12. ORGANIC FACIES OF CRETACEOUS SEDIMENTS FROM DEEP SEA DRILLING PROJECT SITES 535 AND 540, EASTERN GULF OF MEXICO

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ABSTRACT

Lower to middle Cretaceous sediments in the eastern Gulf of Mexico are richer in organic matter and have a more marine organic facies than their counterparts in the nearby western North Atlantic, suggesting that the Gulf was the more productive of the two areas. As in the western North Atlantic, the rate of supply of terrestrial organic matter was high when the rate of supply of noncarbonate clastic materials was high (at times of low sea level) and diminished as sea level rose. The rate of supply of marine organic matter was lower in the Early Cretaceous than in the Cenomanian, perhaps in response to the global rise in sea level over this period. Where they are thermally mature, the organic matter-rich units drilled at Sites 535 and 540 should be excellent sources for liquid hydrocarbons. The Pleistocene sediments of the eastern Gulf are dominated by terrestrial organic matter representing Mississippi River effluent.

INTRODUCTION

The history of deposition of different types of organic matter in past ocean basins can provide valuable information about environmental factors like (1) the productivity of surface waters, (2) the degree of oxygenation of bottom waters, (3) the extent of runoff from land, (4) the proximity of the shoreline, and (5) relative changes in sea level (Welte et al., 1979; Tissot et al., 1980; Summerhayes, 1981; Summerhayes and Masran, 1983). In order to obtain this type of information from the eastern Gulf of Mexico, we have examined the distribution of organic matter in sediments recovered at DSDP Sites 535 and 540 (Fig. 1). We have focused on the Early to middle Cretaceous, where organic matter-rich samples were obtained (site chapter, Sites 535, 539, and 540, this volume), but have also analyzed some Cenozoic samples (Appendix). Our study is a follow-up to earlier work on the nature and controls of deposition of the organic facies of the mid-Cretaceous “black shales” that are widespread throughout the deep North Atlantic (Summerhayes, 1981; Masran, 1982; Summerhayes and Masran, 1983). In this report we compare and contrast the sedimentation of organic matter in the Gulf of Mexico with that in the nearby western North Atlantic.

The drilled sections at Sites 535 and 540 together form an overlapping sequence (site chapter, Sites 535, 539, and 540, this volume). In both places there is a veneer of Quaternary sediments designated Unit I, which overlie Tertiary marls and chalks at Site 540 (Unit II). An Upper Cretaceous mudflow deposit at Site 540 (Unit III) follows. It was not analyzed for its organic constituents. It overlies in turn a lower Cenomanian–mid-Albian sequence (Units IV, V, and VI at Site 540). At Site 535, the Cretaceous section extends from the mid-Cenomanian into the lower Valanginian–upper Berriasian through Units II, III, IV, and V (site chapter, Sites 535, 539, and 540, this volume).

METHODS

The LECO analyzer was used to find total organic carbon (TOC) for our samples; the Rock-Eval analyzer was used to do the pyrolysis for hydrogen and oxygen indices; and the transmitted-light-microscopy method of Masran and Pocock (1981) was used for classifying types of organic matter. Our samples came from pieces of core frozen for organic geochemical purposes and are not necessarily fully representative of the sections from which they were obtained. The data are given in the Appendix.

TYPES AND AMOUNTS OF ORGANIC MATTER

Quaternary (Unit I, Sites 535 and 540)

The Quaternary sediments of Site 535 are slightly calcareous to calcareous muds and clays at the distal edge of the Mississippi Fan. They are reported to contain abundant wood fragments and small twigs, and to have an average TOC of 1.17% (site chapter, Sites 535, 539, and 540, this volume). Pyrolysis shows that the organic matter has a low hydrogen index typical of terrestrial organic matter (Type III) (Appendix, and shipboard reports). Analyses by transmitted light microscopy confirm the highly terrestrial nature of the organic facies, which averages 35% structured terrestrial, 7% biodegraded terrestrial, 8% pollen and spores, and 22% charcoal, along with 3% structured marine and 27% amorphous material of indeterminate origin (Appendix).

At the shallower site (Site 540), located above the Fan, the sediments are less terrigenous, the TOC is lower, and there is much more amorphous and structured marine organic matter than at Site 535 (Appendix). Gray amorphous organic matter in highly calcareous sediments like these is usually mainly derived from marine organic remains; because it is abundant in these sediments, we suspect that much of the organic matter here
Figure 1. Locations of DSDP Sites 535, 539, 540.
has a marine rather than a terrestrial source. Nevertheless, the hydrogen index is very low (Appendix) and belongs to the Type III category of Tissot and others (1980), which is usually considered to be terrestrial plant material.

**Tertiary (Unit II, Site 540)**

Highly calcareous mid-Miocene to late Paleocene ooze, chalks, and limestones with 70–90% CaCO₃ are interbedded with marls containing 32–65% CaCO₃ (site chapter, Sites 535, 539, and 540, this volume). They are bioturbated and contain very little organic matter (average = 0.08% TOC; Appendix), indicating deposition under oxidizing conditions. Most of our samples contained too little organic matter to be visually analyzed for organic matter type. The sample that had enough matter yielded results similar to those of Unit I at this site, suggesting a marine character (Appendix). But, the average hydrogen index of these samples is only 188 (Appendix), signifying the Type III category of Tissot et al. (1980).

**Middle Cenomanian (Unit II, Site 535)**

This unit is typically banded into light-colored limestones (CaCO₃ 95%) that tend to be bioturbated, and darker-colored, more marly beds (CaCO₃ 72%) that tend to be laminated (site chapter, Sites 535, 539, and 540, this volume). The limestones contain abundant bioclastic, turbiditic material, though less than in the lower Cenomanian nearby at Site 540. The sedimentation rate is thought to be about 46 m/Ma (site chapter, Sites 535, 539, and 540, this volume).

The shipboard geochemical reports show that TOCs range from 0.3 to 5.4%, and hydrogen indices from 61 to 520 (Type III to Type II). Our careful inspection of the shipboard geochemical data shows that only two samples contain more than 1% TOC (they average 4.7% TOC); the rest have less than 1% TOC and average 0.6% TOC. Average hydrogen indices are 440 for the two rich samples (indicating a mix of Type II and Type III), and 152 for the remaining samples (Type III).

All of the samples that we analyzed from this deposit at Site 535 have about 1% TOC or less (Appendix). Some of them contain abundant structured marine organic matter, others contain abundant gray amorphous material (Appendix). There was almost no recognizable terrestrial organic matter. Hydrogen indices range from 47 (Type III organic matter according to Tissot et al., 1980) to 372 (Type II or a mixture of the Types II and III of Tissot et al., 1980), averaging 214. The sample with the highest TOC also had the highest hydrogen index (Appendix).

**Lower Cenomanian–Late Albian (Unit IV, Site 540)**

This unit is characterized by rhythmic alternations of light-colored limestone (93% CaCO₃) and dark-colored clayey limestone (80% CaCO₃). It has a tendency to be laminated, especially in the darker, more marly units in which CaCO₃ may be as low as 65% (site chapter, Sites 535, 539, and 540, this volume). Its upper part (Cores 540-35 to 540-45) was deposited at moderate rates (24–57 m/Ma). Its lower part (Cores 540-45 to 540-70) contains much slumped material, so it has an artificially high sedimentation rate (119 m/Ma) (site chapter, Sites 535, 539, and 540, this volume).

Shipboard geochemical analyses show that this unit is rich in organic matter, with TOCs ranging from 0.5 to 7.8%. According to shipboard interpretations of pyrolysis data, the organic matter is either marine (Type II), or mixtures of marine and terrestrial material (Types II and III), with hydrogen indices ranging from 176 to 741.

The laminated sections rich in marine organic matter were most probably deposited under reducing conditions, whereas the bioturbated light-colored limestones with low TOCs represent deposition under oxidizing conditions (site chapter, Sites 535, 539, and 540, this volume). This interpretation applies to most of the Cretaceous section.

We did not analyze any samples from this unit.

**Late Albian–Middle Albian (Unit V, Site 540)**

Alternating light and dark limestones also characterize this unit. The darker sections tend to be laminated, the lighter ones to be bioturbated (site chapter, Sites 535, 539, and 540, this volume). Calcium carbonate ranges from 51 to 95%; TOCs are moderate, ranging from 0.8 to 1.8% (shipboard organic geochemical reports). According to shipboard geochemical reports, hydrogen indices range from 100 to 428 and are usually lowest in TOC-poor samples and highest in TOC-rich samples.

The two samples that we analyzed did not contain much organic matter (Appendix). Structured marine organic matter and probably marine-derived gray amorphous organic matter were abundant (average-43%), as were structured terrestrial material and charcoal (average-40%) (Appendix), indicating a mixed marine-terrestrial organic facies. Hydrogen indices were very low (average-77, Appendix), indicating the Type III category of Tissot et al. (1980).

**Middle Albian (Unit VI, Site 540)**

This is mainly a bioturbated, coarse-grained, bioclastic limestone containing shallow-water calcareous components displaced from nearby reefs (site chapter, Sites 535, 539, and 540, this volume). Calcium carbonate is 40–45%, and TOCs are low (0.3–0.4%). According to shipboard geochemical reports, hydrogen indices are 107–190 (Type III). Our analyses of one sample confirm the low TOC (Appendix). We did not have enough organic matter to determine the type of organic matter in the sample, but its hydrogen index confirms that it belongs to the Type III category of Tissot et al. (1980).

**Aptian–Late Hauterivian (Unit III, Site 535)**

This unit consists of light-colored massive limestones (94% CaCO₃) interbedded with laminated light-colored limestones and black marly limestones (CaCO₃ 51%) (site chapter, Sites 535, 539, and 540, this volume). According to shipboard technical reports, TOCs are low in the lighter-colored sediments (0.3%), and rich in the darker-colored sediments (reaching 7.8% and averaging 4.5%), whereas hydrogen indices range from 176 (Type
III) to 720 (Type II), the lowest hydrogen indices correspond to the lowest TOCs.

Our one sample was low in TOC (0.5%) and dominated by amorphous and gray amorphous organic matter with some amorphous round bodies (probably seaweed spores) and a little structured marine material and charcoal (Appendix). The hydrogen index of 362 suggests Type II organic matter or a mixture of Types II and III organic matter.

**Late Hauterivian–Early Valanginian (Unit IV, Site 535)**

This unit consists of alternating limestones (85% CaCO$_3$) and gray and laminated marly limestones (71% CaCO$_3$) grading downwards into limestones and black marly limestones (49% CaCO$_3$) (site chapter, Sites 535, 539, and 540, this volume). Fractures filled with tar and stained with hydrocarbons signal that migration has taken place through this unit (site chapter, Sites 535, 539, and 540, this volume). According to shipboard geochemical reports, TOCs range from 0.12 to 13.2%; hydrogen indices range from 109 (Type III) to 600 (Type II), most indicating mixtures of organic matter Types II and III. Our visual analyses confirm that the richer parts of this unit (TOCs more than 1%) contain abundant marine organic matter; the amorphous material in the rich samples contains remnants of structured marine organic matter (Appendix). There is a minor terrestrial contribution, averaging 8% structured terrestrial material and 9% charcoal. Structured marine material is common (average-15%), along with marine-derived amorphous round bodies (average-7%). The organic matter-rich samples have the highest hydrogen indices (Type II); the organic matter-poor sample has a low hydrogen index typical of Type III organic matter (Appendix).

**Early Valanginian–Late Berriasian (Unit V, Site 535)**

This unit is similar in appearance to Unit III (Site 535), but is mostly bioturbated rather than laminated, suggesting that the depositional environment was oxidizing rather than reducing. It contains some laminated black marly beds (CaCO$_3$ 49%), Shipboard geochemical reports and our Appendix show that TOCs range from 0.17 to 6.6%. Shipboard data show that the rich marly beds have an average hydrogen index of 314 (a mix of Types II and III). We analyzed only organic matter-poor sample and found that they had a mixed marine-terrestrial organic facies and low hydrogen indices (see Appendix).

**DISCUSSION**

**Origin of Organic Matter**

Shipboard geochemical work established that Early to middle Cretaceous sediments at Sites 535 and 540 consist of alternations of organically rich sediment (with more than 1% TOC), usually with a high hydrogen index (200–600), and organically depleted sediment (TOC less than 1%), usually with a low hydrogen index (100–200). In the shipboard reports, this was interpreted as suggesting preservation of mainly marine organic matter under the reducing conditions that gave rise to the laminated organic matter–rich and dark-colored sediments, and of mainly terrestrial organic matter under the oxidizing conditions that gave rise to the bioturbated light-colored organic matter–poor intervals. This type of interpretation is based on the premise that labile marine organic matter is decomposed under oxidizing conditions, leaving refractory components like structured terrestrial material and charcoal.

Our analyses of organic matter types demonstrate that marine organic matter is abundant not only in the TOC-rich, but also in many of the TOC-poor intervals. The low hydrogen indices of the TOC-poor intervals cannot, then, indicate the abundance of terrestrial organic matter, but, instead, may indicate extensive degradation of marine organic matter and loss of hydrocarbon-generating potential during early diagenesis. This explanation seems plausible geologically. In contrast, it seems less plausible geologically to suggest that the bioturbated carbonate-rich units (many with 95% CaCO$_3$) should contain only terrestrial organic matter (which is what a literal interpretation of the pyrolysis data implies). Similar conclusions regarding the significance of low (Type III) hydrogen indices in organic matter–poor carbonate sequences have been reached elsewhere by Pratt (1981) and Demaison and Bourgeois (1982). Our contention that most of the amorphous and gray amorphous organic matter in these carbonate sequences is marine derived is supported by the abundance of these components in samples that have high hydrogen indices.

**Distribution of Organic Matter through Time**

Variations in TOC through a time series cannot be used to interpret the history of supply and preservation of organic matter, because TOC contents are controlled by the rate of accumulation not only of organic matter, but also of carbonate and clastic diluents. This is seen very clearly in the nearby western North Atlantic, where a rise in the CCD at the Barremian/Aptian boundary marks a change from an older, low-TOC carbonate sequence to a younger, TOC-rich clastic sequence (Thierstein, 1979; Summerhayes and Masran, 1983). For this reason, we have examined not the absolute abundance of TOC through time in the eastern Gulf of Mexico, but the rates of accumulation of TOC with time at Sites 535 and 540.

We calculated accumulation rates for TOC and for the carbonate and noncarbonate (clastic) fraction of each unit by using (1) sedimentation rates, (2) porosities (both 1 and 2 from site chapter, Sites 535, 539, and 540, this volume), (3) TOCs from shipboard organic geochemical reports and from our Appendix, (4) CaCO$_3$ values from shipboard organic geochemical reports, and (5) an assumed bulk dry-sediment density of 2.65 g/cm$^3$. Rates of accumulation of TOC fall into two main populations, one with rates less than 0.04 mg/cm$^2$ per yr., representing what we shall refer to as “background” rates of TOC accumulation, and another with higher rates that we shall refer to as “peak” TOC accumulation rates. Peak rates are typical of laminated beds and represent good preservation of organic matter under reducing conditions. Background rates are typical of biotur-
Carbonate accumulation dominates the section (Fig. 2). The jump in accumulation rates between Unit III at Site 535 and Unit VII at Site 540 apparently reflects an increase in the lateral supply of shallow-water bioclastic material from nearby reefs, rather than an increase in productivity (site chapter, Sites 535, 539, and 540, this volume). This jump takes place after the late Aptian drop in sea level (cf. Figs. 2 and 3). Thereafter, carbonate supply seems to remain more or less constant regardless of changes in sea level (Figs. 2 and 3).

The relationships between the peak and background rates of accumulation of TOC are weak. Both show a tendency to increase in younger beds, as does the rate of carbonate accumulation. In part, this could reflect increasing preservation of organic matter as the rate of burial increases (both in oxidizing and reducing environments). However, it may also in part be a productivity signal resulting from an increase in productivity as sea level rises through the Cretaceous, which was recognized in the nearby western North Atlantic by Summerhayes and Masran (1983).

Comparison with Deep Western North Atlantic

Both peak and background rates of TOC accumulation are higher in the Gulf than in the nearby western North Atlantic by a factor of about 4 (cf. Summerhayes and Masran, 1983). In contrast, carbonate rates of accumulation are about the same in both areas for the pre-middle Albian section (average = about 2.5 mg/cm² per yr. in the western North Atlantic), and clastic accumulation rates are also about the same (average = 1.5 mg/cm² per yr. in the western North Atlantic). Because deposition of organic matter-rich sediment took place under reducing conditions in both areas, we interpret these data to suggest that productivity was higher in the Gulf than in the western North Atlantic, so that much more of the organic matter in the Gulf, even in organic matter-poor sediments, is marine.

As mentioned above, the pattern of productivity increasing with time as sea level rises is repeated in the western North Atlantic. Summerhayes and Masran (1983) attribute this to a gradual increase in the nutrient budget of the Atlantic by the introduction at intermediate depths of nutrient-enriched subsurface waters from the Pacific. As the Gulf and Atlantic were linked at this time, it is not surprising that the same phenomena are recognized in both areas.

A major difference between the Gulf and the western North Atlantic is that the post-Barremian Hatteras Formation, a siliceous unit deposited beneath the CCD in the Atlantic, is represented in the Gulf by a carbonate sequence. This is because the paleodepth of Site 535 was
probably 1500–1700 m, while the Hatteras Formation was deposited at depths greater than ~3000 m (site chapter, Sites 535, 539, and 540, this volume). These depth differences suggest to us that the thickness of anoxic bottom waters in the western North Atlantic region (including the Gulf of Mexico) probably extended throughout the water column from deeper than 3000 m up into the depth range of today’s oxygen minimum zone (about 200–1500 m). Possibly the entire lower water column was anoxic, as in the Black Sea today. In this context it may be significant that late Albian organic matter–rich laminated sediments occur also at Site 538 in the eastern Gulf (Fig. 1) atop an elevated fault block (site chapter, Sites 535, 539, and 540, this volume).

As in the western North Atlantic (Summerhayes and Masran, 1983), the timing of organic enrichment does not follow closely the pattern of “oceanic anoxic events” described by Schlanger and Jenkyns (1976) and Jenkyns (1980). Deposition of sediment rich in organic matter in the Gulf was not confined to a Barremian-Aptian “oceanic anoxic event,” but continued at high rates throughout the Early Cretaceous, possibly because the North Atlantic (and its offshoot, the Gulf of Mexico) were separated from the rest of the world’s oceans by sills.

CONCLUSIONS

Early to middle Cretaceous sediments from DSDP Sites 535 and 540 in the eastern Gulf of Mexico are carbonate rich and consist of alternations of dark, laminated beds that were deposited under reducing conditions and contain abundant organic matter, and lighter-colored, bioturbated beds that were deposited under oxidizing conditions and are poor in organic matter.

We conclude that:

1) The organic facies of both types of beds contain abundant recognizable remains of marine plants or amorphous organic matter, some of which contains recognizable remains of marine plant tissue.

2) The rate of supply of marine organic matter to the seabed was higher in the eastern Gulf than at comparable distances from shore in the nearby western North Atlantic.

3) The rate of supply of terrestrial organic matter was high when the rate of supply of noncarbonate clastic sediment was high, at times of low sea level; both diminished as sea level rose.

4) The rate of supply of clastic sediment was about the same in the eastern Gulf as in the nearby western North Atlantic.

5) The hydrogen index of organic matter cannot be used as a reliable guide to the marine versus terrestrial derivation of the organic fraction of the sediments; in these carbonate-rich sequences, low hydrogen indices may represent highly degraded marine organic matter, rather than terrestrial organic matter.

ACKNOWLEDGMENTS

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REFERENCES


APPENDIX

Total Organic Carbon (TOC), Pyrolysis Data, and Organic Matter Types, Sites 535 (3450 m water depth) and 540 (2926 m water depth)

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<th>Sub-bottom depth (m)</th>
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<th>Lithology</th>
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<th>Organic matter type&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>Pl.</td>
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Note: TOC analyzed by LECO; pyrolysis by Rock-Eval; organic matter types by Th. C. Mazan (in percent of kerogen fraction) using organic matter classification scheme of Mazan and Pock (1981). Blanks indicate "not present."

<sup>a</sup> Pl. = Plinian; Ce. = Cenomanian; Ap. = Aptian; Ha. = Hauterivian; Va. = Valanginian; Be. = Berriasian; Mi. = Miocene; Oi. = Oligocene; Eo. = Eocene; Al. = Albian.

<sup>b</sup> ST = structured terrestrial; PS = pollen and spores; C = charcoal; BT = biodegraded terrestrial; AM = Amorphous, with m = marine structural remnants; GA = gray amorphous; SM = structured marine; RB = amorphous round bodies (probably algal).

<sup>c</sup> HI = hydrogen index (mg hydrocarbons/g TOC).

<sup>d</sup> OI = oxygen index (mg CO2/g TOC). High oxygen indices probably result from some decomposition of carbonate minerals and/or extensive oxidation of organic matter.