fractions that is poor in amino acids (Carter and Mitterer, 1978). Particulate organic matter, especially, can be expected to exhibit major differences between the two environments. Clastic sediments, derived from continental sources, contain varying amounts of terrigenous plant material. Carbonate environments generally receive minimal clastic and terrigenous plant input. These fundamental differences in the nature of the organic matter may account for different hydrocarbon distributions in ancient carbonate and clastic sequences.

In addition to adsorbed and particulate organic matter, biogenic carbonate sediments contain an organic matrix within the mineral structure that is largely protein in composition. Non-biogenic calcium carbonate, such as ooids, also contain an organic

matrix that is entrapped within the ooid layers from previously adsorbed humic substances (Mitterer and Cunningham, 1985); ooids also contain infestations of algae and fungi (Harris *et al.*, 1979). Except for pyrolytic studies of organic matter in ooids (Ferguson and Ibe, 1982; Ferguson *et al.*, 1984), the role of the organic matrices in carbonates in hydrocarbon generation has been virtually unexplored. Generation of hydrocarbons from proteins and amino acids has been suggested and demonstrated in laboratory experiments (Philippi, 1977). Typical products are a suite of low molecular weight aliphatic and aromatic hydrocarbons. These results indicate that proteins and amino acids in carbonate shells may be important sources of low molecular weight hydrocarbons. The organic matrix of ooids has less of a proteinaceous and more of a humic character. Accordingly, both low and high molecular weight *n*-alkanes have been detected in modern carbonate ooids (Ferguson and Ibe, 1981, 1982). Low molecular weight hydrocarbons are in the C<sub>1</sub>–C<sub>5</sub> range while the heavier *n*-alkanes are in the C<sub>15+</sub> fraction. As with hydrocarbons from known carbonate source rocks, the C<sub>15+</sub> *n*-alkanes in modern ooids have an even carbon dominance. Heating experiments of carbonate ooids in seawater result in the generation of additional gaseous and C<sub>15+</sub> hydrocarbons (Ferguson *et al.*, 1981, 1984).

Carbonate rocks are excellent hydrocarbon sources as well as reservoirs. Good carbonate source rocks usually reflect deposition of organic matter-rich laminated carbonate muds in deeper water anoxic environments. However, carbonates today are not accu-

mulating significantly in anoxic environments, and prior to the Jurassic, carbonate sediments originated and accumulated predominantly in shallow water environments. Thus, throughout the Paleozoic and Mesozoic most carbonates were deposited in shallow water, probably oxic, environments. In modern settings, shallow water carbonate sediments generally contain abundant organic matter, and as Gehman (1962) noted, these sediments have adequate amounts of organic matter to be considered as potential source rocks. Ancient carbonates are usually low in organic carbon as a consequence of the effects of fresh water diagenesis, which causes recrystallization of unstable carbonate constituents and oxidation of organic matter. The major factor then that determines whether shallow water carbonates will be good source rocks may be preservation of the organic matter after burial. Thus, shallow water carbonates may have good source potential but poor preservation potential. Under optimum conditions of continuous burial without exposure and absence of fresh water influence, shallow water carbonates may become source rocks. The purpose of the present survey is to evaluate the hydrocarbon source potential of typical shallow water carbonate sediments.

#### STUDY AREA AND METHODS

##### Setting

Florida Bay, located at the southern end of the Florida mainland, is the only region of extensive active carbonate sedimentation in the contiguous United States. The Everglades, a swampy region of peat formation on the mainland, lies to the north, and the Florida Keys, a chain of Pleistocene coral islands trending northeast-southwest, form the eastern and

southern boundary. The western side of the bay is open to the Gulf of Mexico (Fig. 1). No rivers enter into the bay, but fresh water drains from the mainland especially during rainy spells.

An extensive network of shallow mud banks forms an irregular lacy pattern surrounding basins of about 3 m depth (Enos and Perkins, 1979). The percentage of the bay area occupied by mudbanks increases markedly from the restricted northeastern portion toward the open western end. Approximately one-third of the entire bay area is comprised of mudbanks. Numerous islands or keys, which are sites of supratidal carbonate sedimentation, have developed on portions of the mudbanks.

Plant life is a major factor in mudbank and island development within the bay. Calcareous algae, especially *Penicillus* sp., contribute the bulk of the carbonate mud that forms the banks (Stockman *et al.*, 1967). Banks are stabilized by dense growths of marine grass (*Thalassia testudinum*), and islands are sites of thick growths of mangrove trees. Algal mats cover open supratidal flats on the islands. Organic matter in the bay is derived from three major sources: (1) sea grass on mud banks, (2) terrestrial run-off from the Florida mainland (Everglades), and (3) marine phytoplankton.

The shallow waters of the bay are mixed by the wind and by limited circulation due to tidal currents. Because of the shallow water depth, the water column is oxic. Bioturbation of the sediments is extensive (Enos and Perkins, 1979).

##### Analytical

Several 1 m cores were collected in Florida Bay by hand pushing a coring tube into the soft sediment.

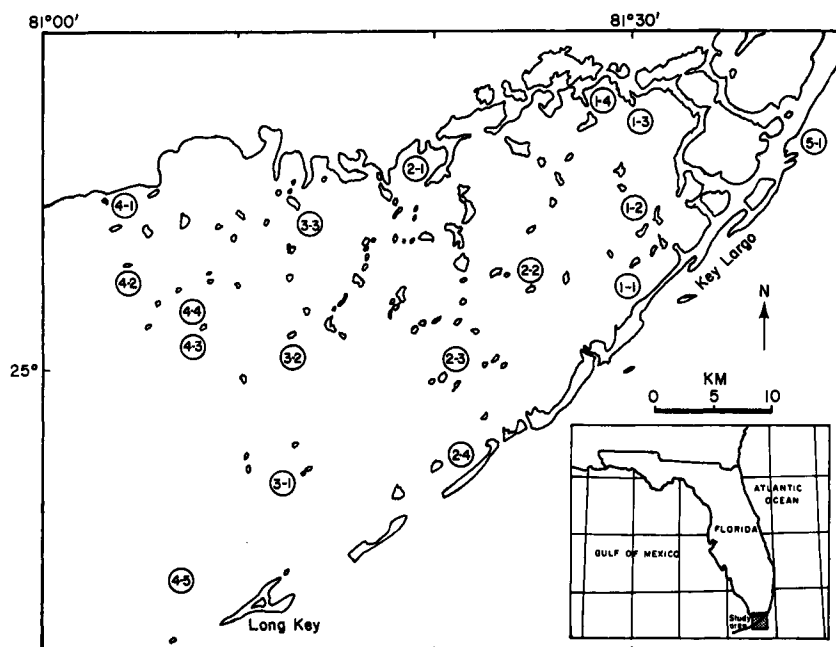


Fig. 1. Location map of Florida Bay with sampling localities.

The cores were immediately extruded, sectioned and stored frozen until analysis. Pore waters were extracted by centrifugation from some unfrozen sediments after collection and analyzed for sulfate. After returning to the laboratory thawed sediment was dried at 40°C and pulverized. Organic carbon was determined with a LECO Carbon Analyzer. Samples were treated with 20% reagent grade HCl prior to organic carbon analysis. Some loss of soluble organic matter may have occurred during the acid leach, and the organic carbon values should be considered as minimal. For anhydrous pyrolysis, weighed sediments were pyrolyzed in a stainless steel high pressure bomb under nitrogen for 72 h at 250°C. For hydrous pyrolysis the bomb was filled with 40 g of ground sediment and 40 ml distilled water, purged with nitrogen, and heated for 72 h at 250°C. Gases and low molecular weight hydrocarbons were not analyzed in the bomb pyrolyzates.

Unheated and pyrolyzed sediment was extracted with chloroform in a Soxhlet apparatus for 24 h. Asphaltenes were removed from the extract by soaking for one hour in heptane, and the extract was then separated by silica gel chromatography into saturate, aromatic and polar fractions.

Programmed pyrolysis also was carried out on a variety of carbonate samples including ooids, carbonate mud, carbonate sand, and individual mollusk shells. Pyrolysis conditions differed from those described above for the carbonate core sediments from Florida Bay. For individual carbonate samples, pyrolysis was conducted in 9 mm diameter evacuated sealed glass tubes in a programmed (120–600°C at 25°C/min with final temperature held for 9 min) Geochemical Analysis System Pyrolyzer. Separate samples were analyzed for gaseous and  $C_{15+}$  products. Liquid products were separated by HPLC prior to gas chromatography. Because the conditions of pyrolysis for the individual carbonate samples are different from those employed in the pyrolysis of carbonate sediment from Florida Bay, the data are not quantitatively comparable. However, two samples of carbonate mud were pyrolyzed with the individual carbonate samples, and these muds provide some comparison with the muds pyrolyzed in bombs.

Routine gas chromatographic separations of alkanes were performed on a Perkin-Elmer 3920 equipped with a one meter packed column coated with SE-30 and flame ionization detector. Some analyses were also made on a Hewlett-Packard 5890A equipped with a 25 m fused silica capillary column.

## RESULTS AND DISCUSSION

### Organic carbon

Three major sources of organic matter exist in and around the bay. Higher plant sources are important adjacent to the northern and eastern parts of the bay

Table 1. Carbon isotope values for organic matter in pore waters and NaOH sediment extract from selected Florida Bay core samples.

| Locality | Depth (cm) | $\delta^{13}C$ (PW) | $\delta^{13}C$ (Ext.) |
|----------|------------|---------------------|-----------------------|
| 1-1      | Surface    | -                   | -11.2                 |
| 1-1      | 12-24      | -                   | -13.2                 |
| 1-2      | 15-27      | -10.9               | -11.4                 |
| 1-3      | 12-24      | -15.1               | -                     |
| 1-4      | 12-24      | -24.0               | -                     |
| 2-1      | Surface    | -                   | -15.7                 |
| 2-1      | 15-27      | -                   | -16.5                 |
| 2-4      | 12-24      | -14.3               | -                     |
| 3-2      | 12-24      | -                   | -10.9                 |
| 4-5      | 12-24      | -8.4                | -                     |

on the mainland and the Keys. In most of the bay, marine sources dominate, with amorphous organic matter and marine grasses (predominantly *Thalassia testudinum*) important. Carbon isotopic analyses confirm this pattern (Table 1). Terrestrial plant contribution ( $\delta^{13}C \approx -24$ ) is found adjacent to the Everglades, while sea grasses ( $\delta^{13}C \approx -10$ ) dominate the carbon isotope signature in open portions of the bay. An intermediate isotopic value ( $\delta^{13}C \approx -16$ ), indicative perhaps of input from multiple sources, occurs adjacent to the Florida Keys tract. The presence of amorphous organic matter derived from phytoplankton cannot be ascertained isotopically as the expected  $\delta^{13}C$  values fall between the ranges for terrestrial organic matter and sea grasses. However, qualitative visual characterization of organic matter in three locations documents the presence of amorphous, herbaceous and woody plant material.

Organic carbon ranges from about 0.7–2.1 weight percent, with highest values in surface samples or in upper portions of cores. Similar organic carbon contents in various carbonate sediments, including those in Florida Bay, have been noted by Gehman (1962). The organic carbon content of Florida Bay carbonate sediments also is comparable to the organic carbon content of fine-grained, non-carbonate sediments deposited in a variety of environments (Tissot and Welte, 1984). In all cases, organic carbon decreases down core [Fig. 2(a)]. Average organic carbon in all surface samples is 1.3%. Average organic carbon in deepest core sections (84–96 cm) is 1.0% for an average decrease in organic carbon from surface to core bottom (approximately 1 m depth) of 23%. Down core decrease in organic carbon in individual cores ranges from 20 to 50%. Most of this decrease occurs within the upper 40 cm. There is a broad areal trend in organic carbon content of all samples (surface and depth), with sediments in the northeastern part of the bay averaging 1.4% organic carbon while the comparable value for all sediments from the southwestern portion is 1.0%.

Down core decreases in organic carbon are routinely observed in non-carbonate sediments (Berner, 1980); destruction of the organic matter by aerobic and anaerobic bacteria accounts for this decrease. Estimates of organic carbon loss during shallow

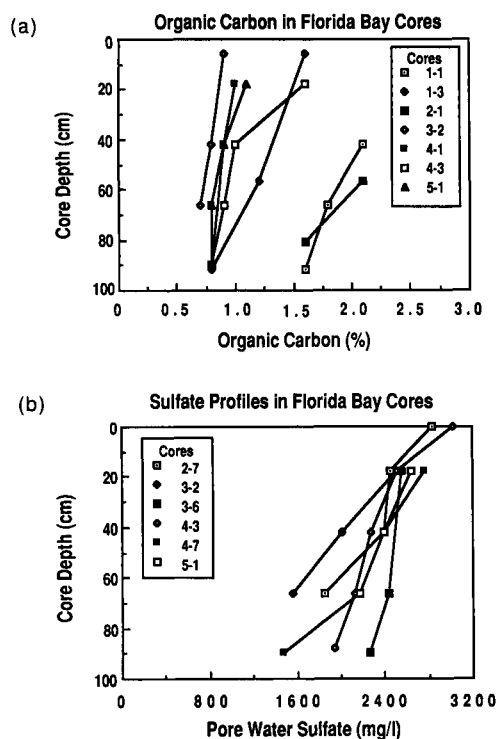


Fig. 2. (a) Organic carbon and (b) pore water sulfate in cores from Florida Bay. Data are plotted at center of 6 cm core segments used for analyses.

burial in different sedimentary regimes are from 20 to 50% (Berner, 1980), which is the same range of values noted above for Florida Bay sediments. Data from the present and previous investigations show that destruction of organic matter is most intense within the upper few tens of centimeters, below which generally uniform organic carbon values are obtained.

Although the shallow water column is well-mixed and oxygenated, and the sediments are extensively bioturbated, some sulfate-reduction is occurring within the sediments. Analyses of pore waters show a partial depletion of sulfate with depth [Fig. 2(b)]. The low energy of the environment and the availability of abundant organic matter counter the effects of bioturbation and establish an anoxic regime at depth. Under these conditions, sulfate-reducing bacteria extract the available sulfate and reduce it to hydrogen sulfide. In clastic muds, where reactive iron is usually abundant, sulfide combines with iron to form pyrite (Berner, 1980). In carbonate muds with much less reactive iron, sulfide is converted to free sulfur, some of which becomes incorporated in residual organic matter during diagenesis (Tissot and Welte, 1984).

#### Extractable organic matter

In sediments of the more restricted northeastern portion of the bay extractable organic matter (EOM),

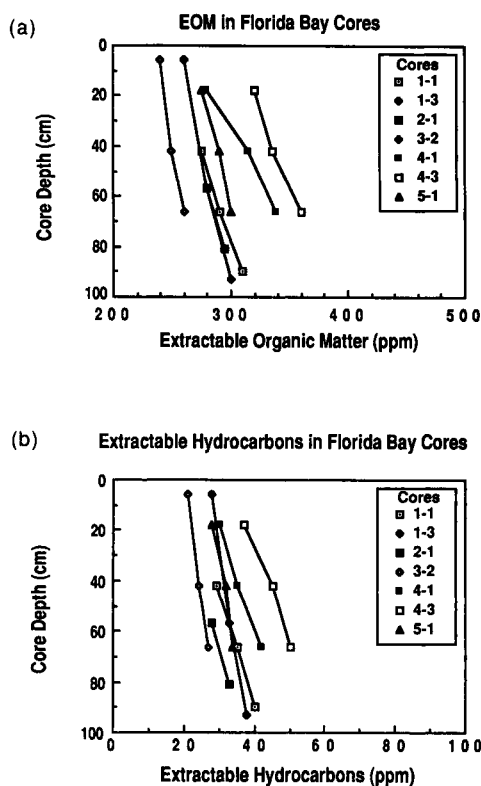


Fig. 3. (a) Extractable organic matter and (b) hydrocarbons in cores from Florida Bay. Data are plotted at center of 6 cm core segments used for analyses.

or bitumen, ranges from 230 to 310 ppm and averages 268 ppm. In the open southwestern portion, bitumen content ranges from 270 to 360 ppm and averages 309 ppm. The bitumen is composed of 80–85% NSO compounds, 5–10% aromatic hydrocarbons, and 5–10% saturated hydrocarbons. This distribution is similar to the composition of organic matter extracted from modern clastic sediments (Tissot and Welte, 1984). Extractable hydrocarbon contents are generally below 50 ppm and are also comparable to values reported for clastic sediments (Hunt, 1970; Tissot and Welte, 1984).

Extractable organic matter and total hydrocarbon concentrations show opposite distributions to organic carbon with depth in cores [Figs 3(a) and 3(b); Table 2]. Both properties systematically increase with depth despite the decrease in organic carbon. The trends can be explained by the effects of early diagenesis, with metabolism of the organic matter by sulfate-reducing bacteria leading to an overall decrease in organic carbon but to an enrichment of lipids due to preferential metabolism of non-lipid components.

#### Normal alkanes

As for the bulk parameters, the *n*-alkane distribution is a function of sample locality within the bay. Sediments from the restricted portion of the bay

Table 2. Organic geochemical data for Florida Bay sediments.

| Locality                 | Depth (cm) | Org. C (%) | EOM (ppm) | HC (ppm) | NSO (ppm) | HC/EOM (%) | EOM/OC (%) | HC/OC (%) |
|--------------------------|------------|------------|-----------|----------|-----------|------------|------------|-----------|
| <i>Northeastern Part</i> |            |            |           |          |           |            |            |           |
| 1-1                      | 36-48      | 2.1        | 275       | 29       | 246       | 11         | 1.3        | 0.1       |
|                          | 60-72      | 1.8        | 290       | 35       | 255       | 12         | 1.6        | 0.2       |
|                          | 84-96      | 1.6        | 310       | 40       | 270       | 13         | 1.9        | 0.3       |
| 1-2                      | Surface    | 1.6        | 265       | 29       | 236       | 11         | 1.7        | 0.2       |
| 1-3                      | Surface    | 1.6        | 260       | 28       | 232       | 11         | 1.6        | 0.2       |
|                          | 51-63      | 1.2        | 280       | 33       | 247       | 12         | 2.3        | 0.3       |
|                          | 87-99      | 0.8        | 300       | 38       | 262       | 13         | 3.8        | 0.5       |
| 1-4                      | Surface    | 0.9        | 235       | 22       | 213       | 9          | 2.6        | 0.2       |
| 2-1                      | 51-63      | 2.1        | 280       | 28       | 252       | 10         | 1.3        | 0.1       |
|                          | 75-87      | 1.6        | 295       | 33       | 262       | 11         | 1.8        | 0.2       |
|                          | Surface    | 1.2        | 250       | 25       | 225       | 10         | 2.1        | 0.2       |
| 2-2                      | Surface    | 2.0        | 270       | 28       | 242       | 10         | 1.4        | 0.1       |
| 2-3                      | Surface    | 0.9        | 240       | 21       | 219       | 9          | 2.7        | 0.2       |
| 3-2                      | 36-48      | 0.8        | 250       | 24       | 226       | 10         | 3.1        | 0.3       |
|                          | 60-72      | 0.7        | 260       | 27       | 233       | 10         | 3.7        | 0.4       |
|                          | Surface    | 0.8        | 230       | 20       | 210       | 9          | 2.9        | 0.3       |
| Average                  |            | 1.4        | 268       | 29       | 239       | 11         | 2.2        | 0.2       |
| <i>Southwestern Part</i> |            |            |           |          |           |            |            |           |
| 2-4                      | Surface    | 1.4        | 306       | 37       | 269       | 12         | 2.2        | 0.3       |
| 3-1                      | Surface    | 0.8        | 270       | 29       | 241       | 11         | 3.4        | 0.4       |
| 4-1                      | 12-24      | 1.0        | 280       | 30       | 250       | 11         | 2.8        | 0.3       |
|                          | 36-48      | 0.9        | 315       | 35       | 280       | 11         | 3.5        | 0.4       |
|                          | 60-72      | 0.8        | 338       | 42       | 296       | 12         | 4.2        | 0.5       |
| 4-2                      | Surface    | 1.4        | 310       | 38       | 272       | 12         | 2.2        | 0.3       |
| 4-3                      | 12-24      | 1.6        | 320       | 37       | 283       | 12         | 2.0        | 0.2       |
|                          | 36-48      | 1.0        | 335       | 45       | 290       | 13         | 3.4        | 0.5       |
|                          | 60-72      | 0.9        | 360       | 50       | 305       | 14         | 4.0        | 0.6       |
| 5-1                      | 84-96      | 0.8        | -         | -        | -         | -          | -          | -         |
|                          | 12-24      | 1.0        | 275       | 28       | 242       | 10         | 2.8        | 0.3       |
|                          | 36-48      | 0.9        | 290       | 32       | 258       | 11         | 3.2        | 0.4       |
|                          | 60-72      | 0.9        | 300       | 34       | 266       | 11         | 3.3        | 0.4       |
| Average                  |            | 1.0        | 308       | 36       | 271       | 12         | 3.1        | 0.4       |

typically have a bimodal *n*-alkane distribution with major components from *n*-C<sub>17</sub> to *n*-C<sub>19</sub> and from *n*-C<sub>23</sub> to *n*-C<sub>27</sub> [Figs 4(a), 4(b) and 5(a)]. Alkanes from *n*-C<sub>21</sub> to *n*-C<sub>31</sub> show a pronounced odd-to-even predominance with a Carbon Preference Index as high as 2.4. A few samples have relatively high concentrations of *n*-C<sub>21</sub> and *n*-C<sub>23</sub>, which are the most abundant *n*-alkanes in *Thalassia*, and they are probably derived in part from this commonly occurring sea grass (Attaway *et al.*, 1970). The *n*-alkanes in sediments from the open part of the bay also exhibit a bimodal pattern, but the distribution differs from that in the northeastern sediments; maxima in the sediments from the marine-dominated southwestern region occur at *n*-C<sub>17</sub> or *n*-C<sub>18</sub> and *n*-C<sub>23</sub> or *n*-C<sub>24</sub> with a slight even carbon-number dominance when *n*-C<sub>24</sub> is prevalent [Fig. 4(c)]. Normal alkanes greater than C<sub>27</sub> with an odd carbon-number predominance are less abundant in sediments collected in the southwestern half of the bay. There is a slight increase in even carbon-number predominance with depth.

An even carbon-number predominance at about *n*-C<sub>22</sub> or *n*-C<sub>24</sub> has been noted previously and is considered to be characteristic of carbonate and evaporite environments (Welte and Ebhard, 1968; Dembicki *et al.*, 1976; Tissot and Welte, 1984).

Reduction of even carbon-number fatty acids and alcohols under highly reducing conditions has been suggested as the probable source of the even carbon-number *n*-alkanes (Welte and Ebhard, 1968; Welte and Waples, 1973). The inference of this interpretation is that carbonate and evaporite environments are highly reducing and more reducing than their non-carbonate counterparts. There is no evidence to support this inference, and there is no reason to believe that carbonate and evaporite environments are more or less reducing than non-carbonate environments. As the results in the present study demonstrate, even carbon-number predominance occurs in carbonate sediments that are bioturbated, that are experiencing partial but not complete sulfate reduction, and that are not highly reducing.

Recent investigations have emphasized a combination of reducing conditions as well as contributions from a variety of microbial sources as being important in establishing an even carbon-number predominance in non-carbonate environments (Johnson and Calder, 1973; Cranwell, 1976; Hatcher *et al.*, 1977; Debyser *et al.*, 1977; Nishimura and Baker, 1986; Grimalt and Albaiges, 1987). Nishimura and Baker (1986) and Grimalt and Albaiges (1987) note the presence of even carbon-number preference in a

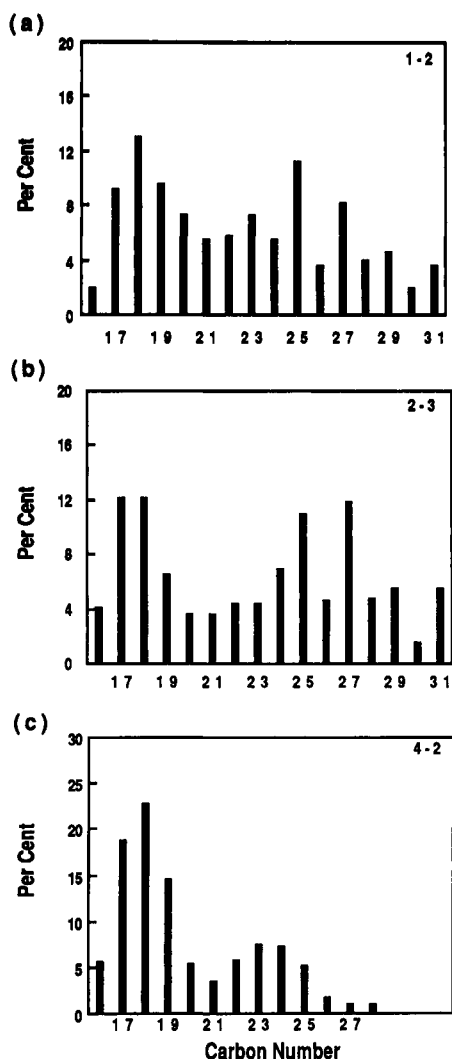


Fig. 4.  $C_{15+}$   $n$ -alkane distributions in surface sediments from three stations across Florida Bay.

variety of sedimentary environments, both oxic and anoxic, and both fresh water and marine settings. Because of the lack of parallelism between the  $n$ -alkane distribution and other straight-chain lipid constituents, and because of the presence of an even carbon-number predominance in  $n$ -alkanes produced by many bacterial, fungal and algal species, Nishimura and Baker (1986) and Grimalt and Albaiges (1987) propose that the sources for even carbon-number predominance of  $n$ -alkanes in sediments are marine and fresh water bacteria, fungi and algae. The results of the present and previous studies indicate, therefore, that even carbon-number predominance is due to the types of organisms present rather than to the nature of the sedimentary environment or its reducing power.

In summary, Florida Bay sediments from near the mainland and the Keys contain  $n$ -alkanes attributable to higher plant waxes and to marine autochthonous origins, whereas sediments in the open bay

further from terrestrial sources of organic matter contain  $n$ -alkanes derived almost entirely from marine sources. These  $n$ -alkane distributions occur in carbonate sediments that are only mildly reducing.

#### Biomarkers

Although the primary focus of this study was to conduct a broad survey of  $n$ -alkane distributions, preliminary biomarker analyses were obtained on one sample. Various biomarker maturity indicators are consistent with the immature nature of the organic matter. The presence of  $C_{31}$   $\beta\beta$  hopane and the presence only of the 22R epimers of the  $C_{31}$  homohopanes and bishomohopanes (i.e. 17 $\alpha$ (H), 21 $\beta$ (H), 22(R)-homohopane and 17 $\alpha$ (H), 21 $\beta$ (H), 22(R)-bishomohopane) indicate an immature source, as expected for these modern sediments.

#### Pyrolysis

The second part of this study examines simulated thermal maturation of modern carbonate sediment organic matter by hydrous and anhydrous pyrolysis in order to compare the products with the original constituents and with the organic matter in carbonate source rocks. The presence of water in wet pyrolysis experiments yields hydrocarbon products that are more saturated than those obtained during dry pyrolysis conditions (Lewan *et al.*, 1979). The present study expands the use of hydrous pyrolysis in one of the first detailed applications to modern sediments within a single sedimentary environment and explores its usefulness as a thermal simulation technique for generating hydrocarbons from modern organic matter.

Both hydrous and anhydrous pyrolyses of Florida Bay muds resulted in about a tenfold increase in extractable organic matter (EOM) from two to three percent of the organic carbon in the unheated sediment to as high as 28% of the organic carbon in a pyrolyzed sample (Table 3). The EOM values for pyrolyzed Florida Bay carbonates are comparable to data reported for the Upper Cretaceous Austin Chalk (Grabowski, 1984), a known carbonate source rock, indicating that pyrolysis of modern Florida Bay sediments is capable of generating extractable organic matter in concentrations comparable to those in carbonate source rocks. Comparison of the hydrocarbon content between unheated and heated samples clearly shows that heating also causes a significant increase in extractable hydrocarbons. After heating, the sediments contain up to seven times as much  $C_{15+}$  hydrocarbons. The hydrocarbon content as a proportion of organic carbon increases from 0.24 to 2%. As a proportion of EOM, however, the hydrocarbon content decreases from 11 to 12% of EOM in unheated sediments to 6–8% in pyrolyzed sediment. Clearly, at the given experimental conditions pyrolysis generates a greater proportion of NSO compounds compared to hydrocarbons in these sediments, although continued heating or higher

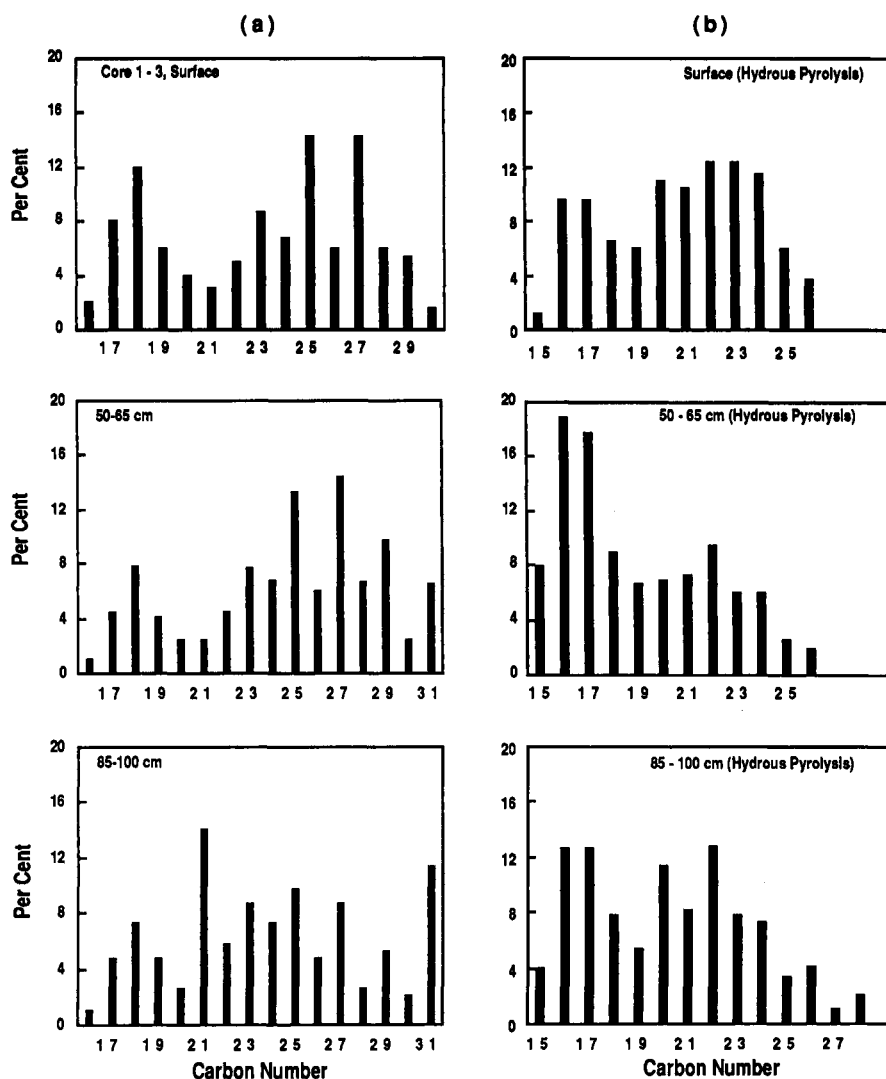


Fig. 5. (a)  $C_{15+}$   $n$ -alkane distributions at three depths in a core, and (b)  $n$ -alkanes generated by hydrous pyrolysis in the same samples.

temperatures might have increased the hydrocarbon yield. The quantity of newly extractable hydrocarbons is mainly a function of the amount of organic matter in the starting material. The amount of generated hydrocarbons decreases downcore because the organic carbon content also decreases down-core. Hydrous pyrolysis consistently generates slightly greater yields than anhydrous pyrolysis for all parameters.

The yields of EOM and hydrocarbons from pyrolyzed sediment are consistently different for the two regions of the bay. Although EOM is comparable for both regions, the quantity of generated hydrocarbons is greater in the southwestern part. Due to the lower average organic carbon content in this marine-dominated region, EOM and hydrocarbon yields as a function of organic carbon are consistently greater, reflecting the greater propensity of marine organic matter to generate liquid hydrocarbons.

Most pyrolyzates have a similar  $n$ -alkane distribution, exhibiting a bimodal pattern with maxima at  $C_{16}$  or  $C_{17}$  and  $C_{22}$  [Fig. 5(b)]. The exceptions are essentially unimodal at  $C_{21}$  or  $C_{22}$  with a very subdued or no second mode at  $C_{17}$  (Fig. 6). All the newly generated hydrocarbons are different from those of the original sediment extracts in the northern portion of the bay, with little or no odd carbon preference from  $C_{25}$  to  $C_{31}$  and significant amounts of compounds with less than 27 carbon atoms [Fig. 5(b)]. The overall hydrocarbon patterns generated by wet and dry pyrolyses exhibit no significant differences, except for the presence of unsaturated homologs in the dry pyrolyzates. In the only prior investigations in which modern carbonate sediments were heated under hydrous conditions, an even predominance, with  $C_{20}$  and  $C_{22}$  most abundant, was produced (Ferguson *et al.*, 1984; Shinn *et al.*, 1984).

Previous studies have shown that dry pyrolysis of

Table 3. Organic geochemical data for wet pyrolyzed Florida Bay sediment.

| Locality                 | Depth<br>(cm) | Org. C<br>(%) | EOM<br>(ppm) | HC<br>(ppm) | NSO<br>(ppm) | HC/EOM<br>(%) | EOM/OC<br>(%) | HC/OC<br>(%) |
|--------------------------|---------------|---------------|--------------|-------------|--------------|---------------|---------------|--------------|
| <i>Northeastern Part</i> |               |               |              |             |              |               |               |              |
| 1-1                      | 36-48         | 2.1           | 4163         | 245         | 3918         | 5.9           | 20            | 1.2          |
|                          | 60-72         | 1.8           | 3514         | 210         | 3304         | 6.0           | 20            | 1.2          |
|                          | 84-96         | 1.6           | 3260         | 196         | 3064         | 6.0           | 20            | 1.2          |
| 1-2                      | Surface       | 1.6           | 3200         | 198         | 3002         | 6.2           | 20            | 1.2          |
| 1-3                      | Surface       | 1.6           | 3026         | 192         | 2834         | 6.3           | 19            | 1.2          |
|                          | 51-63         | 1.2           | 2300         | 141         | 2159         | 6.1           | 19            | 1.2          |
|                          | 87-99         | 0.8           | 1500         | 95          | 1405         | 6.3           | 19            | 1.2          |
| 1-4                      | Surface       | 0.9           | 1664         | 108         | 1556         | 6.5           | 19            | 1.2          |
| 2-1                      | 51-63         | 2.1           | 4258         | 250         | 4008         | 5.9           | 20            | 1.2          |
|                          | 75-87         | 1.6           | 3300         | 208         | 3092         | 6.3           | 21            | 1.3          |
| 2-2                      | Surface       | 1.2           | 2254         | 138         | 2116         | 6.1           | 19            | 1.2          |
| 2-3                      | Surface       | 2.0           | 3848         | 225         | 3623         | 5.8           | 19            | 1.1          |
| 3-2                      | Surface       | 0.9           | 1786         | 114         | 1672         | 6.4           | 20            | 1.3          |
|                          | 36-48         | 0.8           | 1558         | 94          | 1464         | 6.0           | 20            | 1.2          |
|                          | 60-72         | 0.7           | 1486         | 90          | 1396         | 6.1           | 21            | 1.3          |
| 3-3                      | Surface       | 0.8           | 1602         | 100         | 1502         | 6.2           | 20            | 1.3          |
| <i>Average</i>           |               | 1.4           | 2670         | 163         | 2507         | 6.1           | 20            | 1.2          |
| <i>Southwestern Part</i> |               |               |              |             |              |               |               |              |
| 2-4                      | Surface       | 1.4           | 3453         | 263         | 3190         | 7.6           | 25            | 2            |
| 3-1                      | Surface       | 0.8           | 2120         | 170         | 1950         | 8.0           | 27            | 2            |
| 4-1                      | 12-24         | 1.0           | 2460         | 195         | 2265         | 7.9           | 25            | 2            |
|                          | 36-48         | 0.9           | 2170         | 180         | 1990         | 8.3           | 24            | 2            |
|                          | 60-72         | 0.8           | 1910         | 158         | 1752         | 8.3           | 24            | 2            |
| 4-2                      | Surface       | 1.4           | 3472         | 280         | 3192         | 8.1           | 25            | 2            |
| 4-3                      | 12-24         | 1.6           | 4253         | 370         | 3883         | 8.7           | 27            | 2            |
|                          | 36-48         | 1.0           | 2540         | 199         | 2341         | 7.8           | 25            | 2            |
|                          | 60-72         | 0.9           | 2492         | 197         | 2295         | 7.9           | 28            | 2            |
|                          | 84-96         | 0.8           | -            | -           | -            | -             | -             | -            |
| 5-1                      | 12-24         | 1.0           | 2372         | 188         | 2186         | 7.9           | 24            | 2            |
|                          | 36-48         | 0.9           | 2340         | 184         | 2156         | 7.9           | 26            | 2            |
|                          | 60-72         | 0.9           | 2200         | 180         | 2020         | 8.2           | 24            | 2            |
|                          |               | 0.8           | -            | -           | -            | -             | -             | -            |
| <i>Average</i>           |               | 1.0           | 2649         | 214         | 2435         | 8.1           | 25            | 2            |

a variety of sediments results in the generation of a suite of *n*-alkanes dominated by even carbon-numbers (e.g. Mitterer and Hoering, 1968; Ishiwatari *et al.*, 1977; Douglas *et al.*, 1977). Free or esterified fatty alcohols, after dehydration and hydrogenation, were suggested as a source for even predominance in the C<sub>20</sub>-C<sub>28</sub> range (Douglas *et al.*, 1977). Results from some pyrolysis studies suggest that formation of an even carbon-number predominance of *n*-alkanes could be temperature-dependent (Ishiwatari *et al.*, 1977; Douglas *et al.*, 1977). At temperatures below 200°C there is a little change in original hydrocarbon distribution of pyrolyzed sediment. Preferential production of even carbon-number *n*-alkanes occurs between 200 and 300°C, with gradual disappearance of carbon-number preference above 300°C and CPI values approaching unity (Douglas *et al.*, 1977). It is possible, therefore, that even predominance in pyrolyzates may be a function of experimental conditions. While the conditions of pyrolysis experiments are more extreme than those under which petroleum hydrocarbons are generated naturally in sedimentary rocks, the resulting distributions of hydrocarbon products are nevertheless quite comparable. The hydrocarbons in extracts from Cretaceous carbonate rocks from South Florida (Palacas *et al.*, 1984) and from the Cretaceous Austin Chalk (Grabowski,

1984) exhibit bimodal patterns, which are very similar to those generated during pyrolysis of modern carbonates.

#### *Pyrolysis of individual carbonate samples*

EOM of pyrolyzed ooid and shell samples ranges from 500 to 6700 ppm and is roughly proportional to organic carbon content. The hydrocarbon content ranges from 2 to 34% of EOM and is inversely proportional to it; that is, the smaller the EOM, the greater the relative hydrocarbon content (Table 4). The yield of hydrocarbons is greatest in the ooid and mud samples and lowest in the shell samples. Ooids and mud, containing humic substances, algal material and particulate organic matter, undoubtedly have a larger indigenous lipid content than shells, which are dominated by protein. The yield of EOM and hydrocarbons in these higher temperature programmed pyrolyzates of carbonates is significantly greater than comparable yields for the lower temperature bomb-pyrolyzed Florida Bay muds. The contrast is probably due to the different methods used for pyrolysis; consequently, the data are only qualitatively comparable.

The distribution of hydrocarbons in the C<sub>15+</sub> fraction is surprisingly uniform considering the diversity of sample types and their organic constituents. The



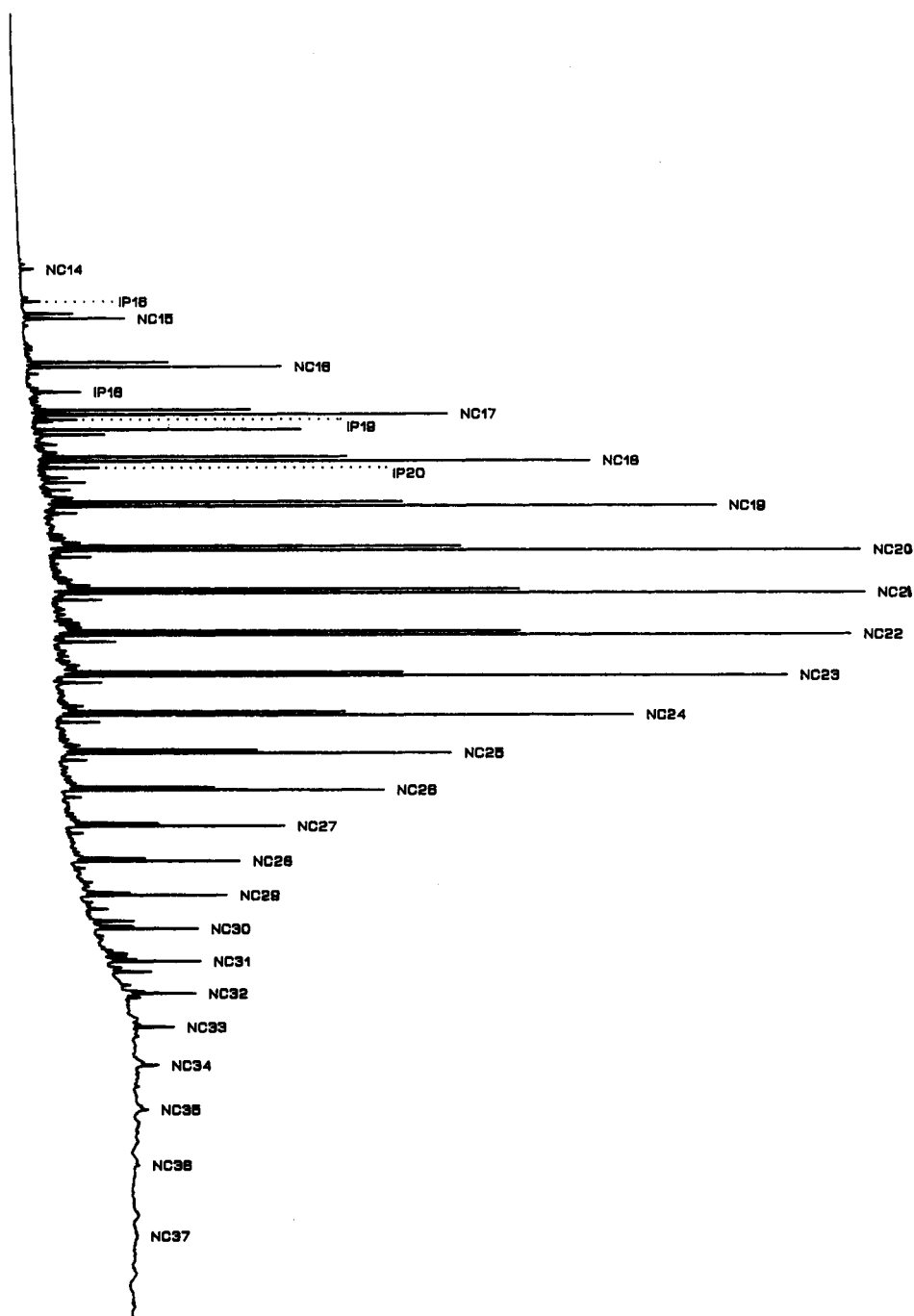


Fig. 6. Gas chromatogram of hydrocarbons generated by anhydrous pyrolysis of a sample of supratidal carbonate mud. The numbered peaks are saturated hydrocarbons; the smaller peaks preceding the *n*-alkanes are the corresponding *n*-alkenes formed under anhydrous conditions.

*n*-alkane pattern is generally unimodal at  $C_{22}$ , with an envelope of hydrocarbons ranging from  $C_{15}$  to  $C_{30+}$  [Figs 7(a) and 7(b)]. Phytane always exceeds pristane, with pristane/phytane values ranging from 0.52 to 0.66. One sample of carbonate mud collected on a supratidal mud flat covered by cyanobacterial mats has a different *n*-alkane pattern, with a unimodal hydrocarbon distribution peaking at  $C_{17}$  and  $C_{18}$ .

These *n*-alkane distributions are similar to those described previously for the bomb-pyrolyzed bay sediments and for carbonate source rocks such as the Cretaceous Sunniland Limestone of South Florida and the Austin Chalk of South Texas.

While the heavy hydrocarbon distributions in these samples are not unexpected for ooid and mud samples, which contain proto-kerosen and humic sub-

Table 4. Organic geochemical data for pyrolyzed carbonate samples.

| Sample | OC <sup>a</sup><br>(%) | EOM<br>(ppm) | Alkane<br>(ppm) | Arom.<br>(ppm) | NSO<br>(ppm) | HC/EOM<br>(%) |
|--------|------------------------|--------------|-----------------|----------------|--------------|---------------|
| Ooid   | -                      | 1365         | 299             | 205            | 1066         | 22            |
| Ooid   | -                      | 799          | 117             | 91             | 682          | 14            |
| Mud    | 0.5                    | 1178         | 403             | 243            | 775          | 35            |
| Mud    | 0.9                    | 4760         | 729             | 373            | 2384         | 23            |
| Sand   | 0.1                    | 645          | 171             | 84             | 474          | 27            |
| Shell  | 0.1                    | 510          | 59              | 33             | 439          | 12            |
| Shell  | 0.4                    | 6749         | 188             | 94             | 6427         | 2             |
| Shell  | 0.5                    | 3722         | 73              | 28             | 2882         | 3             |

<sup>a</sup>Values are minimal due to removal of acid-soluble organic matter during acid leach.

stances, the *n*-alkane pattern is surprising for the shell and carbonate sand samples. Pigments, lipoproteins, or other minor lipid constituents may be the sources of C<sub>15+</sub> *n*-alkanes, pristane and phytane. Amino acids and amino sugars, the dominant monomers of the organic matrix in biogenic carbonates, are expected to yield predominantly gaseous hydrocarbons. Indeed, low molecular weight hydrocarbons from C<sub>1</sub> to C<sub>3</sub> are major products of the programmed pyrolyses [Figs 8(a) and 8(b)]. Methane is the dominant hydrocarbon gas, with decreasing concentrations of C<sub>2</sub> through C<sub>7</sub> gases with increasing molecular weight. Shell samples generally have higher C<sub>2</sub> and C<sub>3</sub> and lower C<sub>1</sub> concentrations than ooid and mud samples, probably reflecting a greater concentration of two and three carbon amino acid compounds in the organic matrix of shells. One sample, the subtidal mud, has a different abundance distribution of hydrocarbon gases with nearly equal concentrations of C<sub>1</sub> and C<sub>2</sub>.

Rock-Eval parameters of Hydrogen Index (HI) and T<sub>max</sub> provide further insight into the nature of the organic matter in these carbonate samples (Fig. 9). The two samples of carbonate mud, including the one from a supratidal algal mat, are examples of Type I organic matter. Ooids, containing marine humic substances, consist of Type II, while three of the shell samples contain organic matter intermediate between Types II and III. One shell sample and the carbonate sand consist of Type III. The position of the samples on the HI-T<sub>max</sub> plot correlates roughly with organic carbon, EOM and hydrocarbon content of the pyrolyzed sediments. The two samples of Type III organic matter have lowest organic carbon and EOM and generally lowest hydrocarbon yield.

#### SUMMARY AND CONCLUSIONS

Carbonate environments may have multiple sources of organic matter. Although they are marine deposits, and are not associated with large river discharges, near-shore carbonate environments can have a significant input of terrestrial organic matter due to storm drainage of fresh water from the adjacent

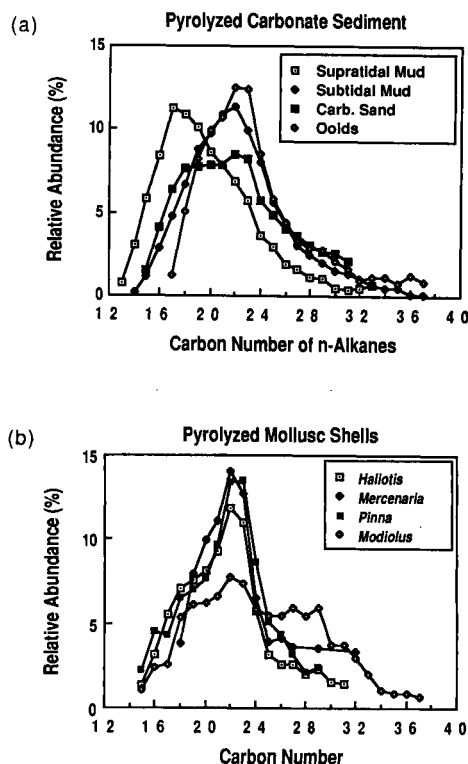


Fig. 7. C<sub>15+</sub> *n*-alkane distribution in (a) non-skeletal carbonates and (b) mollusc shells generated by anhydrous pyrolysis.

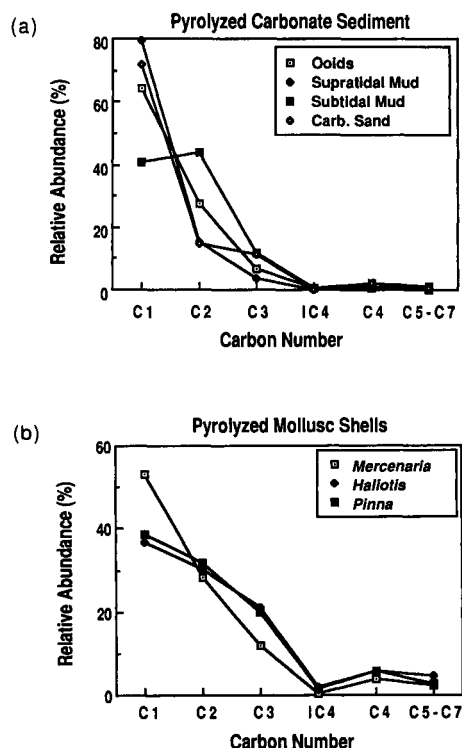


Fig. 8. Low molecular weight hydrocarbons in (a) non-skeletal carbonates and (b) mollusc shells generated by anhydrous pyrolysis.

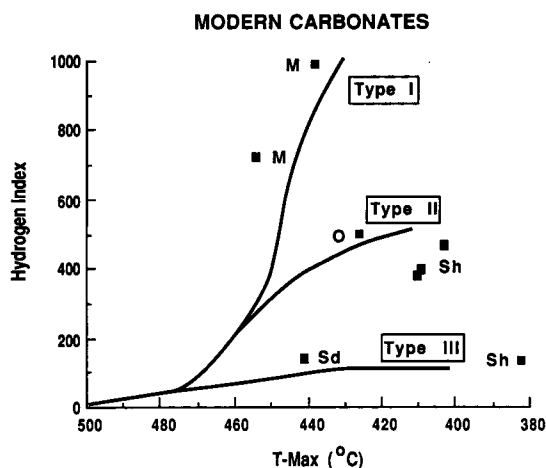


Fig. 9. Rock-Eval Hydrogen Index vs  $T_{max}$  for skeletal and non-skeletal carbonate samples. Samples are carbonate mud (M), ooids (O), sand (Sd) and shells (Sh).

mainland and through tidal circulation. The resulting nearshore to offshore decreasing gradient of terrestrial organic matter, although largely localized close to the source, may be comparable to that seen in non-carbonate environments. This pattern has a number of implications. First, it may be useful in determining shoreline direction. Second, the *n*-alkane distribution will exhibit either a terrestrial, marine, or mixed signature, depending on the location of the sample. Such a variety of signals can confuse the correlation of oils to source rocks. Third, a single or even a few analyses may not adequately characterize the organic matter in a carbonate environment; two-dimensional surveys are necessary to map the potential variability in organic matter.

Marine organic matter in carbonate environments also has multiple sources and includes phytoplankton, bacteria, marine grasses and the organic matrix within grains. Marine grasses contribute significantly to the organic carbon budget, and their presence or absence exerts an important influence on the organic carbon content of the sediments as well as on the biochemical make-up of the sedimentary organic matter. In the absence of marine grasses, the sediments may have a dominant phytoplanktonic biochemical imprint.

The influence of the organic matrix on sedimentary organic matter is also somewhat variable due to different compositions. Skeletal organic matter is predominantly proteinaceous and is largely gas prone, although pigments and minor lipid constituents may contribute to the formation of liquid hydrocarbons. The organic matrix of ooids consists of adsorbed and entrapped marine humic substances and algal and fungal infestations, all of which may be oil prone. Thus, the sedimentary carbonate facies will exert some influence on the composition of the organic matter and ultimately on the hydrocarbons

generated from it. As modern, and presumably many ancient, carbonate settings contain a number of facies, the potential for a significant range in composition of carbonate-sourced oils exists.

Finally, as Gehman (1962) noted, and the results of the present study confirm, shallow water carbonate sediments have a high potential for generating hydrocarbons. Continuous burial of carbonate sediments without exposure will tend to preserve this hydrocarbon potential.

**Acknowledgements**—Appreciation is extended to colleagues at the Technology Center, Sun Exploration and Production Co., Dallas, Texas, for assistance. Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. Contribution No. 554 of the Geosciences Department, The University of Texas at Dallas.

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