

### 3. INTERSTITIAL WATER STUDIES, LEG 15 – DISSOLVED GASES AT SITE 147<sup>1</sup>

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#### ABSTRACT

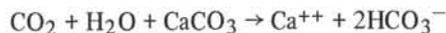
Ten gas pocket samples were collected at DSDP Site 147 in the Cariaco Trench. Gas chromatographic analysis showed them to range in concentration as follows: 85 to 95% CH<sub>4</sub>; 1 to 13% CO<sub>2</sub>; 1 to 2% H<sub>2</sub>O; 0 to 3% N<sub>2</sub>; and 0.004 to 0.05% C<sub>2</sub>H<sub>6</sub>. Gas pocket *p*CO<sub>2</sub> is consistent with punch-in *p*H measurements within 0.2 *p*H units. Conversion of gas pocket data to in situ concentrations is hindered by the difficulty in determining the ratio of gas pocket volume to interstitial water volume. Development of a device for collecting samples at the in situ pressure would eliminate this problem. Visual estimates of gas content do not resolve the anticipated methane increase with depth. The best estimate of in situ concentrations in the interstitial water is [CH<sub>4</sub>]<sup>o</sup> = 20 mmol ±50%, [C<sub>2</sub>H<sub>6</sub>]<sup>o</sup> = 1 to 10 mmol/l ±100%, and [N<sub>2</sub>]<sup>o</sup> = 0.7 to 0.0 mmol/l ±50%. This corresponds to the conversion of about 1.5% of the organic carbon into methane.

Zobell (1947) has shown that H<sub>2</sub> is a likely product in the anaerobic decomposition of organic matter by bacteria, but that it is rapidly utilized by other bacteria as an electron source. Assuming this to be true, the reactions N<sub>2</sub> + 3H<sub>2</sub> → 2NH<sub>3</sub> and Ca<sup>++</sup> + 2 HCO<sub>3</sub><sup>-</sup> + 4H<sub>2</sub> → CaCO<sub>3</sub> + 3H<sub>2</sub>O + CH<sub>4</sub> should occur, accounting for observed decreases in alkalinity and dissolved nitrogen. It is possible that the dissolved nitrogen decrease may be due to extensive gas loss and consequently the best estimates of [C<sub>2</sub>H<sub>6</sub>]<sup>o</sup> and [CH<sub>4</sub>]<sup>o</sup> are each an order of magnitude low. The ethane/methane ratio in the sediment is lower than in the overlying water column but increases with depth. This is attributed to different mechanisms of production in the two regions.

#### INTRODUCTION

The Cariaco Trench, an elongated depression off the coast of Venezuela, is surrounded by a sill at 150 meters depth which inhibits exchange with the deep ocean. This restricted circulation, coupled with high productivity in the coastal waters, has created anoxic conditions in the deep waters (Richards, 1960), and has resulted in the preservation of large amounts of organic debris in the sediment, typically 2 to 5% carbon (dry weight) (T. Edgar, personal communication). During diagenesis, bacteria attack this debris, producing a plethora of compounds, including CO<sub>2</sub> and probably H<sub>2</sub>, which can then be used by other bacteria, first to reduce SO<sub>4</sub><sup>=</sup> to S<sup>=</sup>, and then to reduce CO<sub>2</sub> to CH<sub>4</sub> (Zobell, 1947; Thimann, 1963). Net

production of CO<sub>2</sub> in the upper region of the sediment drives the reaction



and alkalinity increases down to 100 meters. Significant methane production does not occur above 40 meters, the depth at which gas pockets begin to appear.

When cores were taken at Site 147, the pressure reduction from in situ to one atm. allowed the methane to form gas pockets. Dissolved CO<sub>2</sub>, N<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> equilibrated with this gas phase. Samples were collected using the Horowitz-Takahashi device described in detail elsewhere (Horowitz et al., this volume). Briefly, the procedure was to punch a needle through the plastic core liner, measure the gas pocket pressure, and collect a sample in an evacuated flask. These samples were returned to Lamont-Doherty Geological Observatory for gas chromatographic analysis. An aliquot of these samples was sent to Graeme Lyon in New Zealand for isotopic analysis of C<sup>13</sup>, O<sup>18</sup>, and deuterium (Lyon, this volume).

<sup>1</sup>Lamont-Doherty Geological Observatory Contribution No. 1833.

## ANALYTICAL PROCEDURE

Analyses were performed using a gas chromatograph with dual thermal conductivity detectors (Varian Aerograph model 1720) and a potentiometric recorder with disk integrator (Varian Aerograph model 20). Since the gas composition was unknown initially, several different sets of column operating conditions were used (Table 1) to effect component separations. Conditions 4 to 5 were used for one sample (147B-9-4) and when the Ar/O<sub>2</sub> ratio was found to be close to the atmospheric value, the remaining samples were analyzed using conditions 1, 2, and 3. Individual components detected were O<sub>2</sub> (including Ar), N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and H<sub>2</sub>O. Response of the detector to the total of these gases was 100±1% of detector response to dry air standards run simultaneously. Since 1% is about the sum of precisions of sample size and of peak area measurement, the amount of undetected components is probably much less than 1%. Analytical conditions were selected to detect H<sub>2</sub>, CO, N<sub>2</sub>O, and H<sub>2</sub>S. Since none of these were observed, upper limits can be placed on their abundance: H<sub>2</sub> and CO, 0.05%; N<sub>2</sub>O, 0.1%; and H<sub>2</sub>S, 0.5%. Detector sensitivity to CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub> was determined by using standards supplied by the Matheson Company (purity >99.5%). Detector response to each was found to be linear to better than 2% over the observed sample concentration ranges. Dry air was used to calibrate the detector for N<sub>2</sub> and O<sub>2</sub> + Ar. Air with 2.9% H<sub>2</sub>O was used to calibrate for H<sub>2</sub>O.

The composition of the gas pockets is listed in Table 2, along with estimated random and systematic errors. All oxygen detected was attributed to contamination of the sample with air during collection and analysis. This estimate of contamination was used to convert the total N<sub>2</sub> measured into gas pocket N<sub>2</sub>. Although air contamination is usually only about 3%, it introduces a large uncertainty in the gas pocket N<sub>2</sub> because the latter quantity is small.

## DISCUSSION

The general features of Table 2 indicate that the gas pockets are primarily methane and are similar in composition to a variety of natural gases and marsh gases (Zobell, 1947). The CO<sub>2</sub> fraction rises to a maximum of about 12% in the 83 to 128 meter interval and then decreases, reflecting the changes in alkalinity (Gieskes, this volume) and CO<sub>2</sub> (Hammond, this volume). Nitrogen decreases with depth, which could be due to either in situ destruction or increasing dilution with methane. The ethane systematically increases with depth.

The total gas pressure of each pocket is listed in Table 3 and can be used to calculate partial gas pressures. The vapor pressure of water can be used to estimate sampling temperature (Table 3). The scatter is primarily due to the unfavorable shape of the water peak, which makes its area difficult to measure accurately, but the median of 17°C seems reasonable as it is the same as the temperature of bottom water in the trench (Richards, 1960).

pCO<sub>2</sub> (Table 3 and Figure 1) and the titration alkalinity (Gieskes, this volume) were used to calculate the pH of the

pore water. Details of the calculation are given elsewhere (Hammond, this volume), but when temperature corrections were made, calculated results were consistent with punch-in electrode measurements made in nearby regions (Table 3). This is significant because it establishes the reliability of punch-in electrode measurements as better than 0.2 pH units. The pCO<sub>2</sub> profile shows a maximum near 100 meters which corresponds with the alkalinity maximum and may be interpreted as the boundary between regions of net CO<sub>2</sub> production (above) and net CO<sub>2</sub> destruction (below).

The best observation that can be made about pCH<sub>4</sub> (Figure 2 and Table 3) is that it is constant with depth at 1.2 atm pressure. The profile is probably mainly a function of the confining pressure of the soft sediment plugs around each sample in each section of core liner and is not a reliable indicator of the gas content of a given region.

The pressure, temperature, and composition in each gas pocket are known, but to calculate the in situ gas concentrations in the interstitial water requires determination of V<sub>R</sub>, the ratio of gas pocket volume to pore water volume. Visual estimates at the time of sampling were that gas constituted 20% of the core by volume. The porosity is nearly constant at 70% (T. Edgar, personal communication). Thus, assuming that the gas is totally dissolved originally and that the sediment plus water volume comprises 80% of the core on shipboard

$$V_R = \frac{\text{gas volume}}{(\text{sediment} + \text{water volume}) \times \text{porosity}} = \frac{20\%}{80\% \times 70\%} = 0.36$$

It is, however, unlikely that V<sub>R</sub> is constant, as the gas content can be expected to increase with depth. A method is needed to determine V<sub>R</sub> for each sample.

N<sub>2</sub>, molecular nitrogen, is conservative in seawater. If this is also true in sediment, and the in situ [N<sub>2</sub>]<sup>o</sup> can be estimated, gas pocket p<sub>N<sub>2</sub></sub> can be used to calculate V<sub>R</sub> for each sample:

$$1) V_R = RT \frac{[N_2]^o}{p_{N_2}} - \frac{17^\circ}{\alpha_{N_2}}$$

where

R = ideal gas constant

T = 290°K

α<sub>N<sub>2</sub></sub> = solubility of nitrogen

The first term in the parentheses dominates the right side of the equation and is the most difficult to estimate.

The present temperature and salinity in the deep water of the Cariaco Trench are 17°C and 36‰ (Richards, 1960). Dissolved nitrogen should be very close to solubility equilibrium with the atmosphere at these conditions, although it has been suggested (Richards and Vaccaro, 1956; Richards and Benson, 1961) that [N<sub>2</sub>]<sup>o</sup> may be increased up to 3% by in situ bacterial reduction of nitrate. Since paleotemperatures and salinities in this basin are unknown, the solubility equilibrium value for present conditions of 4.44 × 10<sup>-4</sup> mol/l (Weiss, 1970) is the best choice for [N<sub>2</sub>]<sup>o</sup>. It is important to point out that oxygen

TABLE 1  
Column Operation Parameters

| No. | Packing Material                    | Size      | Temperature (°C) | He Carrier Flow Rate (scc/min) | Elution Order   |
|-----|-------------------------------------|-----------|------------------|--------------------------------|---|
| 1   | Molecular Sieve No. 5A (30/50 mesh) | 4½' × ¼'' | 105              | 30                             | O <sub>2</sub> + Ar, N <sub>2</sub> , CH <sub>4</sub>                                     |
| 2   | Porapak Q (150-200 mesh)            | 5' × ¼''  | 50 <sup>a</sup>  | 55                             | Air, CH <sub>4</sub> , CO <sub>2</sub>  |
| 3   | Porapak Q (150-200 mesh)            | 5' × ¼''  | 105 <sup>a</sup> | 55                             | Air, CH <sub>4</sub> , CO <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> , H <sub>2</sub> O |
| 4   | Porapak Q (150-200 mesh)            | 5' × ¼''  | 0                | 85                             | Air, CH <sub>4</sub> , CO <sub>2</sub>  |
| 5   | Porapak Q (150-200 mesh)            | 9' × ¼''  | -78              | 135                            | N <sub>2</sub> , O <sub>2</sub> , Ar, CH <sub>4</sub>                                     |

<sup>a</sup>Programmed at 10°C/minute after CH<sub>4</sub> peak.

TABLE 2  
Gas Pocket Composition

| Sample                | Depth (m) | Air Contamination (%) | Normalized to 100%  |                     |                      |                                   |                    | N <sub>2</sub> Error as ΔN <sub>2</sub> /N <sub>2</sub> (%) |
|-----------------------|-----------|-----------------------|---------------------|---------------------|----------------------|-----------------------------------|--------------------|---|
|                       |           |                       | CH <sub>4</sub> (%) | CO <sub>2</sub> (%) | H <sub>2</sub> O (%) | C <sub>2</sub> H <sub>6</sub> (%) | N <sub>2</sub> (%) |   |
| 147-6-4               | 47        | 5.7                   | 95.4                | 1.16                | 0.9                  | 0.004                             | 2.45               | 7   |
| 147B-6-2              | 51        | 3.1                   | 92.5                | 4.61                | 1.6                  | 0.023                             | 1.17               | 8   |
| 147B-7-4              | 63        | 3.5                   | 92.7                | 5.57                | 1.1                  | 0.012                             | 0.53               | 30  |
| 147-10-3              | 82        | 3.1                   | 91.3                | 6.84                | 1.5                  | 0.015                             | 0.35               | 29  |
| 147B-9-4 <sup>a</sup> | 83        | 3.4                   | 86.1                | 13.5                | —                    | —                                 | 0.44               | 57  |
| 147B-11-3             | 100       | 3.5                   | 85.8                | 12.3                | 1.8                  | 0.014                             | 0.16               | 63  |
| 147-14-3 <sup>a</sup> | 118       | 3.3                   | 87.8                | 11.9                | —                    | 0.020                             | 0.27               | 32  |
| 147C-2-2              | 128       | 4.8                   | 85.9                | 12.8                | 1.1                  | 0.025                             | 0.16               | 100   |
| 147C-4-4              | 148       | 3.3                   | 87.5                | 10.6                | 1.4                  | 0.034                             | 0.42               | 23  |
| 147C-7-3              | 175       | 2.6                   | 91.8                | 6.70                | 1.4                  | 0.047                             | 0.07               | 170   |

Error as

$\frac{\Delta \text{ gas}}{\text{ gas}}$  (%)

|             |   |   |    |    |
|-------------|---|---|----|----|
| Random      | 2 | 3 | 20 | 30 |
| Calibration | 2 | 3 | 10 | 20 |

<sup>a</sup>Calculated on a water-free basis.

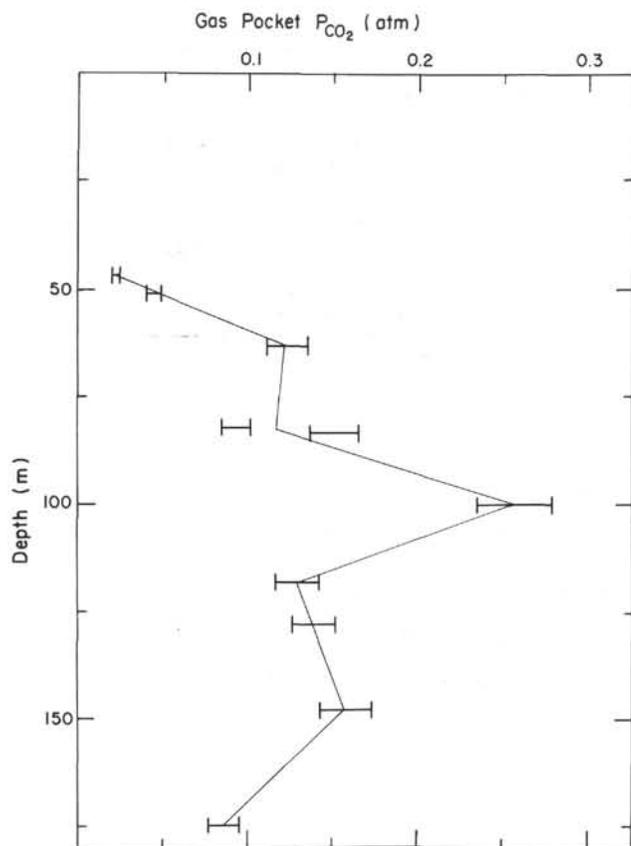
TABLE 3  
Gas Pocket Partial Pressures

| Sample    | Depth (m) | Gas Pocket Pressure (atm) | pH <sub>2</sub> O (mm Hg) | T <sup>c</sup> (°C) | pCO <sub>2</sub> × 10 <sup>3</sup> (atm) | Calc. pH (25°C) | Meas. pH (25°C) | pCH <sub>4</sub> (atm) | pN <sub>2</sub> × 10 <sup>3</sup> (atm) | V <sub>R</sub> <sup>b</sup> | [CH <sub>4</sub> ] <sup>a,b</sup> (mmol/l) | ρCH <sub>4</sub> <sup>a,b</sup> (atm) |
|-----------|-----------|---------------------------|---------------------------|---------------------|--|-----------------|-----------------|------------------------|---|-----------------------------|--|---------------------------------------|
| 147-6-4   | 47        | 1.87                      | 13                        | 15                  | 21.7                                     | 7.14            |                 | 1.79                   | 46.                                     | 0.22                        | 19   | 16                                    |
| 147B-6-2  | 51        | 0.96                      | 12                        | 14                  | 44.3                                     | 6.84            | 7.04            | .89                    | 11.                                     | 0.9                         | 36   | 31                                    |
| 147B-7-4  | 63        | 2.21                      | 19                        | 22                  | 123.                                     | 6.75            | 6.77            | 2.05                   | 12.                                     | 0.9                         | 81   | 86                                    |
| 147-10-3  | 82        | 1.36                      | 15                        | 18                  | 93.                                      | 6.96            | 6.65            | 1.24                   | 4.8                                     | 2.2                         | 116  | 144                                   |
| 147B-9-4  | 83        | 1.12                      | —                         | —                   | 151.                                     | 6.75            | 6.71            | 0.96                   | 4.9                                     | 2.2                         | 89   | 99                                    |
| 147B-11-3 | 100       | 2.08                      | 29                        | 29                  | 256.                                     | 6.61            | 6.73            | 1.78                   | 3.3                                     | 3.3                         | 250  | 420                                   |
| 147-14-3  | 118       | 1.09                      | —                         | —                   | 130.                                     | 6.89            |                 | 0.96                   | 3.0                                     | 3.6                         | 150  | 250                                   |
| 147C-2-2  | 128       | 1.09                      | 9                         | 11                  | 139.                                     | 6.85            |                 | 0.94                   | 1.7                                     | 6.2                         | 240  | 400                                   |
| 147C-4-4  | 148       | 1.50                      | 16                        | 19                  | 159                                      | 6.77            |                 | 1.31                   | 6.2                                     | 1.7                         | 96   | 110                                   |
| 147C-7-3  | 175       | 1.29                      | 13                        | 16                  | 86.5                                     | 6.92            |                 | 1.18                   | 0.9                                     | 12.                         | 600  | 1000                                  |
| Median    |           | 1.33                      | 17                        |                     |  |                 |                 | 1.2                    |   | 2.2                         |  |                                       |

<sup>a</sup>Represents in situ quantity.

<sup>b</sup>Assuming N<sub>2</sub> is conservative.

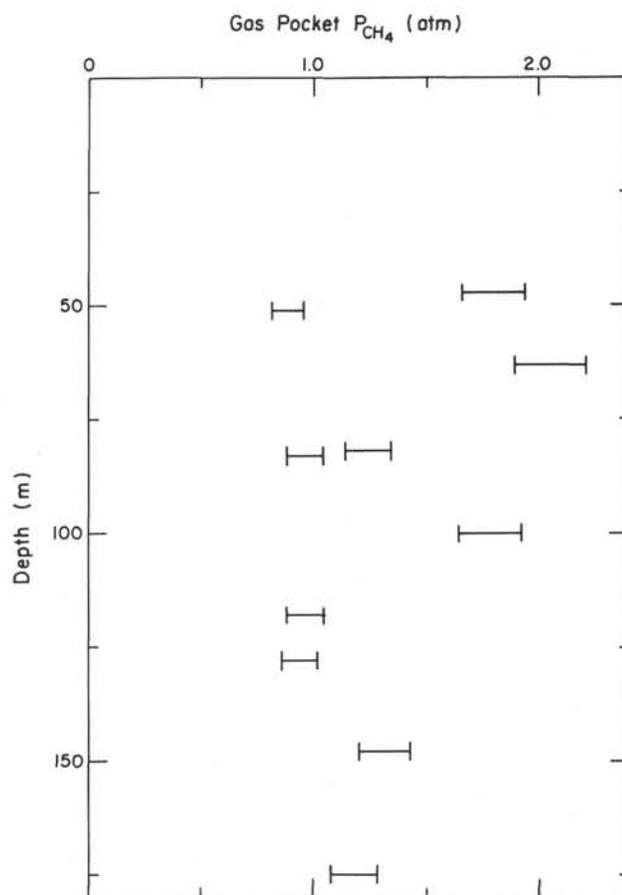
<sup>c</sup>Gas temperature calculated from pH<sub>2</sub>O.

Figure 1. Gas pocket  $p_{CO_2}$ .

isotope measurements are forams indicate that at no time in the past 800,000 years has the surface Caribbean been warmer than  $30^\circ\text{C}$  (Broecker and van Donk, 1970). Nitrogen is only 20% less soluble at this temperature than at  $17^\circ$ . Thus, the  $[N_2]^\circ$  selected should have a maximum error of 20%.

The error in each total gas pocket pressure measurement is estimated at 5% and so the error in  $p_{N_2}$  (Figure 3) is essentially the fractional error in gas pocket percent  $N_2$  ( $\Delta N_2/N_2$  in Table 2) which ranges between 7 and 100%, generally increasing with depth. This error and the error in  $[N_2]^\circ$  indicate that the  $V_R$  calculated should be no more than 50% off in the upper part of the hole and 100% off for most of the lower part of the hole.

Using  $p_{N_2}$  (Table 3) and equation (1),  $V_R$  was calculated for each sample (Table 3) and found to be far greater than the estimated value of 0.35. A 50% error in the visual estimate of gas volume could make the observed  $V_R = 0.6$ , still only about one-third the minimum value permitted by the maximum error in  $[N_2]/p_{N_2}$ . Below 80 meters, the two methods of estimating  $V_R$  differ by a factor of about 10, implying either roughly 90% of the gas was lost during drilling and recovery or  $[N_2]$  is not a conservative property of sediment. The latter explanation seems more likely.

Figure 2. Gas pocket  $p_{CH_4}$ .

If nitrogen is conservative and gas loss occurred, the in situ  $[CH_4]^\circ$  can still be calculated from  $p_{CH_4}$ ,  $T$ , and  $V_R$  by rearranging equation (1)

$$[CH_4]^\circ = p_{CH_4} \frac{V_R}{RT} + \frac{17^\circ}{\alpha_{CH_4}}$$

Results appear in Table 3. Culberson and McKetta (1951) measured the solubility of methane in distilled water as a function of pressure. At one atm, the solubility of  $N_2$ , Ar, and  $CO_2$  in seawater of  $35^\circ/_{\infty}$  salinity is 20% less than that in distilled water (Weiss, 1970). Applying the same "salting out" effect to methane solubility allows calculation of the in situ  $p_{CH_4}^\circ$ . The total hydrostatic pressure at 80 meters in the sediment (960 m below sea level) is about 120 atm. The gas loss hypothesis predicts that below this point, interstitial water is saturated or supersaturated with methane in situ. Water saturated with methane at 120 atm should release a gas phase 1.6 times its volume when the pressure is lowered to 1.5 atm. This implies that the gas volume of the core should have been roughly 80%, about four times what was observed. Disturbance during drilling could have caused bubble formation and some gas loss, but when the core liner captures the sediment and is raised, gas

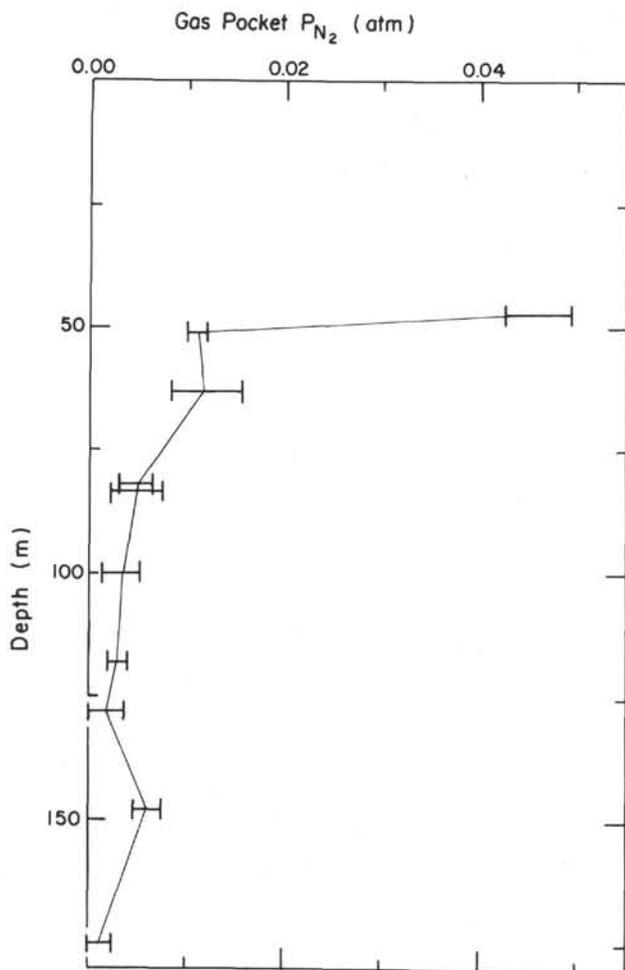
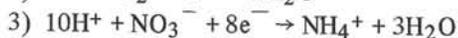
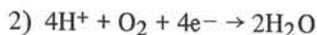


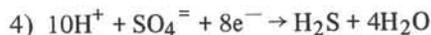
Figure 3. Gas pocket  $p_{N_2}$ .

bubbles which form subsequently should be trapped by the plugs of sediment surrounding them. Perhaps this gas could have been lost during core recovery, but it is hard to conceive a gas pocket which could form during recovery, bleed 75% of its volume, and then stop, remaining pressurized at 1.5 atm. Excessive gas loss cannot be absolutely ruled out by this argument, but it seems unlikely.

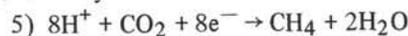
The second possibility is that  $[N_2]$  is not conservative in strongly reducing sediments. Zobell (1947) has shown that  $H_2$  is produced from a variety of organic substrates by several types of anaerobic bacteria found in petroleum and marine sediments.  $H_2$  can be rapidly utilized by other bacteria as an electron source. Treating the problem as one of oxidation reduction (Stumm and Morgan, 1967), as hydrogen of other electron sources are added to the depositional environment,



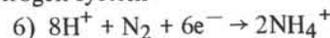
completely remove  $O_2$  and  $NO_3^-$  from Cariaco Trench deep water. In the upper 5 meters of the sediment,  $SO_4^{2-}$  is completely reduced:



The formation of methane below 40 meters in the sediment by the reaction



indicates the environment has become highly reducing.  $pe$ , the negative log of electron activity reaches  $-4.20$  (for  $p_{eO_2} = 0.093$  atm; alkalinity = 28.5 meq/kg (Gieskes, this volume);  $[CH_4] = 20$  mmol/l (Table 4) at 82 meters. If the nitrogen system



is in equilibrium with the carbon system, the  $[N_2]/[NH_4^+]^2$  ratio should be  $2.6 \times 10^{-10}$ , or  $[N_2] = 1 \times 10^{-11}$  mmol/l. Although it is unlikely that equilibrium conditions prevail, thermodynamics predicts that reaction 6 should accompany reaction 5 if a suitable metabolic pathway exists as a catalyst. Thimann (1963) cites evidence that anaerobic bacteria of the genus *Clostridium*, among others, can form ammonia from nitrogen and hydrogen, and Zelitch (1951) has shown that *Cl. Pasteurianum* fixed  $N_2$  in the presence of  $NH_3$ . If this occurred, it is masked by amino acid decomposition, since  $[NH_3]$  increases from 2.7 mmol/l at 5 meters to 3.4 mmol/l at 56 meters to 6.4 mmol/l at 84 meters (Gieskes, this volume).  $4.4 \times 10^{-4}$  mol/l of  $N_2$  would produce only 0.9 mmol/l of  $NH_3$ . It appears, therefore, that  $[N_2]$  is not conservative in strongly reducing environments due to its consumption by bacteria.

It is interesting to note that significant quantities of methane are not produced in sediments from Sites 147 and 148 until all sulfate is utilized (Jaw-Long Tsou, personal communication about observations on anoxically stored sediment samples). The redox potentials may actually reflect the order in which reactions 2 to 6 occur. This is consistent with the  $p_{N_2}$  data which shows a sharp decrease between 40 and 80 meters, the same region in which reaction 5 becomes important (as indicated by the appearance of gas pockets).

Since  $[N_2]$  seems unsuitable as an internal standard, the best assumption that can be made is to choose  $V_R$  as constant at 0.35. This is probably not true and has the unfortunate consequence that the calculated  $[CH_4]^\circ$  will be approximately constant. It is likely that  $V_R$  may increase by a factor of about two, a change which cannot be resolved by visual observations. The in situ concentrations are listed in Table 4 and can be compared with dissolved gas concentrations in deep water of the trench.

The sulfate data (Sayles et al. and Presley et al., this volume) indicate that pore water may be contaminated with 5 to 10% seawater. This would explain the  $[N_2]^\circ$  observed below 80 meters. The high  $[N_2]^\circ$  at 46 meters indicates  $V_R$  probably is less than 0.35 in this part of the hole. The  $[N_2]^\circ$  profile should probably show seawater values down to about 40 meters and then a rapid drop to zero at about 80 meters, as the redox potential becomes more negative.

The mechanism of methane formation is difficult to characterize in these sediments. Probably most carbohydrates and fatty acids are broken down in the water

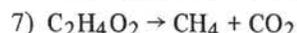
TABLE 4  
In Situ Gas Concentrations for  $V_R = 0.35$

| Sample                       | Depth (m) | [CH <sub>4</sub> ] <sup>a</sup> (mmol/l) | <i>p</i> CH <sub>4</sub> <sup>a</sup> (atm) | [N <sub>2</sub> ] <sup>a</sup> (mmol/l) | [C <sub>2</sub> H <sub>6</sub> ] <sup>a</sup> (μmol/l) | $\frac{[C_2H_6]}{[CH_4]} \times 10^4$ |
|------------------------------|-----------|--|---|---|--|---------------------------------------|
| 147-6-4                      | 47        | 28                                       | 24  | 0.70                                    | 1.   | 0.4                                   |
| 147B-6-2                     | 51        | 14                                       | 12  | 0.17                                    | 3.5  | 2.5                                   |
| 147B-7-4                     | 63        | 32                                       | 27  | 0.18                                    | 4.3  | 1.3                                   |
| 147-10-3                     | 82        | 20                                       | 17  | 0.07                                    | 3.2  | 1.6                                   |
| 147B-9-4                     | 83        | 15                                       | 12  | 0.07                                    | —  | —                                     |
| 147B-11-3                    | 100       | 28                                       | 24  | 0.05                                    | 4.5  | 1.6                                   |
| 147-14-3                     | 118       | 15                                       | 12  | 0.05                                    | 3.5  | 2.3                                   |
| 147C-2-2                     | 128       | 14                                       | 12  | 0.03                                    | 4.1  | 2.9                                   |
| 147C-4-4                     | 148       | 21                                       | 17  | 0.09                                    | 8.2  | 3.9                                   |
| 147C-7-3                     | 175       | 19                                       | 16  | 0.01                                    | 9.7  | 5.1                                   |
| Cariaco Basin:<br>Deep Water |           | 0.007 <sup>b</sup>                       |   | 0.44                                    | 0.003 <sup>b</sup>                                     | 3.6                                   |

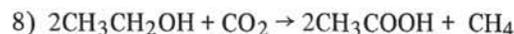
<sup>a</sup>Represents in situ quantity.

<sup>†</sup>Lamontagne et al., 1972.

column and the dominant organic materials in the sediment are cellulose (approximately C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) and some protein. It is deceiving to write the reaction



because there is no evidence that the bacterial degradation is complete. Initial degradation should occur at functional groups, such as OH on cellulose, where the bacteria can attack in the presence of CO<sub>2</sub> to liberate CH<sub>4</sub>. The fermentation reaction,

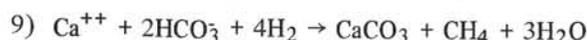


$$\Delta F \approx -4 \text{ kcal/mol}$$

utilized by *Methanobacterium omelianski* (Doelle, 1969), is an example of this type of degradation.

Zobell (1947) shows that some marine anaerobes attack cellulose and produce H<sub>2</sub>. The mechanism of this attack is unknown, but pH of 5.5 to 9.2 and redox potentials less than -0.05 volts provide favorable conditions. Reactions 2 to 6 might all have been written with organic material as the hydrogen source, omitting the likely intermediate H<sub>2</sub>. Regardless of the details of the process, it seems likely that most methane is produced by the reduction of CO<sub>2</sub> by bacteria that employ reactions similar to 8 or by hydrogen production plus reaction 5. The approximate isotopic equilibrium observed in reaction 5 and the extremely light  $\delta D = -178^\circ/\text{‰}$  observed by Lyon (this volume) are consistent with this hypothesis.

At Site 147, alkalinity decreases by about 8 meq/kg between 100 and 175 meters. Where methane production exceeds CO<sub>2</sub> production, reaction 5 can occur as



(I. Kaplan, personal communication). [CH<sub>4</sub>]<sup>o</sup> (Table 4) is sufficiently abundant (20 mmol/l) to suggest reaction 9 may have caused the alkalinity decrease, but the lack of resolution in  $V_R$  precludes definite conclusions.

The ethane/methane ratio in the sediment is smaller than in the deep water (Lamontagne et al., 1972), although both compounds are present in greater abundance. This may

reflect different mechanisms of production. In deep water, C<sub>2</sub>H<sub>6</sub> is a by-product of the breakdown of complex molecules, while in sediments, ethane may be produced as a by-product of carbon dioxide reduction. It should be a more favored product as the demand for hydrogen increases or the hydrogen supply decreases.

## CONCLUSIONS

Several useful conclusions have been extracted from the gas pocket data:

1) The consistency of gas pocket *p*CO<sub>2</sub> and punch-in pH measurements establishes the reliability of the latter as better than 0.2 pH units.

2) CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O compose 100±1% of the samples. H<sub>2</sub> is significantly absent or in low abundance, although it is expected as a major product in the bacterial decomposition of organic matter. Its absence is attributed to the occurrence of reactions 2 to 6, and it may be that hydrogen production is the rate-limiting step in methane production. Methane is probably produced by bacterial reduction of CO<sub>2</sub>. Assuming the sediment to be 2% organic carbon, sediment density 2.0 g/cc, porosity 70%, and [CH<sub>4</sub>]<sup>o</sup> 20 mmol/l indicates roughly 1.5% of the organic carbon is converted to methane.

3) Roughly 90% of the anticipated nitrogen is missing from gas pockets below 80 meters. While excessive gas loss cannot be definitively ruled out as the explanation for this, it is more likely that nitrogen is not conservative in strongly reducing sediments and is converted to ammonia through bacterial metabolic pathways.

4) A gaseous tracer in the interstitial water is needed to determine the ratio of gas pocket volume to water volume and define the anticipated increase in methane content with depth. Ne<sup>20</sup> might be useful if extreme care was taken to avoid air contamination during sampling. A better approach would be to develop a sampler which would confine sediment and gas at the in situ pressure during retrieval, eliminating this difficulty and the problem of gas loss. In the absence of such a tracer or special sampler, the approximation must be made that [CH<sub>4</sub>]<sup>o</sup> may increase by

a factor of about two between 40 and 175 meters in the sediment but is roughly uniform at 20 mmol/l.

5) Although the methane profile cannot be clearly defined, CH<sub>4</sub> is sufficiently abundant (20 mmol/l) to suggest that reaction 9 occurs, causing the alkalinity decrease (8 meq/l) observed below 100 meters at Site 147. This may also occur below 70 meters at Site 148. Reaction 9 is probably not important until all [SO<sub>4</sub><sup>2-</sup>] is utilized by reaction 4 which competes for H<sub>2</sub>.

6) The ethane/methane ratio in the sediment is lower than in the overlying water column, but increases with depth. This is attributed to two different ethane production mechanisms.

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