by reactions in the atmosphere. Although the fluorine atoms released by similar reactions can also destroy O_3 catalytically, the reaction $CH_4 + F \rightarrow CH_3 + HF$ will terminate the fluorine chains more quickly than $CH_4 + Cl \rightarrow CH_3 + HCl$ does for chlorine. Further, reinitiation of fluorine chains will not proceed via $HF + OH \rightarrow F + H_2O$, whereas $HCl + OH \rightarrow Cl + H_2O$ does reinitiate the chlorine chains.

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16. Both D. D. Davis and D. D. Garvin (personal communication) have suggested that $ClO + NO \rightarrow Cl + NO_2$, which couples ClO_x and NO_x cycles, is important for stratospheric chlorine chemistry. This reaction and $H_2 + Cl + HCl + H$ were subsequently included in model studies by Wofsy and McElroy (*7*).
17. We computed photolysis rates for $CFCl_3$ and CF_2Cl_2 versus altitude and time through an implicit numerical solution of the diffusion equation with 10-day time steps and altitude steps ΔZ of 1 km. These loss rates for CF_xCl_y then served as chlorine production rates, Q, in the photochemical, vertical transport model for ClX. Table 1 shows an example of Q along with selected input data. The OH profile was taken from (*12*); the reaction rate for $HCl + OH \rightarrow Cl + H_2O$ was $2 \times 10^{-12} \exp(-335/T)$ (where T is the absolute temperature) (J. G. Anderson, personal communication). The remainder of the photochemical scheme and input data were adopted from (*6*). For the ClX calculations the boundary conditions were: zero flux at the upper boundary (80 km), ground upward flux of 2×10^{10} cm^{-2} sec^{-1} [see (*7*)], and diffusion to the ground at a velocity of 0.4 cm sec^{-1}. These conditions yield ground-level concentrations of 1 part per billion (ppb), consistent with data from C. Junge [*Tellus* **9**, 528 (1957)], an initial stratospheric concentration of 0.55 ppb, below the 0.8 ppb estimated for HCl at 16 km by C. B. Farmer (paper presented at the 3rd Conference on the Climatic Impact Assessment Program, Cambridge, Massachusetts, 27 February 1974). A 10-day rainout period (0 to 5 km), tapering to 100 days at 10 km, was assumed for HCl. The initial ClX profile, though not critical for the present problem, implies a column-integrated O_3 destruction rate of 2×10^{12} cm^{-2} sec^{-1}.
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Methane Production in the Interstitial Waters of Sulfate-Depleted Marine Sediments

Abstract. *Methane in the interstitial waters of anoxic Long Island Sound sediments does not reach appreciable concentrations until about 90 percent of seawater sulfate is removed by sulfate-reducing bacteria. This is in agreement with laboratory studies of anoxic marine sediments sealed in jars, which indicate that methane production does not occur until dissolved sulfate is totally exhausted. Upward diffusion of methane or its production in sulfate-free microenvironments, or both, can explain the observed coexistence of measurable concentrations of methane and sulfate in the upper portions of anoxic sediments.*

Amounts of methane in the marine environment in excess of that resulting from equilibration with the atmosphere most frequently occur in anoxic waters such as those found in fjords (*1, 2*) and in the interstitial water of anoxic sediments (*3–6*). In the absence of sources associated with shipping and industrial activity or natural seeps from oil and gas reservoirs (*7*), most of this methane results from anaerobic bacterial decomposition of organic matter. Methane bacteria are readily found in anoxic environments, where they are terminal organisms in the microbial food chain (*8*); moreover, there is some evidence that methane is not produced until dissolved sulfate has been previously removed by sulfate-reducing bacteria (*5, 6*).

The interstitial waters of Recent organic-rich marine sediments are ideal for studying the relation between methane and dissolved sulfate distributions because of the large concentration changes over short depth intervals that result from high bacterial activity. In this report we present the results of a study of methane and dissolved sulfate in the interstitial waters of Long Island Sound sediments which suggest that significant production of methane does not begin until dissolved sulfate concentrations approach zero. Results of laboratory studies of time-dependent changes in the chemistry of anoxic marine sediments indicate that sulfate reduction and methane production are mutually exclusive metabolic processes.

Gravity cores were collected at three stations in Long Island Sound. Station TH is located approximately 2 km south of the coastal town of Guilford, Connecticut, at a water depth of approximately 7 m. Stations BS and SC are located in two shallow harbors near Guilford. The water depths at these two stations ranged from 1.5 to 4 m because of tidal fluctuations. Interstitial waters were sampled without coming into contact with air by transferring sediments from sealed core liners to a filter-press type squeezer through an interlock flushed with CO_2 or He (*9*). Dissolved methane was measured by liquid stripping techniques developed for measuring dissolved gases in seawater by Swinnerton *et al.* (*10*) and applied to interstitial water measurements by Reeburgh (*11*). Dissolved sulfate was measured by gravimetric analysis as $BaSO_4$. Blank corrections for precipitation of nonsulfate material led to uncertainties of ± 0.5 mmole liter^{-1} in dissolved sulfate concentrations.

Concentrations of methane and dissolved sulfate in the interstitial waters are plotted as a function of depth in Fig. 1. Differences in the depth of complete sulfate reduction at the three stations are probably a result of variations in sedimentation rates and the content of organic matter in the sediments. The leveling off of methane concentrations at station SC at about 1.0 mmole liter^{-1} is consistent with reaching saturation with respect to methane. The solubility of methane calculated from the Setchénow relation by using solubility data from Winkler (*12*) and Atkinson and Richards (*2*) ranges from 1.1 to 2.3 mmole liter^{-1} (25 to 51 ml liter^{-1}) for the temperature range (4° to 28°C) and salinity range (27 to 31 per mil) encountered in these sediments.

Reeburgh (*4*) has presented evidence of methane saturation in Chesapeake Bay sediments, which results in the formation of trapped methane bubbles that strip other dissolved gases such as N_2 and Ar from interstitial waters in the sediments. We infer from the low concentrations of dissolved N_2 and Ar at station SC that this process may be taking place there (*13*).

The data in Fig. 1 show that in the interstitial waters of Long Island Sound sediments high methane concentrations do not occur unless sulfate concentrations have been appreciably lowered. Only where dissolved sulfate concentrations approach zero do concentrations of methane attain saturation.

Four alternative hypotheses can be used to explain these results. The first is that methane is produced at roughly the same rate throughout the sediment column by methane bacteria but is consumed by sulfate-reducing bacteria through the reaction

$$CH_4 + SO_4^{2-} + 2H^+ \rightarrow H_2S + CO_2 + 2H_2O$$

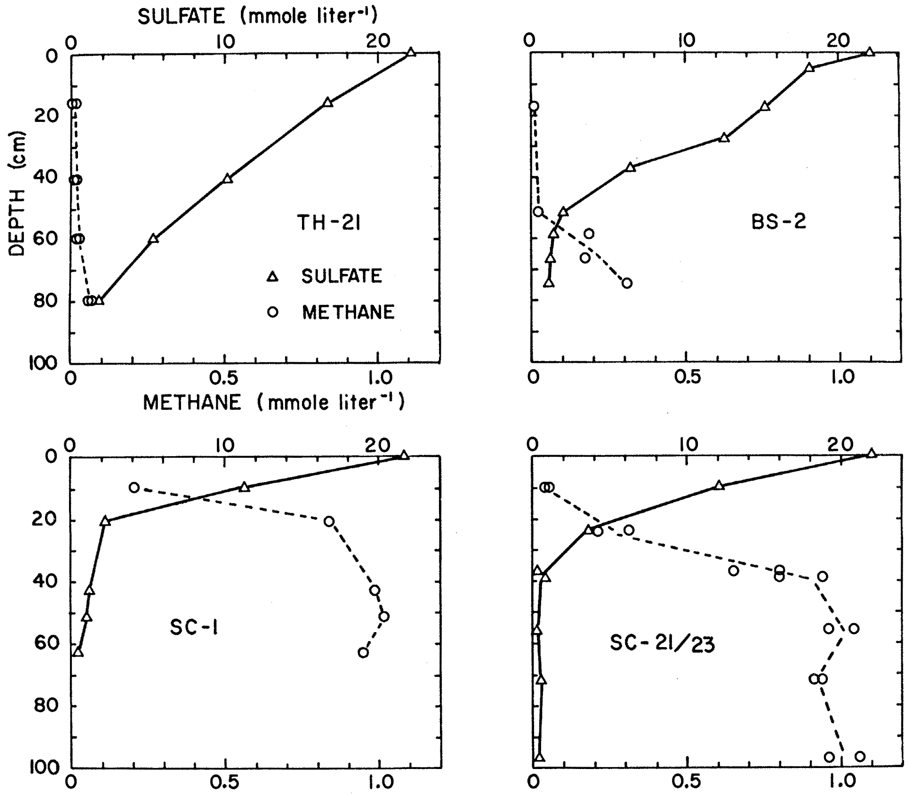

Fig. 1. Concentrations of methane and dissolved sulfate in the interstitial waters of Long Island Sound sediments. Core SC 21/23 data are from a combination of two cores taken together at station SC. The legends shown on the axes for the TH-21 data also apply to the BS and SC core data. Sulfate concentrations below 1.0 mmole liter^{-1} may represent precipitation of nonsulfate material (see text).

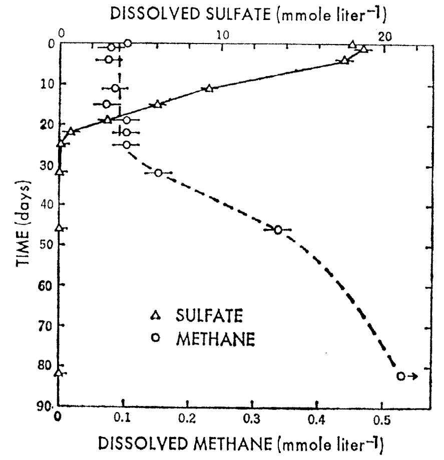

Fig. 2. Concentrations of methane and dissolved sulfate in the interstitial waters of salt marsh pan sediments sealed in jars plotted against the time when the jars were opened. The methane concentration in the 82-day jar is shown as a lower limit (indicated by arrow) because methane was lost through cracks in the lid of the jar caused by gas pressure buildup.

This reaction has been considered by Feely and Kulp (*14*) during studies of sulfate reduction by various hydrocarbons associated with petroleum. The reaction is energetically possible; however, the direct reduction in the absence of bacteria does not appear to occur at an appreciable rate below 500°C. The reaction may be catalyzed by bacteria present in our sediments (*15*), although most methane-oxidizers are aerobic (*16*). Studies of the anaerobic oxidation of ^{14}C-labeled methane by the sulfate-reducing bacteria, *Desulfovibrio desulfuricans*, indicate that they do carry out this reaction, but at a very slow rate (*17*). Apparently the bacteria prefer other organic compounds (such as those present in abundance in our sediments) as energy sources.

The second explanation is that methane is produced only in the absence of dissolved sulfate below the zone of sulfate reduction and that coexistence of the two is due simply to interdiffusion. Mutual exclusivity of production can be explained on the basis of equilibrium thermodynamic calculations (*18*), relative energy yield models (*6*), or kinetic models involving competition for available hydrogen (*5*); in all these explanations the organisms capable of greatest metabolic energy production will dominate (*19*). Relative energy yield models have been successfully used to explain the observed sequence of aerobic respiration, nitrate reduction, and sulfate reduction in the marine environment (*1, 2, 20*). Claypool and Kaplan (*6*) have calculated energy yields to demonstrate that sulfate reduction and methane production should be mutually exclusive in marine sediments. They suggest, in agreement with previous workers (*5, 15*), that the most important mechanism for methane formation in the marine environment is reduction of CO_2 by biologically produced hydrogen

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

This reaction is thought to account for the methane concentrations found in Lake Kivu, an African rift lake, although the carbon dioxide and hydrogen are attributed to abiogenic rather than biogenic sources (*21*).

The third alternative is that methane is produced only in the absence of dissolved sulfate, as described in alternative 2. However, this methane, on diffusing upward, is then consumed by sulfate reducers as described in alternative 1.

The fourth alternative is that methane is produced to a limited extent in the presence of sulfate-reducing bacteria but is not utilized by them. For example, methane would be formed when sulfate reduction was complete in organic-rich microenvironments such as the interior portions of decaying organisms, while at the same time sulfate reduction continued in the surrounding sediment matrix. The result, when methane diffuses away from the microenvironments, is the presence of low concentrations of methane coexisting with sulfate. Then, on reduction of all or nearly all of the sulfate, the concentration of methane rises as much more methane is generated throughout the sediment. The methane maximum observed in the water column at normal seawater sulfate concentrations in locations such as the western Gulf of Mexico (*7*) may also be the result of production of methane in microenvironments such as decaying particulate organic matter or the guts of living organisms.

To test the various hypotheses we made a laboratory study of sulfate reduction and methane production with natural sediments. A large sample of sediment from the surface of a salt marsh pan was collected near Guilford. The sediments were quickly brought to the laboratory, homogenized by stirring in a large plastic bucket, and loaded into airtight glass jars, which were immediately sealed. The jars were stored at 22°C in the laboratory (close to the 17°C field temperature at time of collection) and opened sequentially for analysis of dissolved sulfate and methane over an 82-day period. The experimental results are summarized in Fig. 2 (*22*).

The methane concentration of the sediments remained at its original value until dissolved sulfate was totally exhausted at about 32 days. At this time methane production began and a maximum production rate of approximately 13 μmole liter^{-1} day^{-1} was observed. The apparent drop-off in this production rate based on the methane concentration after 82 days was at least partially due to loss of methane through observable cracks in the lid of the 82-day jar caused by gas pressure buildup. The salinity and concentrations of other ions in this jar rose because of evaporation through the cracks. These problems were not encountered with the other jars.

The significant result of the jar experiment is that methane originally present in the salt marsh sediments neither increased nor decreased during sulfate reduction. To the extent that the jar experiment mimics nature (*23*) this suggests that sulfate reduction and methane production are mutually exclusive processes and that oxidation of methane by sulfate-reducing bacteria is not responsible for the observed distributions in Long Island Sound sediments. Instead, the observed coexistence of measurable concentrations of methane and sulfate ions may be accounted for by interdiffusion combined with limited production of methane in sulfate-free microenvironments as described in alternatives 2 and 4 above. Before a firm choice of hypotheses can be made, however, more data from both pore waters and laboratory experiments, especially combined with microbiological identifications, are needed.

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23. The rate of sulfate reduction observed in the laboratory jar experiment, about 2.8×10^{-1} mole liter^{-1} year^{-1}, approximates the highest rates calculated for marine sediments (M. Goldhaber and I. R. Kaplan, *J. Soil Sci.*, in press).
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Melatonin: Its Inhibition of Pineal Antigonadotrophic Activity in Male Hamsters

Abstract. *Exposure of male hamsters to short daily photoperiods (1 hour of light and 23 hours of darkness daily for 9 weeks led to total involution of the testes and accessory sex organs (seminal vesicles and coagulating glands). Pituitary levels of immunoreactive prolaction also decreased by about 60 percent after dark exposure. The inhibitory effects of darkness on the reproductive organs were prevented either by pinealectomy or by the subcutaneous implantation of a melatonin-beeswax pellet into the animals each week. Both pinealectomy and melatonin treatment also returned pituitary levels of prolactin toward normal. The results suggest that melatonin is not the pineal antigonadotrophic factor in the male golden hamster.*

A considerable amount of evidence suggests that *N*-acetyl-5-methoxytryptamine (melatonin) may be a pineal antigonadotrophic factor in the rat (*1*). In the golden hamster, however, melatonin has repeatedly failed to exhibit gonad-inhibiting activity (*2*). Yet, in both males and females of the species the pineal gland is known to be strongly suppressive to the reproductive system (*3*). However, melatonin may yet play some role in determining the ability of darkness to influence reproductive physiology in photosensitive species. The results of the present experiment show that melatonin acts in a heretofore unreported manner to prevent the pineal gland from inducing gonadal degeneration in dark-exposed male hamsters.

Forty young adult male hamsters (*Mesocricetus auratus*) (60 to 75 g) were purchased from Lakeview Hamster Colony, Newfield, N.J. Six of these were maintained in long daily periods of light (14 hours of light and 10 hours of darkness in each 24 hours) (LD 14 : 10) throughout the study. The remaining 34 hamsters were subdivided into four groups which were maintained in short daily light periods (1 hour of light and 23 hours of darkness in each 24 hours) (LD 1 : 23).

Of the four dark-exposed groups, one group received no further treatment, one group was pinealectomized by use of a standard procedure (*4*), one group received a weekly subcutaneous implant of a beeswax pellet (25 mg), and the final group received weekly a beeswax pellet that contained 1 mg of melatonin (*5*). Administration of melatonin in this manner has been found to produce endocrine effects (*6*). Nine weeks after the onset of the experiment the hamsters were decapitated and trunk blood was collected in heparinized tubes. Body, testicular, accessory organ (seminal vesicles and coagulating glands), and anterior pituitary gland weights were recorded. Pituitaries and plasma samples were analyzed by radioimmunoassay for prolactin by using an established technique (*7*). Data were statistically analyzed on a Programma