

21. MICROBIAL GASES IN SEDIMENTS FROM THE SOUTHWEST AFRICAN MARGIN¹

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ABSTRACT

High concentrations of microbial methane and carbon dioxide are present in sediments cored during Leg 175 on the southwest African margin. Headspace carbon dioxide concentrations increase quickly below the seafloor. In contrast, headspace methane concentrations do not increase until after interstitial sulfate is depleted. Only a small fraction of the available carbon is microbially converted into interstitial gases. No geochemical evidence was found either for migration of hydrocarbon gases from deeper, thermally mature sediments or for formation of well-developed gas hydrate layers, even though seismic data suggest that both processes occur along this margin.

INTRODUCTION

High amounts of gas were present in sediments cored during Leg 175. The possible origins of these sedimentary gases are (1) production as a result of microbial degradation of sediment organic matter, (2) in situ thermal decomposition of sediment organic matter, and (3) thermal degradation of deeply buried organic matter and migration into shallower sediments. The elevated hydrostatic/lithologic pressures and low temperatures that exist beneath the seabed typically keep gases dissolved in the interstitial fluids of most sediment sequences. In some sediments, gas is sufficiently abundant to exist in the free state or as gas hydrate. During core recovery, gases exsolve from solution as a result of the release of pressure and from warming of the sediment. Gas bubbles and gas expansion pockets were common features of cores recovered during Leg 175.

DEPOSITIONAL REGIMES

The 13 Leg 175 drill sites (Fig. 1) encompass a variety of oceanic settings and passive-margin depositional environments (see Pufahl et al., Chap. 18 and Wefer et al., Chap. 16, both this volume). The amounts and types of gases found in the sediments from the various locations are influenced by the differences among the sites. The 13 drill sites may be grouped into four sedimentary regimes, as follows.

Lower Congo Basin Sites 1075–1077

Drilling at three drill sites on the lower continental margin explored the Quaternary history of fan-margin sedimentation north of the Congo River Canyon. This depositional regime is located under a neritic environment dominated by the freshwater contributions of the Congo River, seasonal coastal upwelling, and incursions of open-ocean water from the South Equatorial Countercurrent. The three drill sites are close to areas of commercial petroleum exploration, and drilling at these sites was limited to 200 meters below seafloor (mbsf) because of safety concerns. Predrilling seismic surveys detected evidence of gas chimneys, which indicate free gas, and abun-

dant bottom-simulating reflectors (BSRs) in the regions of the three Lower Congo Basin drill sites.

The three sites constitute a depth transect that provides a composite picture of hemipelagic sedimentation across this margin (Fig. 1). Site 1075 (4°47'S, 10°05'E) is located in 2995 m water depth. Sediments at this site consist of Pliocene–Pleistocene greenish gray diatomaceous clay and nannofossil-bearing diatomaceous clay having an average sedimentation rate of 100 m/m.y. Sediments from Site 1077 (5°11'S, 10°26'E; water depth 2392 m) are composed of intercalations of greenish gray diatom-rich, diatom-bearing, nannofossil-bearing, and nannofossil-rich clay. Site 1076 (5°04'S, 11°06'E) is situated in 1404 m water. Its sediments consist of Pleistocene diatom-bearing olive-gray clay and greenish gray clay that accumulated at rates that varied between 50 and 200 m/m.y. Sediments from all three sites are bioturbated and contain an average of 2.5 wt% organic carbon.

Angola Margin Sites 1078 and 1079

Two drill sites on the upper continental margin of Angola provide a history of upper Quaternary sedimentation in a setting that is free of strong fluvial or upwelling influences. The moderately productive coastal environment of this depositional regime contrasts with the more productive Lower Congo Basin sites and to the upwelling-dominated sites south of the Angola-Benguela Front. The Angola margin drill sites are close to areas of commercial petroleum production, and drilling at these sites was limited to 200 and 120 mbsf because of safety concerns. Predrilling seismic surveys detected evidence of gas chimneys and of abundant BSRs in the regions of the two drill sites.

The two sites describe a transect across the upper continental slope (Fig. 1). Site 1078 (11°55'S, 13°24'E) is located in 438 m water depth. Site 1079 (11°56'S, 13°19'E) is downslope in 749 m of water. Flaring of gas from a production platform that was ~25 mi distant could be observed from Site 1078, imparting special importance to the safety aspect of the shipboard gas analyses. Sediments at both sites consist of olive-gray silty clay with varying amounts of nannofossils and foraminifers. Sedimentation rates are high because of inputs of terrigenous materials from the arid and elevated coastal regions of Angola. The rates average between 600 and 400 m/m.y. over the upper two-thirds (260 k.y.) of Sites 1078 and 1079, respectively, before dropping to ~50 m/m.y. in deeper sediments. The shallow water depths and elevated sedimentation rates combine to improve organic matter preservation. The elevated preservation is reflected in organic carbon concentrations of ~2.5 wt%, which is greater than that anticipated from the moderate marine productivity in this sedimentary regime.

¹Wefer, G., Berger, W.H., Richter, C., et al., 1998. *Proc. ODP, Init. Repts.*, 175: College Station, TX (Ocean Drilling Program).

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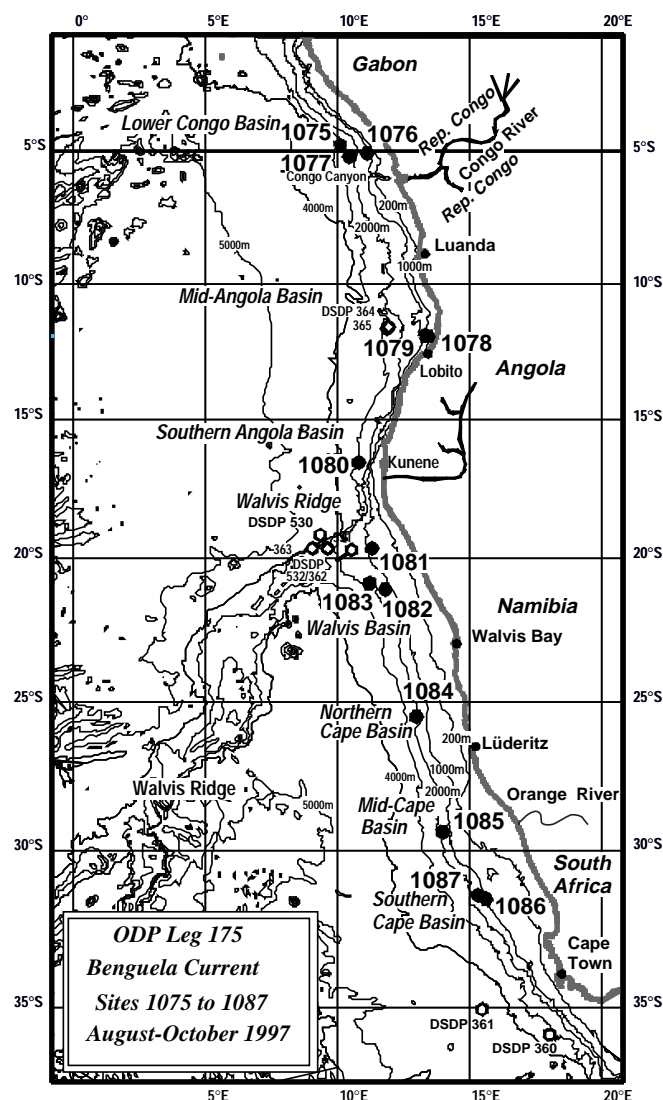


Figure 1. Locations of Leg 175 drill sites on the southwest African margin. Bathymetry is in meters.

Angola-Namibia Upwelling Sites 1080–1084

Sedimentary sequences at the drill sites in this depositional regime provide a composite latest Miocene–present history of the major upwelling system that extends from the mid-Namibia margin to north of the Walvis Ridge. The drill sites (Fig. 1) are seaward of the upwelling centers, but they contain second-order signals of enhanced marine productivity associated with the upwelling signals that are transported to their respective locations by the Benguela Current and its meanders and eddies.

Site 1080 (16°36'S, 10°49'E) is located south of the Angola-Benguela Front in water 2778 m deep. Sediments consist of dark greenish gray to olive-gray diatom-bearing to diatom-rich silty clays with varying amounts of calcareous microfossils. The sedimentary sequence is incomplete and disturbed, possibly involving turbidite deposition. Site 1081 (19°37'S, 11°19'E) is situated on the Walvis Ridge in water 794 m deep. Sites 1082 (21°06'S, 11°49'E; water depth 1280 m) and 1083 (20°57'S, 11°13'E; water depth 2180 m) are in the Walvis Basin on the southern flank of the ridge. Site 1084 (25°31'S, 13°02'E) is in 1992 m of water south of the Walvis Ridge on the northern landward edge of the Cape Basin. The sediments at the four

sites contain similar alternations of bioturbated olive-gray to black clays rich in nannofossils and diatoms that overlie an olive-gray clayey nannofossil ooze. Sedimentation rates vary from 40 to 200 m/m.y. in the various lithostratigraphic units and subunits of these sites. Most of the sediments of this depositional regime are notably rich in marine organic matter; organic carbon concentrations exceed 10 wt% in many parts of the sequences.

Benguela Current Sites 1085–1087

A record of sediment accumulation from the middle Miocene to the latest Pleistocene is provided by the three sites in this depositional regime. These sites (Fig. 1) are south of the main high-productivity zone of the Benguela upwelling system, yet they all lie under the cold waters of the Benguela Current.

Site 1085 (29°22'S, 13°59'E) is at a water depth of 1725 m on the Namibia slope. Sediments at this site are greenish gray, foraminifer-bearing nannofossil oozes. Site 1086 (31°33'S, 15°40'E) lies in 782 m of water on the northern part of the Orange River paleofan. Sediments consist of bioturbated olive nannofossil oozes with varying amounts of foraminifers, silt, and clay. Site 1087 (31°28'S, 15°19'E) is in 1383 m of water on the South Africa slope. Sediments are greenish gray nannofossil oozes with varying amounts of foraminifers and clay. Sedimentation rates in this depositional regime are low, ranging between 20 and 70 m/m.y. at these three drill sites. Organic carbon concentrations in these sites are fairly low (averaging 1 wt%), which reflects the low-to-moderate productivity of this region.

GAS ANALYSIS METHODS

Gas samples were obtained by two different methods. The primary method was the headspace procedure (Kvenvolden and McDonald, 1986), which involves placing a nominal 5-cm³ plug of sediment into a septum-sealed vial that is then heated at 60°C for 30 min to evolve sediment gases. The secondary procedure was used occasionally when gas expansion pockets appeared in cores before they were cut into 1.5-m sections. A heavy-duty needle was used to puncture the butyrate core liner, and an attached syringe was employed to collect the gas.

Methane and ethane contents of gas samples were analyzed using a Hewlett Packard 5890 II Plus gas chromatograph equipped with a 2.4 m × 3.2 mm stainless steel column packed with HaySep S connected to a flame ionization detector (FID). Additional gas contents were analyzed using a Hewlett Packard 5890 II Plus gas chromatograph equipped with a 60 m × 0.32 mm DB-1 capillary column connected to an FID to measure hydrocarbons from methane to hexane and a packed column connected to a thermal conductivity detector to measure nonhydrocarbon gases, such as CO₂ and H₂S. Both instruments were calibrated using Scotty IV gas mixtures, and gas concentrations are reported in parts per million by volume (ppmv).

The Ocean Drilling Program (ODP) gas analysis techniques are designed to provide quick determinations of the relative amounts and possible origins of the residual interstitial gases recovered during drilling. In particular, they help avoid situations where dangerously elevated concentrations of thermogenic gas might occur. The procedures were not designed to deliver quantitatively correct in situ concentrations of the gaseous components of sediments, but rather the concentrations of gas that remain after core recovery. Although samples for gas analysis are collected almost immediately after sediment cores reach the ship, a significant amount of the gas may be lost because of the decrease in pressure and increase in temperature experienced by the cores. The results of the gas analysis techniques nonetheless provide useful comparisons of the relative amounts and compositions of sedimentary gases at different depths at a single drill site and between drill sites.

REPRESENTATIVE CONCENTRATION PROFILES OF HEADSPACE GAS, CALCIUM CARBONATE, AND ORGANIC CARBON

Significant to high concentrations of residual headspace methane and CO₂ were found in sub-bottom sediments at all of the Leg 175 sites. Carbon dioxide concentrations generally increased quickly with depth in the drill holes, whereas methane concentrations did not begin to increase until interstitial sulfate was depleted. In addition, the odor of H₂S was often noted, especially in the upper parts of the sedimentary sequences, but detectable concentrations (>1ppmv) of this gas were rarely found. Total gas pressures typically became great enough in sediments cored below 10 to 20 mbsf to require perforating core liners to relieve the pressure and prevent excessive core expansion. Nevertheless, gas-expansion pockets developed in many cores. Headspace gas profiles from representative sites in each of the four depositional regimes are described below.

Site 1076: Lower Congo Basin

Concentrations of CaCO₃ are low in Site 1076 sediments. The maximum is 16 wt%, and most sediment samples contain <5 wt% CaCO₃. These generally low concentrations reflect the paucity of coccolith microfossils and the high abundances of opaline and continental clastic material in these sediments. In contrast, total organic carbon (TOC) values are elevated; they range from 0.9 to 4.3 wt% (Fig. 2) and average 2.6 wt%. The organic matter appears to be predominantly marine in origin (see “Organic Geochemistry” section, “Site 1076” chapter, this volume).

A succession of relatively abundant gases exists in sediments from Hole 1076A. Hydrogen sulfide could be detected by its odor, but not by H₂S sensors having a sensitivity of ~1 ppmv, in Cores 175-1076A-3H through 5H (18–39 mbsf). Methane first appears in headspace gas samples from Hole 1076A sediments at 12.5 mbsf. Concentrations rapidly increase and become significant in sediments below 30 mbsf (Fig. 2). Gas pressures became great enough in sediments below Core 175-1076A-15H (138 mbsf) to require perforating the core liner to relieve the pressure and to alleviate core expansion. Analyses of gas in expansion pockets showed that much of this gas was CO₂ (see “Organic Geochemistry” section, “Site 1076” chapter, this volume).

Site 1078: Angola Margin

As in the Lower Congo Basin, concentrations of CaCO₃ are low (Fig. 3). They vary between 11 and 25 wt% in Site 1078 sediments. TOC values range from 1.1 to 5.3 wt% (Fig. 3) and average 2.5 wt%. The organic matter appears to be predominantly marine in origin (see “Summary” section, “Site 1078” chapter, this volume).

As found at Site 1076, a succession of relatively abundant gases exists in sediments from Site 1078. Although hydrogen sulfide could be detected by its odor, it remained below the instrumental detection limit of ~1 ppmv in Cores 175-1078A-1H through 3H (1.5–26.5 mbsf). Methane first appears in headspace gas samples from Site 1078 sediments at 6 mbsf. Concentrations rapidly increase and become significant in sediments between 20 and 35 mbsf, below which they decrease (Fig. 3). Gas pressures became great enough in sediments below Core 175-1078A-4H (36 mbsf) to require perforating the core liner to relieve the pressure and alleviate core expansion. Analyses of expansion pockets showed that most of this gas was CO₂.

Site 1084: Northern Cape Basin Upwelling

Concentrations of CaCO₃ in Site 1084 sediments fluctuate between 0.5 and 69 wt% (Fig. 4). The fluctuations consist of (1) closely

spaced changes related to light–dark color changes and (2) more gradual downhole increases and decreases in concentration. TOC concentrations change in both short-term and longer term patterns (Fig. 4). Dark-colored sediments have higher TOC values than light-colored layers. TOC concentrations also differ in Hole 1084A lithostratigraphic units, averaging 8.2 wt% in Subunit IA, 7.0 wt% in Subunit IB, 4.9 wt% in Subunit IC, 3.4 wt% in Unit II, 4.5 wt% in Unit III, and 2.9 wt% in Unit IV. The organic matter appears to be predominantly marine in origin (see “Organic Geochemistry” section, “Site 1084” chapter, this volume). The high TOC concentrations in the upper 200 mbsf (Fig. 4) are a consequence of the elevated paleoproductivity of the Benguela Current upwelling system.

High concentrations of H₂S, methane, and CO₂ were found in sediments from Site 1084. The odor of H₂S was noted throughout most of the sequence, and detectable concentrations of this gas were found in upper parts of Hole 1084A (see Table 15 in the “Site 1084” chap-

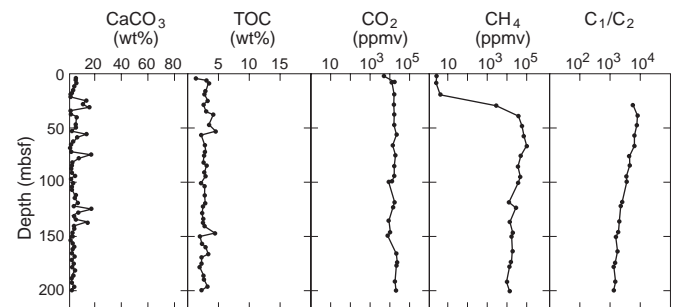


Figure 2. Concentrations of CaCO₃, TOC, and headspace CO₂ and methane in sediments from Site 1076 in the Lower Congo Basin depositional regime. Elevated C₁/C₂ ratios indicate microbial origins for these hydrocarbon gases.

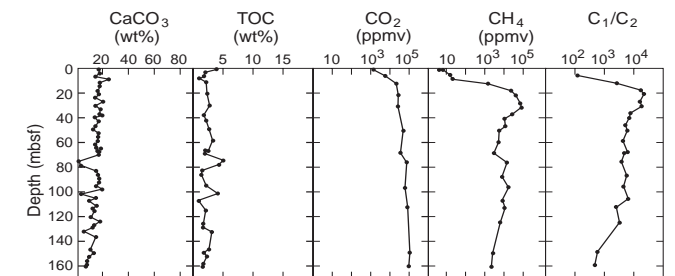


Figure 3. Concentrations of CaCO₃, TOC, and headspace CO₂ and methane in sediments from Site 1078 in the Angola margin depositional regime. Elevated C₁/C₂ ratios indicate microbial origins for these hydrocarbon gases.

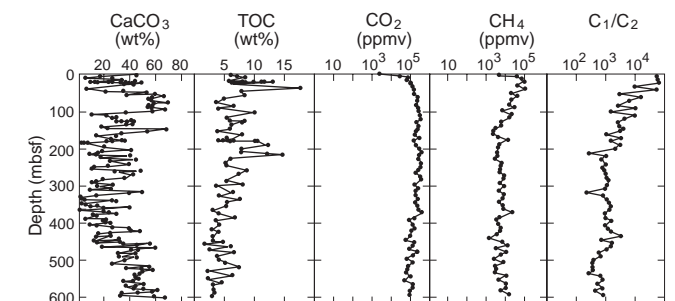


Figure 4. Concentrations of CaCO₃, TOC, and headspace CO₂ and methane in sediments from Site 1084 in the Angola-Namibia upwelling depositional regime. Elevated C₁/C₂ ratios indicate microbial origins for these hydrocarbon gases.

ter, this volume). Much of the sedimentary sequence had an offensive odor, which may have resulted from microbial production of organo-sulfur gases, such as dimethyl sulfide and carbon disulfide, in this sulfur-rich sequence. Methane (C_1) concentrations increase rapidly with depth in headspace gas samples from Hole 1084A sediments. Concentrations become significant in sediments below 6 mbsf (Fig. 4). High methane/ethane (C_1/C_2) ratios (Fig. 4) and the absence of major contributions of higher molecular weight hydrocarbon gases (see Table 15 in the "Site 1084" chapter, this volume) indicate that the gas is microbial, as opposed to thermal, in origin. Total gas pressures became great enough in sediments below Core 175-1084A-2H (6 mbsf) to require perforating the core liner to relieve the pressure and prevent excessive core expansion. The most abundant headspace gas was CO_2 ; concentrations of this gas remained high throughout the 600-m-deep Hole 1084A (Fig. 4).

Site 1085: Benguela Current

Concentrations of $CaCO_3$ are generally high in Site 1085 sediments, varying between 28 and 85 wt% (Fig. 5). The concentrations vary in two ways: (1) closely spaced changes related to light-dark color fluctuations and (2) more gradual downhole increases and decreases. TOC amounts change in both short-term and longer term patterns (Fig. 5). TOC concentrations are low, averaging ~1 wt% over the sedimentary sequence. These TOC values reflect a history of moderate-to-low productivity in the southern portion of the Benguela Current system.

Moderately high amounts of methane and CO_2 were found in sediments from Site 1085 (Fig. 5). Methane first appears in headspace gas samples from Hole 1085A sediments at 17.7 mbsf. Concentrations become significant in sediments below 46 mbsf. High C_1/C_2 ratios (Fig. 5) and the absence of major contributions of higher molecular weight hydrocarbon gases (see "Organic Geochemistry" section, "Site 1085" chapter, this volume) indicate that the gas is microbial, rather than thermal, in origin. The most abundant gas was methane, not CO_2 , as in the other depositional regimes. Headspace concentrations of methane remained high, whereas those of CO_2 gradually diminished with depth in sediments from Hole 1085A (Fig. 5).

DISCUSSION

TOC concentrations of sediments from the 13 Leg 175 drill sites are greater than the average of 0.3 wt% given by McIver (1975) based on Deep Sea Drilling Project (DSDP) Legs 1–33, a value that can be considered representative of typical deep-sea sediments. The elevated TOC concentrations are probably a consequence of the combination of elevated paleoproductivities, which would have delivered abundant organic matter to the sediments, and the high accumulation rates of sediments, which would have improved preservation of the organic matter. Associated variations in $CaCO_3$ concentrations reflect varying combinations of changes in delivery of calcareous material, dilution by noncalcareous components, and carbonate dissolution fueled by oxidation of organic matter.

Source of the gases

Sedimentary gases are elevated at all 13 drill sites on the southwest African margin. Both CO_2 and methane are abundant in the cored sediments. The most likely source of the CO_2 is from oxidation of some of the marine organic matter that is present in the sediments. The evolution of dissolved interstitial CO_2 from oxidation of organic matter involves a sequence of terminal electron acceptors—first interstitial oxygen, followed by nitrate, manganese (IV) oxides, iron (III) oxides, and finally sulfate—in the transition from oxic to suboxic to anoxic sediment conditions (Froelich et al., 1979; Schulz et al., 1994).

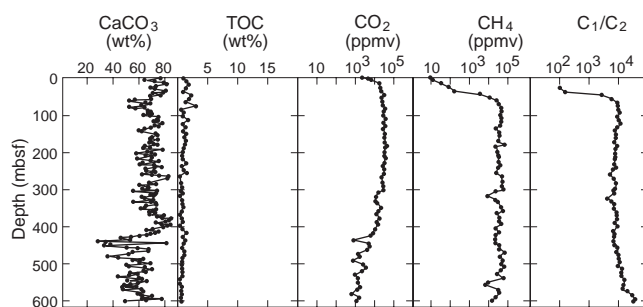
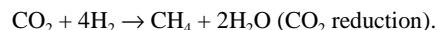
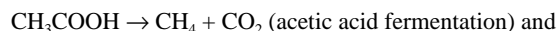


Figure 5. Concentrations of $CaCO_3$, TOC, and headspace CO_2 and methane in sediments from Site 1085 in the Benguela Current depositional regime. Elevated C_1/C_2 ratios indicate microbial origins for these hydrocarbon gases.

Dissolved oxygen and nitrate tend to disappear rapidly with depth in marine sediments; sulfate is then used as a source of oxygen in generating CO_2 . Oxidation continues deeper into the sediments until interstitial sulfate is exhausted. It should be recognized that only a small fraction of sedimentary organic matter needed to be oxidized to markedly increase dissolved interstitial CO_2 levels.

Two sources of the abundant methane are possible. First, hydrocarbon gases from deeper, thermally mature sediments may have migrated into the gas-rich zone. Evidence for migration of methane into porous sediments from deeper sources has been found at Sites 762 and 763 on the Exmouth Plateau, where a thermogenic source exists in underlying Jurassic rocks (Meyers and Snowdon, 1993). Mesozoic sources of thermogenic gas are indeed known on the African margin between the Niger delta and the Walvis Ridge. However, high C_1/C_2 ratios, which are representative of microbial gases (Claypool and Kvenvolden, 1983; Whiticar, 1996), and the absence of major contributions of higher molecular weight hydrocarbon gases (see individual site chapters, this volume) indicate that little, if any, of the gas in the sites drilled during Leg 175 is derived from the thermal degradation of organic matter.

A second possible source of methane, the dominant hydrocarbon gas in these sediments, is in situ formation by methanogenic microorganisms. Methanogenesis becomes important in sediments that lack interstitial sulfate but contain metabolizable organic matter. This process has two stages in which a consortium of microorganisms first converts the various forms of organic matter into short-chain alcohols and acids, CO_2 , and H_2 . In the second stage, some of these products are converted to methane by a metabolically limited group of obligate anaerobic microbes (Mechalas, 1981; Whiticar, 1996). The general reactions that represent the production of methane in the second stages are these:



The reduction of CO_2 to methane is the dominant process in marine sediments (Wiese and Kvenvolden, 1993; Whiticar, 1996).

At all 13 Leg 175 drill sites, a correspondence between the disappearance of interstitial sulfate and the increase in methane concentrations was found (see individual site chapters, this volume). A microbial origin of methane is supported by this observation, inasmuch as Claypool and Kvenvolden (1983) observe that the presence of interstitial sulfate inhibits microbial methanogenesis in marine sediments. Similar in situ microbial production of methane has been inferred for high gas concentrations in Pliocene–Pleistocene sediments from DSDP Site 532 nearby on the Walvis Ridge (Meyers and Brassell, 1985), Sites 897 and 898 on the Iberian Abyssal Plain (Meyers and

Shaw, 1996), and also in middle Miocene sediments from Site 767 in the Celebes Sea (Shipboard Scientific Party, 1990). Moreover, Cragg et al. (1992) report the existence of viable microbes to depths of ~500 mbsf in the sediments of the Japan Sea. The abundance of microbial gases in sediments from Sites 1084 and 1085 suggests the similar presence of viable microbial communities to sub-bottom depths as great as 600 mbsf along the southwest African margin.

The origin of the methane probably involves a reduction mainly of the abundant interstitial CO₂ in the sediments and minor in situ microbial fermentation of marine organic matter. Because these two processes are carried out by distinct microbial populations, the abundance of methane ultimately depends on satisfying the metabolic requirements of both pathways. Comparison of the carbon-isotopic contents of CO₂ and methane in ODP Site 533 sediments has indicated that most of the methane originates from the reduction of CO₂ (Galimov and Kvenvolden, 1983). Inasmuch as the obligate anaerobes involved with CO₂ reduction are particularly metabolically limited (Mechalás, 1981; Whiticar, 1996), this pathway can become blocked, despite an abundance of interstitial CO₂.

Comparison of Gas Profiles and Sediment Carbon Contents

Considerable differences in the concentrations of CaCO₃ and TOC exist in the sediments from the four depositional regimes, yet the gas profiles are similar. For example, CaCO₃ concentrations differ by about a factor of 10 in sediments from Sites 1076 and 1085, whereas the residual CO₂ and methane concentrations are virtually the same (Figs. 2, 5). Similarly, TOC concentrations in Site 1076 sediments are about twice those at Site 1985, yet this difference does not appear in the gas concentrations. The sediments having the highest concentrations of organic carbon, those at Site 1084, also have the highest concentrations of CO₂; this is understandable given that oxidation of organic matter leads to CO₂ production. Surprisingly, these same sediments have the lowest methane concentrations throughout much of the sequence (Fig. 4), which implies that the metabolic requirements of the CO₂-reducing microbes were poorly satisfied at this location. It may be significant that much of the sedimentary sequence from Site 1084 smelled strongly of organo-sulfur compounds, as opposed to simply H₂S. This observation may reflect fundamental biogeochemical differences that limited microbial CO₂ reduction at Site 1084.

Moreover, the general lack of correspondence between concentrations of carbonate carbon and organic carbon and concentrations of CO₂ and methane in sediments from the four depositional regimes implies that only a small percentage of organic matter is converted to gas. For example, even at saturation, methane represents only ~0.1% of the organic matter that is present in unconsolidated sediments (Whiticar, 1996). The limiting factor to microbial gas production is generally not the availability of organic matter, but the availability of terminal electron receptors.

Comparison of Headspace and Gas-Pocket Analyses

Sedimentary sequences from the 13 Leg 175 drill sites typically did not contain enough gas to develop gas-expansion pockets until below the sub-bottom depth where interstitial sulfate was depleted. Concentrations of headspace methane often reached a maximum somewhat deeper than the sulfate depletion depth, but concentrations of headspace CO₂ commonly continued to increase with depth in the sequences (Figs. 2–4). In these patterns, the concentrations of headspace CO₂ and methane were approximately the same. Compositions of gases from expansion pockets were usually similar to those of the headspace gases from the same cores. A significant difference, however, between the compositions of headspace and expansion-pocket gases was found in the sedimentary sequences from the Angola-

Namibia upwelling regime. Methane typically was three to four times more abundant than CO₂ in the gas-pocket compositions of these sediments, whereas methane was at equal or lesser concentrations than CO₂ in the headspace samples.

Several possibilities may contribute to this difference between gas compositions. First, most of the sites in the Angola-Namibia upwelling regime were drilled to 600 m, which is deeper than those in the other depositional regimes. The solubility of methane increases rapidly with increasing pressure (Culberson and McKetta, 1951), which increases with sub-bottom depth. The sediments from deeper in the upwelling regime may have actually had higher in situ concentrations of methane. Second, interstitial alkalinity reaches very high levels in the sediments from Sites 1082 and 1084 (see individual site chapters, this volume). Much of this alkalinity increase involves the addition of CO₂ from organic matter degradation. This gas becomes incorporated into the bicarbonate-dominated inorganic carbon equilibria. When sediment cores are brought onto the *JOIDES Resolution*, in situ pressures are released. If abundant methane is dissolved in sediment pore waters, it bubbles out of solution. Elevated pressures also increase the solubility of CO₂, but incorporation of this gas into the carbonate equilibria delays its exsolution when pressures are released. The period of heating that is part of the headspace procedure compensates for the slower release of CO₂ from solution. The greater proportion of methane in the expansion-pocket gases than in the headspace gases may consequently reflect the difference in the mobilities and solubilities of CO₂ and methane, rather than their true in situ concentrations.

A third possibility exists. The two factors that make the mobilities of sedimentary CO₂ and methane different may systematically bias the headspace procedure results toward lower methane concentrations. Because the plug of sediment that is used in the headspace technique is not collected until the core is cut into 1.5-m sections some 10–15 min after arrival on deck, a significant fraction of the interstitial methane may exsolve, either escaping to the atmosphere in the space between the core and core liner or collecting in the gas pockets, where it is lost when they are punctured to minimize core expansion. A further consequence of this potential biasing of headspace analyses toward lower methane values is that gas-pocket analyses may be simultaneously biased toward higher methane concentrations.

Tests for Presence of Gas Hydrate

Gas hydrate formation can greatly increase the concentration of gases present in sediments above the limit of their solubility in interstitial water. In gas hydrate, water crystallizes into a cubic lattice rather than the hexagonal lattice of pure water. Large volumes of low molecular weight gases—methane, ethane, CO₂, H₂S, and nitrogen—fit into the cubic lattice. Methane is easily accommodated into the three-dimensional framework of water molecules. As much as 170 volumes of methane (at standard temperature and pressure) can theoretically be accommodated by one volume of hydrate (Kvenvolden and McMenamin, 1980). Actual accommodation values commonly are less, as exemplified by hydrate recovered from the Peruvian margin at ODP Sites 685 and 688, in which ~100 volumes of methane evolved from one volume of solid hydrate (Kvenvolden and Kastner, 1990). Gas hydrate forms under specific pressure and temperature combinations that are satisfied at water depths as shallow as 500 m at temperatures of 4° to 6°C (Claypool and Kvenvolden, 1983). The presence of gas hydrate is often inferred from acoustic BSRs in the seabed, and BSRs were detected near some of the planned Leg 175 drill sites during precruise seismic surveys.

The presence of substantial amounts of gas in the Lower Congo Basin and Angola margin depositional regimes was implied by features in the seismic traces made during predrilling site surveys. Drill sites were ultimately selected to avoid what appeared to be gas chimneys, but BSRs were so extensive that they were unavoidable. After

two sites (six holes) had been drilled in which little direct evidence of gas hydrate had been found, a special test was conducted to search for the existence of hydrate layers. Headspace gases were sampled at 3-m intervals between 100 and 130 mbsf at Hole 1077B to detect the presence of methane hydrate that might be responsible for a conspicuous seismic reflector seen at this level. No extraordinary amounts of methane were found; headspace concentrations ranged between 7,000 and 41,000 ppmv. Furthermore, none of the frothing of sediments, the disruption of sediment structures, the frosting of the outside of the core liner, or the dilution of interstitial chloride that accompanies the endothermic decomposition of hydrate and the release of its contents (Kvenvolden and Barnard, 1983) were observed. It was concluded that despite the common occurrence of BSRs, gas hydrate is not strongly developed along this part of the southwest African margin.

A possible alternate explanation for the conspicuous seismic reflectors on this margin is that they represent lenses of dolostone. These rocky layers were encountered at several sites north of the Walvis Ridge, and they presented obstacles to drilling. For example, the two holes at Site 1080 were terminated prematurely at 37 and 52 mbsf, respectively, because of drilling refusal from these layers. The dolostones could be formed by precipitation of diagenetic dolomite as a result of alkalinity increases that follow in situ oxidation of organic matter, with consequent oversaturation of interstitial bicarbonate.

SUMMARY

Concentrations of methane and CO₂ inferred from headspace analyses are significant to high in sub-bottom sediments in the four depositional regimes on the southwest African margin that are encompassed by the 13 Leg 175 drill sites. Residual CO₂ concentrations generally increased quickly with depth in the cores, whereas methane concentrations did not begin to increase until interstitial sulfate was depleted, usually within a few tens of meters below the seafloor. The origins of these gases appear to be from in situ microbial production. Carbon dioxide is released during the degradation of organic matter; methane is produced primarily by microbial reduction of CO₂. No evidence of migration of hydrocarbon gases into the drilled sequences from deeper, thermally mature sediments was found.

Little correspondence exists between concentrations of the microbial gases and the availability of either organic carbon or carbonate carbon in these sedimentary sequences. This lack of correspondence indicates that only a small fraction of the available carbon is converted to gaseous components by microbial processes.

Despite the widespread occurrence of strong bottom-simulating seismic reflectors along the Congo and Angola margins, physical evidence of gas hydrate layers was not found. Dolostone lenses may be the cause of the seismic reflectors.

Results of analyses of headspace gases and of expansion-pocket gases generally agreed well, but systematic differences were observed at Sites 1082, 1083, and 1084. The greater mobility of methane is probably responsible for the elevated concentrations of this gas that were measured in expansion pockets from these three sites.

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