40. GEOCHEMISTRY SUMMARY—LEG 96—THE MISSISSIPPI FAN[1]

Jean K. Whelan, Woods Hole Oceanographic Institution[2]

ABSTRACT

Generally, organic lean sediments (organic carbon 0.5–1.5%) and pyrolyzable organic carbon (50–100 mg/g organic carbon) prevail at both Mississippi Fan and intraslope basin sites of Deep Sea Drilling Project (DSDP) Leg 96 in the Gulf of Mexico. The strong contribution of terrigenous organic matter is shown by the $\delta^{13}C$ of the sediment organic matter (−28 to −26‰) and the strong n-C_{27}, n-C_{29}, and n-C_{31} n-alkane signal in the extractable organic matter. The compositions and low levels of extractable hydrocarbons are consistent with either organic matter recycled from continental sources or traces of petroleum hydrocarbon migration. Distinct geochemical differences occur between middle fan overbank and channel-fill sites including higher levels of extractable hydrocarbons and elevated pore-water levels of calcium, magnesium, lithium, and sulfate (but not sodium or chloride) at the overbank sites. Depleted pore-water sulfate levels, indicative of either rapid sediment deposition or oxygen-depleted bottom waters, were found in channel-fill sites. Clay mineral composition on the fan is distinctly different from that of the more hemipelagic intraslope basin sites. Changes both in clay composition and extractable organic matter at the bottom of basin Site 619 are consistent with the presence of slumped material in that interval (below about 150 m sub-bottom). Trace metals associated with the mineral phases are diagnostic of minimal alteration/re-equilibration between pore-water and mineral phases. Bacterial culturing experiments showed the presence of anaerobic microorganisms in sediments recovered from a maximum depth of 167 m sub-bottom (85,000 to 110,000-yr.-old sediments) at Site 619. Microbiological activity was also detected in sediments recovered from Orca Basin Site 618 and fan Site 622. Pore-water geochemistry, suggestive that the organisms may also have been active at depth, shows that sulfate reduction is important in shallower sediments until pore-water sulfate is depleted. In deeper zones where gas pocket methane occurs, bacterial carbon dioxide reduction appears to have been the major methane production path based on $\delta^{13}C$ and deuterium isotopic data. Labeling experiments and pore-water data show that methylamine and acetate reduction may also be minor bacterial methane contributors. Pore-water sugar levels correlate with gas pocket methane profiles at intraslope basin Site 619. Elevated pore-water acetate levels occur at the sediment/water interface at Site 618 (>1225 μM) and at the boundary between the sulfate reduction and methane production zones at Site 619 (100 μM).

INTRODUCTION

During DSDP Leg 96, nine sites (Sites 614–617 and 620–624) were drilled in the middle and lower Mississippi Fan (see site chapters, this volume). The sections obtained are terrigenous sediments characterized by very high sedimentation rates (6–11 m/1000 yr.). These sediments, predominantly deposited during late Wisconsin glacial time, provide an excellent opportunity to examine the geochemical characteristics of deep-ocean sediments derived from redeposited continental sources. For comparison, sediments were also examined from two intraslope basins (Sites 618 and 619), which contain higher proportions of hemipelagic material of equivalent age.

ORGANIC GEOCHEMISTRY

General

The amount of organic carbon at all of the fan and intraslope basin sites tends to be fairly uniform (0.5–1.5%) even though the latter sites contain a much greater proportion of hemipelagic material. Both carbon-isotope data ($\delta^{13}C$ ranging from −25.5 to −28‰) and distributions of extractable C_{15+} hydrocarbons (containing high concentrations of n-C_{27}, n-C_{29}, and n-C_{31} typical of land plant waxes) are consistent with a predominantly terrigenous carbon source for both fan and basin sediments (Kennicutt et al., this volume; Requejo et al., this volume). At fan sites, the general increase with depth in extractable hydrocarbons including the unresolved complex mixture (UCM, typical of petroleum), together with a decrease in the carbon preference index (CPI), is consistent with the presence of small amounts of petroleum hydrocarbons. These could either be migrating up from depth or may represent redeposited terrigenous material delivered by the ancestral Mississippi River. The total amounts of petroleum hydrocarbons present in fan and basin sites, as shown by both solvent extraction (Kennicutt et al., this volume; Requejo et al., this volume) and pyrolysis analyses (results summarized later), are less than normally found for sediments containing migrated petroleum, implying that these hydrocarbons may represent recycled material (Whelan and Tarafa, this volume).

Pyrolysis shows low amounts of both generated petroleum (P_1 or S_1 in a plot of evolved hydrocarbons versus temperature, called a pyrogram; see Whelan and Tarafa, this volume) and pyrolyzable organic matter (P_2 or S_2, related to the total petroleum the sediment could produce upon further burial) in an extensive suite of samples from both fan and intraslope basin sites (Whelan and Tarafa, this volume). Production index (PI) values ($P_1/(P_1 + P_2)$) are generally low (always <0.1 and generally <0.05), typical of sediments containing immature organic matter. For comparison, sediments containing mature organic matter generally have PI values >0.1,

[1] Bouma, A. H., Coleman, J. M., Meyer, A. W., et al., *Init. Repts. DSDP*, 96: Washington (U.S. Govt. Printing Office).

[2] Address: Chemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543.

and sediments containing migrated petroleum usually give values of >0.2 and often >0.5 (Espitalié et al., 1977). Thus, PI values of Leg 96 sediments are not typical of sediments that contain more than very small amounts of migrated hydrocarbons.

Pyrolyzable organic carbon values (P_2) average about 50–100 mg hydrocarbon per gram organic carbon, as compared to typical petroleum source rock values that generally are about 10 times higher (Mukhopadhyay et al., 1985). For comparison, high P_2 values (>300) are generally observed in rapidly deposited sediments, such as those in upwelling regions, whereas very low values (<10) are typical of slowly deposited open-ocean sediments. The relatively low values observed at the Mississippi Fan sites, in spite of the high sedimentation rates, are typical of deltaic sediments where Type II organic matter from marine organisms is oxidized to Type III because of high activity of the deltaic environment. This material is further diluted with additional Type III carbon originating from terrigenous organic matter.

Specific Organic Geochemical Changes

Some specific intervals within the Leg 96 drill sites where changes in organic compounds appear to correlate with changes in lithology and/or paleontology are summarized:

1. The pristane/phytane ratio and odd/even hydrocarbon ratio show a gradual increase with depth at Site 619 from 112 to 167 m sub-bottom, suggesting a greater input of terrigenous organic matter in that interval. Low n-C_{17}/n-C_{29} ratios observed in this interval also support this interpretation (Requejo et al., this volume). A change in a number of profiles, including n-C_{17}, n-C_{20}, odd/even carbon ratio, and $\delta^{13}C$, occur below about 150 m sub-bottom where slumping is thought to be important (see Site 619 chapter, this volume).

2. An increase in all extractable organic compounds occurs from 250 to 460 m sub-bottom at lower fan Site 615. The upper part of this interval corresponds to a section containing *Tasminidies* (algal clasts originating from shallow littoral waters; Kohl et al., this volume), suggesting that a change in sediment type is responsible for the hydrocarbon profiles. The CPI gradually decreases in the same interval, which is consistent with a greater marine input. All organic compounds decrease in the deeper carbonate section of the same hole (490–520 m).

3. Amounts of extractable hydrocarbons (n-C_{17}, n-C_{20}, pristane, phytane, and UCM) are somewhat higher in overbank than in channel-fill sediments in the middle fan (Kennicutt et al., this volume) and generally show an increase with depth in deeper sections of the overbank. Total organic carbon generally remains very constant (0.8–1.2%) in the same interval. The slightly higher amounts of n-C_{17}, n-C_{20}, and a slightly lower CPI for the overbank sites suggests either preferential petroleum seepage into overbank sites or better preservation of marine organic matter in overbank as compared to channel-fill sites. The former possibility seems unlikely because channel-fill sediments tend to be coarser grained and, therefore, should provide better petroleum migration conduits than overbank sediments. However, these clays tend to be highly underconsolidated and could have some permeability.

Pyrolysis data show that high molecular weight organic matter is also higher in overbank than in channel-fill sites (Whelan and Tarafa, this volume). Thus, better presentation of all organic matter appears to occur in overbank (as compared to channel-fill) sites.

4. Total extractable lipid material (TEM) for the intraslope basin sites is relatively high and exceeds that reported for many surface sediments including some from the northeastern Gulf of Mexico continental shelf (Requejo et al., this volume). Only about 10% of the TEM consists of hydrocarbons that could have been derived from petroleum. The remainder includes more polar lipid material derived from biological sources—either preserved by rapid burial or associated with sediment anaerobic microorganisms.

5. The compositions (but not total amounts) of pyrolysis products [as determined by capillary-gas chromatography (GC) and gas chromatography mass spectrometry (GCMS)] remain fairly constant throughout Site 623 on the lower fan and are similar to those found at intraslope basin Site 619 and lower fan Site 615 (Whelan and Tarafa, this volume). The uniformity suggests a similarity in the diagenetic history of the organic carbon throughout the area, even though the original sources of sediments in the fan sites may have been somewhat different from those of the intraslope basin sites (as suggested by differences in clay mineral compositions discussed later).

Total amount of pyrolyzable organic matter increases with increasing depth in two sequences in lower fan Site 623. These values are generally higher in the coarse-grained than in the fine-grained sediments, which contradicts trends observed at other sites (Whelan and Tarafa, this volume). These trends suggest that the deeper sediments in each of these sequences were deposited more rapidly than the shallower ones.

6. Requejo et al. (this volume) show the presence of C_{27}–C_{29} steranes and triterpanes typical of immature sediments at the basin sites. The same authors also report an increase in perylene below 100 m sub-bottom at basin Site 619, which is probably related either to an increased input of terrigenous organic matter or to the presence of anaerobic methanogenic microorganisms or both.

PORE-WATER CHEMISTRY

General

Interstitial waters were studied extensively by Ishizuka, Kawahata, et al. (this volume) and by Presley and Stearns (this volume). Agreement between the two laboratories is excellent even though different analytical methods were used in some cases (Table 1). Measurements of inorganic constituents include pH, alkalinity, salinity, calcium, magnesium, chloride, sulfate, potassium, strontium, manganese, lithium, silica, and iron. Dissolved carbon dioxide and sulfate values are also reported by Kennicutt et al. (this volume). Ishizuka et al. (this volume) have also analyzed the associated clay mineral composition as well as dissolved organic carbon (DOC) and sug-

Table 1. Leg 96 pore-water summary, average values.

Site (interval, m sub-bottom)	Number of samples	Sulfate (g/kg) (P)	Sulfate (mM) (I)	Calcium (mg/kg) (P)	Calcium (mM) (I)	Magnesium (mg/kg) (P)	Magnesium (mM) (I)	Chloride (g/kg) (P)	Chloride (g/kg) (I)	Sodium (g/kg) (P)	pH (I)
Seawater (S&M)[a]		2.7	28	400	10	1312	54	19.5	—[c]	10.8	7.89
(P), (I)[b]				397		1188	54	—	—	9.9	8.25
616 (1.4–145)	12	3.3 ± 0.2	33 ± 3	610 ± 72	18 ± 3	1455 ± 128	63 ± 3	18.8 ± 0.9	17.8 ± 0.2	10.2 ± 0.4	6.8 ± 0.2
617 (30–184)	14	3.3 ± 0.15	35 ± 3	690 ± 38	21 ± 1.6	1355 ± 76	60 ± 2	19.5 ± 1.0	18.1 ± 0.4	10.4 ± 0.4	7.1 ± 0.2
620 (130–281)	7	3.0 ± 0.2	30 ± 2	698 ± 25	19 ± 3	1374 ± 51	64 ± 2	19.3 ± 0.2	18.1 ± 0.2	10.4 ± 0.2	6.9 ± 0.2
623 (19–124)	6	3 ± 0.04	30 ± 0.6	629 ± 52	9 ± 1	1417 ± 48	61 ± 2	19.0 ± 0.3	18.0 ± 0.1	10.3 ± 0.2	6.9 ± 0.2
615 (1.4–240)	13	2.4 ± 0.15	24 ± 1	501 ± 95	15 ± 2	1322 ± 222	58 ± 2	18.6 ± 1.2	18.0 ± 0.2	10.2 ± 0.6	7.3 ± 0.4
(306–506)	8	0.8 ± 0.8	8 ± 6	293 ± 135	10 ± 4	1094 ± 197	46 ± 5	19.2 ± 0.67	18.0 ± 0.2	10.5 ± 0.3	7.5 ± 0.2
621 (10.9–177)	22	0.11 ± 0.2	2 ± 1	262 ± 35	7 ± 0.8	1154 ± 203	49 ± 4	19.2 ± 0.3	18.0 ± 0.2	10.2 ± 0.2	7.2 ± 0.2
622 (27–129)	7	0	2 ± 1	228 ± 41	6.9 ± 0.7	1146 ± 73	50 ± 1	19.3 ± 0.1	18.1 ± 0.1	10.1 ± 0.2	7.2 ± 0.3
(144–179)	2	1 ± 0.2	11 ± 3	390 ± 90	8.4 ± 5	1135 ± 50	50 ± 0.2	19.6 ± 0.1	18.2 ± 0.1	10.2 ± 0.1	7.1 ± 0.04
618 (12.4–90.5)	10	0	1.6 ± 1	295 ± 63	9 ± 2	1131 ± 91	49 ± 5	42 ± 18	38.8 ± 15.8	23 ± 11	7.6 ± 0.2
619 (10–42.5)	5	2 ± 0.4	19 ± 3	441 ± 53	14 ± 1	1210 ± 23	57 ± 2	19.0 ± 0.2	18.0 ± 0.02	10.3 ± 0.1	6.9 ± 0.1
(71.6–189)	13	0.03 ± 0.07	1.7 ± 0.6	222 ± 44	8 ± 2	939 ± 139	44 ± 2	18.7 ± 2.5	18.4 ± 0.2	9.8 ± 1.4	7.4 ± 0.3

Note: Values on left from Presley and Sterns (P); values on right from Ishizuka et al. (I). Average and 1σ standard deviation are shown for all samples within the indicated depth interval.

[a] Strumm and Morgan, 1970.

[b] Taken from surface seawater measurements of Presley and Sterns (P) and Ishizuka et al. (I), this volume.

[c] — means not determined.

ars in pore waters for the intraslope basin sites and one lower fan site. Other measurements of pore-water organics include acetate and methylamine, which also were carried out as part of microbiological investigations of these cores (Whelan et al., this volume). Hydrocarbon and isotopic ($\delta^{13}C$ and deuterium) compositions of pore gases were measured (Pflaum et al., this volume; Burke et al., this volume, and reported later under the section on core gases).

Pore-Water Differences between Channel-Fill and Overbank Sites

Elevated calcium, magnesium, and sulfate (but not sodium or chloride) are observed in the middle and lower fan regions at slump Site 616 (1–145 m sub-bottom), midfan overbank Site 617 (30–184 m sub-bottom), midfan overbank Site 620 (139–281 m sub-bottom), and lower fan Site 623 (19–124 m sub-bottom, containing interbedded channel and overbank sequences) (Table 1). Because smooth depth profiles for these constituents were observed in the same intervals by at least two different laboratories and squeezing was carried out on refrigerated samples in the accepted manner (either immediately on board ship or on shore within a few weeks after the cruise), there is no reason to believe that the sulfate, calcium, and magnesium results represent an artifact caused by sulfur oxidation during core storage. This appears to be the first authentic case where elevated levels of sulfate occur without concurrent elevated sodium and chloride (as would be observed if dissolution of salt diapirs were the cause).

Sulfate is either normal or depleted for lower fan Site 615 and midfan channel Sites 621 and 622, as well as for the two intraslope basin Sites 618 and 619 (Table 1). The depleted sulfate in channel sites versus the high levels in overbank sites suggests either the presence of oxygen-depleted waters within the channels as compared to the overbank sites as postulated by Presley and Stearns (this volume) or more rapid deposition at the channel than at the overbank sites as postulated by Berner (1978) for other areas showing sulfate depletion. Average deposition rates for overbank and channel-fill sites in the midfan region are estimated to be about equal (~1200 cm/1000 yr.; site chapters, this volume). However, there is also evidence that deposition at channel sites was probably faster and occurred primarily as near-instantaneous events. Rapid deposition of relatively unreworked organic matter at the channel sites is supported by the finding of abraded shallow-water benthic foraminifers dispersed throughout coarser sections. In addition, some clay fractions from Sites 621 and 622 contain well-preserved shallow-water specimens that were probably transported as part of a density flow (site chapters, this volume).

The cause of elevated sulfate, calcium, and magnesium in the overbank sites is unknown. It is postulated that because the relatively finer grained sediments in the overbank sites (as compared to coarser grained sediments in channel-fill sites) spend longer in the water column before deposition, organic matter in this fine fraction, as well as reduced sulfur (possibly eroded from marine sediments during lowering of sea level, as suggested by Presley and Stearns, this volume), may have been subjected to greater aerobic oxidation before deposition. Oxidation of reduced sulfur would produce sulfuric acid, which, if sediments were subsequently buried relatively rapidly, would remain in the sediments to produce *in situ* dissolution of carbonate minerals, explaining the observed excesses of calcium and magnesium. Pore-water pH data support this hypothesis: acidities are slightly higher in overbank sections that show elevated sulfate levels (Table 1).

Such a process might also explain the presence of higher levels of typically marine hydrocarbons (C_{17} and C_{20}) in the overbank compared to channel-fill sediments (as observed by Kennicutt et al., this volume, and discussed previously). Their presence would seem to contradict the hypothesis of organic matter reworking of fine-grained overbank sediments prior to deposition, since these compounds should normally have been rapidly biodegraded and therefore depleted before sediment removal from the active zone. However, if these compounds were originally protected by inclusion in organisms with carbonaceous shells, they might have been released upon burial and exposure of the overbank sediments to the sulfuric acid produced by oxidation of reduced sulfur produced during deposition. It is well known from petroleum-source rock analyses that dissolution of carbonate minerals with acid in the laboratory often releases significant quantities of bitumen.

Pore-Water Characteristics Associated with Anaerobic Bacteria

The highest level of pore-water acetate (>1225 μM) ever measured in a sediment occurs just below the interstitial water salinity maximum in intraslope basin Site 618 sediments (15 m sub-bottom). Site 618 is located in Orca Basin, which contains anoxic and high salinity (230‰ at the sediment/water interface) bottom waters (Whelan et al., this volume; Ishizuka, Kawahata, et al., this volume). This anomalously high acetate level, which should be checked in future work, may be related to the activities of anaerobic microorganisms in this high salinity environment. Elevated levels of pore-water acetate (>500 μM) have been reported at the base of the sulfate reduction zone at a much shallower depth (8–15 cm) by Martens and Crill (1984). Abnormally high pore-water acetate and volatile fatty acid levels have also been observed for anoxic solar salt ponds (Klug et al., 1984).

Site 619 in the adjacent Pigmy Basin, a rapidly sedimented intraslope basin containing oxic bottom waters, shows pore-water profiles in which sediments gradually change with depth from showing characteristics of anaerobic microbial sulfate reduction into deeper zones showing methane production. Pore-water sugar profiles correlate with gas pocket methane concentrations in lower sections of basin Site 619 (Ishizuka, Ittekkot, et al., this volume).

At Orca Basin Site 618, a highly elevated salinity at the sediment/water interface (230‰; Ishizuka, Kawahata, et al., this volume) decreased exponentially with depth to a somewhat elevated level (as compared to normal seawater) of about 50‰ for all sediments below 30 m sub-bottom. Thus, the high salinity waters appear to be migrating laterally (rather than vertically) into the Orca Basin bottom waters and surface sediments. In addition, Presley and Stearns (this volume) have interpreted the slightly elevated salinities in sediments deeper than 30 m sub-bottom to imply that anoxic bottom waters have existed in the Orca Basin for at least the last 50,000 yr.

Below the very highest salinity layer near the sediment/water interface, the high salinities do not seem to have stopped microbial processes as shown both by microbiological experiments and pore-water profiles of typical microbial nutrients and products such as sulfate, acetate, and methane (Ishizuka, Kawahata, et al., this volume; Whelan et al., this volume).

Radio-labeling studies show the presence of viable anaerobic microorganisms in sediments recovered from Sites 618, 619, and 622. Changes in pore-water constituents in the same intervals where microbial growth was detected suggest that the organisms may also have been active at depth (Whelan et al., this volume).

Pore-Water Changes Related to Depositional Environment

1. The slumping in surface sediments at Site 618 in the Orca Basin (see Site 618 chapter, this volume) does not seem to have affected the pore-water profiles, which generally show smooth changes with depth.
2. Changes in lithium correlate with calcium and show elevated levels in overbank as compared to channel sites. Thus, in this area lithium appears to correlate with carbonate precipitation–dissolution rather than with volcanic activity, as often observed in other areas (Presley and Stearns, this volume).
3. Pore waters for the massive slump deposit at Site 616 are enriched in sulfate, calcium, magnesium, and lithium, very similar to those of the overbank sediments discussed before. This similarity suggests that the slump sediments were deposited via a mechanism similar to that of the overbank sediments prior to the slumping event.
4. A strong increase in strontium and a decrease in manganese occur below 450 m sub-bottom at Site 615. The increase is just above an abrupt lithologic change at 485 m with Ericson Zone Y terrigenous clay and silt above and Ericson Zone X calcareous ooze below (site 615 chapter, this volume). High deposition rates just above this zone (300–460 m) are indicated by pore-water profiles typical of sulfate reduction, namely sulfate depletion and an alkalinity maximum. Berner (1978) has observed a relation between sulfate reduction and deposition rate in a number of areas. Higher deposition is also suggested by higher concentrations of extractable organics in roughly the same interval (300–460 m sub-bottom; Kennicutt et al., this volume). Sulfate levels then decrease and extractable organics increase slightly in the calcareous ooze at the bottom of the hole (490–510 m sub-bottom) deposited during the Wisconsin interglacial (Ericson Zone X) at much slower sedimentation rates than the overlying clay and silt (Wetzel and Kohl, this volume).

CORE GASES

Core gases were detected at intraslope basin Sites 618 and 619 and midfan Sites 620 and 621. Most of the gas was biogenic methane, as shown by high C_1/C_2 ratios (>3000 at Site 618 and $>20,000$ at the other sites) and $\delta^{13}C$ values of less than -70‰ (Pflaum et al., this volume; Burke et al., this volume). In addition, the hydrogen-isotope values of -184‰ for methane in Site 618 sediments show that methanogenic CO_2 reduction is the major methane production path (Burke et al., this volume).

Amounts of biogenic methane were high enough to form small amounts of gas hydrates, usually in silty mud sections, at Orca Basin Site 618 between 20 and 40 m sub-bottom. Isotopic values of these hydrates are similar to those of the nearest gas pockets, implying hydrate formation from predominantly biogenic methane without isotopic fractionation (Pflaum et al., this volume).

Amounts of methane in core gas pockets from intraslope basin Sites 618 and 619 increase substantially below the zone where pore-water sulfate decreased to near zero, as found at other DSDP sites (Rice and Claypool, 1981; Claypool and Kaplan, 1974). These methane levels also correlate with methanogenic microbiological activity as determined by incubation of sediments with radiolabeled substrates. The results imply that viable methanogenic bacteria may have operated *in situ* to a maximum sub-bottom depth of at least 167 m in Site 619 sediments (Whelan et al., this volume), which are between 85,000 and 110,000 yr. old (Williams and Kohl, this volume).

CHEMICAL ANALYSIS OF CLAY MINERALS

A very uniform clay composition occurs at all of the fan sites showing a predominance of smectite (generally about 50%) over smaller but approximately equal amounts of chlorite and kaolinite (about 20% each) and only traces of illite (Pickering et al., this volume; Ishizuka, Kawahata, et al., this volume). This composition is very typical of Cretaceous and younger Gulf Coast sediments that have not undergone significant thermal alteration (Grim, 1968). The only exception is Site 615, which shows a general decrease in smectite with depth as well as a sharp decrease of the proportion of smectite in several samples below 413 m sub-bottom, particularly in the calcareous ooze section below 485 m sub-bottom.

Trace elements in sediment mineral phases generally correlate with clay minerals rather than with pore-water constituents, implying minimal alteration–re-equilibration between minerals and pore fluids for these rapidly deposited recent sediments (Pickering et al., this volume; Ishizuka, Kawahata, et al., this volume).

The intraslope basin sites have a different clay composition than the fan sites (Ishizuka, Kawahata, et al., this volume). For example, a smaller proportion of smectite occurs in the intraslope basin sites (generally ~20%) as compared to the fan sites (50%). This trend is consistent with the basin sediments being generally hemipelagic. The percentage of smectite at basin Site 619 increases to about 50% below 150 m (Ishizuka, Kawahata, et al., this volume) where it is believed that slumping, possibly from the shelf, may have been important (Site 619 chapter and Williams and Kohl, this volume).

REFERENCES

Berner, R. A., 1978. Sulfate reduction and the rate of deposition of marine sediments. *Earth Planet. Sci. Lett.*, 37:492–498.

Claypool, G. E., and Kaplan, I. R., 1974. The origin and distribution of methane in marine sediments. *Natural Gases in Marine Sediments:* New York, (Plenum Press) pp. 99–139.

Espitalié, J., Madec, M., Tissot, B., Mennig, J. J., and Laplat, P., 1977. Source rock characterization method for petroleum exploration. *Proc. Offshore Tech. Conf.*, 9(3):439–444.

Grim, R. A., 1968. *Clay Mineralogy:* New York (McGraw-Hill), pp. 532–533.

Klug, M., Francois, R., Gyure, R., Javor, B., Tribble, G., and Vairavamurthy, A., 1984. Sulfur reduction in sediments of marine and evaporite environment. *EOS Trans. Am. Geophys. Union*, 65:919.

Martens, C. S., and Crill, P. M., 1984. Acetate cycling at the base of the sulfate reduction zone in an organic-rich coastal sediment. *EOS Trans. Am. Geophys. Union*, 65:905.

Mukhopadhyay, P. K., Hagemann, H. W., and Gormly, J. R., 1985. Characterization of kerogens as seen under the aspect of maturation and hydrocarbon generation. *Erdoel Kohle*, 38:7–18.

Rice, D. D., and Claypool, G. E., 1981. Generation, accumulation and resource potential of biogenic gas. *Am. Assoc. Pet. Geol. Bull.*, 65:5–25.

Strumm, W., and Morgan, J. J., 1970. *Aquatic Chemistry:* New York (Wiley).

Date of Initial Receipt: 26 June 1985
Date of Acceptance: 8 October 1985