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OBSERVATIONS OF GASES IN CHESAPEAKE BAY SEDIMENTS¹

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ABSTRACT

Summer and winter depth distributions of Ar, N₂, CH₄, and total CO₂ in Chesapeake Bay sediments are reported. Methane increased with depth in the sediment from undetectable quantities at the surface to concentrations of 150 and 85 ml/liter in water depths of 30.4 and 15.2 m. The observed maximum concentrations agree well with values calculated assuming that the CH₄ is controlled by ebullition from the sediment. Argon and N₂ in the surface sediments were present in concentrations near that of the overlying water and decreased with depth to values of 0.1 and 2 ml/liter. Depth variations of the N₂:Ar ratio indicate selective removal of N₂. Stripping by bubbles of CH₄ accounts for the selective removal of N₂ and the decrease with depth of both Ar and N₂. Total CO₂ increased with depth to concentrations of 1,500 ml/liter and pH remained uniform with depth at about 7. Low values of total H₂S and an abundance of acid-labile sulfides in the sediments indicate that sulfide species are removed by mineral formation. All depth variations showed a break at about 25-cm depth, indicating that mixing takes place to this depth.

INTRODUCTION

Following the introduction of sediment squeezers as a means of obtaining reliable samples of interstitial water, a number of papers have been published reporting measurements of various chemical elements with depth in sediments. Most of these investigations have involved measurement of the more abundant elements in seawater (e.g., Ca, Mg, Na, K, Cl) to try to detect compositional changes in the interstitial water resulting from early diagenesis, while a few papers have dealt with species existing in more than one oxidation state (e.g., Fe, Mn, S). Large variations with depth were expected initially but were not observed. Little is known about the extent of physical mixing in sediments.

Large qualitative and quantitative differences are observed between the gases in surface waters and those present in sediments in interstitial waters. For both situations, the gas content is controlled by three factors: exchange across the interface, internal mixing, and biological pro-

cesses. Since gases in sediments may be either produced biologically within the sediment or mixed in from the overlying water, they offer an opportunity to study both chemical and physical processes in sediments. In interstitial waters, the presence of appreciable quantities of organic detritus and the large proportion of solid material with a high surface area permit the growth of large and diverse bacterial populations which deplete dissolved O₂, producing anoxic conditions. Methane, CO₂, and H₂S are produced in the biochemical degradation of organic material and can be analyzed as gases. Since sulfate reduction and methane production are performed by obligate anaerobes, depth distributions of these gases in sediments may be used to infer a limit of oxygen penetration. The inert gas Ar is present in measurable concentrations and should be affected by physical processes only.

Koyama (1953) and Emery and Hoggan (1958) have attempted quantitative measurements of gases in sediments. Gases were extracted from slurries of gas-free water and sediment by stripping or by vacuum, and analyses were performed by mass spectrometry, manometry, or gas chromatography. The observed quantities of gas were converted to concentrations expressed as milliliters per liter of intersti-

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tial water either by parallel determinations of sediment water content or by assuming the concentration of N_2 to be identical in the sediment and overlying water and using it as an internal standard. Koyama's studies were limited to the upper 30 cm of Japanese lake and paddy sediments, while Emery and Hoggan sampled deep-sea basins at 1-ft (0.3 m) intervals over several feet. These sampling intervals did not provide reliable depth distributions. Duplicate measurements were not performed and both sets of data suggest contamination by atmospheric gases.

METHODS

The method used for gas analysis in this study has been described (Reeburgh 1968). Interstitial water was separated from sediment samples with a core squeezer (Reeburgh 1967) and varying volumes sampled in triplicate and analyzed using a liquid stripping gas chromatographic technique similar to that of Swinnerton, Linnenbom, and Check (1962). Sediment samples were extruded directly into the squeezers from suitable depths in a gravity core. To avoid contamination by atmospheric gases, the squeezers were loaded in a well-flushed, helium-filled glove bag. Analyses were performed using a gas partitioner (Fisher model 29) with helium carrier gas. Argon, nitrogen, and methane were separated on a molecular sieve 5A column after oxygen had been removed by reduction with a chromous sulfate solution. On a separate sample, total carbon dioxide was released from solution with a dilute solution of sulfuric acid and was separated from the other gases on a short silica gel column. Triplicates gave relative standard deviations of 5% or less on natural samples and 1% for distilled water standards.

Temperatures at various positions along the coring tube were measured with a handheld thermistor probe, inserted in holes drilled in a core liner before coring and designed to stop with the temperature-sensitive element at the center of the core. The holes were covered with plastic tape during coring to prevent sample loss. Cores

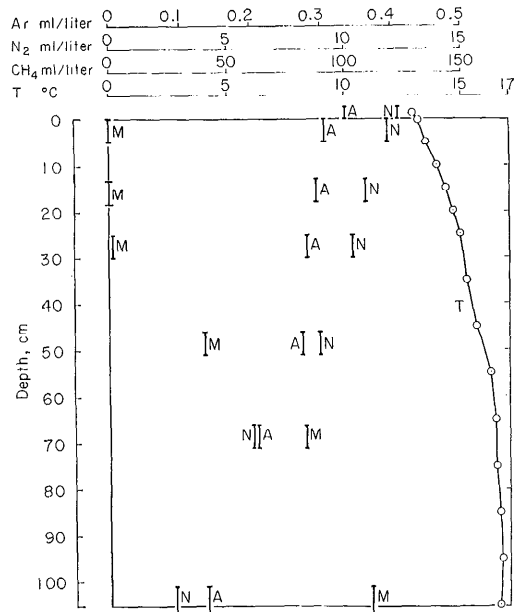


FIG. 1. Depth distributions of argon, A; nitrogen, N; methane, M; and temperature, T, in Chesapeake Bay sediments. Station 858-D, 17 November 1966, 15.2 m.

were processed immediately after retrieval, and temperature drift because of warming did not exceed 0.2°C.

RESULTS

Two stations in Chesapeake Bay were occupied on several occasions throughout a year. Station 858-C ($38^{\circ}57'43''$ N lat, $76^{\circ}22'49''$ W long, 30.4 m) lies in the axial trough of the bay and is occasionally exposed to anoxic bottom water during summer stratification. Station 858-D ($38^{\circ}57'56''$ N lat, $76^{\circ}23'50''$ W long, 15.2 m) lies to the west of the axial trough and has been exposed to oxygenated bottom water for the last several years. Sediments at both stations are black muds.

Representative depth distributions of Ar, N_2 , CH_4 , and temperature at both stations under summer and winter conditions are shown in Figs. 1-4, and Figs. 5 and 6 show depth distributions of total CO_2 and pH at both stations. Each point is the mean of three determinations. The length of the vertical lines represents the sample depth

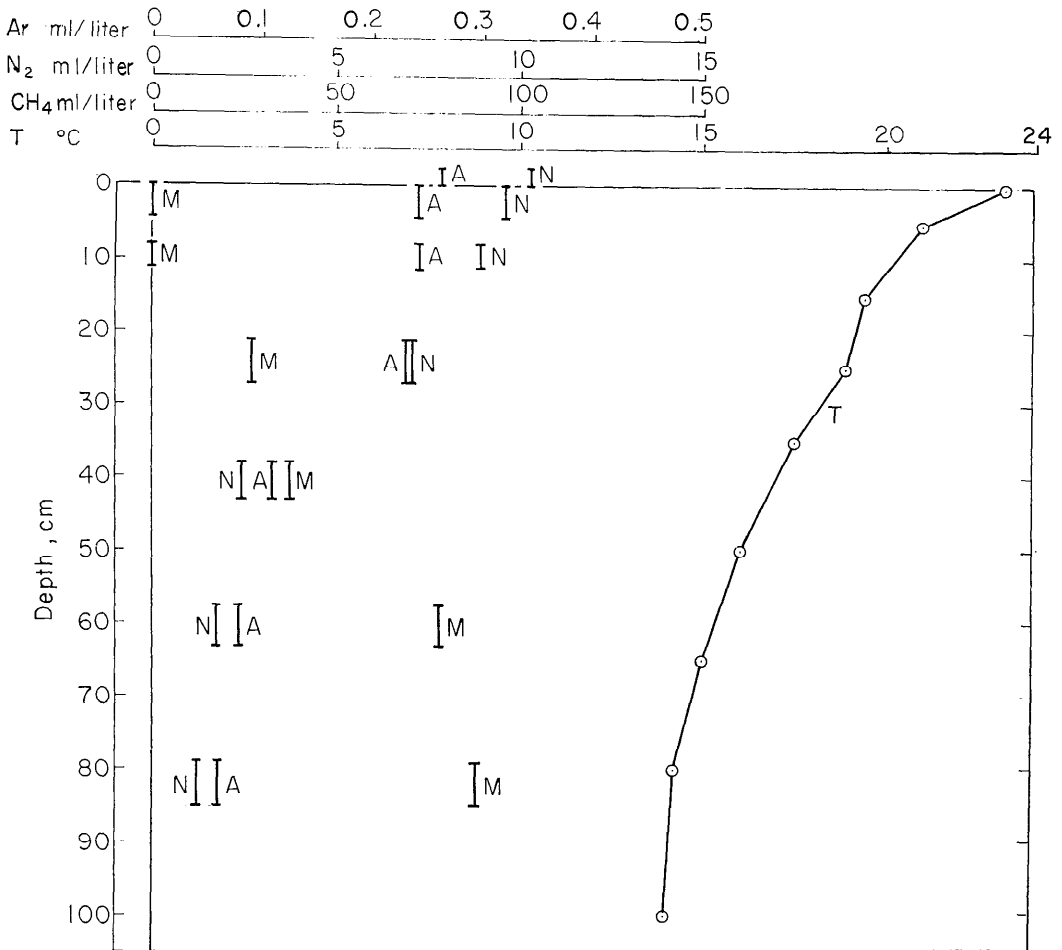


FIG. 2. Depth distributions of argon, A; nitrogen, N; methane, M; and temperature, T, in Chesapeake Bay sediments. Station 858-D, 17 August 1967, 15.2 m.

interval as determined by measurements of the extruding piston position on the core barrel.

DISCUSSION

Methane

Methane was not detected in the overlying water or the upper 10 to 20 cm of each core, but it increased with depth in the sediment to concentrations up to 150 ml/liter. Higher maximum concentrations were observed at station 858-C (30.4 m) than at the shallower 858-D (15.2 m).

Methane may be formed by anaerobic bacterial decomposition of organic matter through a number of pathways. ZoBell

(1939) and McCarty (1964) regarded anaerobic fermentation of carbohydrates as the primary source. Under aerobic conditions, CH_4 may be consumed as an energy source.

Swinnerton and Linnenbom (1967) observed CH_4 in the open ocean in a range of 2.8 to 0.2×10^{-4} ml/liter while Atkinson and Richards (1967) reported maximum concentrations of 1.6 ml/liter in anoxic basins. Koyama (1964) measured CH_4 production rates in Japanese paddy soils, obtaining an average value at 15°C of about $1,200 \text{ ml liter}^{-1} \text{ yr}^{-1}$, which is probably high for an estuarine environment. An estimate for Chesapeake Bay can be obtained from

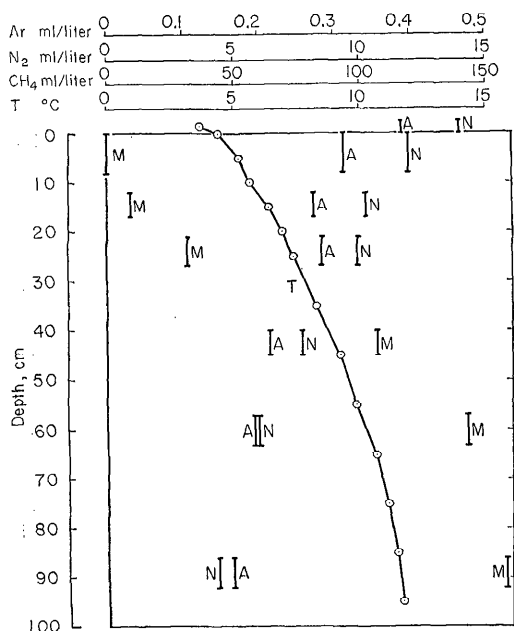


FIG. 3. Depth distributions of argon, A; nitrogen, N; methane, M; and temperature, T, in Chesapeake Bay sediments. Station 858-C, 5 January 1967, 30.4 m.

the data of Biggs (1967), who found organic carbon concentrations of 3% (dry wt basis) in surface sediments of Chesapeake Bay. Using his observed decrease in carbon with depth of 1% per inch, and assuming that the decrease is due solely to CH₄ production, that the water content of the sediments is 50%, and that the deposition rate is 1 mm/yr, a methane production rate of 22 ml liter⁻¹ yr⁻¹ is obtained. This rate may be low owing to losses of volatile compounds during drying. Koyama (1954) has also observed a depth variation with CH₄ in his studies of lake sediments and has suggested that CH₄ is lost from the sediments as bubbles. Bubble formation would be expected if the partial pressure of a gas exceeded the *in situ* pressure. Instead of calculating pCH_4 , the ambient pressure and CH₄ solubility coefficients can be used to calculate critical CH₄ concentrations, as suggested by Klots (1961). If the measured concentration is greater than the critical concentration at a station, bubble formation is possible.

Since solubility coefficients for CH₄ in seawater are not available, a salt correction was applied to the distilled water CH₄ solubility coefficients reported by Winkler (1901). The solubility coefficients for Ar, N₂, and O₂ are similar in magnitude to those of CH₄ and decrease by about 1% per chlorinity unit, so this correction was applied to Winkler's values. The maximum observed CH₄ concentrations are within 10% of the calculated critical concentrations. Since seasonal warming of 10C would cause CH₄, in equilibrium at a low temperature, to exceed the new critical concentration by about 30%, it seems clear that CH₄ bubbles can form and that ebullition of CH₄ controls the maximum concentration of this gas in the sediment. It appears that CH₄ is not released from the sediments during coring. No bubbles were observed beneath the check valve of the corer or along the walls of the coring tube until the cores had stood on deck for some time.

Argon and nitrogen

The depth distributions of Ar and N₂ are similar, decreasing with depth in the sediments from concentrations near those of the overlying water to concentrations of about 0.1 and 2 ml/liter, respectively, at a depth of 1 m. The concentrations below 25 cm are much lower than summer concentrations of the overlying water. Argon and N₂ in the surface sediments appear to track seasonal variations in the overlying water. The N₂:Ar ratios decrease with depth from values representing equilibration with the atmosphere (38:1, Benson and Parker 1961) to values of 20:1 at 1 m in the sediment, indicating selective removal of N₂. The removal of Ar can only be accounted for by a physical process.

The principal source of Ar and N₂ in interstitial waters is the overlying water. The production rate of Ar by ⁴⁰K decay is too low (10⁻⁴ ml liter⁻¹ per 10⁶ yr) to affect the depth distributions of Ar in these sediments. Nitrogen can be fixed by hydrogenase-producing sulfate-reducing bacteria (Sisler and ZoBell 1951). Richards

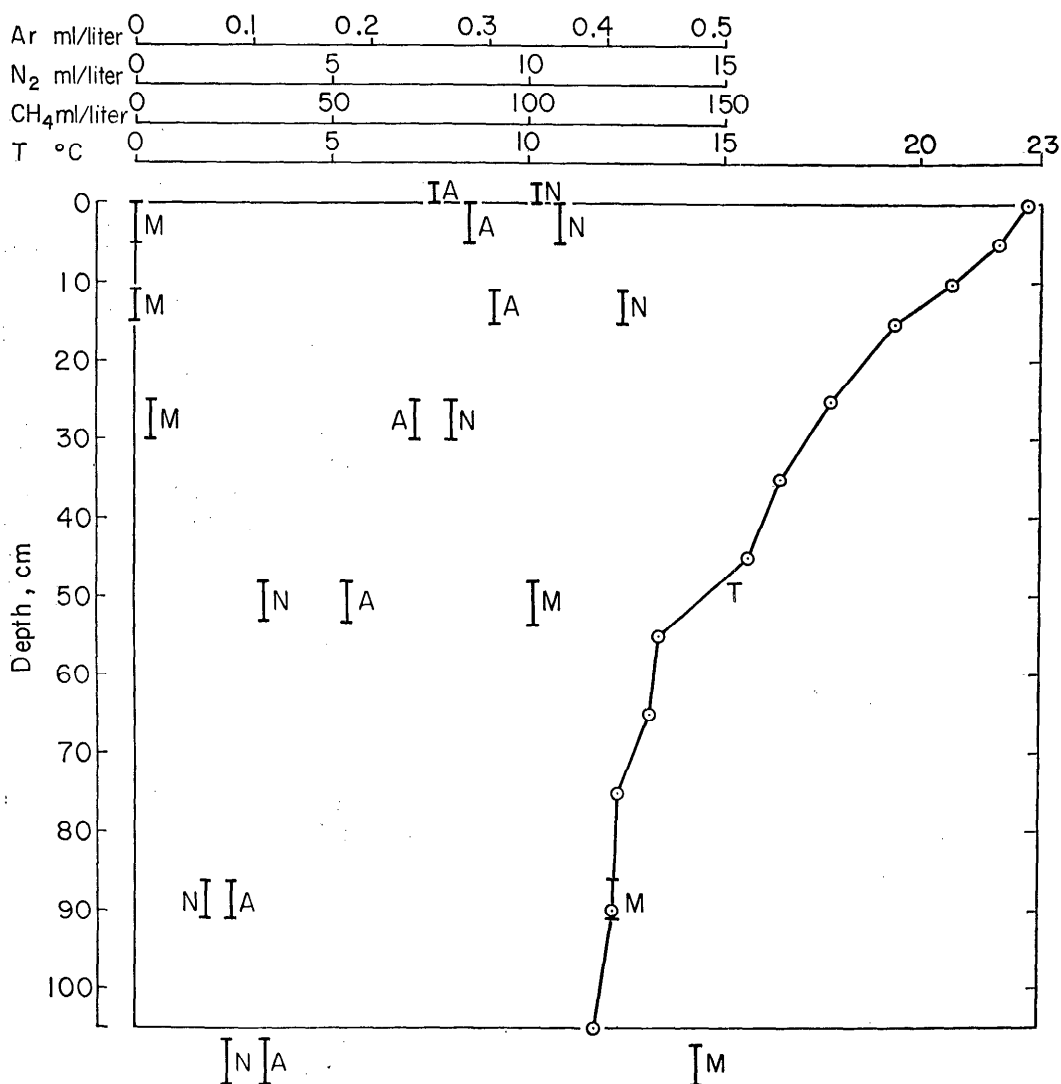


FIG. 4. Depth distributions of argon, A; nitrogen, N; methane, M; and temperature, T, in Chesapeake Bay sediments. Station 858-C, 15 August 1967, 30.4 m.

and Benson (1961) have shown that reduction of nitrite and nitrate in anoxic basin and fjord waters accounts for the small (3%) excess of N₂ there. Several reactions involving oxidation of amino or ammonia-N to N₂ are thermodynamically possible, but none of these has been demonstrated in sediments.

Since CH₄ can be lost from the sediments as bubbles, a stripping process might account for the low Ar and N₂ con-

centrations at depth. This stripping process can be treated quantitatively by calculating the volume of gas phase required to contain the Ar and N₂ lost from the interstitial water and be in equilibrium with the residual Ar and N₂ in the interstitial water. This volume of stripping gas is a minimum estimate of the volume required and implies an equilibrium stripping process if the calculated stripping volumes for both Ar and N₂ are equal.

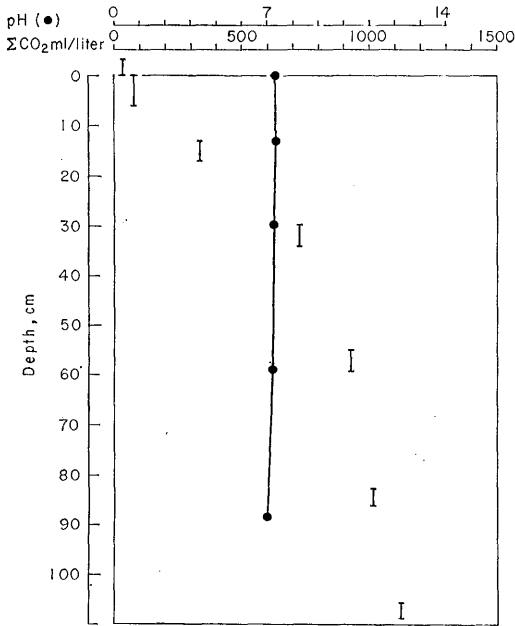


FIG. 5. Depth distributions of total carbon dioxide and pH (●) in Chesapeake Bay sediments. Station 858-D, 15 May 1968, 15.2 m.

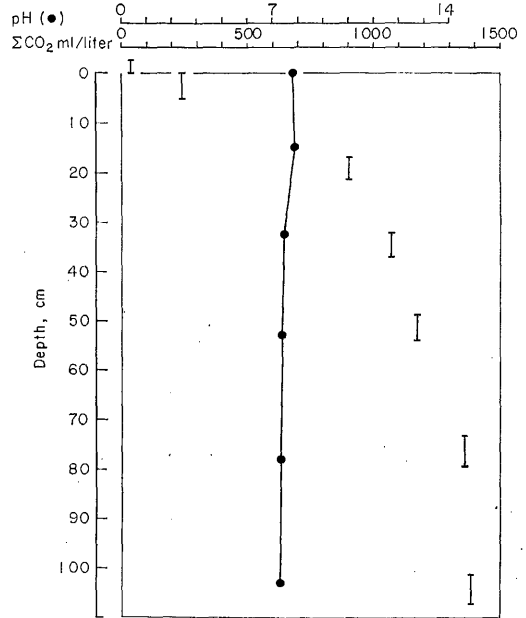


FIG. 6. Depth distributions of total carbon dioxide and pH (●) in Chesapeake Bay sediments. Station 858-C, 23 May 1968, 30.4 m.

The Ar and N₂ data used in this calculation are from three cores taken at the same station and sampled at the surface and 1-m depth (Table 1, Reeburgh 1968). The number of moles of Ar and N₂ lost to the gas phase for each liter of interstitial water was taken as the difference between the surface and 1-m Ar and N₂ concentrations. The observed 1-m Ar and N₂ concentrations were converted to the corresponding partial pressures in the gas volume using the appropriate solubility coefficients at 10°C and 10‰ chlorinity. From the estimated number of moles of gas and the partial pressure, the corresponding volume for both Ar and N₂ was calculated. These calculated stripping gas volumes for Ar and N₂ were, respectively, 80.3 and 81.3 ml/liter of interstitial water. Since uncertainties in the gas measurements are greater than the difference between these two estimates, the stripping gas volumes may be considered equal, indicating that Ar and N₂ are stripped from interstitial water in equilibrium ratios. The lower solubility of N₂ relative to Ar is the

cause of its selective removal. Biological processes may also be affecting the nitrogen distributions, but their effects are overwhelmed by the CH₄ stripping process.

Total CO₂

Total CO₂ increased with depth in the sediments from concentrations of about 100 ml/liter to concentrations over 1,000 ml/liter. The pH was constant with depth at values between 7 and 8. The maximum total CO₂ concentrations do not exceed their critical concentrations. The total CO₂ concentrations observed are much higher than those observed by previous investigators. Emery and Hoggan (1958) did not obtain measurements of total CO₂ because their vacuum extraction technique involved no acidification.

Carbon dioxide is introduced to these sediments with the overlying bay water in concentrations of about 25 ml/liter. It can be produced internally both aerobically and anaerobically in quantities equal to or in excess of CH₄, depending on conditions. Dissolution of CaCO₃ minerals in the sedi-

ments may account for a portion of the total CO_2 , but relatively large quantities of carbonate minerals must be dissolved (1 g/liter CaCO_3 yields 224 ml/liter CO_2) to produce noticeable effects on the total CO_2 distribution.

Considering the pH values and the observed alkalinities of 50 meq/liter, the CO_2 must exist in solution predominantly as HCO_3^- . Unlike CH_4 , most of the CO_2 remains in the sediments as complexes or is neutralized by cations produced or released within the sediments. Explanation of these high concentrations will require careful measurement of both Ca and NH_4^+ .

The possibility that the high total CO_2 concentrations are the result of solution of filter-passing carbonate minerals can be discounted by considering the few measurements of total H_2S . The sediments contain large quantities of acid-labile sulfides, but the interstitial waters contain less than 1 ml/liter total H_2S , indicating that neither sulfide minerals nor carbonate minerals pass the filters in the squeezers. Simultaneous measurements of total H_2S and total CO_2 were attempted using a long DEHS (di-2-ethylhexylsebacate) column followed by a short silica gel column. A H_2S trap consisting of CuSO_4 -coated Celite followed the DEHS column. Such large volumes of total CO_2 were encountered that it was necessary to limit sample size to the point where reliable quantitative measurements of total H_2S were impossible. The low total H_2S concentrations and the presence of large quantities of acid-labile sulfide minerals indicate that H_2S in these sediments is controlled by precipitation.

CONCLUSIONS

The concentrations of Ar and N_2 observed in the upper 25 cm of the sediments are near those of the overlying water and track seasonal variations in the overlying water concentration. They are probably due to admixture of the overlying water. Oxidation of CH_4 or low production account for its absence or low concentration in the upper 25 cm.

Below 25 cm the concentration of CH_4

is controlled by loss as bubbles. The stripping action of these bubbles removes Ar and N_2 from the sediments in equilibrium ratios, leading to a decrease in the N_2 :Ar ratio. Any changes in N_2 by biological activity are masked by the stripping process.

Carbon dioxide remains in the sediment as HCO_3^- , while H_2S is precipitated as iron sulfides.

These measurements shed some light on problems encountered by geologists working with subbottom profilers. These workers sometimes observe almost complete attenuation of their signals, and CH_4 bubbles offer a reasonable explanation of this phenomenon.

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