40. SOURCES, PRESERVATION, AND MATURATION OF ORGANIC MATTER IN PLIOCENE AND QUATERNARY SEDIMENTS OF THE GULF OF CALIFORNIA: A SYNTHESIS OF ORGANIC GEOCHEMICAL STUDIES FROM DEEP SEA DRILLING PROJECT LEG 64[1]

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ABSTRACT

This synthesis of organic geochemical studies from Leg 64 was designed to answer fundamental questions about the source, deposition, preservation, and alteration of organic matter in the Gulf of California. The answers to these questions help to determine the extent and degree of influence not only of paleoenvironmental factors, but also of geothermal processes; understanding both these features was among the main objectives of drilling on this leg.

The organic matter is mostly marine, and was deposited as pelagic sediment. Deep in the Guaymas Basin at Sites 477, 478, and 481, turbidites containing terrigenous organic matter are abundant. Total organic carbon (TOC) is most abundant at Sites 479 and 480 in the oxygen-minimum zone on the continental margin. Deeper-water sites contain much less organic matter, and generally their organic contents decrease with depth downhole in response to diagenetic processes. There are local exceptions to this general rule, for instance (1) deep in Hole 476, where there are some fossil(?) lagoonal deposits, rich in organic matter, (2) deep in Hole 478, where laminated sediments rich in organic matter represent a period of stagnation of bottom water in the Guaymas Basin, and (3) 15–20 meters sub-bottom throughout the Gulf, probably in response to some basinwide productivity event in the Holocene transgression.

Despite high heat flow, most of the sediments drilled are immature, except close to sills and in Guaymas Basin Hole 477, where the heat flow reaches 20 HFU. Thermogenic methane is widespread as a minor component of gases near the spreading center in the Guaymas Basin, and is a major component of gas deep in Hole 477. Small amounts of light (gasoline-range) hydrocarbons are being generated within the deeper parts of the drilled section in the Guaymas Basin, close to sills throughout the Gulf, and on the Guaymas margin (Site 479). Migration of these light hydrocarbons is most apparent near sills.

INTRODUCTION

The unravelling of major geological problems can be greatly helped by studying the organic matter in deep sea sediments. Organic matter preserves a record of sedimentary transport processes, of surface water productivity, of the degree of oxygenation of bottom waters, and of the magnitude of subsurface diagenetic processes. Moreover, it is far more sensitive than are other geological thermometers to thermal effects.

Our approach to Leg 64 has been to use organic geochemistry to address several major questions of geological importance:

1) Where did the organic matter come from—terrigenous or marine sources?

2) How was it deposited—as pelagic sediment or by turbidites, for instance?

3) How was it preserved—were bottom waters oxidizing or reducing?

4) What paleoenvironmental changes can be detected from the interplay of source, deposition, and preservation?

5) How much has the organic matter been altered by the high heat flow of the region and by the intrusion of sills?

6) What are the products of this catagenesis, and to what extent have they migrated through the section?

We have tackled these fundamental questions by reviewing the organic geochemical reports published in this volume, and by synthesizing the data and interpretations given in those reports. Our review is in three parts, one for each of the major geological environments drilled on this DSDP leg:

1) Baja California (Cabo San Lucas): typical passive margin, with some sills (Sites 474, 475, and 476).

2) Guaymas Basin: spreading center with high heat flow, sills, and turbidites (Sites 477, 478, and 481).

3) Guaymas continental slope: oxygen-minimum zone on continental slope (Sites 479 and 480). At Site 480 the hydraulic piston corer provided undisturbed laminated sediments (Schrader et al., 1980).

Sedimentation rates were calculated from radiocarbon ages (Spiker and Simoneit, this volume, Pt. 2). There was disagreement between these ages and those determined biostratigraphically at Sites 478 and 481, and radiometrically determined ages are younger than biostratigraphic ages at Sites 474, 476, 477, and 479, suggesting faster rates of sedimentation.

There are three limitations to our interpretation of the available geochemical data. First, there is a bias in the fact that most analyses are from cores that were frozen specifically for organic geochemical work. These frozen cores may not be fully representative of the sections from which they were taken. Second, the various investigators received samples from different depths within each frozen core. Differences in lithology between these subsamples may lead to differences in the results obtained by the different investigators. Third, each investigator may have chosen to analyze a different set of the frozen cores. In our synthesis we have tried to minimize the effects of sampling bias.

BAJA CALIFORNIA–CABO SAN LUCAS SITES

Sites 474–476 were drilled along a transect of the Baja California continental margin. Site 474 is located on oceanic crust overlain by 500 meters of diatomaceous mud and turbidites at a water depth of 3023 meters. Sites 475 and 476 were drilled on the lower continental slope at 2631 and 2400 meters water depths, respectively. Both sites penetrated primarily hemipelagic sediments and a minor carbonaceous mudstone overlying a conglomerate. The geological structure of this margin is dominated by horst and graben tectonics and by rotational listric faulting. Sites 475 and 476 lie on the two lowest and most deeply subsided blocks (Curray et al., this volume, Pt. 2).

Important questions that concerned us were the nature of the organic matter in this hemipelagic environment and the effect of turbidites on the distribution of terrigenous organic matter in an open ocean setting.

Site 474

Total organic carbon (TOC) is generally high throughout the sediment column, although actual values range from 0.2 to 3.1%, probably in response to alterations between hemipelagic and turbiditic sedimentation. At 20 meters sub-bottom there is a TOC maximum (3.1%); a shallow TOC maximum like this is common to all of the deep-water sites from Leg 64. Levels of TOC decrease over the top 150 meters of this hole to 1.5–2.0%— a level that persists for most of the deeper section. Low TOC levels occur near intrusive sills deep in the section and close to the basalts that form the basement at this site, probably in response to thermal degradation of organic matter.

Depositional Environment

Different investigators come to different conclusions about the oxic versus anoxic nature of the depositional environment at this site. Pristane/phytane ratios greater than 1.0 suggest that the depositional environment was oxidizing (Galimov et al., this volume, Pt. 2; Simoneit, this volume, Pt. 2), as do the absence of perylene and free sulfur (Simoneit, this volume, Pt. 2). In contrast, Rullkötter et al. (this volume, Pt. 2) found evidence that the depositional environment was reducing—their pristane/phytane ratios were less than 1.0, they found perylene to be a major component of the aromatic hydro-

carbons, and they detected a variety of alkylated thiophenes, which are probably formed under reducing conditions in the presence of free sulfur. Low oxygen concentrations in the sediments at this site are suggested by the high methane concentrations measured here. The methane values are attributed to methanogenic bacterial activity that would be enhanced at low oxygen concentrations (Whelan and Hunt, this volume, Pt. 2).

Although we cannot resolve these discrepancies, we can point out three possible ways in which they may have arisen. First, indicators of reducing versus oxidizing conditions may pertain not to the bottom waters but to conditions at or immediately below the sediment/water interface. The cores are not laminated, suggesting that bottom waters were always oxidizing to some degree. In the subsurface, conditions may have fluctuated, with time, from oxidizing to reducing. Second, different investigators may have received different parts of turbidite units, or pelagic rather than turbiditic sediments. Third, there may have been important differences between the various extraction and separation procedures used in the laboratories prior to the analyses.

Source of Organic Matter

There is also a disagreement about the nature of the organic matter at this location (Table 1). Elemental analyses of kerogens, and $\delta^{13}C$ values averaging $-21.3‰$, suggest that most of the organic matter is marine (Simoneit, this volume, Pt. 2). Isotopic analyses by Galimov et al. (this volume, Pt. 2) support this interpretation. Gilbert and Summerhayes (this volume, Pt. 2) considered the oozes and turbidites separately, and found that although both lithologies were dominated by amorphous organic matter, there was more subordinate terrestrial organic matter in turbidites than in oozes; they inferred that much of the amorphous organic matter was marine-derived. This agrees with optical studies by Rueda et al. (this volume, Pt. 2). From Rock-Eval pyrolysis data, Deroo et al. (this volume, Pt. 2) determined that most of their Site 474 samples contained type II (probably marine) organic matter. They found type III (probably terrigenous) organic matter only near the sill at the bottom of this hole. In contrast, Rullkötter et al. (this volume, Pt. 2) found that type III (probably terrigenous) organic matter predominated in their samples. Terrigeous material is, indeed, locally abundant—Gilbert and Summerhayes report up to 25% recognizable terrigenous organic remains in one of the turbidite samples that they analyzed. Thus, although most of the organic matter may be marine, it is usually mixed with some land-derived material that may be locally dominant. The presence of recycled organic matter does not explain why radiocarbon ages for organic matter are younger than the paleontological ages of the host sediments throughout the sites at the mouth of the Gulf (Spiker and Simoneit, this volume, Pt. 2). Most of the organic matter near the sediment/basement contact appears to be land-derived, on the basis of Rock-Eval data (Deroo et al., this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2). This fits well with the interpretation of

Table 1. Sources of organic matter in unaltered sediments from the Gulf of California.

Site	Interstitial Gas	Lipids[a]	Kerogen[a]	Reference (this volume, Pt. 2)
Cabo San Lucas				
Site 474		*Marine*/terrigenous	Marine	Simoneit
		Marine	Marine	Galimov et al.
		Terrigenous/marine	Terrigenous	Rullkotter et al.
	Biogenic/thermogenic			Galimov and Simoneit
	Biogenic			Whelan and Hunt
	Thermogenic (near sill)		*Marine*/terrigenous	Gilbert and Summerhayes; Deroo et al.
Site 476		Marine	Marine	Simoneit
			Marine	Deroo et al.; Kendrick
Guaymas Basin				
Site 477		Terrigenous	Marine	Galimov et al.
		Terrigenous/*marine*	Marine	Simoneit and Philp
			Marine	Gilbert and Summerhayes
Site 478		*Terrigenous*/marine	Marine	Galimov et al.
		Terrigenous/*marine*	Marine	Simoneit and Philp
		Terrigenous		Rullkotter et al.
			Marine/terrigenous	Deroo et al.; Kendrick; Gilbert and Summerhayes
	Biogenic			Galimov and Simoneit
Site 481		*Terrigenous*/marine	Marine	Galimov et al.; Simoneit and Philp
		Terrigenous	Terrigenous	Rullkotter et al.
		Marine		Thomson et al.
			Marine/terrigenous	Deroo et al., Gilbert and Summerhayes
	Biogenic/thermogenic			Galimov and Simoneit; Schoell; Whelan and Hunt
Guaymas Slope				
Site 479		*Marine*/terrigenous	*Marine*/terrigenous	Galimov et al.; Simoneit and Philp; Simoneit
		Terrigenous/marine	*Marine*/terrigenous	Rullkotter et al.
			Marine/terrigenous	Gilbert and Summerhayes; Kendrick; Deroo et al.; Peters and Simoneit
	Biogenic/thermogenic			Simoneit and Galimov; Whelan and Hunt; Simoneit; site chapter
Site 480		*Marine*/terrigenous		Simoneit
			Marine/terrigenous	Peters and Simoneit
	Biogenic			Site chapter; Simoneit

[a] The dominant source is italicized.

an active turbidite basin already in existence at the time interval where this hole terminated (Curray et al., this volume, Pt. 2).

A similar data conflict is apparent in the analyses of the lipid fraction, and probably stems from the same problem—that is, some investigators analyzed more terrigenous organic facies than others. Sterols, *n*-alkanes, and *n*-alkanoic acids primarily from marine sources dominate samples analyzed by Simoneit (this volume, Pt. 2), although land plant waxes were important in one of his shallow samples. Hydrocarbon data from Galimov et al. (this volume, Pt. 2) confirm a marine origin for the lipids in their samples. Rullkötter et al. (this volume, Pt. 2) find larger concentrations of terrigenous lipids at this site. From the predominance of long-chain *n*-alkanes, and the high Carbon Preference Index (CPI), they deduce that land-derived materials dominate the lipid fraction. All of the hydrocarbon patterns of Site 474 samples show mixtures of terrigenous and marine lipids. It is likely that in a turbiditic sequence such as this one, the proportions of these components change according to the intensity of turbidite development.

Alteration of Organic Matter

Most of the section at Site 474 shows only mild thermal alteration. The CPI of *n*-alkanes does not change with depth, and remains fairly high, averaging about 2

(Galimov et al., this volume, Pt. 2). Pyrolysis shows that the kerogens are immature (Deroo et al., this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2). This is confirmed by the low vitrinite reflectances and thermal alteration indexes of most samples (Rullkötter et al., this volume, Pt. 2; Gilbert and Summerhayes, this volume, Pt. 2). Light hydrocarbons indicate a biogenic rather than a thermogenic origin (Whelan and Hunt, this volume, Pt. 2), a conclusion supported by methane $\delta^{13}C$ values near $-75‰$ in shallow sediments (Galimov and Simoneit, this volume, Pt. 2). Mild diagenetic alteration is indicated by the presence of Ni-porphyrins (Galimov et al., this volume, Pt. 2; Louda and Baker, this volume, Pt. 2).

Close to dolerite sills at the bottom of this hole the organic matter has been thermally altered. TOC levels decrease, the ratio of hydrocarbons/TOC increases (Galimov et al., this volume, Pt. 2), the $\delta^{13}C$ of methane drops to about $-50‰$ (Galimov and Simoneit, this volume, Pt. 2), and there are lower ratios of $C_1/(C_2 + C_3)$ and of C_1/C_2 (Gilbert and Summerhayes, this volume, Pt. 2; site chapter, this volume, Pt. 1), indicating thermal generation of light hydrocarbons. Moderate heating between the deep sills has produced some metalloporphyrins (Louda and Baker, this volume, Pt. 2). In these sediments a thermal alteration index of 2 indicates the threshold of extensive generation of hydrocarbons (Gilbert and Summerhayes, this volume, Pt. 2).

Sites 475 and 476

Levels of TOC here range from 0.4 to 3.4%, with considerable local variability between closely spaced samples (Simoneit and Bode, this volume, Pt. 2). There is a subsurface TOC maximum at 10 meters depth at Site 475, and at 20 meters depth at Site 476. As discussed later, this maximum may record a basinwide event affecting organic matter sedimentation in the Gulf. Levels of TOC generally decrease with depth. An anomalously high TOC level (7.1%: Simoneit and Bode, this volume, Pt. 2) characterizes the glauconitic, phosphatic, carbonaceous mudstone of Unit V, which is a shallow-water sediment overlying subaerial conglomerates of probable late Miocene age (Curray et al., this volume, Pt. 2).

Depositional Environment

The depositional environment seems to have been predominantly oxidizing. Pristane/phytane ratios average 1.4, and there is no perylene or free sulfur (Simoneit, this volume, Pt. 2). There is somewhat less methane at these sites than at Site 474, again suggesting a more oxidizing environment (Whelan and Hunt, this volume, Pt. 2).

Source of Organic Matter

The organic matter is mostly marine. According to Rock-Eval data (Deroo et al., this volume, Pt. 2; Kendrick, this volume, Pt. 2), the kerogen is mostly marine type II. It is aliphatic and has $\delta^{13}C$ values of $-20.6‰$, indicating a marine source (Simoneit, this volume, Pt. 2). In the lipid fraction a predominantly marine origin is indicated by n-alkane and n-alkanoic acid distributions and by the types of steroid and triterpenoid compounds (Simoneit, this volume, Pt. 2). Optical examination of kerogen shows that most is amorphous, with lesser, more or less equal amounts of algal and higher plant remains. From the abundant bitumen extract, Gilbert and Summerhayes (this volume, Pt. 2) suggest that much of this amorphous material is marine-derived. Rueda et al. (this volume, Pt. 2) agree that most of the kerogen is marine.

Alteration of Organic Matter

Because the heat flow is low in this area and the sediments have not been buried to any great depths, there are no signs of thermal alteration at these two sites. The kerogen is immature (Deroo et al., this volume, Pt. 2; Kendrick, this volume, Pt. 2; Gilbert and Summerhayes, this volume, Pt. 2), and there were no gas shows (site chapter, this volume, Pt. 1; Simoneit, this volume, Pt. 2; Galimov and Simoneit, this volume, Pt. 2).

GUAYMAS BASIN

The Guaymas Basin is an actively spreading ocean basin that includes two well-defined rifts separated by a 20-km-long transform fault (Curray et al., 1979). The high sedimentation rates keep the basin floor covered while new ocean crust forms. Site 477 is located in the southern rift, Site 481 in the northern one, and Site 478 is adjacent to the transform fault zone on slightly older crust just north of the southern rift (Curray et al., 1979). The sediments are diatomaceous oozes and turbidites, intruded by dolerite sills. Site 477 had the highest heat flow (20 HFU), and Site 481 had slightly higher heat flow (about 4 HFU) than Site 478 (site chapter, this volume, Pt. 1).

The major questions that we address here are the sources of the organic matter and the extent to which it has been affected by thermal stress from both the high heat flow and the intrusion of sills.

Source of Organic Matter

The sources of the organic matter in the sediments of the Guaymas Basin have been interpreted to be both terrigenous and marine (Table 1). The terrigenous components of the lipids appear to be more dominant at Site 481, which is closer to the mainland and the outflow of the Yaqui River, than at the other two sites. Site 477, farthest from the river, has the least terrigenous character (Simoneit and Philp, this volume, Pt. 2). The same trend is seen in the kerogens.

At Site 477, the n-alkanes of unaltered samples exhibit a dominance of the odd-carbon-number homologs larger than C_{27}, indicative of terrigenous sources, with significant components lower than C_{21} that are of marine origin (Galimov et al., this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2). However, the stable carbon isotope compositions of the total lipid extract (which is dominated by polar components) fall within the range typical of marine detritus ($\delta^{13}C$ about $-22‰$; Galimov et al., this volume, Pt. 2). In the shallow sediments molecular markers such as steroids and triterpenoids have distributions and stereochemistries indicative of recent marine biosynthesis (Simoneit and Philp, this volume, Pt. 2).

The lipids of the shallower samples from Site 478 are derived from marine and terrigenous sources in approximately equal proportions (Table 1; Simoneit and Philp, this volume, Pt. 2; Galimov et al., this volume, Pt. 2), or are composed of dominantly terrigenous material (Rullkötter et al., this volume, Pt. 2). These interpretations are based primarily on the homolog distributions in hydrocarbon fractions, or, in some cases, in fatty acid fractions. The $\delta^{13}C$ data for the total lipids indicate a marine origin (Galimov et al., this volume, Pt. 2). As at Site 477, trace molecular markers in the lipids of shallow samples have distributions and stereochemistries indicating a recent marine microbial origin (Simoneit and Philp, this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2).

At Site 481, the lipids in the shallow samples are dominated by terrigenous components (Table 1; Galimov et al., this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2), except for one sample that has a largely marine origin (Thomson et al., this volume, Pt. 2). This terrigenous influence is probably due to the proximity of continental sources and the abundance of turbidites at this site. These interpretations are based primarily on the homolog distributions and the nature of the minor molecular markers in the hydrocarbon fractions, and,

for some samples, also the fatty acid fractions. Again, the $\delta^{13}C$ data for the total lipid fractions indicate an overall marine source (Galimov et al., this volume, Pt. 2), which is probably due to the large amount of polar, marine detritus (e.g., carbohydrates and proteinaceous material) present in extracts from such recent sediments.

The kerogen fraction is dominantly marine in some samples, terrigenous in others, or a more equal mixture of marine and terrigenous materials (Gilbert and Summerhayes, this volume, Pt. 2). The main component is usually amorphous. Pyrolysis confirms this wide variation, some samples being classified as type II (probably marine), others as type III (probably terrigenous), and others as mixtures of types II and III (Deroo et al., this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2; Kendrick, this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2). The wide variations in organic facies result from the interplay of pelagic and turbidity-current deposition. As for the lipid fractions, there seems to be an increase in terrigenous influence from Site 477 through Site 478 to Site 481.

There is a wide range in TOC levels, from about 0.3 to more than 3% (Simoneit and Bode, this volume, Pt. 2). As at the Cabo San Lucas sites, there is a subsurface TOC maximum which reaches 3.3% (12 m sub-bottom) at Site 477, 3.6% (about 10 m sub-bottom) at Site 478, and 4.3% (about 13 m sub-bottom) at Site 481. The considerable variation in TOC with depth, especially at Site 481, probably represents the interplay between pelagic sedimentation and turbidite deposition. A deeply buried TOC high at about 300 meters at Site 478 occurs in laminated diatomaceous sediment and may represent a period when bottom waters were anoxic.

Depositional Environment

Various indicators in the lipid fraction, for example pristane/phytane ratios of less than 1.0, and the presence of perylene, pigments, and sulfur, suggest that depositional conditions were reducing (Didyk et al., 1978; Galimov et al., this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2). Perylene has been invoked as a terrigenous indicator (Rullkötter et al., this volume, Pt. 2). This may be misleading, as it is a common constituent of DSDP Leg 63 sediments (Louda and Baker, 1981; Rullkötter et al., 1981; Simoneit and Mazurek, 1981) and is generally ubiquitous in Recent sediments (Wakeham et al., 1979; LaFlamme and Hites, 1978; Hites et al., 1977, 1980). The presence of perylene in a sediment may indicate deposition under anoxic conditions, where it may form from precursors of either terrigenous or marine origin. Since these sediments are not laminated and there is a tendency toward an exponential decline in TOC beneath the sediment/water interface, it seems unlikely that the bottom waters are themselves anoxic. Calvert (1964) reports that bottom water in the Guaymas Basin contains up to about 1.0 ml/l O_2. These different lines of evidence suggest that the anoxic conditions that have influenced the lipid fraction prevailed at or beneath the sediment/water interface periodically in the Holocene and did not extend into the overlying bottom water.

Alteration of Organic Matter

Interstitial gases and fixed gases (H_2S and CO_2) appear to be of biogenic origin in the shallow section. This is true of all three Guaymas Basin sites and nearby gravity core station 30G (site chapter, this volume, Pt. 1; Whelan and Hunt, this volume, Pt. 2; Simoneit, this volume, Pt. 2; Simoneit and Galimov, this volume, Pt. 2; Gilbert and Summerhayes, this volume, Pt. 2; Simoneit et al., 1979).

Various lipids (e.g., chlorins, steroid residues) undergo diagenetic alteration in the shallow sequences. At greater depths they experience more rapid diagenesis under the influence of thermal stress (Galimov et al., this volume, Pt. 2; Louda and Baker, this volume, Pt. 2; Thomson et al., this volume, Pt. 2). The total organic matter tends to decrease exponentially with depth (see plots of TOC versus depth in the site chapters, this volume, Pt. 1). The exponential change (which is locally obscured by the influence of turbidites) could be attributed to diagenesis involving microbial degradation of labile organic matter. Methanogenic bacteria are present in the very shallow sediments (Oremland et al., this volume, Pt. 2), but they comprise only a part of the total microbial population. The exponential decrease in TOC occurs below the subsurface TOC maximum, which (as at the Cabo San Lucas sites) may represent some paleoceanographic event, perhaps heightened productivity at the start of the Holocene transgression 10 ky. ago. A pulse of foraminifers and coccolithophores was observed in Site 480; it corresponds to an approximate 10–11 ky. switchover (site chapter, this volume, Pt. 1).

The general effects of the thermal stress imposed on the organic matter by the various sill intrusions and high heat flow are greatest at Site 477, intermediate at Site 481, and lowest at Site 478. Near sills, samples contain gasoline-range hydrocarbons; the abundance of these components decreases exponentially close to the sills, where thermal stress has been highest (Whelan and Hunt, this volume, Pt. 2; site chapters, this volume, Pt. 1; Simoneit, this volume, Pt. 2). At Site 477 the gas contained only a limited range of hydrocarbons and large amounts of CO_2 and H_2S (site chapter, this volume, Pt. 1; Simoneit, this volume, Pt. 2). Methane, ethane, benzene, and toluene dominate the light hydrocarbons, indicating high-temperature thermogenesis (Whelan and Hunt, this volume, Pt. 2). High thermal stress is confirmed by the $\delta^{13}C$ values of methane (Galimov and Simoneit, this volume, Pt. 2). At Site 478 there is no sign in the gas data of major thermal stress from the upper sill intrusions, and there was no thermogenic H_2S at depth (site chapter, this volume, Pt. 1; Simoneit, this volume, Pt. 2). The $\delta^{13}C$ data for methane suggest that thermogenic methane increases with depth (Galimov and Simoneit, this volume, Pt. 2). The minimal influence of the shallow sill intrusion is confirmed by the gasoline-range hydrocarbon data (Whelan and Hunt, this volume, Pt. 2), in that there were no unusual concentrations of ethane or the aromatic hydrocarbons. At Site 481, the gas data are more complicated and do show a strong thermogenic influence. The C_3–C_5 hydrocarbon distributions

above the upper sill complex exhibit a triple maximum that is less well developed for methane and ethane (Simoneit, this volume, Pt. 2; Einsele et al., 1980; Galimov and Simoneit, this volume, Pt. 2). This may indicate a multiple-pulsed sill emplacement that caused distinct diffusion maxima. The $\delta^{13}C$ data for methane suggest an admixture of thermogenic and biogenic gas, with the thermogenic component increasing with depth (Galimov and Simoneit, this volume, Pt. 2). Thermogenic H_2S was not detected at this site. The multiple maximum for the C_3-C_5 hydrocarbons was not detected in the gasoline-range hydrocarbons desorbed from frozen core samples, but there was a general increase in the C_5-C_8 hydrocarbons above the sill complex (Whelan and Hunt, this volume, Pt. 2). From the relatively small amounts of aromatic compounds it seems that there was less thermal stress at this site than at Site 477.

The lipids (bitumen) have been significantly altered by thermal stress. This effect is most dramatic at Site 477, where the CPI approaches 1.0 at depth (Simoneit and Philp, this volume, Pt. 2). Moreover, lipid/TOC ratios increase toward the sill, then decrease with increasing depth, indicating severe alteration (Galimov et al., this volume, Pt. 2). With increasing thermal stress the chlorins are first converted to metalloporphyrins and then destroyed at very high temperatures (Galimov et al., this volume, Pt. 2; Louda and Baker, this volume, Pt. 2). In samples located close to the sill, at sediment depths greater than 130 meters, the hydrocarbon distributions resemble those of petroleum, but amounts of n-alkanes larger than C_{27} are smaller than in samples from shallower depths, and the CPI is about 1.0 (Simoneit and Philp, this volume, Pt. 2). These and equivalent samples from Site 481 contain major amounts of terminal olefins, which are stable for only short periods and are generated by pyrolytic processes (Simoneit and Philp, this volume, Pt. 2). These compounds suggest that the thermal stress occurred very recently and at significantly high temperatures. Laboratory simulation experiments suggest that olefin generation begins at about 250°C (Simoneit et al., unpublished data), and the operating temperatures for catalytic petroleum cracking systems are 450–600°C (e.g., Shreve, 1956). In addition to this evidence, the molecular marker compounds have a mature appearance. Their distributions (e.g., steroids and triterpenoids) and stereochemistries show the effects of thermal stress, and these compounds are almost completely destroyed or otherwise removed in the deepest samples from Site 477. These data are consistent with the interpretations of a deep-seated heat source below the bottom of the hole causing severe thermal alteration in the deep samples and of limited stress from the now-cooled upper sill in the sediments near it.

The lipids from samples from Site 478 have experienced a milder thermal history. Their n-alkane patterns are essentially unaltered, except very close to sill intrusions (Galimov et al., this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2). The pattern of total hydrocarbon yields versus depth suggests that the onset of maturation has been reached between the upper sills (Galimov et al., this vol-

ume, Pt. 2) and is enhanced near sill contacts (Simoneit and Philp, this volume, Pt. 2). Molecular marker compounds were only in samples well away from sills and appear to be immature (Rullkötter et al., this volume, Pt. 2).

At Site 481, the lipids have been exposed to thermal stress greater than at Site 478 but less than at Site 477. The n-alkanes have an essentially unaltered distribution, except close to sills, where thermal products become more dominant (Rullkötter et al., this volume, Pt. 2; Galimov et al.,, this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2). The total hydrocarbon content increases relative to TOC close to sills (Galimov et al., this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2). The same is true for the fatty acids, which have primarily unaltered biogenic character (Simoneit and Philp, this volume, Pt. 2). Steroidal and triterpenoidal residues do show the effects of maturation from thermal stress near sills (Simoneit and Philp, this volume, Pt. 2). As in the highly altered samples from Site 477, the most thermally stressed samples here contain terminal olefins and indicate a high degree of thermal stress from sill intrusion (Simoneit and Philp, this volume, Pt. 2).

The kerogen data confirm that thermal alteration is highest at Site 477 (Gilbert and Summerhayes, this volume, Pt. 2; Jenden et al., this volume, Pt. 2). Although the section above the main sill (at 58 m) is immature, that below the sill has a thermal alteration index of 2+, equivalent to a vitrinite reflectance value of 0.7–0.9% R_0, and is probably in the oil window (Dow, 1977). As the sill is approached, maturation increases to a thermal alteration index of 3 (R_0 equivalent is about 1.2%, near the bottom of the oil window according to Dow, 1977); this degree of maturation occurs 15 meters below the sill and implies that the sediments nearer to the sill have been baked and may have lost their potential to generate liquid hydrocarbons (Gilbert and Summerhayes, this volume, Pt. 2).

Curie Point pyrolysis-GC (Cupy-GC) data for kerogens of samples taken near the sill show the effects of this thermal stress (Simoneit and Philp, this volume, Pt. 2). The pyrolysis yields drop dramatically, and the products change from higher to lower molecular weight. The organic matter at depth was described by Rueda et al. (this volume, Pt. 2) as coaly and highly altered. The atomic N/C, carbon isotope composition, and electron spin resonance (ESR) spin density of the kerogens all demonstrate the effects of thermal stress near the sill contact (Jenden et al., this volume, Pt. 2). The N/C decreases to 0.025 near the sill and the $\delta^{13}C$ values decrease by 1 to 1.5‰. The ESR spin density exhibits an intense maximum at lower H/C values next to the sill.

At Site 478, both the vitrinite reflectance (R_0) (Rullkötter et al., this volume, Pt. 2) and the thermal alteration indices (Gilbert and Summerhayes, this volume, Pt. 2) show that the section is immature. A downhole increase in R_0 values to 0.37 at about 250 meters (Rullkötter et al., this volume, Pt. 2) suggests that this is a hot area (heat flow is 3.65 HFU; site chapter, this volume, Pt. 1). The top of the oil window may be as shallow as 450–550 meters. As the sill at 340 meters is ap-

proached, the thermal alteration index rises to $2+$ (R_0 approx. 0.7–0.9%), probably in response to the intrusion (Gilbert and Summerhayes, this volume, Pt. 2). There is, however, a conflict in the available data. Kendrick (this volume, Pt. 2) reports vitrinite reflectance values that are immature in Section 478-35-5 (about 305 m sub-bottom), where Gilbert and Summerhayes (this volume, Pt. 2) find a thermal alteration index of $2+$. It is possible that the vitrinite data are in error, because this deep sample has the same R_0 (0.31) as Kendrick's samples from much shallower in the core, and it is much less mature than a sample from about 240 meters sub-bottom analyzed by Rullkötter et al. (this volume, Pt. 2), which had an R_0 value of 0.37. We believe that the overall sediment sequence is immature, except near sills.

The Cupy–GC data for kerogen samples taken at depth and on either side of a sill intrusion clearly show the effects of thermal stress. Amounts of pyrolysate decrease, and the molecular distributions are different, compared with unaltered samples (Simoneit and Philp, this volume, Pt. 2). The kerogens from Site 478 near the sill reflect the thermal stress least of the three Guaymas Basin sites. The N/C near the sills remains as high as 0.05 and the $\delta^{13}C$ increases slightly (Jenden et al., this volume, Pt. 2). The ESR spin density shows a lesser maximum at higher H/C values than for Sites 477 and 481. Microscopic examination of organic matter by Rueda et al. (this volume, Pt. 2) confirms that the kerogen has been altered near sills.

At Site 481, which is also a "hot" hole (with 4 HFU; site chapter, this volume, Pt. 1), the vitrinite reflectance data (Rullkotter et al., this volume, Pt. 2) and thermal alteration indices (Gilbert and Summerhayes, this volume, Pt. 2) suggest that the section is immature down to 280 meters. As the sills at 160 meters and at 330 meters are approached, there is a slight increase in the thermal alteration index (Gilbert and Summerhayes, this volume, Pt. 2).

The Cupy–GC data for kerogens from the upper sill complex reflect the thermal stress in showing a decrease in pyrolysis products with increasing proximity to sills (Simoneit and Philp, this volume, Pt. 2). However, one sample from close to the sill did have a significant amount of pyrolysate; this may be a "bituminized kerogen" of the type described from Site 368 (Peters et al., 1978). The Cupy–GC trace for a sample from 233 meters sub-bottom showed an essentially unaltered pattern (Simoneit and Philp, this volume, Pt. 2), confirming the results of vitrinite and thermal alteration index analyses. Again, the N/C, $\delta^{13}C$, and ESR spin density of the kerogens demonstrate the effects of thermal stress near the sill contacts, as was described for Site 477 (Jenden et al., this volume, Pt. 2).

Migration

Migration of gases and of certain components of the lipid fraction has occurred in response to the development of high thermal gradients in the Guaymas Basin. Migration of gas into shallow sediments was recognized in a gravity core (30G) near Site 481 prior to Leg 64 (Simoneit et al., 1979). Simple fluorescence measurements show that lipids have migrated away from sill

intrusions at Sites 478 and 481 (Simoneit, this volume, Pt. 2), and this migration has been confirmed by lipid analysis (Galimov et al., this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2). The approximate distances of upward and downward migration from intrusions in these unconsolidated sediments are about the same as observed in lithified Cretaceous black shales from Site 368, which were intruded by diorite in the Miocene (Simoneit et al., 1978, 1981). Preliminary data show that lipid products from thermogenic processes at depth are brought to the seabed by hydrothermal circulation. The less volatile and less soluble compounds condense at the sea floor as oil in moundlike mineral deposits over hydrothermal vents (Simoneit, unpublished data).

The residual carbon remaining in the sediment after liquid hydrocarbon generation was detected at Sites 477 and 478 (site chapter, this volume, Pt. 1; Simoneit, this volume, Pt. 2). It consists of fine-grained carbon with adsorbed interstitial gas and traces of adsorbed bitumen residues (Simoneit, this volume, Pt. 2; Simoneit and Philp, this volume, Pt. 2).

Gases and Light Gasolines

Thermogenic gas was identified deep in Holes 477 and 481 (Gilbert and Summerhayes, this volume, Pt. 2). The thermogenic gas contribution increases downhole toward the sill at Site 477, and is very high below the sill (methane $\delta^{13}C$ values drop to -45 or -40‰; Simoneit and Galimov, this volume, Pt. 2). The same is observed in the analyses of light hydrocarbons, which increase toward the sill and are most abundant beneath it (Whelan and Hunt, this volume, Pt. 2). The C/N ratio also increases strongly in the mature section beneath the sill (Simoneit, this volume, Pt. 2; Simoneit and Bode, this volume, Pt. 2). These various data suggest that gas, but not necessarily light-gasoline-range components, may be migrating up into the deeper section.

At Site 478, ethane shows a slight increase with depth toward the shallow sill at 200–250 meters, then a decrease, followed by an increase toward the deeper sill at 350 meters (Galimov and Simoneit, this volume, Pt. 2). The immaturity of the sedimentary section is confirmed by the downhole change in the $\delta^{13}C$ values of methane, from -80‰ (biogenic) at surface to -60‰ (slight thermogenic input) at depth (Galimov and Simoneit, this volume, Pt. 2). Gilbert and Summerhayes (this volume, Pt. 2) also interpret the gas to be biogenic rather than thermogenic. Whelan and Hunt (this volume, Pt. 2) confirm that thermal stress has had little influence on the light hydrocarbons at this site.

At Site 481, Galimov and Simoneit (this volume, Pt. 2) find that, in response to thermal stress, the C_2/C_1 ratio increases and the $\delta^{13}C$ value of methane decreases as the sills are approached (see also Gilbert and Summerhayes, this volume, Pt. 2; Schoell, this volume, Pt. 2). Between the sills there is evidence for only mild thermal alteration, the $\delta^{13}C$ of methane being about -60‰ (Schoell, this volume, Pt. 2; Galimov and Simoneit, this volume, Pt. 2). Mild thermal stress is indicated also by the light-gas and gasoline-range data (Whelan and Hunt, this volume, Pt. 2).

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GUAYMAS SLOPE

Sites 479 and 480

Sites 479 and 480 are situated on the Mexican continental slope almost due north of the Guaymas Basin, and within the present oxygen-minimum zone. Laminated diatomaceous sediments are deposited throughout the northern Gulf of California, wherever the oxygen-minimum zone contains less than 0.2 ml/l O_2 (Calvert, 1964). Alternations of laminae rich in diatoms or in terrigenous clay apparently reflect seasonal variations in productivity or runoff, or some combination of these (Calvert, 1964; Schrader et al., 1980). Lamination, then, is a response to both source variations (marine versus terrigenous input) and preservation (a reducing or anoxic water column prevents significant bioturbation and favors preservation of organic matter as well as laminations). Sites 479 and 480 were occupied in the hope that detailed sampling of these laminated sequences would provide information about past climatic changes and cycles, changes in circulation patterns, in the depth or intensity of development of the oxygen minimum zone, in sea level, in diagenesis, and in the floral and faunal assemblage of surface and bottom waters.

Unfortunately, drilling disturbed the sediments at Site 479, making it difficult to ascertain whether the first 200 meters of diatomaceous ooze were laminated or not. At Site 480, which is about 6 km from Site 479, Leg 64 scientists obtained a 150-meter-long hydraulic piston core containing an undisturbed, laminated, sediment column thought to be equivalent in age to the upper section from Site 479. Laminated zones alternate with homogeneous zones that lack laminations and are bioturbated, at least in places.

Geochemical techniques, especially pyrolysis data, confirm that the sediments at Site 480 are more or less identical to those at Site 479 (see Fig. 1; based on data from Peters and Simoneit, this volume, Pt. 2). Alternations of laminated with unlaminated zones are probably responses to changes in the degree of oxygenation of bottom waters (see later in this chapter for more discussion of paleoenvironmental changes). The deeper sections at Site 479 are more indurated than the shallow sections and thus have been less disturbed by drilling. Laminated sediments continue to the bottom of the hole.

Source of Organic Matter

Marine-derived organic matter dominates the section at Sites 479 (Units I and II) and 480 (Table 1). Much of this material is present as liptinitic amorphous organic matter with some as algal remains (Rullkötter et al., this volume, Pt. 2; Gilbert and Summerhayes, this volume, Pt. 2; Kendrick, this volume, Pt. 2; Deroo et al., this volume, Pt. 2). There are substantial minor terrigenous components in some samples, consisting of admixed structured terrestrial materials and coaly material or inertinite (Table 1). The mixed nature of the sediment is confirmed by isotopic analyses, lipid analyses, and pyrolysis. For instance, the $\delta^{13}C$ carbon isotope values of samples from Site 479, Units I and II, fall between

-20.5 and $-23.4\%_0$, indicating that they are planktonic to mixed planktonic–higher land plant in character (Galimov et al., this volume, Pt. 2). Lipids in one sample (Section 497-29-5) analyzed by Simoneit and Philp (this volume, Pt. 2) have mixed marine terrigenous character, although a Cupy–GC pyrolysate of a kerogen from that same sample resembles one from unaltered pure diatom ooze from Walvis Bay. Long-chain terrigenous plant waxes dominate the n-alkane distribution of the lipid extracts, probably because the large marine component of the sediment contains few n-alkanes. Rock-Eval pyrolysis confirms that the organic matter mostly consists of type II (marine) organic matter, or of mixtures of types II (marine) and III (terrigenous) organic matter, with an average hydrogen index of about 350 mg HC/g C_{org} (Deroo et al., this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2). This interpretation of the pyrolysis data is confirmed by elemental analyses of kerogen extracted from the samples. H/C ratios average 1.13 (Deroo et al., this volume, Pt. 2), 1.12 (Peters and Simoneit, this volume, Pt. 2), and 1.3 (Kendrick, this volume, Pt. 2), in Units I and II at Site 479, and average 1.15 at Site 480 (Peters and Simoneit, this volume, Pt. 2). These ratios confirm that the organic matter is most probably a mixture of types II and III.

Peters and Simoneit (this volume, Pt. 2) obtained pyrolysis data that differ considerably from those of the other analysts; the reasons for this discrepancy are discussed below.

Unit III, at the base of Site 479, has a different organic facies: most of its organic matter is land-derived. Rock-Eval pyrolysis data show that samples from this unit (e.g., Section 479-47-4) consist almost entirely of type III (probably terrigenous) organic matter (Rullkötter et al., this volume, Pt. 2; Deroo et al., this volume, Pt. 2; Peters and Simoneit, this volume, Pt. 2). The H/C ratios of kerogens of this unit are lower than those in Units I and II, suggesting a greater terrigenous influence (Deroo et al. found ratios of 1.09; Kendrick found ratios of 1.19). Isotopic data confirm the increasingly terrigenous character of this unit, which has a $\delta^{13}C$ value of $-23.4\%_0$ for the organic matter in Section 479-43-1 (Galimov et al., this volume, Pt. 2). The terrigenous signal could reflect increasing terrigenous influx or diagenetic removal of the labile marine fraction but may also indicate that productivity was low in surface waters at this time.

Preservation of Organic Matter

The TOC seems to be controlled by the preservation of marine organic matter (Fig. 2). Samples having higher content of marine (or marine-derived amorphous) organic matter, also had higher TOC values. Sediments with low TOCs, like those in Unit III at Site 479 (Fig. 1). are usually dominated by terrigenous organic matter (Fig. 2). This applies not only at Sites 479 and 480, but also at the other sites in the Gulf of California, although there is less terrigenous organic matter for a given TOC at the Cabo San Lucas sites than elsewhere (Fig. 2). Downhole at Site 479, the hydrogen index is high where the TOC is high, and low where the TOC is low (see Fig.
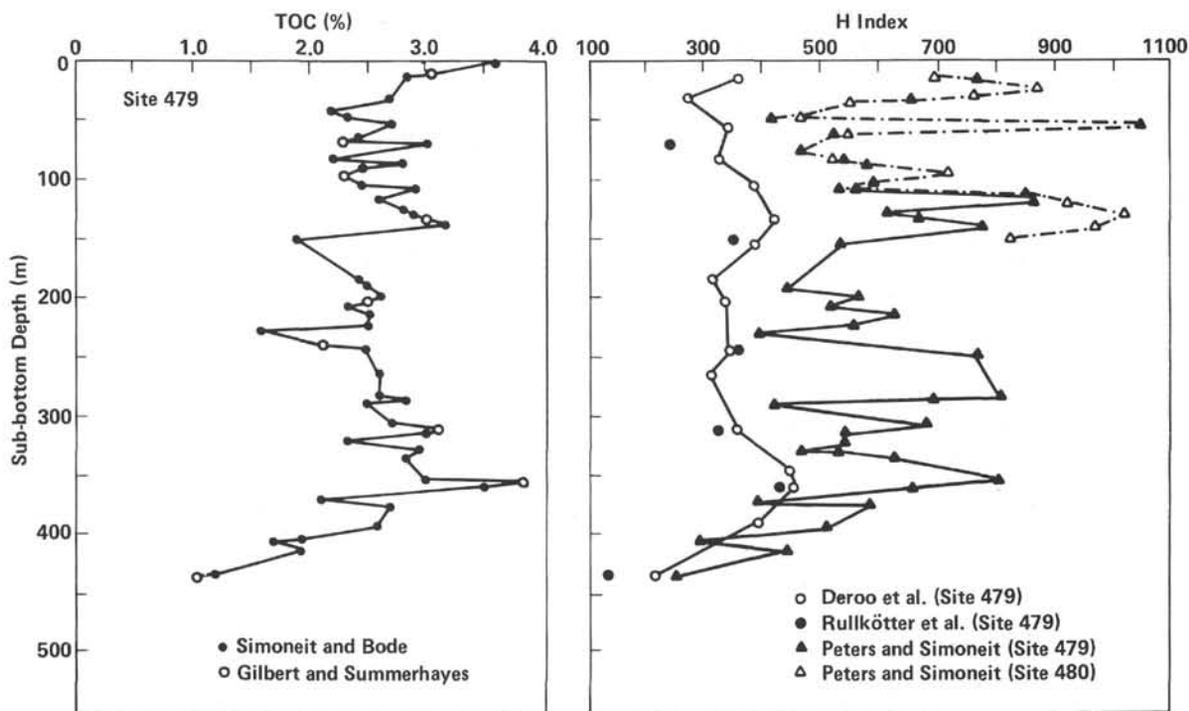
Figure 1. Downhole variations in TOC and hydrogen index (mg hydrocarbons/g TOC), from references in this volume. Note that H-index data for Sites 479 and 480 fall along the same curve for top 100 meters, indicating a comparable depositional history.
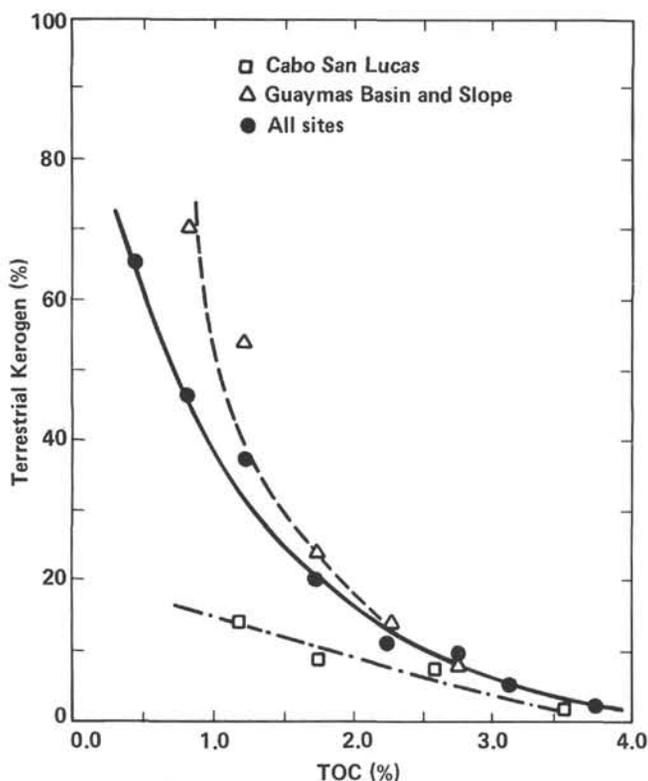
Figure 2. Interdependence of TOC and organic matter type, based on data from Gilbert and Summerhayes (this volume, Pt. 2). Preservation of marine amorphous material dilutes terrigenous organic matter and increases TOC. The background of terrigenous organic matter is lowest off Cabo San Lucas, because the source area is more arid than the mainland.

1; Peters and Simoneit, this volume, Pt. 2; Kendrick, this volume, Pt. 2). Again, this suggests that the preservation of lipid-rich marine organic matter controls the TOC, as seen in other environments (Summerhayes, 1981). That preservation is the main control on the abundance of marine organic matter is implied in the association between high TOC and periods of deposition of laminated, as opposed to homogeneous, sediments (Peters and Simoneit, this volume, Pt. 2; Schrader et al., 1980).

Alteration

Diagenesis by sulfate-reducing bacteria is one possible explanation for the exponential decrease in TOC from the surface (3.6% TOC) to a depth of 30–40 meters (2.5% TOC) at Site 479 (Fig. 1). An exponential decrease of sulfate from the surface (30 mM) to about 10 meters sub-bottom (3 mM) is also observed at this site (Gieskes et al., this volume, Pt. 2). This indicates that sulfate reduction is essentially complete below that depth. However, the decrease in TOC is accompanied by a change from laminated (surface) to homogeneous (subsurface) sediments in the contemporaneous sediments of Site 480, so it may instead reflect TOC preservation at time of deposition, rather than diagenetic change.

C/N ratios do not change significantly with depth (Simoneit, this volume, Pt. 2; Simoneit and Bode, this volume, Pt. 2), suggesting that diagenetic changes may not be very important. However, there is evidence for early thermal generation of hydrocarbons with depth at Site 479, so the C/N ratio may not be a good indicator of downhole changes in organic matter, except under

very high thermal stress (Site 477, Simoneit, this volume, Pt. 2). Most of the diagenetic loss of nitrogen leading to the high C/N values typical of the sediments penetrated on Leg 64 (C/N ratios are typically 11 or more; Simoneit, this volume, Pt. 2; Simoneit and Bode, this volume, Pt. 2) may take place in the upper few meters of the sediment column (Emery, 1960).

Within the oxygen-minimum zone, microbially mediated diagenesis has probably been restricted by the lack of oxygen (in comparison with the other sites, which are presently bathed in oxygenated water). That would explain why the average TOC at Sites 479 and 480 (about 2.5%) is much higher than at the other sites in the Gulf.

Some degree of diagenesis, perhaps thermally stimulated, is evident from the development of Ni-porphyrins at depth in the core. Surface samples from this area generally contain chlorins, not porphyrins (Galimov et al., this volume, Pt. 2).

The entire section of Site 479 is thermally immature. Vitrinite reflectance (R_0) values increase gradually downhole to a maximum of 0.38% (Fig 3: based on Kendrick, this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2; and Peters and Simoneit, this volume, Pt. 2). Agreement is good except for two of Kendrick's deeper samples. The vitrinite histograms of Rullkötter et al. (this volume, Pt. 2) show a reliable primary vitrinite popula-
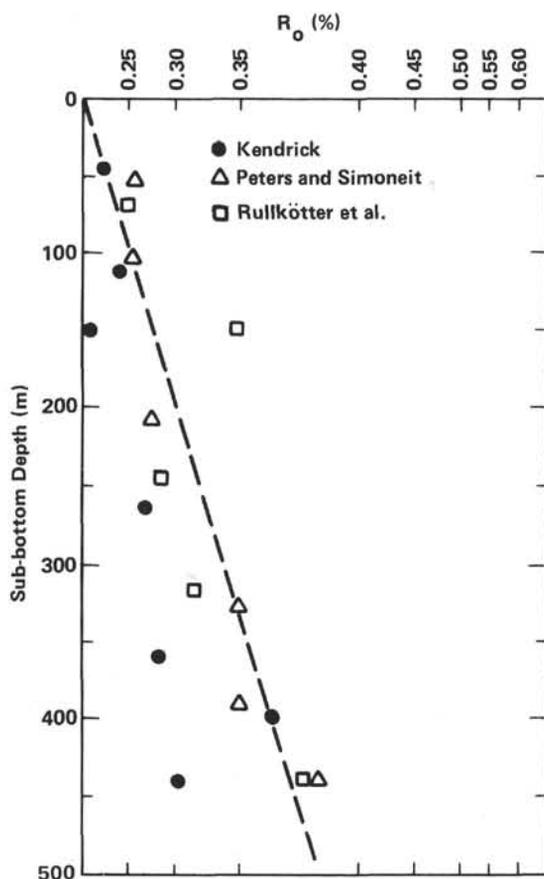
Figure 3. Downhole increase in thermal maturity as measured by vitrinite reflectance (% R_0) at Site 479. Dashed line is our best fit to available data.

tion, as well as much reworked material of higher reflectance that was not included in their reflectance calculations for maturity at this site. Thermal alteration indices as determined from spores and pollen (Deroo et al., this volume, Pt. 2; Gilbert and Summerhayes, this volume, Pt. 2) are not reliable at this site. There is too much marine and amorphous organic matter, and too little terrigenous material; besides, much of the terrigenous material is reworked.

Other indications of immaturity are (1) the absence of any free hydrocarbons in pyrolysis analyses (Peters and Simoneit, this volume, Pt. 2), (2) the low T_{max} measured during pyrolysis (Peters and Simoneit, this volume, Pt. 2), (3) the unaltered appearance of the n-alkanes as deep as Section 479-43-1 (where there is also a high ratio of phytane/nC_{18} as well as a high CPI—Galimov et al., this volume, Pt. 2), (4) the unaltered $\delta^{13}C$ isotope pattern in the separated bitumen fractions deep in the hole (Galimov et al., this volume, Pt. 2), and (5) the lack of downhole increase in extractable bitumens relative to TOC (Rullkötter et al., this volume, Pt. 2). This last point is countered by a moderate increase in the ratio of hydrocarbons to TOC in Section 479-43-1 (Galimov et al., this volume, Pt. 2).

Generation of hydrocarbons with increasing depth is most apparent in the gas- and gasoline-range hydrocarbon data (Whelan and Hunt, this volume, Pt. 2). The C_2–C_8 components show an exponential increase downhole, signifying that generation of hydrocarbons is taking place. This trend is somewhat obscured by the tendency of the hydrocarbons to reflect the abundance of the parent material (TOC) (Whelan and Hunt, this volume, Pt. 2). We remove that effect by making a ratio of the hydrocarbons to the TOC. The relation between these ratios and maturation indicators (R_0) suggests that the downhole increase in these components is caused by maturation rather than migration (Fig. 4). There is a parallel increase downhole in the nC_5/iC_5 ratio from 250 meters downward, another signal of increasing thermal stress (Whelan and Hunt; this volume, Pt. 2). The downhole increase in ethane below 250–300 meters noted by Galimov and Simoneit (this volume, Pt. 2) is a further indication of the approach of maturation.

Methane does not show the dependence on thermal stress that is evident in the gasoline-range components. Its carbon isotope composition remains about the same (−60‰) over much of the sediment sequence at Site 479, suggesting its derivation mostly from bacterial degradation of organic matter (Schoell, this volume, Pt. 2; Galimov and Simoneit, this volume, Pt. 2). The generation of gasoline-range components should be accompanied by the generation of at least some thermogenic methane; conceivably, the volume of biogenic methane at this site is so large that the thermogenic contribution is not obvious.

Paleoenvironmental Changes

The main paleoenvironmental information here is that changes in the degree of oxygenation of the bottom water are obvious from both the abundance of marine organic matter and the presence of laminations. Thus,
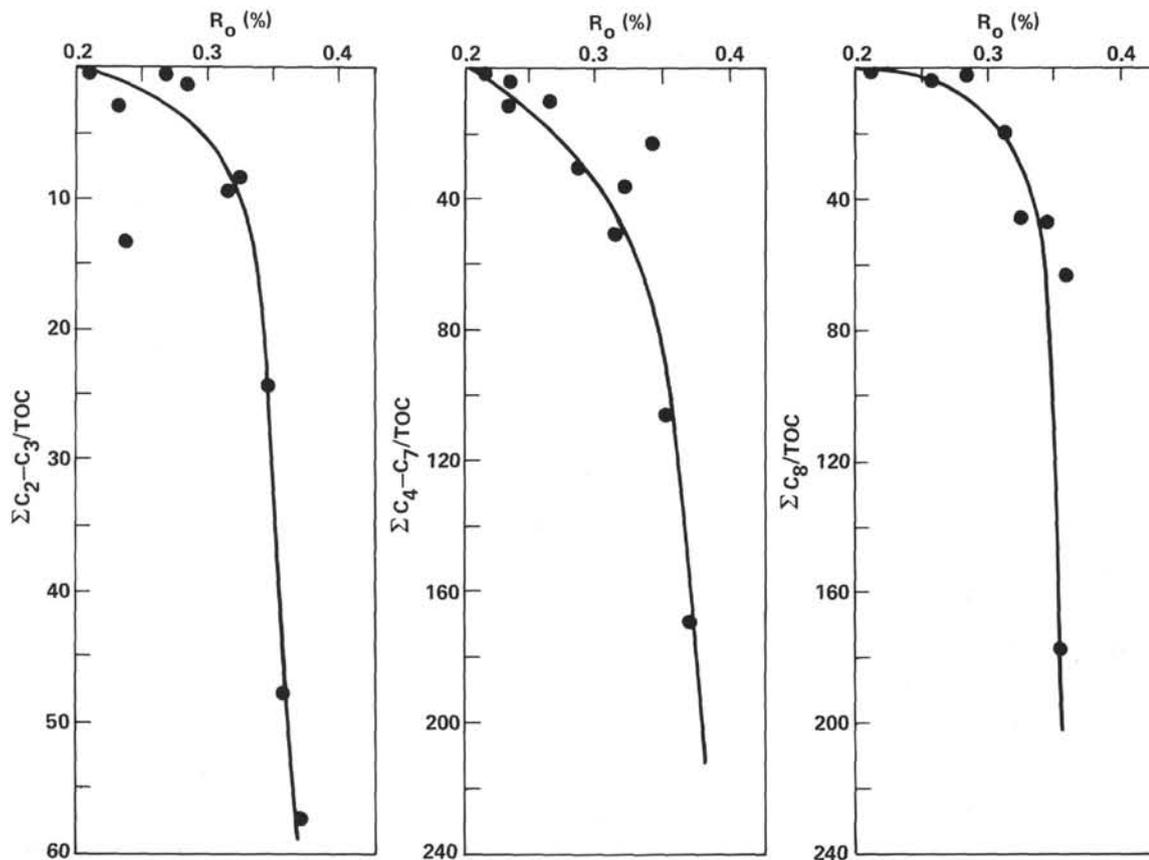
Figure 4. Interdependence of maturation (vitrinite reflectance—% R_0) and light hydrocarbon concentration at Site 479. R_0 data interpolated from best-fit line of Figure 3; ratios calculated from data in Whelan and Hunt (this volume, Pt. 2). Nature of section argues against diffusion and in favor of generation as an explanation of the trends.

high levels of TOC and of marine organic matter tend to occur only when bottom waters are anoxic enough to permit the preservation of laminations (essentially by eliminating benthic organisms). Under more oxidizing conditions, benthic organisms populate the sediment, metabolize the organic matter, and cause bioturbation.

That the sediments were reducing, at least immediately beneath the sediment/water interface, is suggested by the pristane/phytane ratios of less than 1.0, the abundant perylene, and the common sulfur compounds (Simoneit and Philp, this volume, Pt. 2; Simoneit, this volume, Pt. 2; Rullkötter et al., this volume, Pt. 2).

The long record of laminations, extending back into Unit III (which is poor in organic matter) suggests that we are looking at long-term climatic stability, probably reflecting seasonal runoff. The increase in TOC from Unit III up into Unit II tells us that bottom waters were possibly not anoxic during Unit III times. Alternatively, bottom waters were anoxic (giving laminations), but surface waters were not highly productive (giving low TOC). Seasonal productivity during deposition of Unit III is reflected in the presence of very thin laminae consisting of fish scales and organic matter, but the amount of organic matter preserved is small compared with Unit II. As diatoms and nannofossils are not abundant in Unit III, it appears that productivity was low at this time. We interpret these data to suggest that there was

an increase in both productivity and anoxia from the time of Unit III into that of Unit II.

Analytical Discrepancies at Sites 479 and 480

The main discrepancy here is in the pyrolysis data (see Fig. 1). The data of Deroo et al. (this volume, Pt. 2) and Rullkötter et al. (this volume, Pt. 2) are in good agreement with each other, with the elemental analyses, with the kerogen analyses, and with the lipid geochemistry, in suggesting that the source of the material is marine or a marine-terrigenous mixture (type II, or II mixed with III). Kendrick (this volume, Pt. 2) reports that his pyrolysis data show the organic matter to be type II and III mixed, while his elemental analyses of kerogens suggest type II. Conceivably the elemental data are in error, as his elemental ratios average 1.3, much higher than the H/C ratios of the other analysts. The hydrogen indices and the oxygen indices calculated by Peters and Simoneit (this volume, Pt. 2) from their pyrolysis analyses are much higher than those of other analysts and suggest that the organic matter is pure algal (type I) (Fig. 1); this interpretation disagrees with their own elemental ratios for kerogen (which suggest a type II + III mixture). We consider that the hydrogen indices of Deroo et al., and Rullkötter et al., are probably valid (Fig. 1). Those of Peters and Simoneit (Fig. 1) faithfully reflect changes in TOC, but are probably too high.

CONCLUSIONS

1. Much of the organic matter reaching the bottom is marine rather than terrigenous and deposited by processes of pelagic sedimentation.

2. Terrigenous organic matter is an important minor constituent and may be a major constituent especially where turbidity currents bring in land-derived organic matter. The Guaymas Basin contains the most land-derived organic matter.

3. Organic enrichment is a function of the preservation of marine and amorphous (usually marine-derived) organic matter.

4. TOCs are consistently highest at Sites 479 and 480, in the oxygen-minimum zone. Here the highest TOCs occur in laminated sediments that were deposited beneath anoxic bottom waters. Fluctuations from anoxic to oxidizing conditions caused changes from laminated (high TOC) to homogeneous (lower TOC) sediments. At the bottom of Hole 479, laminated sediments are poor in TOC, nannofossils, and diatoms; this may represent a period of lower productivity. Laminations in these sediments represent responses to runoff that are preserved because bottom waters were anoxic.

5. Phosphatic sediment rich in organic matter near the base of Unit IV of Hole 476 may be a fossil lagoonal deposit or an oxygen-minimum-zone deposit brought to its present depth by subsidence.

6. A subsurface peak in the concentration of TOC at 15–20 meters depth in all deep-water sites (excepting 479 and 480) averages 3.3% TOC compared with an average surface TOC of 2.1%. The age determinations of Spiker and Simoneit (this volume, Pt. 2) suggest that this subsurface peak is about 10 ky. old, on the average. It may represent a basinwide event that occurred at the beginning of the Holocene transgression. At that time, as sea level began to rise, there may have been a marked increase in upwelling and productivity, perhaps coupled with a decrease in the oxygen content of all Gulf waters. Alternatively, these sediments could have slumped in from the oxygen-minimum zone, though there is no clear geological evidence to support this idea.

7. A deep peak in TOC concentration at Site 478 occurs in laminated sediments and represents a period of anoxia in the depths of Guaymas Basin.

8. At several sites, the top 50 meters of sediments have more TOC, on the average, than do deeper samples. Most probably this reflects the effects of diagenesis, aided at Site 477 by thermal processes.

9. Pristane/phytane ratios and the abundance of certain sulfur compounds and perylene suggest that oxidizing conditions have dominated on the Baja margin, whereas conditions within the sediments elsewhere have been mainly reducing. We are not confident that these chemical indicators can be used to characterize the nature of deep bottom waters.

10. Although methane at Site 479 is mainly biogenic and the section is immature, small amounts of gasoline-range hydrocarbons are being generated at depth. Baja margin samples are immature and contain biogenic gas except near sills at Site 474.

11. Guaymas Basin sediments are mostly immature thermally, despite high heat flow, at Sites 478 and 481, except in close proximity to sills. At Site 477, where the heat flow is exceptionally high, much of the section is thermally mature.

12. Although thermogenic methane is widespread locally as a minor component of gas in Guaymas Basin sediments (and as a major component deep at Site 477), other hydrocarbons show little or no signs of extensive migration of the products of heating organic matter. For instance, the hydrocarbon signature at the bottom of Hole 479 appears to be due to *in situ* generation, rather than migration (as was thought during drilling), and perhaps should not have been considered a potential hazard to continued drilling at that site.

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