# Methane in marine sediments

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**Abstract**—Interstitial methane profiles from six sediment cores taken on the slope and abyssal plain of the Gulf of Mexico can be explained by simple kinetic modeling. Methane is apparently produced at a constant rate and microbially consumed in the sulfate-reducing zone. Rates of production and consumption are estimated from best-fit solutions to a steady-state diagenetic equation. Production and consumption balance to form uniform concentrations of 5 to $10 \, \mu l \, l^{-1}$ in the first few meters of slope and abyssal sediments. Effects of upward diffusion from large accumulations of methane in sulfate-free zones deeper than about 10 m are not detectable.

## INTRODUCTION

HIGH concentrations of methane have been measured in sediments of estuaries, marshes, river deltas, and isolated marine basins (EMERY and HOGGAN, 1958; REEBURGH, 1969; REEBURGH and HEGGIE, 1974; WHELAN, 1974; MARTENS and BERNER, 1974; BARNES and GOLDBERG, 1976; REEBURGH, 1976; MARTENS and BERNER, 1977). These accumulations are generally found below the depth where microorganisms have effectively reduced all the interstitial sulfate to sulfide. Except for a thin layer of oxygenated surface sediment, the region above this sulfate-free zone is generally termed the 'sulfate-reducing' zone.

Two basic questions have been raised from investigations of methane in marine sediments. These are:

1. Is methane produced in the sulfate-reducing zone?
2. Is methane consumed in the sulfate-reducing zone?

CLAYPOOL and KAPLAN (1974) concluded from relative energy-yield calculations that methane-producing bacteria should not be active in the presence of dissolved sulfate. MARTENS and BERNER (1977) supported this view using measured methane and sulfate distributions, concluding that methane is most likely produced only in the absence of dissolved sulfate and is consumed in the sulfate-reducing zone upon diffusing upward.

Several other investigators have also observed this apparent consumption. The upward-concave methane profiles in sediments observed by BARNES and GOLDBERG (1976) and REEBURGH and HEGGIE (1977) as well as methane distributions in the Cariaco Trench (REEBURGH, 1976) can best be explained by the postulation of a methane sink in these anaerobic, sulfate-reducing environments. A likely removal process is oxidation by the sulfate-reducing bacteria. Sulfate reducers capable of oxidizing methane and other hydrocarbons using lactate as the principle carbon source have been cultured by DAVIS and YARBROUGH (1966). In contrast, SOROKIN (1957) could not detect methane consumption by sulfate reducers when methane was the sole carbon source. This is not

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surprising, however, because there are no known anaerobic microorganisms capable of using methane as the sole carbon source (QUAYLE, 1972). MARTENS and BERNER (1977) showed that methane could not be the chief carbon substrate for the sulfate reducers in anoxic Long Island Sound sediments because too much sulfate is reduced per mole of methane consumed. In summary, it appears that sulfate reducers can better use other organic compounds, but can use methane as a secondary carbon source.

Regarding methane production in the sulfate-reducing zone, BARNES and GOLDBERG (1976) suggested that methane generation and sulfate reduction are not mutually exclusive processes. Rather, low concentrations of methane in the sulfate-reducing zone represent a balance between production by methanogenic bacteria and consumption by sulfate reducers. This hypothesis implies that methane is produced in the sulfate-reducing zone at a rate comparable to that below the depth of sulfate disappearance. Nearly all of the methane produced in the sulfate-reducing zone must then be oxidized to carbon dioxide to account for the observed low methane concentration. However, preliminary studies by the author indicate that there is insufficient isotopic change in $\Sigma CO_2$ in this region for methane to be produced and consumed at such a high rate. Alternatively, methane may be produced to a limited extent, but at a much smaller rate than below the sulfate-reducing zone. As an example, MARTENS and BERNER (1974) suggested that methane could be produced in the presence of interstitial sulfate within organic-rich, sulfate-free microenvironments such as the interior portions of decaying organisms. Similarly, BERNARD, BROOKS and SACKETT (1978) have reported that vertical methane concentration profiles in the top few meters of Texas shelf sediments having near-seawater interstitial sulfate concentrations exhibit maxima in the top 40 cm, apparently due to enhanced microbial methane production within organic-rich microenvironments.

CAPPENBERG (1974a, b) demonstrated an ecological succession with a slight overlap in distributions whereby the sulfate reducers are found above the methanogens in lake sediments. This succession was attributed to the toxic effect of sulfide on the methanogenic bacteria. OREMLAND and TAYLOR (1978) found that the sulfate reducers and methanogens compete for available hydrogen produced from the degradation of organic matter by fermentative bacteria. However, methanogens are not nearly so efficient in competing for hydrogen when sulfate is abundant, and sulfate reducers effectively consume the available hydrogen produced in the sediment. When sulfate is reduced to insufficient concentrations to support cell growth of sulfate reducers, hydrogen becomes available to the methane producers. In fact, the authors pointed out that in the absence of sulfate, sulfate-reducing bacteria *generate* hydrogen by degradation of organic matter. Hydrogen for the reduction of carbon dioxide by methanogenic bacteria would then be provided in part by the sulfate reducers. These observations suggest that neither sulfate nor hydrogen sulfide is inhibitory to methanogenesis, rather that a limited amount of methane could be produced in the sulfate-reducing zone as a result of incomplete hydrogen utilization by the sulfate reducers, even without so-called sulfate-free microenvironments.

Time-restricted laboratory culture experiments have, to date, failed to confirm or refute methane consumption or establish rates of methane production in the presence of sulfate, simply because of the exceedingly slow rates involved in these natural processes. Marine sediments, on the other hand, provide excellent 'laboratories' for the geochemical approach to the problems. For example, MARTENS and BERNER (1977) were able to model vertical methane distributions in Long Island Sound sediments using a steady-state

30°

Galveston

28° ———— 200 m ———

3
4
1000 m
6  5
2

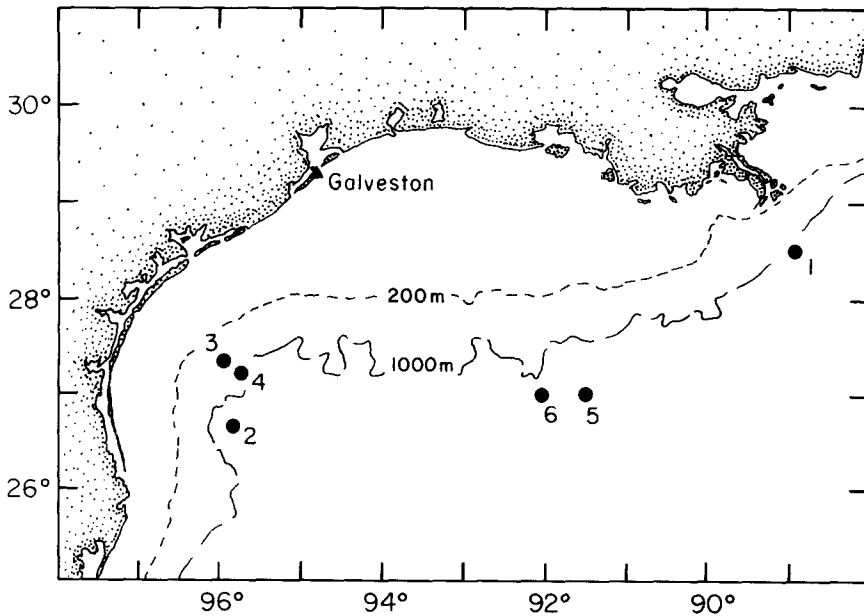26°

96°        94°        92°        90°

Fig. 1.   Station locations in the northwest Gulf of Mexico.

diagenetic equation incorporating effects of diffusion, sediment accumulation, and consumption. In such highly-reducing sediments, however, the depth of sulfate disappearance and corresponding high methane concentration is too close to the sediment surface to study the extent of methane production in the sulfate-reducing zone. Investigations of more mildly reducing shelf and slope sediments, where sulfate exists much deeper and diffusional effects of high methane concentrations do not dominate in the top few meters, can shed light on both production and consumption of methane in the sulfate-reducing zone. It is the purpose of this paper to demonstrate that methane is produced as well as consumed in the sulfate-reducing zone and to estimate these natural reaction rates in open marine sediments.

## ANALYTICAL METHODS

Sediment samples from six Gulf of Mexico locations (Fig. 1) were obtained using standard gravity and piston coring techniques. The sites are all in the slope-abyssal region of the northwestern Gulf. Methane in 5-cm sediment sections was determined by partitioning sediment gases into container headspaces with subsequent gas chromatographic analysis of the headspace gases as described by BERNARD et al. (1978). Sulfate was determined on interstitial water samples by barium sulfate gravimetry (VOGEL, 1961). Methane concentrations are reported as microliters per liter interstitial water ($\mu l \, l^{-1}$) and sulfate as millimoles per liter interstitial water (mM).

## DISCUSSION

### Upper sulfate-reducing zone

When attempting mathematically to model the behavior of a pore water species such as methane, all major factors affecting the concentration profile should be considered and

expressed mathematically. To simplify the mathematics involved, imprecise influences such as bioturbation and other biological effects are initially expressed as simply and as reasonably as possible, and minor and secondary effects are ignored. If horizontal gradients are assumed to be negligible, the behavior of the species can be described by the equation:

$$(\partial C/\partial t)_x = dC/dt - \omega(\partial C/\partial x) \qquad (1)$$

where $C$ is the concentration of the dissolved species, $t$ is time, $x$ is sediment depth measured positively downward from the moving sediment-water interface, and $\omega$ is the net rate of sediment accumulation (BERNER, 1974). The total derivative $dC/dt$ contains all processes affecting the concentration of the dissolved species except those due to advection (sediment accumulation). For methane, changes due to mineral precipitation, dissolution, and sorption reactions are ignored to a first approximation, and only diffusive and biological effects need be considered. Mathematically:

$$dC/dt = D(\partial^2 C/\partial x^2) + dC/dt_{biol}, \qquad (2)$$

where $D$ is the effective diffusion coefficient for methane in the pore water-sediment system and $dC/dt_{biol}$ describes effects due to biological production and consumption of the gas.

Strictly speaking, the effects of porosity changes and compaction on the advective and diffusive terms should be included in equations 1 and 2 (BERNER, 1975), but the assumptions that pore water velocity is equal to sediment grain velocity and that $D$ is constant with depth greatly simplify initial solutions. Likewise, no attempt is made here to correct for possible mixing by bioturbation (SCHINK and GUINASSO, 1977), a phenomena restricted to the upper several centimeters of slope and abyssal sediments.

Before pursuing the kinetic descriptions of biological effects, it is helpful to consider what gross effects the processes of diffusion, advection, consumption, and production have on vertical methane concentration profiles. At the sediment interface, the concentration of methane in slope and abyssal regions is essentially zero for these purposes (deep water concentrations are less than $50 \, nl \, l^{-1}$). Ideally, sulfate decreases to zero at some sediment depth in this region of the gulf, and methane increases to as high as several hundred milliliters per liter pore water. The sulfate-reducing zone is several meters deep on the inner shelf, several tens of meters deep on the outer shelf, and possibly several hundreds of meters deep in slope and abyssal sediments. If diffusion and sediment accumulation were the only controlling factors, methane concentrations in this zone would increase essentially linearly with depth from 'zero' at the sediment interface to the high concentration of the methane 'horizon' at the zero-sulfate depth. Rates of sediment accumulation on the outer shelf, slope, and abyssal plain are so low that the advective effect would be dominated by the linear diffusional gradient. In addition to diffusing, if methane is consumed in the sulfate-reducing zone, the overall vertical concentration profile would appear concave-upward, and if methane is produced (but not consumed) in this zone the profile would appear concave-downward. These effects are illustrated in Fig. 2. In each of these three cases, the concentration profile is always downward-increasing.

Figure 3 shows the methane profile observed from a piston core at Sta. 1. Superficially, the profile resembles that of Fig. 2c, the simple diffusion-production description. However, sulfate and methane both indicate that the core represents only the top portion of the sulphate-reducing zone (methane concentrations certainly do not approach the high values expected for the methane horizon). Methane does not increase

downward continually as illustrated in Fig. 2 but approaches a constant value with depth. This asymptotic behavior cannot be explained by simple diffusion-production or diffusion-consumption, rather it suggests that both consumption and production are taking place at 'balanced' rates and can be used to postulate the rates of these natural biological reactions.

The kinetics of biological methane production and consumption have not been well described. Bacterial consumption or production of a chemical species in the sediment pore water has generally been assumed to be first order with respect to the material undergoing decomposition (BERNER, 1974; LERMAN, 1977). The assumption that methane is
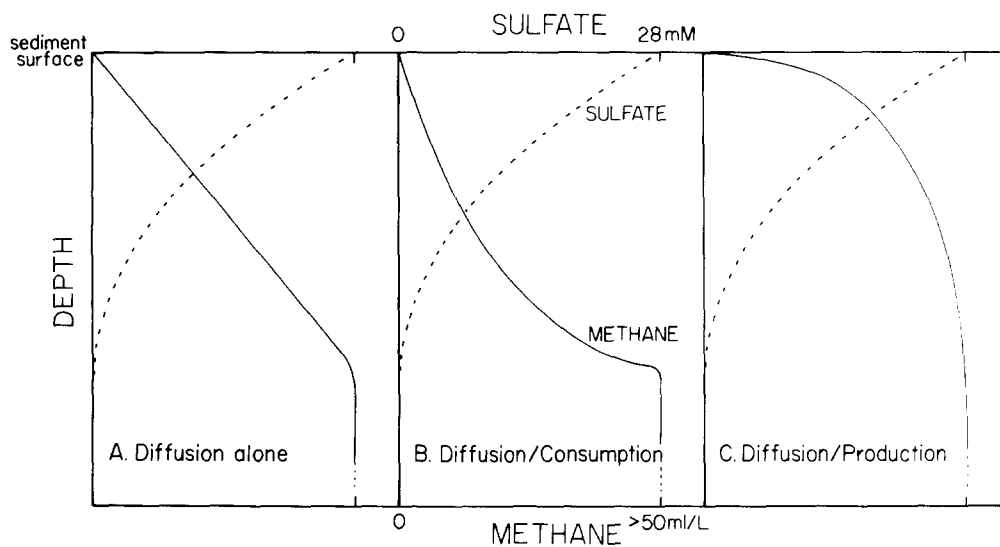


Fig. 2.   Idealized methane and sulfate profiles in the sulfate-reducing zone.

microbially consumed following first order kinetics has been used to explain methane profiles in anoxic marine sediments (MARTENS and BERNER, 1977) and waters (REEBURGH, 1976). Therefore, it is postulated here that methane is consumed in the zone of active sulfate reduction at a rate proportional to its concentration. Methane consumption can be represented mathematically by:

$$(\partial C/\partial t)_{cons} = -KC \tag{3}$$

where $K$ is the rate constant for methane consumption $(s^{-1})$ and $C$ is the concentration of methane $(\mu l\,l^{-1})$.

In the production of methane, the role of hydrogen is apparently critical. The sulfate reducers control the availability of hydrogen so that methane cannot be produced extensively until sulfate essentially disappears. OREMLAND and TAYLOR (1978) attributed their observations of limited methane production in the presence of sulfate to interaction of methanogens with anaerobes other than sulfate reducers, which could directly provide hydrogen for methanogenesis. Another possibility is that the sulfate reducers cannot utilize hydrogen below some threshold concentration, so that this 'residual' hydrogen is available to the methane producers. The result would be a slight production of methane
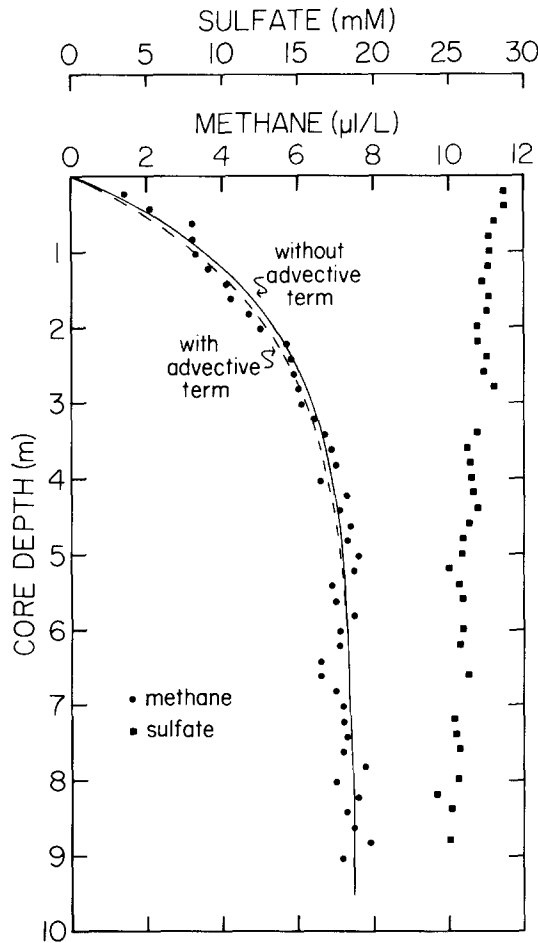
Fig. 3.    Interstitial methane and sulfate at Sta. 1.

with the rate limited by hydrogen availability in the sulfate-reducing zone and extensive production when sulfate is depleted. In reality, the production rate must be some function of hydrogen concentration $(C_H)$ and the amount of available organic matter $(G)$:

$$(\partial C/\partial t)_{prod} = f(C_H, G) \qquad (4)$$

but at the presumed low concentrations of hydrogen in the sulfate-reducing zone, hydrogen rather than organic matter would be rate-limiting and production might simply be considered first order with hydrogen:

$$(\partial C/\partial t)_{prod} = K'C_H \qquad (5)$$

In any case, if consumption is assumed to follow the first order kinetics of equation 3, then:

$$dC/dt_{biol} = (\partial C/\partial t)_{prod} + (\partial C/\partial t)_{cons} = f(C_H, G) - KC \qquad (6)$$

Now the effect of diffusion on the methane concentration profile shown in Fig. 3

disappears with depth because it takes the mathematical form of a negative exponential $(A\,e^{-ax})$, so the asymptotic behavior of the methane with depth at Sta. 1 is a result of the biological effects only. This constant concentration with depth implies that there is a balance achieved between production and consumption to maintain a constant methane concentration with time. Assuming steady-state conditions, equation 6 becomes:

$$f(C_H, G) - KC = 0 \qquad (7)$$

or

$$C = f(C_H, G)/K \qquad (8)$$

If methane concentration $(C)$ is *observed* to be constant with depth, then the production function must also be constant with depth:

$$f(C_H, G) = J \qquad (9)$$

where $J$ represents a constant production of methane with time. This conclusion based on the measured methane profile is supported by the following argument. A presumed threshold hydrogen concentration controlled by the sulfate reducers would be fairly constant in the sulfate-reducing zone. From equation 5, production of methane should be proportional to the hydrogen concentration so:

$$(\partial C/\partial t)_{prod} = K'C_H = J \qquad (10)$$

In summary, if consumption of methane in the sulfate-reducing zone is assumed to follow first order kinetics, measured concentrations and theoretical considerations suggest that methane is concurrently produced at an essentially constant rate. These rate functions for production and consumption are admittedly oversimplified, as both reactions are certainly related to the interstitial sulfate distribution. As interstitial hydrogen is produced rather than consumed by sulfate reducers in the absence of sulfate, methane production rates are not truly constant with depth but increase drastically at the depth of sulfate disappearance. Similarly, methane cannot be consumed below this depth, so a first order consumption rate is applicable only in the sulfate-reducing zone. These simple descriptions seem to be adequate, however, for explaining methane concentrations in the upper portion of the sulfate-reducing zone, where effects of the deep methane horizon are negligible. Conversely, observed methane profiles can be used to assess the extent of production and consumption in the sulfate reducing zone.

Assuming steady-state conditions for the distribution of methane with time yields:

$$(\partial C/\partial t)_x = D(\partial^2 C/\partial x^2) - \omega(\partial C/\partial x) - KC + J = 0 \qquad (11)$$

If the concentration of the species approaches a constant value with 'infinite' depth, the solution to equation 11 is given by LERMAN (1977), who demonstrated that the rate of sediment accumulation (advective term) can be neglected if $\omega^2/4D \ll K$ in equation 11. This simplification is valid for methane diagenesis in slope and abyssal sediments (as will be shown) so equation 11 reduces to:

$$D(d^2 C/dx^2) - KC + J = 0 \qquad (12)$$

If $C = C_0$ at the sediment-seawater interface $(x = 0)$ and $C \to C_x$ as $x \to \infty$, the solution

to equation 12 is given by:

$$C = J/K + (C_0 - J/K) \exp\left[-x(K/D)^{1/2}\right] \tag{13}$$

The ratio $J/K$ has units of concentration and represents the constant level of methane ($C_x$) resulting from the balance of production and consumption as diffusive effects disappear with increasing sediment depth. The reciprocal of $(K/D)^{1/2}$ has units of length and represents the scale length (l/e length) set by diffusion and consumption. This scale length is the depth at which methane concentrations are within $\sim 37\%$ ($e^{-1} \times 100$) of the asymptotic value, $C_x$.

The exact depth of sulfate disappearance is unknown for most areas of the Gulf of Mexico, but the existence of a methane horizon at some sediment depth has been observed commonly by seismic techniques on the Texas–Louisiana shelf (ROEMER, 1976) and in the abyssal region by Deep-Sea Drilling Project borehole cores (CLAYPOOL, PRESLEY and KAPLAN, 1973). In the highly reducing, rapidly accumulating Mississippi Delta sediments, interstitial sulfate is quickly depleted and extensive microbial production of methane occurs a few centimeters below the seawater-sediment interface. This methane horizon occurs progressively deeper in the sediment in an offshore direction, the depth being a function of sedimentation rate, temperature, organic input, and oxygen diffusion from overlying water.

The existence of this drastic increase in methane concentration at some sediment depth contradicts the assumption made for the solution of equation 12 that concentrations approach a constant value with infinite depth. The methane horizon is deep enough in slope and abyssal sediments of the gulf, however, that the effects of upward diffusion of methane from the horizon are negligible in the upper part of the sulfate-reducing zone due to overriding effects of local consumption and production. Thus, vertical profiles in the top few meters of sediment can first be approximated by equation 13.

As discussed earlier, Fig. 3 shows interstitial methane and sulfate concentrations (measured every 20 cm in a 9-m piston core) for Sta. 1 plotted against sediment depth. A concentration profile described by equation 13 is also shown on the figure using $C_0 = 0$ (the overlying water methane concentration in this region was about $0.05 \,\mu l \, l^{-1}$) and best-fit values for $(D/K)^{1/2}$ and $J/K$. The slight change in the profile due to the inclusion of the advective term of equation 11 using a sedimentation rate of $0.05 \, cm \, y^{-1}$ (SHOKES, 1976) is illustrated by the dashed line. Because the solution profile of Fig. 3 is only slightly shifted by the advective term, precision indicated by data scatter does not justify the inclusion of this complicating term. For the data presented here, advective effects due to sedimentation will be ignored because the data can be described adequately without them, and the simpler kinetic description of equation 12 will be used.

The measured methane concentrations at Sta. 1 level off at $7.5 \,\mu l \, l^{-1}$ with depth, indicating a balance between production and consumption. In equation 13, the magnitude of the ratio of production to consumption, $J/K$, is simply this constant methane concentration of $7.5 \,\mu l \, l^{-1}$. The scale length $(D/K)^{1/2}$ can be estimated by a best-fit curve of equation 13 to the data to be 160 cm and if a reasonable value of $D$ is assumed, values for $K$ and $J$ can be established.

The diffusion coefficient of methane at infinite dilution in water at various temperatures is given by SAHORES and WHITHERSPOON (1970). Calculation assuming a pore water temperature of $4.5°C$ and salinity of $35\%_{00}$ results in a value of $8.3 \times 10^{-6} \, cm^2 \, s^{-1}$. Correcting for the effects of porosity and tortuosity of the sediments (LI and GREGORY,
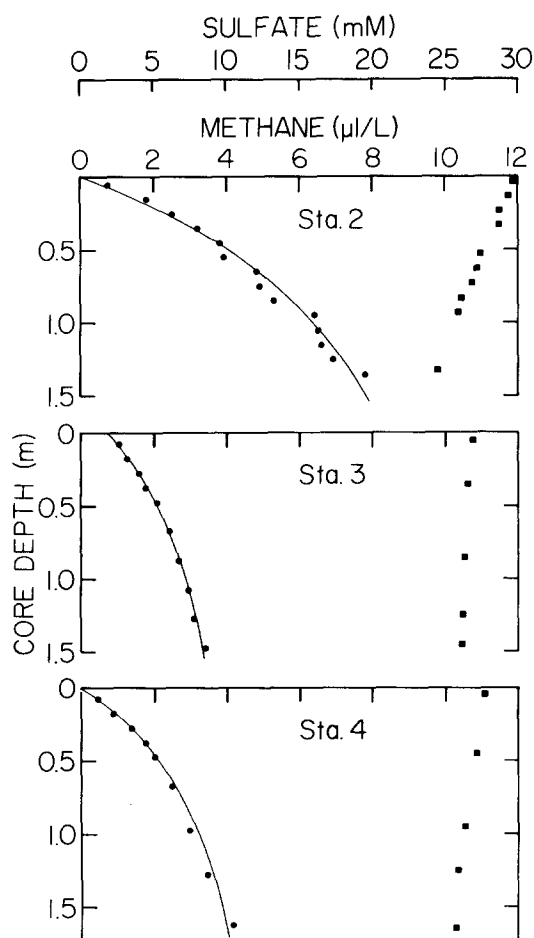
Fig. 4. Interstitial methane and sulfate at Stas 2, 3, and 4.

1974) yields an effective diffusion coefficient of methane through sediments of 4.6 $\times 10^{-6}$ cm$^2$ s$^{-1}$. Estimates of $J$ and $K$ are in error proportionally to any error introduced by this estimate of $D$.

Using a value of $4.6 \times 10^{-6}$ cm$^2$ s$^{-1}$ for $D$, values for $J$ and $K$ are calculated to be $1.3 \times 10^{-9}$ µl l$^{-1}$ s$^{-1}$ and $1.8 \times 10^{-10}$ s$^{-1}$, respectively. MARTENS and BERNER (1977) estimate a consumption rate of $K = 8 \times 10^{-9}$ s$^{-1}$ for the anoxic sediments of Long Island Sound. The consumption rate reported here, 40 times slower than in Long Island Sound, is reasonable considering the lower sediment temperature, sedimentation rate, and organic carbon input. (Note that $K$ is indeed much larger than $\omega^2/4D$ and advective effects can be neglected.)

Methane and sulfate concentrations from gravity cores taken at Stas 2, 3, and 4 are presented in Fig. 4. These cores do not extend to sediment depths where methane concentrations presumably become constant. In these cases, asymptotic methane concentrations representing $J/K$ values as well as estimates of $(D/K)^{1/2}$ can still be projected using best-fit curves generated by equation 13. These theoretical curves are

plotted on Fig. 4 for comparison with the data, and estimates of $J$ and $K$ are listed in Table 1. At Sta. 3, $C_0$ is apparently not near zero as observed for the other stations, but rather about $0.75\,\mu l\,l^{-1}$. This station is on the outer Texas shelf and the observed near-surface methane concentration can be attributed to enhanced microbial production

Table 1.   Rates of production and consumption, minimum horizon depth, scale length, and flux of methane.

| Station | $C_0$ ($\mu l\,l^{-1}$) | $J \times 10^{10}$ ($\mu l\,l^{-1}\,S^{-1}$) | $K \times 10^{10}$ ($S^{-1}$) | Minimum $Z$ (m) | $(D/K)^{1/2}$ (m) | Flux ($nl\,cm^{-2}\,yr^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 0 | 13 | 1.8 | 28.5 | 0.16 | 7 |
| 2 | 0 | 53 | 5.6 | 12.5 | 0.91 | 15 |
| 3 | 0.75 | 20 | 5.1 | 14.0 | 0.95 | 5 |
| 4 | 0 | 32 | 7.1 | 12.0 | 0.81 | 8 |
| 5 | 0 | 150 | 14.4 | 6.85* | 0.57 | 27 |
| 6 | 0 | 65 | 9.0 | 11.0 | 0.71 | 15 |

* Apparent depth rather than a minimum value.

at the sediment surface as described by BERNARD et al. (1978). At all stations, gradual sulfate reduction is observed in the depth interval sampled. Agreement of the interstitial methane data with theoretical profiles suggests that concentrations in the upper portion of the sulfate-reducing zone can be described adequately by a balance of the effects of upward diffusion, microbial consumption, and an essentially constant production due perhaps to a minute 'residual' hydrogen concentration.

### Lower sulfate-reducing zone

In deriving an equation to describe concentrations of methane throughout the entire sulfate-reducing zone and into the methane horizon, the assumptions and boundary conditions used in equation 13 are no longer valid. As interstitial sulfate disappears, the production term $(\partial c/\partial t)_{prod}$ can no longer be considered constant because increasing amounts of hydrogen become available for methane production. Also, the sulfate reducers no longer have sulfate available to drive the presumed oxidation of methane so that the consumption term $(\partial c/\partial t)_{cons}$ should disappear. These two terms are both functions of the interstitial sulfate concentration, which itself has been kinetically modeled (BERNER, 1974; SHOKES, 1976). A comprehensive model for methane and sulfate in highly reducing sediments that will take these interactions into account is in preparation. However, this type of model is not easily confirmed in mildly reducing open marine sediments because accurate methane concentrations throughout a sulfate-reducing zone several tens or hundreds of meters deep have not yet been measured. Some interesting predictions concerning the depth of the methane horizon in open marine sediments can be made, however, by examining the top few meters of sediment. For example, Fig. 5 shows interstitial methane and sulfate concentrations in a gravity core taken from an intra-slope basin (Sta. 5). Sulfate decreases more rapidly with sediment depth at Sta. 5, approaching half of the overlying water concentration at a depth of 2 m. An 'exponental' extrapolation of the interstitial sulfate concentration to zero suggests that the depth of complete removal is 5 to 7 m. The methane horizon should occur just below this depth. Methane concentrations do not approach a constant value in the first 2 m but continue to increase with depth. Upward diffusion from the methane horizon apparently causes the downward-increasing methane profile of Sta. 5.
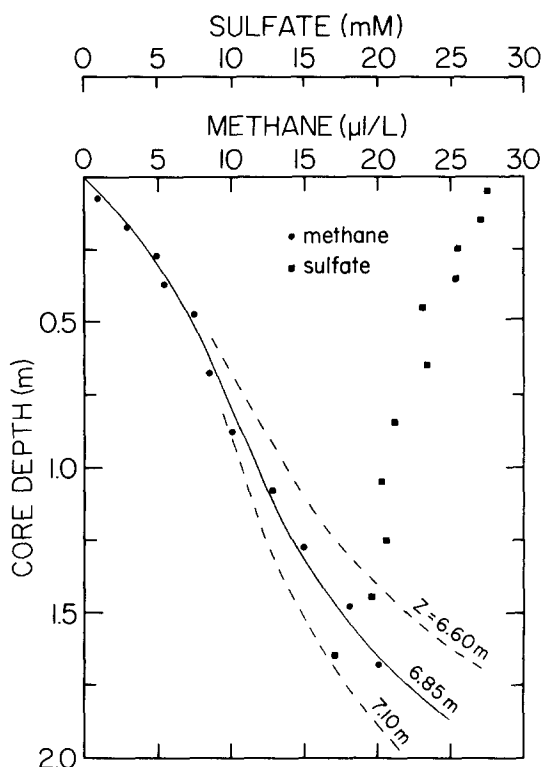
Fig. 5. Interstitial methane and sulfate at Sta. 5.

To express mathematically the concentration profile, step functions for production and consumption of methane (discontinuous at the horizon depth) could be considered in the diagenetic equation. It is less confusing for these purposes, however, simply to set the lower boundary of equation 12 at the methane horizon and derive the theoretical methane concentration profile down to that depth. Boundaries of $C = C_0$ at $x = 0$ and $C = C_x$ at $x = Z$ can be applied to equation 12, where $C_x$ represents the methane concentration at the depth of the methane horizon, $Z$. The solution to equation 12 using these boundaries is considerably more complex, but it can be simplified using two assumptions: (1) $C_x \gg J/K$ and (2) $Z > 4(D/K)^{1/2}$. The first assumption is justifiable for methane because concentrations at the methane horizon $(C_x)$ are generally greater than $50 \, \mathrm{ml \, l^{-1}}$, whereas $J/K$ in the sulfate-reducing zone is generally less than $10 \, \mu\mathrm{l \, l^{-1}}$. The second assumption requires that the depth of the methane horizon be greater than about four times the scale length set by diffusion and consumption (the value 4 is used because $e^4 \gg e^{-4}$). The validity of assumption 2 is not quite so apparent, but will be demonstrated later when minimum values of $Z$ are presented.

The modified solution of equation 12 using the new boundary conditions and assumptions is given by:

$$C = A + (J/K) + B \qquad (14)$$

where

$$A = (C_0 - J/K)\exp\left[-x(K/D)^{1/2}\right]$$

and

$$B = C_x[\exp(x-Z)(K/D)^{1/2} - \exp(-x-Z)(K/D)^{1/2}]$$

Three observations about equation 14 should be noted:

(1) The terms $A + (J/K)$ are identical to equation 13 and control the distribution described by equation 14 in the upper part of the sulfate-reducing zone.

(2) The value of $J/K$ controls the methane concentration where diffusive effects are negligible between the boundary regions, representing a balance between production and consumption.

(3) The terms $(J/K) + B$ control methane concentrations near the depth of the methane horizon (as $x \to Z$), representing the effects of upward diffusion of methane from the horizon to the lower part of the sulfate-reducing zone.

Equation 14 has been best-fit to the measured methane concentration of Sta. 5 and is represented by the solid line on Fig. 5. The methane data from this station agree with the theoretical profile of equation 14 using $J$, $K$, $C_x$, and $Z$ values of $1.5 \times 10^{-8}\,\mu l\,l^{-1}\,s^{-1}$, $1.4 \times 10^{-9}\,s^{-1}$, $100\,ml\,l^{-1}$, and $6.85\,m$, respectively. The $Z$ value of $6.85\,m$ agrees with the earlier extrapolation of decreasing interstitial sulfate to zero at 5 to $7\,m$. It will be shown that the exact value of $C_x$ is relatively unimportant as $C_x \gg J/K$. The depth of the horizon $(Z)$ is important, however, as illustrated by the effect on the Sta. 5 solution profile of 'raising' and 'lowering' the horizon only $25\,cm$, shown by the dashed lines on Fig. 5. This effect can be used to predict a minimum methane horizon depth for the other stations by shifting the depth of a hypothetical horizon until its diffusive effect becomes significant at the depth where data are available and begins to distort the theoretical profile in conflict with the observed methane distribution. As an example, methane and sulfate data from Station 6 are presented in Fig. 6 along with solution curves (equation 14) using various values for the hypothetical horizon depth, $Z$. Values for $J$, $K$, $C_0$, and $C_x$ are held constant at $6.5 \times 10^{-9}\,\mu l\,l^{-1}\,s^{-1}$, $9.0 \times 10^{-10}\,s^{-1}$, $0$ and $100\,ml\,l^{-1}$, respectively. For $Z$ values $12\,m$ and greater, effects of upward diffusion from the horizon are negligible and the resulting solution curves do not change significantly within the depth range of available data. When the hypothetical horizon is raised to $11\,m$, only a slight shift in the solution curve results. A $Z$ value of $10\,m$ produces a more significant shift, and 9- and 8-m horizons obviously conflict with the observed data. The curves of Fig. 6 demonstrate that the minimum depth at which the methane horizon could exist at Station 6 is approximately $11\,m$. If a value for methane concentration at the horizon of 50 rather than $100\,ml\,l^{-1}$ is used, virtually the same curves are generated if $Z$ values of 11.5, 10.5, 9.5, 8.5, and $7.5\,m$ are used in place of 12, 11, 10, 9, and $8\,m$, respectively. Likewise, doubling the $C_x$ value to $200\,ml\,l^{-1}$ raises the $Z$ values corresponding to the curves of Fig. 6 by $0.5\,m$. Thus, if the assumed $C_x$ is in error by a factor of 2, the minimum depth of the methane horizon is in error by only $0.5\,m$.

Minimum values of $Z$ can be approximated as for the other stations. Estimated values of $J$, $K$, $(D/K)^{1/2}$, and minimum $Z$, using a $C_x$ value of $100\,ml\,l^{-1}$ for all stations, are given in Table 1. Values of $J$ and $K$ generally vary inversely with minimum $Z$ because the three parameters are all functions of temperature, sedimentation rate, and organic input of an area, i.e. $Z$ should increase and $J$ and $K$ should decrease with increasing water depth.
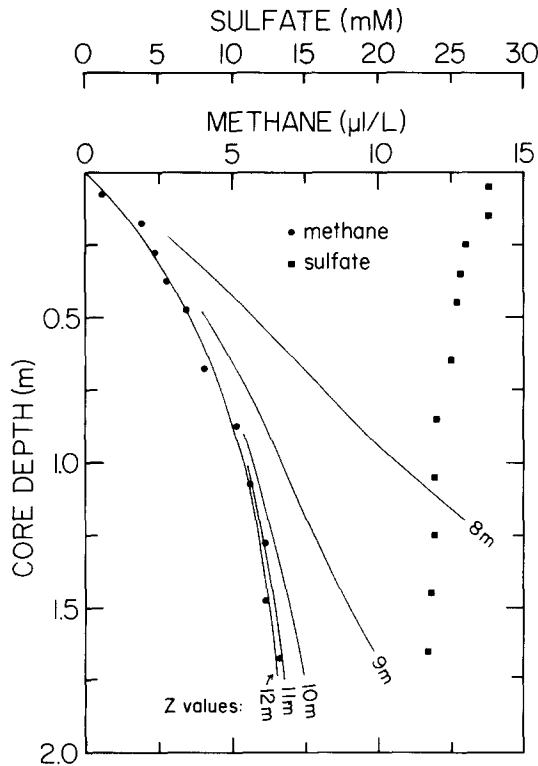
Fig. 6.   Interstitial methane and sulfate at Sta. 6.

Values of $(D/K)^{1/2}$ are listed to demonstrate that these values are always much less than $Z/4$, satisfying the second assumption postulated earlier.

Fluxes of methane out of the sediments can be calculated from equation 14 using Fick's first law:

$$F = -D(\partial C/\partial x)|_{x=0} \qquad (15)$$

In this case, the methane flux out of sediments is given by:

$$F = (J/K - C_0)(KD)^{1/2} \qquad (16)$$

Calculated fluxes are listed in Table 1 for each station in units of $nl\,cm^{-2}\,yr^{-1}$. Although these flux magnitudes are generally related to water depth in the Gulf of Mexico, they vary from area to area and are influenced to a large degree by the local bacterial populations involved in the processes of production and consumption. These flux calculations do not take into account consumption of methane by aerobic bacteria near the sediment surface, so they should be considered upper limits only. If an overall average flux of $10\,nl\,cm^{-2}\,yr^{-1}$ is assumed from Gulf of Mexico slope and abyssal sediments covering a total area of $10^{16}\,cm^2$, the annual input of methane into gulf waters is $10^8$ l. This contribution is miniscule compared to the large inputs from rivers, deltas and marshes, shelf sediments, natural gas seepage, in situ water column production, and underwater venting and brine discharge from petroleum production activities in the gulf.

## SUMMARY AND CONCLUSIONS

Vertical methane concentration profiles in sediments of the Gulf of Mexico can be explained mathematically by simple kinetic modeling. Relative rates of diffusion, advection, production, and consumption of methane determine solutions to a steady-state diagenetic equation. These solutions describe methane concentrations as a function of sediment depth in the sulfate-reducing zone. Correlations of the solutions with observed methane profiles indicate that methane is consumed at a rate proportional to concentration. Profiles indicate that methane is also apparently produced at a limited and essentially constant rate throughout the sulfate-reducing zone. Rates of methane production and consumption generally vary with water depth and can be estimated from best-fit solutions of the kinetic model to the observed profiles.

Diffusive effects are significant only near the sediment surface and near the depth of the methane horizon deeper in the sediment. Between these depths, the effects of production and consumption balance to form uniform concentrations of methane with depth. In the top few meters of the sulfate-reducing zone, upward diffusion from large accumulations of methane deeper than about 10 m is masked by the more localized production and consumption. The conclusions presented here imply that the presence of deep gas pockets cannot be detected at the sediment surface unless conduits such as faults or fractures are present to enhance the upward migration of the gas.

This kinetic model is admittedly an oversimplified description of the processes controlling interstitial methane, but it seems to predict methane concentration as a function of depth surprisingly well. Future work should include attempts to reach the methane horizon when coring and to incorporate isotopic changes of methane, consumption of sulfate, and production of $CO_2$ into a comprehensive model. The methane horizon depth should not be regarded as a boundary condition, but rather a depth at which rates of production and consumption of methane change.

## REFERENCES

BARNES R. O. and E. D. GOLDBERG (1976) Methane production and consumption in anoxic marine sediments. *Geology*, **4**, 297–300.

BERNARD B. B., J. M. BROOKS and W. M. SACKETT (1978) Light hydrocarbons in recent Texas continental shelf and slope sediments. *Journal of Geophysical Research*. In press.

BERNER R. A. (1974) Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus, and silicon in anoxic marine sediments. In: *The sea*, Volume 5, *Marine Chemistry*, E. D. GOLDBERG, editor, John Wiley & Sons, pp. 427–450.

BERNER R. A. (1975) Diagenetic models of dissolved species in the interstitial waters of compacting sediments. *American Journal of Science*, **275**, 88–96.

CAPPENBURG T. E. (1974a) Interrelations between sulfate-reducing and methane-producing bacteria in bottom deposits of a fresh-water lake. I. Field observations, *Antonie van Leeuwenhoek*, **40**, 285–295.

CAPPENBURG T. E. (1974b) Interrelations between sulfate-reducing and methane-producing bacteria in bottom deposits of a freshwater lake. II. Inhibition experiments, *Antonie van Leeuwenhoek*, **40**, 297–306.

CLAYPOOL G. E. and I. R. KAPLAN (1974) The origin and distribution of methane in marine sediments. In: *Natural gases in marine sediments*, I. R. KAPLAN, editor, Plenum Press, pp. 99–139.

CLAYPOOL G. E., B. J. PRESLEY and I. R. KAPLAN (1973) Gas analyses in sediment samples from legs 10, 11, 13, 14, 15, 18, and 19. In: *Initial Reports of the Deep Sea Drilling Project*, XIX, U.S. Government Printing Office, pp. 879–884.

DAVIS J. B. and H. F. YARBROUGH (1966) Anaerobic oxidation of hydrocarbons by *Desulfovibrio desulfuricans*. *Chemical Geology*, **1**, 137–144.

EMERY K. O. and D. HOGGAN (1958) Gases in marine sediments. *Bulletin of the American Association of Petroleum Geologists*, **42**, 2174–2188.

LERMAN A. (1977) Migrational processes and chemical reactions in interstitial waters. In: *The sea*, Volume 6, *Ideas and observations on progress in the study of the seas*, E. D. GOLDBERG, editor, John Wiley & Sons, pp. 695–738.

LI Y. H. and S. GREGORY (1974) Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*, **38**, 703–714.

MARTENS C. S. and R. A. BERNER (1974) Methane production in the interstitial waters of sulfate depleted sediments. *Science*, **185**, 1167–1169.

MARTENS C. S. and R. A. BERNER (1977) Interstitial water chemistry of anoxic Long Island Sound sediments. 1. Dissolved gases. *Limnology and Oceanography*, **22**, 10–25.

OREMLAND R. S. and B. F. TAYLOR (1978) Sulfate reduction and methanogenesis in marine sediments. *Geochimica et Cosmochimica Acta*, **42**, 209–214.

QUAYLE J. R. (1972) The metabolism of one-carbon compounds by microorganisms. *Advances in Microbial Physiology*, **7**, 119–203.

REEBURGH W. S. (1969) Observations of gases in Chesapeake Bay sediments. *Limnology and Oceanography*, **14**, 368–375.

REEBURGH W. S. (1976) Methane consumption in Cariaco Trench waters and sediments. *Earth and Planetary Science Letters*, **28**, 337–344.

REEBURGH W. S. and D. T. HEGGIE (1974) Depth distributions of gases in shallow water sediments. In: *Natural gases in marine sediments*, I. R. KAPLAN, editor, Plenum Press, pp. 27–45.

REEBURGH W. S. and D. T. HEGGIE (1977) Microbial methane consumption reactions and their effect on methane distributions in freshwater and marine systems. *Limnology and Oceanography*, **22**, 1–9.

ROEMAR L. B. (1976) Structure and stratigraphy of late Quaternary deposits on the outer Louisiana shelf. Ph.D. dissertation, Department of Oceanography, Texas A&M University, 170p.

SAHORES J. J. and P. A. WHITHERSPOON (1970) Diffusion of light paraffin hydrocarbons in water from 2°C to 80°C. In: *Advances in organic geochemistry*, 1966, G. D. HOBSON and G. C. SPEARS, editors, Pergamon Press, pp. 219–230.

SCHINK D. R. and N. L. GUINASSO JR. (1977) Effects of bioturbation on sediment-seawater interactions. *Marine Geology*, **23**, 133–154.

SHOKES R. F. (1976) Rate-dependent distributions of lead-210 and interstitial sulfate in sediments of the Mississippi River delta. Ph.D. dissertation, Department of Oceanography, Texas A&M University, 122p.

SOROKIN Y. I. (1957) Ability of sulfate reducing bacteria to utilize methane for reduction of sulfates to hydrogen sulfide. *Microbiologiya*, **115**, 816–818.

VOGEL A. I. (1961) *Quantitative inorganic analysis*, John Wiley & Sons, 446p.

WHELAN T. (1974) Methane and carbon dioxide in coastal marsh sediments. In: *Natural gases in marine sediments*, I. R. KAPLAN, editor, Plenum Press, 47–61.