Evolution of the Global Biogeochemical Sulphur Cycle
Edited by P. Brimblecombe and A. Yu. Lein

CHAPTER 6
Interaction of Sulphur and Carbon Cycles in Marine Sediments

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6.1 QUANTITATIVE RELATIONSHIPS BETWEEN SULPHATE REDUCTION AND CARBON METABOLISM IN MARINE SEDIMENTS*

6.1.1 Introduction

Measurements of the quantitative relationships between the oxidation of organic carbon and sulphate reduction in marine sediments are fundamental to the understanding of the biochemical cycling of C and S. These relationships may also reflect the form and amount of these elements at various stages of cycling or the rates at which their diagenesis occur.

A general conclusion of several investigators is that a major portion of the organic carbon deposited in sediments is rapidly oxidized to CO_2 by the sulphate-reducing bacteria (SRB) and that 2 moles of organic carbon are oxidized for every mole of sulphate reduced. However, the degree to which the data that have prompted these conclusions represent the true situation, is constrained. These constraints involve the methodology and the reliability of measured amounts and rates, the complexity of ecosystems, and the variations imposed by seasons, environmental perturbation and patchiness. These topics will be reviewed with the aim of drawing together the data which are concerned with the biogeochemical dynamics of C and S cycling.

6.1.2 Organic substrates for the sulphate-reducing bacteria in marine sediments

Recent studies of the anaerobic oxidation of organic matter in sediments indicate that fatty acids are quantitatively the most significant penultimate end-products (Balba and Nedwell, 1982; Chambers, 1985; Christensen, 1984; Mountfort and Asher, 1981; Sansone and Martens, 1982; Skyring, 1987,

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1988; Sørensen *et al.*, 1981). Sulphate reduction is the most important process in the complete oxidation of these fatty acids in anoxic marine sediments where sulphate is not limiting. Widdel (1980) gives the general equation for the complete oxidation of fatty acids by the SRB as follows:

$$4H(CH_2)_nCOO^- + (3n+1)SO_4^{2-} + H_2O \rightarrow (4n+4)HCO_3^- + (3n+1)HS^- + OH^- + nH^+$$

For example, when acetate is oxidized completely, the atomic ratio of organic carbon oxidized to sulphate-S reduced is 2 : 1. This is the ratio which is usually used to calculate the quantity of organic-C required to support measured sulphate reduction rates. However, as 'n' increases, the C : S ratio decreases and this may affect such calculations in some unusual circumstances. The presently available data suggest that, in most marine environments, acetate is the dominant natural substrate (Balba and Nedwell, 1982; Banat *et al.*, 1981; Chambers, 1985; Christensen, 1984; Sansone and Martens, 1982; Skyring, 1988; Plumb and Reichstein, 1984; Plumb *et al.*, 1983; Sorensen *et al.*, 1981). A consequence of this observation is that the acetate-oxidizing SRB must be ecologically the most important group of SRB in marine environments. However, other low molecular weight fractions of the dissolved organic carbon (DOC) reservoirs have been shown to be quantitatively important substrates for the SRB. Oremland and Silverman (1979) found that sulphate reduction in San Francisco Bay (USA) sediments was stimulated by lactate but not acetate, and lactate may also be an important natural substrate for the SRB in the sediments of the Ems–Dollard estuary, Holland (Laanbroek and Veldkamp, 1982). From molybdate inhibition experiments Sorensen *et al.*, (1981) and Christensen (1984) considered that propionate and butyrate were quantitatively significant substrates for the SRB in European coastal sediments. However, Skyring (1988), on the basis of the observed stoichiometry between acetate oxidation and sulphate reduction in a coastal lake (Lake Eliza; South Australia) sediment, concluded that propionate was probably not a major substrate for the SRB even though it accumulated in molybdate-treated samples. Succinate (Balba and Nedwell, 1982) and formate (Barcelona, 1980) may also be important natural substrates for the SRB in some marine environments.

Skyring (1984) found that sulphate reduction in the cyanobacterial mats of Spencer Gulf, was stimulated twofold by a complex mixture of growth substrates, but not by acetate or lactate. In respect of alternative energy substrates for the SRB, Skyring *et al.* (1977) and Stams *et al.* (1985) described the utilization of amino acids by several strains of marine SRB, and Smith and Klug (1981) suggested that amino acids may be important substrates for the SRB in freshwater sediments. Amino acids excreted into the rhizosphere by plant roots may be important natural substrates for the SRB in sea grass beds, coastal marshlands and mangroves (Jorgensen *et al.*, 1981).

Aizenshtat *et al.* (1984) found that the DOC in the porewaters of Solar Lake (Sinai, Egypt) is mostly amino acids and the concentration increases with depth in the sediment reaching 50 mM. Why these amino acids do not appear to be suitable substrates for the SRB in Solar Lake (since sulphate reduction rates decreased rapidly with the depth of sediment) was enigmatic. The fact that free amino acids accumulate in this environment indicates that there must be very severe restrictions other than substrate availability on microbial activity, including that of the SRB.

Substantial methane oxidation rates have been attributed to the SRB in the subsurface sediments of Saanich Inlet (Devol and Ahmed, 1981; Devol *et al.*, 1984) and other investigators have also suggested that the SRB are involved in methane oxidation in various subsurface marine sediments (Iversen and Blackburn, 1981; Kosiur and Warford, 1979; Martens and Berner, 1977; Reeburgh, 1976, 1980; Zehnder and Brock, 1980). While the geochemical evidence for the coupled methane oxidation and sulphate reduction appears to be convincing, pure cultures of methane-oxidizing SRB, or even active consortia, have not been isolated and recently Reeburgh (see Section 6.3) concluded that the presently known SRB could not be responsible for methane oxidation unless alternative oxidants are involved.

6.1.3 Methods and variability: primary productivity

Hall and Moll (1975) and Bunt (1975) reviewed many of the methods used for assessing aquatic primary productivity and it is evident from recent publications on this topic that the principal methodologies have not changed significantly over the last 10 years*. However, satellite imaging methods for determining pelagic chlorophyll concentrations have greatly improved the database for global oceanic photosynthesis. The synthesis of organic matter by primary producers is the first step in most concepts of biogeochemical cycles since it is this organic matter which is the energy source for the various organisms involved (Trudinger *et al.*, 1979). A review of primary production in aquatic ecosystems is beyond the scope of this contribution. Therefore attention has been restricted to the following ecosystem in which quantitative relationships between the cycling of C and S have been investigated: cyanobacterial and other microbenthic mats, coastal salt marshes, sea grass beds (meadows), and sediments receiving planktonic rain.

Cyanobacterial and microbenthic mats

Cyanobacterial mats were chosen by this SCOPE workshop as model ecosystems for studying the quantitative relationships between the carbon

*Since preparation of this paper, Roberts *et al.* (1985) have extensively reviewed measurement of plant biomass and net primary production.

and sulphur cycles. Cyanobacterial mats are benthic ecosystems, of which many types are present in modern aquatic environments (see Cohen *et al.*, 1984). Some are very simple structures such as the 1 to 2 mm smooth mats in Spencer Gulf (South Australia) in which *Microcoleus* colonizes carbonate sediments (Bauld *et al.*, 1979, 1980; Bauld, 1984; Skyring and Johns, 1980; Skyring *et al.*, 1983). On the other hand, the microbial components of the mats of Solar Lake are multi-layered and quite complex biologically, but are relatively free of clastic material (Krumbein *et al.*, 1977).

One of the most convenient methods for determining primary productivity is to use ^{14}C-bicarbonate as a tracer to monitor the rate of incorporation of ^{14}C into photosynthate. In order to calculate a primary productivity of a mat ecosystem, it is essential to know the concentration of the bicarbonate being assimilated. The simplest way would be to determine the ^{14}C specific activity of the bicarbonate in the water surrounding the mat. However, Revsbech *et al.* (1981) found that, even after two hours, a ^{14}C-bicarbonate tracer had not equilibrated with the bicarbonate in a diatomaceous mat covering the sediments of Randers Fjord (Denmark). They pointed out that specific activities calculated from the concentration of the bicarbonate in the overlying water would have resulted in underestimation of the primary productivity of the mat. Joint (1978) also used a ^{14}C method to measure primary productivity of the benthic phototrophs of estuarine mud flats of the Lyhner River (UK) in which *Enteromorpha* contributed a large amount of organic matter to the sediments. Bauld (1984) and Bauld *et al.* (1979) used a ^{14}C-bicarbonate tracer and determined the bicarbonate concentration in Spencer Gulf seawater by titration with standard acid to determine the primary productivity of cyanobacterial mats. The results were consistent with those determined for other cyanobacterial mat ecosystems (Bauld, 1984). However, in hypersaline environments, an accurate determination of bicarbonate by titration may be complicated by the effect of salt on pH measurements. There are, however, other methods which do not rely on accurate pH measurements. Horner and Smith (1982) described a method for estimating the CO_2 bicarbonate concentration in water by ^{14}C dilution. This method is independent of salinity for the calculation of bicarbonate concentration. Carbon dioxide-specific membrane electrodes are suitable for determining the total CO_2-bicarbonate in natural waters and CO_2 may also be measured by compact, dedicated infrared spectrophotometers or by gas chromatography.

Javor and Castenholz (1984) used slurry suspensions of cyanobacterial mat from Laguna Negro (Mexico) to estimate primary productivity and pointed out that, with this method, light penetration causes some problems in relating experimentally determined productivity with that of the *in situ* mat. In a method developed by Bauld *et al.* (1979, 1984), discs of intact cyanobacterial mat were incubated so that the original orientation of the

mat to light was always preserved. Thus, if it is possible to use discs, this would be the preferred method for estimating cyanobacterial mat primary productivity under conditions that would approximate the *in situ* conditions. In some of the complex mat structures there are layers of photosynthetic sulphur bacteria below the cyanobacteria (Castenholz, 1984; Stolz, 1984). Estimates of the non-oxygenic photosynthesis by these bacteria may be estimated by preferentially inhibiting the cyanobacterial photosystem II with 3-(3,4-dichloropheny)-1,1-dimethyl-urea (DCMU). However, some of the cyanobacteria such as *Oscillatoria limnetica* also oxidize sulphide phototrophically (Cohen, this volume, Section 8.1), and Revsbech and Ward (1984) pointed out that CO_2 fixation in the presence of DCMU does not provide a measure of the importance of anoxygenic phototrophy in the intact oxygen-producing mat. Illumination of the samples with far red (800–900 nm) light specific for bacteriochlorophyll would be preferable for determining bacterial phototrophy (Cohen, this volume, Section 8.1).

The methods for estimating the primary productivity of cyanobacterial mat communities discussed above were generally based on the fixation of $^{14}CO_2$ by small representative samples. Kinsey (1983, 1985) reviewed the monitoring of CO_2 flux in a body of water (marked with dye) for estimating the net carbon metabolism over large areas of various ecosystems of a coral reef. The method relied on the measurement of fluxes of bicarbonate (determined by alkalinity measurements) and oxygen in a marked water body as tidal currents moved the water over metabolizing benthic communities which included extensive cyanobacterial mats occuring in various parts of coral reefs.

Usually, the quantity of ^{14}C fixed as particulate organic carbon (POC) in the photosynthesizing community is used to estimate productivity. However, Plumb *et al.* (1982) estimated that the net quantity of ^{14}C appearing in the dissolved organic fraction (DOC) associated with a cyanobacterial mat was 1–3% of the total productivity. Photo-assimilation and heterotrophic assimilation may complicate the calculation for gross DOC production by cyanobacterial mats (Plumb *et al.*, 1983). Clearly DOC should be estimated when calculating total productivity.

Oxygen production rates, based on bulk-volume analyses, have been used to estimate primary productivity of several cyanobacterial ecosystems. However, Javor and Castenholz (1984) considered that there were many problems associated with this method, mainly because respiration rates in the light and dark are not equal. Recently developed micro-electrode techniques have provided data on the *in situ* rate of O_2 production in intact mats (Jørgensen *et al.*, 1983; Revsbech *et al.*, 1981) and Revsbech *et al.* (1983) comprehensively reviewed the use of both oxygen production and bicarbonate fixation methods for measuring primary productivity. They concluded from their experiments on bacterial and diatomaceous mats, that

the ^{14}C-bicarbonate method was the most reliable because the oxygen method was complicated by the formation of bubbles. Oxygen production by cyanobacterial mats in Solar Lake was further discussed by Jørgensen *et al.* (1983). A summary of the primary production measurements for various microbenthic mats is given in Table 6.1.

Coastal Salt Marsh Ecosystems

Schubauer and Hopkinson (1984) comprehensively reviewed methods for measuring above and below ground productivity by salt marsh macrophytes of which *Spartina*, *Juncus* and *Salicornia* are the main genera. They harvested complete plants at various times of the year to calculate productivity. They concluded from their investigations with *Spartina* (Georgia, USA) that the statistical variations (standard error or deviation) for the living and dead biomass were ± 10–20% and ± 15–27% for above and below ground, respectively. They concluded that various methods for measuring above ground productivity were satisfactory. However, measuring below ground production by separating live and dead tissue was difficult, tedious and expensive. They also concluded that, since root mass was much less than rhizome or dead material, the process could be made more efficient without sacrificing too much accuracy by including the root mass with the dead material.

Schubauer and Hopkinson (1984) found that the below ground production was around 1.6 times the above ground production and that the total plant production was very high at 7620 g (635 mol (C)$m^{-2}a^{-1}$) for *Spartina alterniflora* and *S. cynsuroides*. These values are the highest productivities reported for salt marsh ecosystems. However, they considered that, if anything, the *in situ* production was underestimated. Livingstone and Patriquin (1981) found that the ratio between below and above ground production in a Nova Scotia (Canada) *Spartina* salt marsh was around 1.75, which was very close to that calculated by Schubauer and Hopkinson (1984). The latter also measured turnover rates (productivity/mean biomass) at 5.09 to 5.35 a^{-1} for *Spartina*. Estimates by several methods of above and below ground production for a variety of the salt marsh ecosystems of the eastern USA are available and for detailed information, reference may be made to Pomeroy *et al.* (1981), Valiela *et al.* (1982), Wiegert *et al.* (1981), and Woodwell *et al.* (1973).

High productivity characterizes coastal salt marsh estuarine ecosystems and, consequently, very high rates of microbial activity are characteristic of the sediments (Table 6.1). In addition to the high productivity of the marshland grasses, phytoplankton and benthic algae make a significant contribution to the total productivity of salt marshes; these have been calculated at around 6% and 10%, respectively for Georgia salt marshes (Pomeroy *et al.*, 1981).

Sea grasses

Sea grasses are frequent colonizers of the lower slope of estuarine sediments and shallow seas. Zieman and Wetzel (1980) reviewed the methodology for estimating the productivity of sea grasses and they recommended the method developed by Jacobs (1979) in which production is estimated from various leaf components. However, estimates of net productivities, like those for salt marsh grasses, are complicated by the inadequacies for measuring below ground productivities. Estimates of net annual productivities range from 4 to 8 mol (C) m^{-2} with an exceptionally high value of 83 mol (C) m^{-2} being estimated for the *Zostera* meadows of the Bering Sea (Hood, 1983). Moriarty *et al.* (1985) measured leaf primary productivity for *Zostera capricornia* in subtropical Moreton Bay (Queensland, Australia) and calculated an annual rate of around 40 mol (C) m^{-2}. Jørgensen (1977) estimated (methods not specified) that the organic detritus in Limfjorden (Denmark) was derived mainly from phytoplankton and the eelgrass, *Zostera marina*, and that the average daily input to the sediments was 0.1 mol (C) m^{-2}. The productivity of *Zostera capricornia* was estimated by the rate of leaf elongation by Moriarty *et al.* (1985) at a similar average daily rate of 0.11 mol (C) m^{-2}. Below ground productivity was not measured. Moriarty *et al.* (1985) amended the daily productivity to 1.6 g (0.13 mol) (C) m^{-2} to account for DOC excretion and epiphyte production. Burkholder and Doheny (1968) found that the ratio of leaf to rhizome plus roots of *Zostera marina* was 2 : 3 in sand and 10 : 3 in mud, and Sand-Jensen (1975) calculated that above ground productivity was 2–6 times below ground productivity. In this respect, the above ground production of sea grasses was relatively greater than above ground production in salt marsh grasses.

Planktonic ecosystems

Much of the organic matter in the bottom sediments of estuaries, enclosed seas, unconfined continental shelves, continental slopes, and abysses of the deep ocean is derived from phytoplankton, zooplankton and faecal debris. However, it is probably the phytoplankton (Meadows and Campbell, 1978) which is the largest carbon source for resident heterotrophic microbial populations. Meadows and Campbell (1978) briefly described the various methods used for measuring phytoplankton productivity. The measurements are relatively simple compared to those required for marsh and sea grasses and the standard errors are considerably lower. Forsberg (1985) briefly reviewed the ^{14}C methods for estimating primary productivity of phytoplankton. Problems he discussed were concerned with ^{14}C equilibration, cellular carbon pools, light saturation and culture growth rate. In some instances, primary productivity may be overestimated by as much as 70% although considerable underestimates are also known. Phytoplankton are patchy (see

Table 6.1 Quantitative relationships between primary productivity and sulphate reduction

Ecosystem	Primary productivity m^{-2} mmol day^{-1}	Primary productivity m^{-2} mol a^{-1}	Sulphate reduction m^{-2} mmol day^{-1}	Sulphate reduction m^{-2} mol a^{-1}	Percent carbon oxidized by SRB	References
Cyanobacterial mats						
Solar Lake (Sinai)						
Microcoleus	700–1000		70		14–20	Cohen *et al.*, 1980
Oscillatoria						Jørgensen and Cohen, 1977
						Krumbein *et al.*, 1977
Spencer Gulf (Australia)						
Microcoleus	17–258	13.5	2–104	6.5	80–100	Skyring *et al.*, 1983
Lyngbya	170–241[1]		2–21[2]		12	Bauld, 1984(1)
						Skyring, 1984(2)
Salt marshes						
Great Sipiwissett (USA)						
Spartina alterniflora						
Above ground		17[3]				Valiela *et al.*, 1982(3)
Below ground		58–75[4]	60[5]	18[5]	54[5]	Howes *et al.*, 1985(4)
				75[6]		Howes *et al.*, 1984(5)
						Howarth and Teal, 1979(6)

Sea grass meadows						
Limfjorden (Denmark) *Zostera marina*		14.2	9.5	2.6	53	Jørgensen, 1978
Moreton Bay (Australia) *Zostera capricornia*	107 (aboveground)		10.5		80	Moriarty *et al.*, 1985
Planktonic						
Long Island Sound (USA)		17.4		29–39	11	Aller and Yingst, 1980
The Baltic Sea		5.3 (to sediment)			36	
(Gdansk Basin)		5.2 (to sediment)		4	90	Lein *et al.*, 1982
Coral reef sediments						
The Great Barrier Reef Lagoon sediments	92[6] (benthic)		8[7]		20–32	Kinsey, 1985 Skyring, 1985

SRB : Sulphate-reducing bacteria.

Meadows and Campbell, 1978) in their distribution in the water column and this complicates estimates of primary productivity for large areas (e.g. Alvarez-Borrego, 1983). Estimates of primary productivity of seas and oceans are given by Koblentz-Mishke *et al.* (1970) on the basis of productivity zones which range from the highly productive neritic waters of coastal ecosystems and shallow seas to the lower production areas of the oligotrophic waters of the halistatic subtropics. Accession of organic matter by the sediments decreases exponentially as the depth of water increases and this is reflected in the flux of organic matter depositing on sediment surfaces (Billen, 1982; Suess, 1980; Suess and Muller, 1980). In a wide variety of lakes phytoplankton are consumed in the water column by grazing and metabolic processes. However, in some freshwater lakes, the situation may be different because Forsberg (1985) showed that in Lake Wingra (USA) 42% sank to the sediments.

6.1.4 Methods and variability: sulphate reduction rates

Several methods have been used for estimating sulphate reduction rates in sediments and this subject has been reviewed extensively by Skyring (1987). The following paragraphs summarize the methods briefly.

Mathematical modelling of the depth/concentration profiles of sulphate, sulphide, ammonia and sedimentation rates have been used to calculate sulphate reduction rates for estuarine and deep sea sediments (Aller and Yingst, 1980; Bender and Heggie, 1984; Berner, 1964; Goldhaber *et al.*, 1977; Goldhaber and Kaplan, 1980; Jørgensen, 1978; Murray *et al.*, 1978; Toth and Lerman, 1977; Westrich and Berner, 1984). These modelling techniques have some advantages over direct methods for calculating sulphate reduction rates in deep sea sediments. Release of the enormous pressures on raising the sediments to the surface may adversely affect some microorganisms; however, it appears that high temperatures are more detrimental (Jannasch, 1984). Whatever the environment, simple mathematical methods are only applicable where the sediment is not perturbed by fauna or water currents (Jørgensen, 1978; Westrich and Berner, 1984). Other indirect methods for calculating sulphate reduction rates have involved ammonia turnover rates (Blackburn, 1979) and electrical impedance of porewaters and sediment slurries (Oremland and Silverman, 1979).

Direct chemical methods involving measurements of sulphate depletion and increase of sulphide concentrations have also been used (e.g. Aller and Yingst, 1980; Bågander, 1977). Jørgensen (1978) found that long periods of incubation in a closed vessel resulted in an overestimation of net sulphate reduction rates because the natural rate of aerobic sulphide oxidation was lowered. He thus recommended short incubation periods with the natural orientation of the samples being maintained. In estimating *in situ* sulphate

reduction rates there is a statistical problem in addition to these problems of chemical balances and fluxes. Observations have shown that variations in both sulphide and/or sulphate concentrations of replicate samples are generally too great to permit the recognition of relatively small changes due to sulphate reduction which occurs in short periods (Skyring *et al.*, 1983). Radioactive sulphate (^{35}S) has been used by many investigators (first by Ivanov, 1956) as an extension of the direct methods, to trace the course of sulphate reduction in sediments because the production of very small amounts of radioactive sulphide may be detected. A sulphate reduction rate may be calculated from the specific activity of the sulphate, and the quantity of radioactive sulphide produced over a given period. However, while the principle is simple, there are some problems which may affect the reliability of the results (Howarth and Giblin, 1983; Howarth and Jørgensen, 1984; Jørgensen, 1978; King *et al.*, 1985; Skyring, 1984, 1985, 1987, 1988; Skyring *et al.*, 1979, 1983). Because of important recent developments in this method, some emphasis is given to this topic in the following paragraphs.

Pyrite (FeS_2) is the form in which most of the reduced sulphur exists in subsurface marine sediments (Berner, 1984) and its formation in sediments is complex (Berner, 1970; Hallberg, 1972; Krouse and McCready, 1979; Lindstrom, 1980; Luther *et al.*, 1983; Morozov and Rosanov, 1981; Rickard, 1970; Sweeney and Kaplan, 1980; Trudinger, 1981; Volkov and Rosanov, 1983). However, pyrite is the most stable end-product of sulphate reduction and knowledge of the mechanism and rates of its formation are essential to understand its geochemical significance.

Pyrite is generally thought to form slowly in marine sediments (Berner, 1971) and for this reason, most investigators using ^{35}S-sulphate to determine sulphate reduction rates have considered that pyrite formation during short-term incubations (i.e. hours to days) could not significantly affect the determination if the rate of ^{35}S incorporation into pyrite was omitted. However, in a series of papers on this subject, (Howarth and Teal, 1979; Howarth and Giblin, 1983; Howarth and Marino, 1984; Howarth and Merkel, 1984), Howarth and his colleagues concluded that the formation of pyrite in marine sediments was rapid. They found that the ^{35}S in pyrite was 5 to 9.6 times that which appeared in the H_2S and FeS fractions in Sippiwissett (USA) *Spartina* marsh sediment. They used aqua regia oxidation and chromium reduction (Zhabina and Volkov, 1978) methods for the preparation of pyrite sulphur. Also, Ivanov *et al.* (1976, 1980) and Lein *et al.* (1982) found that most of the reduced ^{35}S-sulphate was in pyrite and organic sulphur when measuring sulphate reduction rates in sediments from the western Pacific Ocean and Baltic Sea. Howes *et al.* (1984) also measured the sulphate reduction rates in sediments from a *Spartina* marsh using similar methods and calculated that a lesser amount (60% and 45%) of the reduced ^{35}S appeared in a Cr-reducible sulphur from the 0–10 cm and 0–2 cm layers

respectively. Subsequent to these studies, King *et al.* (1985) made a detailed study of O_2 uptake, CO_2 production and sulphate reduction in the 0–10 cm layer of Great Sippiwissett Marsh. They calculated that about 50% of the reduced ^{35}S-sulphate occurred in the acid-volatile fraction, 37% in the elemental S fraction, and 13% was presumed to be in the pyrite fraction. These results agree generally with those of Howes *et al.* (1984).

6.1.5 Quantitative relationships between organic carbon oxidation and sulphate reduction

Table 6.1 summarizes some quantitative relationships between primary productivity and sulphate reduction in various marine ecosystems.

Cyanobacterial mats

Cyanobacterial mats should be useful for quantifying the interaction of the carbon and sulphur cycles in marine environments because primary productivity is entirely local and several investigators have shown that most of the sulphate reduction in these ecosystems generally occurred at very high rates (up to 104 mmol m^{-2} d^{-1}) in close proximity or even within the cyanobacterial mat (Cohen, 1984; Jørgensen and Cohen, 1977; Howarth and Marino, 1984; Lyons *et al.*, 1983; Nedwell and Abram, 1978; Skyring, 1984; Skyring *et al.*, 1983). In the simplest systems, the complete set of reactions from the synthesis to the degeneration of organic matter occurs within a millimetre or less (Cohen, 1984; Skyring *et al.*, 1983). Quantitative relationships between primary productivity and sulphate reduction were first calculated for Solar Lake cyanobacterial mats by Jørgensen and Cohen (1977). They found that 14–20% of the daily primary productivity (0.7 to 1.0 mol (organic-C) m^{-2} d^{-1}) was oxidized by the SRB. Skyring *et al.* (1983) investigated a much simpler system in the *Microcoleus* smooth mats of Spencer Gulf, Australia and concluded, from multivariate analysis, that possibly (correlation coefficient, $r=0.7$, probability $p=0.015$) 100% of the organic carbon synthesized by the cyanobacteria in the mat was eventually oxidized by the SRB. They also estimated that the molar ratio between photosynthetically fixed carbon and reduced sulphate was 2 : 1 (±20%). Estimates of quantitative relationships between primary productivity and sulphate reduction in cyanobacterial mats (and also in other sedimentary systems) may be complicated by the fact that most of the photosynthate is not immediately available for oxidation. For example, Skyring *et al.* (1983) showed that sulphate reduction rates correlated positively with primary productivity of the *Microcoleus* mat only when the productivity data were transformed by an equation which accounted for the rate of decomposition

of the photosynthate. They also derived a polynomial equation which described the quantitative relationships between the sulphate reduction rate, available organic carbon, temperature, porewater content and salinity in a cyanobacterial mat ecosystem. The mathematical model was independently consistent for the Spencer Gulf cyanobacterial ecosystem and it may have general applicability for those marine ecosystems where productivity is high and where the SRB populations are numerically similar.

Marshlands, sea grass beds and coastal environments

Quantitative relationships between the cycling of carbon and sulphur in the coastal *Spartina* salt marshes of the eastern USA have been calculated by several investigators (Howarth and Teal, 1979; and Howarth *et al.*, 1983, 1984, 1985; Howes *et al.*, 1984; King *et al.*, 1985; Skyring *et al.*, 1979). However, because of the difficult problems involved in the measurement of the accession of organic matter to the sediments and rates of sulphate reduction, some disparities occur in the data. Howes *et al.* (1984) estimated that the annual sulphate reduction rate accounted for the oxidation of about 40 mol (C) m^{-2} a^{-1} which was considerably lower than the 150 mol (C) m^{-2} a^{-1} calculated by Howarth *et al.* (1979, 1983). The sulphate reduction rates calculated for the sediments of the *Spartina* marshlands of Sippiwissett Marsh and Sapelo Island (USA) (despite some of the problems which are associated with the interpretation of the rate data) all demand an amount of organic matter which has been calculated to be from 30% to 150% of the primary productivity of the *Spartina*. Howes *et al.* (1984) calculated a below ground production rate of 58 to 75 mol (C) $m^{-2}a^{-1}$ for a *Spartina* marsh ecosystem and concluded that around 90% of the organic input to these sediments resulted from the below ground production of *Spartina*. It is clear from these studies on the salt marsh ecosystems of the Great Sippiwissett Marsh and Sapelo Island that calculations of the quantitative relationships between C and S diagenesis in higher plant ecosystems must include above and below ground productivity.

Quantitative relationships between C and S diagenesis in sea grass beds have not been as extensively investigated as those for salt marshes. However, it appears that the SRB are also responsible for the remineralization of significant amounts of photosynthate in these ecosystems. For example, Jørgensen and Fenchel (1974) and Jørgensen (1977) found that in a model system and in *Zostera*-colonized sediments of Limfjorden (Denmark), about 50% of *Zostera* substrate was oxidized by the SRB. Moriarty *et al.* (1985) calculated that the SRB oxidized around 80% of the unexported organic matter in *Zostera capricornia* beds in Moreton Bay, Australia. In both investigations, however, below ground productivity was not measured.

Planktonic ecosystems

Other marine systems may be much more complex because the relationships between the sites of primary productivity and the translocation and deposition of organic matter are difficult to establish both qualitatively and quantitatively. However, pioneering work was undertaken by B.B. Jørgensen and recently there have been estimates of the C/S relationships in several planktonic ecosystems. Aller and Yingst (1980) calculated that the SRB oxidized approximately 35% of organic matter reaching the sediment in Long Island Sound (USA) (11% of planktonic productivity). Lein *et al.* (1982) measured sulphate reduction rates in several Baltic Sea sediments and calculated that only 30% of planktonic primary productivity reached the sediment, around 90% of which was oxidized by the SRB.

6.1.6 Temporal relationships between organic synthesis, preservation and sulphate reduction

Equation (2) was generalized from the reaction for sulphate reduction in marine sediments given by Leventhal (1983) as:

$$2R(CH_2O) + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- + 2R \qquad (2)$$

where R is the residue of organic matter not metabolized, but deposited and preserved in the sediment. The ratios between the reactants may depend on the varying nature of the organic matter (Lerman, 1982). For example, Westrich and Berner (1984) showed that about 35% of planktonic material (Long Island Sound) was decomposed over a much longer time scale than the rapidly metabolized (65%) fraction. Presumably their 35% fraction equates with Leventhal's R (residue) fraction. Volkov and Rosanov (1983) studied the relationship between the percentage of organic matter metabolized and the initial carbon content in deep-water sediments from the Pacific Ocean, the Bering Sea and the Sea of Okhotsk. They concluded that the rate of decomposition of organic carbon during reduction processes (e.g. sulphate reduction) is related to the initial organic concentration and suggested that there is a relatively constant proportion of fresh organic matter which is readily metabolizable. Westrich and Berner (1984) calculated that the kinetics of equation (2) were first order and that sulphate reduction in this planktonic system can be described by the sequential decomposition of two organic fractions with decay constants of $8 \pm 1 a^{-1}$ and $0.94 \pm 0.25 a^{-1}$. From the data of Jørgensen and Cohen (1977) and Skyring *et al.* (1983) it is evident that most cyanobacterial photosynthates have decay constants equivalent to the rapidly metabolized organic fraction described by Westrich and Berner (1984).

Leventhal (1983) and Berner and Raiswell (1983) found that there was a positive correlation between organic carbon and sulphide of the sediments from the Black Sea and other marine environments. The regression lines have the same slope, but that for the Black Sea data intercepts the S axis at 1.5%. Leventhal suggested that this was due to the quantity of sulphide which was not fixed as iron sulphide (thus lost from the systems) and that it was indicative of a euxinic sedimentary environment. He further suggested that such correlations between C and S may be useful for identifying analogous ancient environments. Contemporary and similar studies by Berner and Raiswell (1983) have led to similar conclusions. However, sediments which are very low in Fe, such as many marine carbonates, may not follow these trends (Berner and Raiswell, 1983; Gibson, 1985).

Skyring *et al.* (1983) calculated that most of the photosynthate particulate organic carbon (POC) synthesized by the cyanobacterial mat colonizing intertidal sediments in Spencer Gulf was oxidized by the SRB within the year and most oxidized within a month or two of synthesis. Further, Bauld (1984) reported that cyanobacterial mats from the same ecosystems produced 1–6% DOC during photosynthesis and subsequently Plumb (1985) showed, from molybdate inhibition studies, that this DOC was rapidly oxidized by the SRB. However, the contribution of this low molecular weight (LMW) component to the DOC pool would be too small on most occasions to be reflected in day- and night-time sulphate reduction rates. On the other hand, Howarth and Marino (1984) found a fivefold increase in sulphate reduction rates in cyanobacterial mats (in the Great Sippiwissett Marsh) on cold sunny days as opposed to warm cloudy days and they suggested that this indicated a short-term coupling of mat photosynthesis and sulphate reduction. In a study of several microbial processes occurring in the sediments of the sea grass beds of Moreton Bay, Moriarty *et al.* (1985) showed that there may have been a slight diurnal effect with sulphate reduction rates peaking from noon to 6 pm. This is more likely to have been due to light-induced excretion of DOC by the roots of the sea grass and the observation suggested that the SRB were active in the plant rhizospheres. Recently, Capone *et al.* (1983) isolated polyesters of β-hydroxybutyrate and β-hydroxypentanoate from the cyanobacterial mats and stromatolites from Shark Bay (Western Australia). It is not presently known if these compounds are oxidized by the SRB, but butyrate is a known substrate for several species, and Sørensen *et al.* (1981) calculated (from molybdate inhibition experiments) that around 10% of sulphate reduction could have been coupled to butyrate oxidation in coastal lagoon sediments (Denmark). Krom and Sholkovitz (1977) showed in sediments from Duich, a fjord type estuary, that the high molecular weight (HMW) fraction increased with depth down to 80 cm. They attributed this to a humification process. Once a compound enters this type of HMW reservoir, its residence time in the sediment would be much longer than the

average residence time for LMW/DOC compounds. Krom and Sholkovitz (1977) also found that the LMW/DOC compounds decreased with depth and that the slow oxidation rate of the LMW compounds in the below surface sediments permitted condensation reactions which resulted in the formation of the HMW/DOC.

Studies of temporal relationships between photosynthesis and sulphate reduction have indicated that, in most marine environments, organic matter is turned over rapidly, resulting in little preservation. For example, in the cyanobacterial mats from Spencer Gulf there is very little preservation of organic matter in the sediment and Cohen *et al.* (1980) calculated that only 1% of mat photosynthate was preserved in the sediment in Solar Lake. However, preservation occurs in some marine (or near marine) situations which may be more complex than those in which high organic concentrations in the sediments result from high rates of organic sedimentation (Berner and Raiswell, 1983).

Figure 6.1 is a schematic diagram which relates the diagenetic relationships between various components of biogeochemical carbon reservoirs. High molecular weight (HMW) photosynthate (or particulate organic carbon, POC) is composed of HMW compounds which may be ultimately energy sources but are not directly metabolized by the SRB. The dissolved organic carbon (DOC) reservoir may be crudely divided into HMW and low molecular weight (LMW) fractions and the average residence time for C atoms in each may vary widely, depending on their suitability as substrates for microbial populations. The DOC reservoir in most sediments results from the anaerobic diagenesis of organic matter buried with sediment and in some instances may be a significant proportion of the total organic content. For example, an acid-soluble organic portion, presumably actual or potential DOC, was from 20 to 40% of the total organic carbon in an organic rich sediment from Hamelin Pool, Shark Bay, Western Australia (Skyring, 1985). Also, in cyanobacterial mats and other microbenthic ecosystems, significant amounts of DOC may be produced directly by photosynthesizers (Bauld, 1984; Chambers, 1985). The kerogen reservoir, which may originate in the R-fraction (Leventhal, 1983), is largely composed of water-insoluble HMW compounds and the residence time of compounds in this pool may be billions of years if the sedimentary formation survives crustal weathering and movement.

A detailed examination of the environmental factors which affect the preservation of organic matter is beyond the scope of this presentation. However, it is evident from the various data available that factors which retard sulphate reduction may also be important in retarding the complete oxidation of organic matter. It is possible that hypersalinity may be important in this respect. For example, in Spencer Gulf sediments, sulphate reduction rates correlated negatively with porewater salinity in cyanobacterial mats

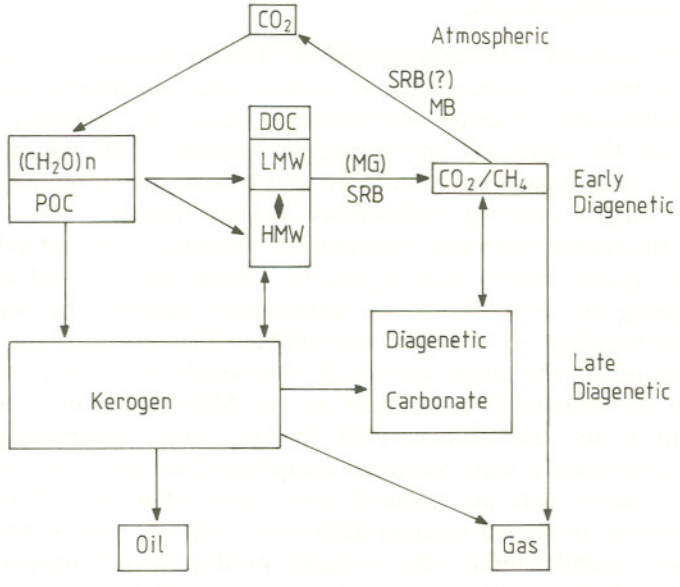

Figure 6.1 Carbon reservoirs and the SRB in marine sediments.
DOC: dissolved organic carbon
POC: particulate organic carbon
LMW: low molecular weight organic compounds
HMW: high molecular weight organic compounds
MG: methanogens
MB: methanobacteria
SRB: sulphate-reducing bacteria

(Skyring *et al.*, 1983) and the cyanobacterial organic matter in the 2000 year old anoxic sediments of Solar Lake is a classic example of preservation in a hypersaline environment. Although the Great Salt Lake is not marine, it is hypersaline and Post (1980) observed that organic matter was best preserved in those sediments of the lake which were associated with saline inundations. Further, Lupton (personal communication) showed that the metabolism of both the SRB and the fatty acid producers in marine sediments from Shark Bay was retarded in hypersaline environments. On the other hand, there are other factors which may contribute to the preservation of organic matter in marine (or sulphate-rich) environments. For example, Aizenshtat *et al.* (1984) found that the secondary enrichment of organic matter with sulphur (from sulphate reduction) is a feature of the well-preserved cyanobacterial material in Solar Lake. They also observed sulphur enrichment of the organic matter in the very early stages of diagenesis pointing to the possibilty of the direct involvement of sulphate reduction in organic preservation.

6.1.7 Concluding remarks

Currently available correlations between primary productivity and sulphate reduction rates are too imprecise to identify exact quantitative relationships between the cycling of carbon and sulphur in marine environments. However, despite all the analytical and statistical problems, there is experimental evidence which indicates that the SRB may oxidize a high proportion of the organic carbon entering sedimentary marine systems. Clearly not all ecosystems are the same with respect to the dynamics of C and S diagenesis; however, cyanobacterial mats appear to provide useful model systems for investigating the process of and quantitative relationships between the biogeochemical cycling of carbon and sulphur. This is because the cyanobacteria are usually the major sources of photosynthate in the ecosystem and most of the organic C is oxidized by the SRB within or in very close proximity to the mat (Cohen, 1984; Skyring, 1984; Skyring *et al.*, 1983). Also, cyanobacterial mats are not as complicated as other ecosystems where organic material may be produced above and below ground, transported long distances or settled through deep water before it enters the sediment. Generally, cyanobacterial mats are highly productive and support very high sulphate reduction rates and it is probable that the rate estimations are representative of the *in situ* condition even though (non-acid volatile sulphide) NAVS data have not been included in the initial calculations (Jørgensen and Cohen, 1977; Skyring *et al.*, 1983). A more precise understanding of important diagenetic reactions may be obtained by a detailed examination of the biogeochemical dynamics of specific C, H and S cycling in an intact but isolated mat.

To date, investigators have relied on destructive methodology, intermittent sampling and insufficient data processing facilities. However, more precise calculations may be realized with the availability of high capacity data processors and the development of non-destructive physical and chemical probes which would permit the continuous, simultaneous monitoring of several key parameters. For example, recent developments in microelectrode (Revsbech and Ward, 1984) technology have resulted in the observation of unexpected and dramatic changes in the porewater chemistry of cyanobacterial mats over micron distances. Geochemical events (which may be irreversible) occur in these micro-layers and over a long period may result in the accumulation of significant quantities of diagenetic products. Also, microprobes employing radioactive tracers and gas chromatographic techniques (Cohen, 1984; Skyring, 1984; Skyring *et al.*, 1983, 1987) have shown that strictly anaerobic processes such as sulphate reduction and methanogenesis occur within the cyanobacterial mat ecosystem. New developments in nuclear magnetic resonance (NMR) spectroscopy and Mössbauer analysis may also provide non-destructive methods for following the dynamics of C and S in intact ecosystems.

It generally appears that organic matter and sulphide are best preserved in marine sediments made anoxic by the activities of the SRB. There are, however, still some gaps with respect to temporal relationships between the formation of various organic carbon reservoirs and sulphate reduction. In particular, more detailed information is required on the very slow carbon and sulphur metabolic rates in subsurface sediments, which may be important in pyrite (and other metal sulphide) formation. Also, the geochemical evidence for methane oxidation by the SRB needs more investigation to show whether or not the SRB can overcome thermodynamic barriers which appear to preclude this metabolic process.

Skyring (1987) drew attention to several important coastal and continental shelf/slope ecosystems where quantitative estimates of the relationships between carbon and sulphur were few or lacking completely. However, even though current knowledge is limited, it appears that 50–90% of global sulphate reduction occurs in coastal, shelf and slope sediments. Global cycles which are important in the burial of organic carbon and sulphur are also important for understanding global fluxes of oceanic and atmospheric constituents, and the formation of oil and some economic minerals.

6.2 INTERACTION OF THE SULPHUR AND CARBON CYCLES IN RECENT MARINE SEDIMENTS*

6.2.1 Introduction

Simulation of the recent sulphur cycle enables one to estimate some of the main fluxes of sulphur in marine sediments. These are: (a) sulphur produced at the early stages of sedimentary diagenesis, (b) sulphur oxidized and returned to the sulphate reservoir and (c) sulphur buried in sediments (Ivanov 1983). As seen in Section 6.1 the biogeochemical cycles of sulphur and carbon are intimately interrelated. Quantitative estimates of the sulphur fluxes made with the help of radioactive isotopes were used by the author to establish the balance of organic carbon in recent oceanic sediments at the stage of their early diagenesis.

6.2.2 Primary production and aerobic mineralization of organic matter in the oceans

Primary production is the initial step of the oceanic carbon cycle. Some estimates of the magnitude of primary production are presently available ranging from $20 \times 10^3 - 55 \times 10^3$ Tg (C) a^{-1} (Ryther, 1969; Romankevitch, 1977; Mopper and Degens, 1979) to 126×10^3 Tg (C)a^{-1}. The latter, long-

*A. Yu. Lein.

considered as overestimates, appear nowadays most reasonable. High estimates of primary production were favoured by the radioisotopic (^{14}C) techniques of measuring the rates of primary production in the oceans and by the researchers' due regard for biomass of *phytoplankton* (Shulenberger and Reid, 1981).

Living organisms are involved in mineralization of some 60–80% of the suspended organic matter in the euphotic layer of the oceans. The quantity of organic matter reaching the ocean floor is variable and depth-dependent. To depths of 100 m, some 40–80% of the organic matter from primary production reaches the ocean floor. The amount of C_{org} reaching the water–sediment interface decreases with depth to 2–10% or less (Jørgensen, 1983). At the sediment–water interface there is a major consumption of C_{org} in aerobic and anaerobic processes. Below, data are presented for oxygen consumption by aerobic respiration in recent sediments of different morphometric oceanic zones (Jørgensen, 1983):

Zone	Depth (m)	Oxygen consumption (mmol m^{-2} day^{-1})
Shelf	0–5	20
	50–200	10
Continental slope	200–1000	3
	1000–4000	0.3
Depressions	over 4000	0.05

Aerobic processes which occur in sediments of the world oceans, over the total surface area of 360×10^6 km^2, consume 527×10^9 mol (O_2) day^{-1} or 6155 Tg (O)a^{-1}.

In addition to the aerobic oxidation of organic matter described by Jørgensen (1983), these processes also embrace oxidation of reduced compounds which migrate from the anaerobic zone of bottom sediments. Most important are the oxidation of hydrogen sulphide, methane and ammonium. Regrettably, methane oxidation and nitrification in bottom sediments of the oceans are still poorly investigated (see Section 6.4). Therefore, our present knowledge is insufficient for estimating oxygen consumption in these processes.

Oxygen consumption for oxidation of biogenic hydrogen sulphide may, in the first approximation, be estimated on the following grounds. Total hydrogen sulphide production during microbial sulphate reduction makes

up 492 Tg (S) a^{-1} (Lein, 1983) of which 111 Tg (S) are buried as sulphide in modern sediments (Volkov and Rosanov, 1983). The remaining 380 Tg (S) are oxidized to sulphate in the reaction:

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-}$$

so it follows that this process requires about 760 Tg (O) a^{-1}.

Subtraction of this value from the total oxygen consumption by bottom sediments gives 5400 Tg (O) for the annual O_2 consumption in oxidation of organic matter.

Aerobic oxidation of organic matter schematized as:

$$(CH_2O) + O_2 \rightarrow CO_2 + H_2O$$

suggests that about 2000 Tg (C_{org}) are absorbed by aerobic processes in the upper horizons of marine mud sediments.

6.2.3 Estimation of organic matter consumption in anaerobic diagenetic processes

The assessment of C_{org} consumption in anaerobic processes which occur in the biogeochemically active sediments of the shelf and continental slope may be approached differently. The first approach is based on due regard for the variation in concentrations of C_{org} and N_{org} in the lower horizons of mud columns compared with their concentrations in the surface horizon which is assumed as the value of primary or initial C_{org} (Emery and Rittenberg, 1952). Firstly, such an approach does not account for possible changes in conditions of sediment formation which affect the magnitude of initial concentrations of C_{org}; secondly, primary production is assumed as the already residual C_{org}, as the most active processes of organic matter destruction take place at the water–sediment interface.

Another approach which is widely used by Soviet researchers estimates C_{org} consumption from the production of reduced compounds of manganese, iron and sulphur in compliance with the balance formulae of Uspensky-Strakhov (Bordovski, 1964; Strakhov and Zalmanzon 1955; Strakhov 1976). This second approach enables one to estimate the consumption of C_{org} on the basis of contents of solid-phase compounds. It essentially accounts for only C_{org} consumption during formation of stable disulphide of iron pyrite, since C_{org} uptake for the reduction of Fe^{3+}, Mn^{4+} and other oxidized

components is extremely low and generally neglected. While substantiating this approach for estimating concentrations of primary C_{org}, Strakhov showed the approximate character of values thus obtained, since organic matter was depleted due to some other transformations, e.g. by splitting off $COOH^-$, CH_4, NH_3 etc. (Strakhov, 1976).

Recent biogeochemical studies suggest that the solid phase of sediments do not absorb all hydrogen sulphide produced *in situ* during bacterial sulphate reduction. The idea of migration and oxidation of a part of hydrogen sulphide in highly reduced sediments is supported by chemical analyses where the interstitial water shows a surface maximum for sulphate ion that is often enriched in the light isotope ^{32}S ($\delta^{34}S$ ranging from -18.8 to $-15.6‰$) compared to the isotopic composition of sulphate sulphur in overlying water (Lein, 1983). The latter fact may be considered as clear evidence of the emergence of a subsurface sulphate maximum from the oxidation of isotopically light metabolic hydrogen sulphide.

Thus the C_{org} consumption in anaerobic bacterial processes in reduced sediments, specifically those containing free H_2S, is significantly underestimated if assesssed on the basis of the pyrite sulphur content of the solid phase.

Taking into account the above arguments, yet another approach was proposed to estimate organic matter mineralized in the course of anaerobic destruction. This method is based on experimental measurements of the rate of biogeochemical processes using the radioisotopes of sulphur and carbon under conditions as close to natural as possible. (Lein, 1983).

Biogeochemical processes of diagenetic transformation of sediments involve microorganisms from various physiological groups: aerobic and anaerobic saprophytic and cellulose-degrading bacteria, sulphate reducers, methanogens, denitrifiers and methylotrophs. The total bacterial population in sediments, excluding the oligotrophic oceanic zones, amounts to several billion cells per gram of wet mud, with a biomass (C_{org}) of 1–100μg (C) per gram of wet mud (Lein and Namsarayev, 1986).

Under anaerobic conditions decomposition of organic matter is a multistage process: primary anaerobes decompose polymeric compounds to monomers which in turn serve as a substrate for fermentation agents and gas-producing bacteria.

Figure 6.2 illustrates anaerobic destruction of organic matter in the sediments of Aden Bay and carries quantitative estimates of specific reservoirs and fluxes (using ^{14}C and ^{35}S). Of particular interest are the so far unique, quantitative estimates of the carbon flux associated with the products of cellulose decomposition. These products are utilized as organic substrates by methanogens and sulphate reducers which bring about most of the consumption of organic matter during early diagenesis.

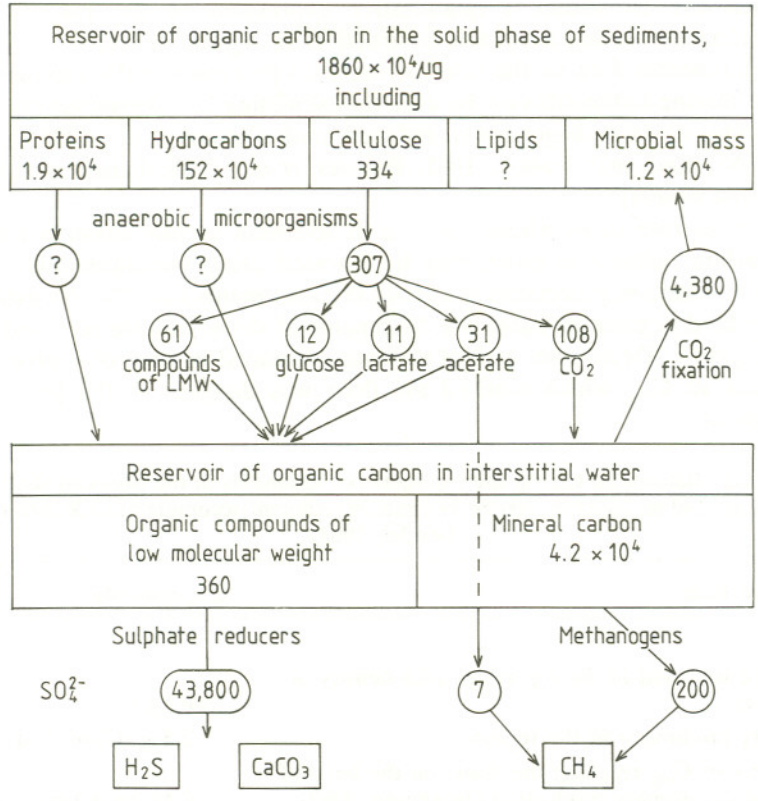

Figure 6.2 Diagram of anaerobic destruction of organic matter. Open boxes indicate reservoirs of C_{org}, µg kg^{-1} dry mud. Numbers within circles are fluxes, µg (C) kg^{-1} a^{-1} dry mud.

6.2.4 Quantitative estimation of C_{org} consumption during anaerobic diagenesis

Earlier studies established that 90–95% of C_{org} involved in anaerobic biogeochemical reactions is consumed by bacterial sulphate reduction (Lein and Ivanov, 1981; Belyaev *et al.*, 1980). Consequently, knowledge of the rate of bacterial sulphate reduction in sediments is sufficient for estimating the magnitude of C_{org} digestion under conditions of anaerobic diagenesis. Simple calculation using the equation of sulphate reduction reaction:

$$SO_4^{2-} + 2C \rightarrow S^{2-} + 2CO_2$$

enables one to obtain a quantitative expression of the rate of C_{org} mineralization during anaerobic destruction of organic matter.

Experimental data on the rates of bacterial processes in the top metre of recent marine sediments may be used for estimating C_{org} consumption under conditions of early diagenesis in reduced muds (Ivanov *et al.*, 1976; Lein *et al.*, 1981; Lein and Ivanov, 1981; Belyaev *et al.*, 1980; Ivanov and Lein, 1980 and others).

In those rare cases where the rate of sediment accumulation is known, the carbon balance in muds may be assessed using measurements of the rates of reduction processes carried out in experiments with ^{35}S. An estimate of this kind is given in Table 6.2. Sediments of the top metre received 1400 $kg(C_{org})m^{-2}$. Twenty per cent of this was consumed in anaerobic processes, whereas all C_{org} which reached the floor was digested in the process of diagenesis.

Table 6.2 Balance of C_{org} in the top metre of sediments in the Mexican shelf (Site 668; depth 140 m; 23°23′N, 106°56′W), rate of sediment accumulation 100 mm/1000 a (Andel, 1964)

Balance item	C_{org} quantity
Mass of wet mud in the top metre with density of 1.5 g cm^{-3}	1500 kg m^{-2}
Primary production in the region	2.5 g (C) m^{-2} d^{-1}
Quantity of C_{org} reaching the floor, on the basis of 15% of the primary production (Jørgensen, 1983)	0.14 kg (C) m^{-2} a^{-1}
Quantity of C_{org} having reached the bottom over the past 10 000 a	1400 kg (C) m^{-2}
Consumption of C_{org} during bacterial sulphate reduction at the sulphate reduction rate of 55.7μg (S) kg^{-1}(wet mud) d^{-1} (Ivanov *et al.*, 1976)	41.8μg (C) $kg^{-1}d^{-1}$
Consumption of C_{org} in bacterial sulphate reduction on the basis of wet mud mass in the uppermost metre of sediment per:	
24 hours	62.7mg (C) m^{-2}
1 year	22.9g (C) m^{-2}
10 000 years	229kg (C) m^{-2}
Quantity of C_{org} remaining over the total volume of wet mud in the top metre with the content of residual C_{org} = 3% dry mud, humidity 60%	18kg (C) m^{-2}
Consumption of C_{org} for aerobic respiration in the top metre over 10 000 a with oxygen absorption in sediments of the shelf of 10 mmol m^{-2} d^{-1} (Jørgensen, 1983)	1168 kg (C) m^{-2}
Total consumption of C_{org} in the top metre of muds (229 + 18 + 1168)	1415 kg m^{-2}

A large body of experimental material hitherto obtained is condensed in Table 6.3 which presents average values for the rates of reduction processes in the top metre of sediments in different morphometric oceanic zones.

In recent years researchers have increased studies of the rate of sulphate reduction in marshlands using ^{35}S (Howarth and Teal, 1979; Howarth and Giblin, 1983; Skyring *et al.*, 1983, and others). The rates of sulphate reduction in the well-studied saline marshes of Sapelo Island and Sippiwissett (USA) are very high at: 40 and 75 mol (S)m^{-2} a^{-1} (Howarth *et al.*, 1984). According to Skyring (see Section 6.1) all of the C_{org} from primary production may be consumed in processes of sulphate reduction in marshes.

The estimation of global C_{org} consumption in sulphate reduction in marshlands is difficult because their total surface area is not known accurately. Assuming a very rough value of 6×10^4 km^2 for the total marshland surface (*The World Ocean Atlas*, 1974, p.37, geomorphological map) and using the average of the two cited rates of sulphate reduction (57 mol (S) m^{-2} a^{-1} or 1.8 kg (S) m^{-2} a^{-1} one finds that the marshes produce up to 100 Tg (S) a^{-1}. This magnitude is of little importance to the sulphur cycle as nearly all of this sulphur is rapidly oxidized and channelled into the marine sulphate reservoir. The magnitude of C_{org} digestion during sulphate reduction in marshlands may, however, amount to 75 Tg (C) a^{-1}, i.e. comparable with C_{org} consumption in sediments of the shelf (Table 6.3). Hence, reliable measurements of total area of marshlands are much called for in view of new data on the rates of sulphate reduction in marshlands. Reverting to Table 6.2 let us underline an important geochemical inference: over 70% of the total mass of C_{org} digested by anaerobic processes, accounting specifically for marshes, is consumed in sediments of near-continental areas of the oceans at depth of 1000 m.

Annual production of metabolic hydrogen sulphide per unit area of sediment surface and consumption of C_{org} in this process were estimated from data on the rate of reduction processes (Table 6.4). The estimated magnitude of C_{org} consumption by anaerobic bacterial diagenesis accounts for about 15% of the total flux of C_{org} to the world ocean floor. The data presented also suggest that the minimum quantity of organic carbon reaching the water column–marine bottom sediment interface is about 2.5×10^3 Tg (C) a^{-1}.

6.3 COUPLING OF THE CARBON AND SULPHUR CYCLES THROUGH ANAEROBIC METHANE OXIDATION*

6.3.1 Introduction

Anaerobic methane oxidation is a process that appears to be important in controlling the flux of methane from anoxic marine sediments. There is

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Table 6.3 Productivity of bacterial sulphate reduction in the top metre of world ocean sediments

Geomorphological zone of the ocean floor	Depth (m)	Zone area (10^6 km^2)	Rate of sulphate reduction: μg (S) kg^{-1} day^{-1}	Rate of sulphate reduction: mg (S) kg^{-1} a^{-1}	Productivity of sulphate reduction g (S) m^{-2} a^{-1}	Flux of H_2S (Tga^{-1})	Consumption of C_{org} in sulphate reduction: Tg (S)a^{-1}	Consumption of C_{org} in sulphate reduction: %
Shelf	0–50	11(2) *	55.6	20.3	26.4	79.2	59.6	16
	50–200	16(3)	37.2	13.6	17.7	53.1	40.0	11
Continental slope	200–1000	(15)	28.2	10.3	13.4	201.0	151.0	41
	1000–3000	(61)	5.5	2.0	2.6	158.6	119.2	32
Slope's foot, depressions, ocean bed	over 3000	257	0.97	0.35	—	—	—	—
Total		360(81)				492.5	369.7	100

* In parentheses: the areas of biogeochemically active sediments where bacterial sulphate reduction takes place. For the shelf zone such areas are calculated on the basis of data on the distribution of recent sand–aleurite–pelitic muds (Lisitsyn, 1978).

Table 6.4 Balance of C_{org} in sediments of the world oceans

Process	Tg (C) a^{-1}	%	Reference
Mineralization of C_{org}			
aerobic	2000	82	Jørgensen, 1983
anaerobic	370	15	see Table 6.2
Burial of C_{org}	85	3	Romankevitch, 1977
Total flux of C_{org} to the floor	2455	100	

general agreement that the process occurs, but the organisms responsible have not been isolated yet, and the mechanism remains unknown. There is a suggested, but unconfirmed, link with the sulphur cycle through sulphate reduction. This section briefly reviews the geochemical evidence for anaerobic methane oxidation and uses measured rates of anaerobic methane oxidation from several environments to make a preliminary estimate of the importance of the process to the global methane and sulphur cycles. Evidence for a link between anaerobic methane oxidation and sulphate reduction is summarized and results from some recent inhibition experiments that provide information on the possible mechanism of anaerobic methane oxidation are presented.

The earliest evidence for anaerobic methane oxidation was presented by Davis and Yarbrough (1966), who reported that methane was oxidized in small quantities by sulphate reducers growing on another substrate. Sorokin (1957) showed that sulphate reducers were unable to oxidize methane when it was the sole substrate. No further work was reported on the subject until the late 1970s, when several papers employing diagenetic models (Berner, 1971) were published.

6.3.2 Geochemical evidence for anaerobic methane oxidation

Anaerobic methane oxidation is a controversial subject among microbiologists, since the responsible organisms and mechanism are unknown. However, a growing body of geochemical evidence supports the occurrence of oxidation of methane in the absence of oxygen, and has been summarized and reviewed in Alperin and Reeburgh (1984). This geochemical evidence favouring anaerobic methane oxidation is derived from three independent approaches: diagenetic modelling, direct *quasi in situ* rate measurements using the radioactive tracer $^{14}CH_4$, and stable carbon isotope budgets. These three independent approaches were applied to samples from a single station in Skan Bay, Alaska (USA) (Alperin and Reeburgh, 1984), and gave consistent results. Figure 6.3 shows a schematic diagram with methane and sulphate depth distributions characteristic of anoxic marine sediments. The most

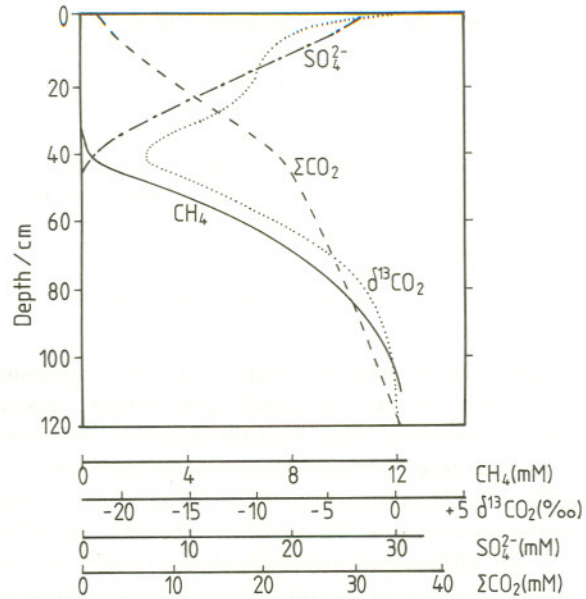

Figure 6.3 Depth distributions of methane, total carbon dioxide, sulphate and the stable isotope ratio of carbon dioxide in interstitial waters of a typical anoxic marine sediment. Note the low methane concentration surface zone, the curved methane distribution, the coincident slope changes and transitions in the distributions, and the minimum in the $\delta^{13}CO_2$ distribution. These distributions suggest that anaerobic methane oxidation occurs in a subsurface depth interval that coincides with the $\delta^{13}CO_2$ minimum. Adapted from Reeburgh (1982)

striking characteristics are the low methane concentration surface zone and the concave-up methane profile. The other distributions all undergo breaks or slope changes over the same depth interval, which is taken to be the zone of methane oxidation. This schematic diagram illustrates how methane diffusing upwards is consumed in the methane oxidizing zone, increasing the upward flux of CO_2 and producing a minimum in the $\delta^{13}CO_2$ distribution as a result of oxidizing isotopically light methane.

6.3.3 Diagenetic models

Diagenetic models and vertical advection–diffusion models (Craig, 1969) are conceptually identical; both balance sedimentation and diffusion (or in the case of advection–diffusion models, vertical advection and eddy diffusion) against reaction. Reeburgh (1976) treated methane data from the Cariaco Trench water column and sediments with vertical advection–diffusion and diagenetic models, respectively, and found that the modelled water column

methane oxidation rates were 10^2–10^3-fold lower than those obtained for the sediments. Barnes and Goldberg (1976) and Martens and Berner (1977) considered methane in Santa Barbara Basin and Long Island Sound (both USA) sediments, respectively. Later model studies include those of Bernard (1979) on Gulf of Mexico sediments, and Whiticar (1982) on Baltic Sea sediments.

All of these model studies showed that a methane consumption process was required to explain the methane depth distributions in the sediment. These environments all contain sulphide and are anoxic, so the process is clearly anaerobic. These model studies all showed that anaerobic methane oxidation occurred in a subsurface zone in anoxic marine sediments and that there was net methane consumption. The model studies are based on actual field data and consider the result of production and consumption reactions, so they yield net rates.

6.3.4 Methane oxidation rate measurements

Tracer techniques using $^{14}CH_4$ following the $^{35}SO_4^{2-}$ sulphate reduction rate method of Jørgensen (1978) have been used in direct measurements of anaerobic methane oxidation rate (Reeburgh, 1980). These studies involve injecting $^{14}CH_4$ either into syringes containing sediment or into intact sediment cores, incubation at *in situ* temperatures and collection of the unreacted methane and CO_2, the product of oxidation. The diagenetic models predict that anaerobic methane oxidation will be restricted to a narrow subsurface zone. Measured anaerobic methane oxidation rate depth distributions from several studies and environments (Reeburgh, 1980; Alperin and Reeburgh, 1984; Devol, 1983; Devol *et al.*, 1984; Iversen and Jørgensen, 1985) show this subsurface maximum in methane oxidation, which is illustrated in Figure 6.4. The locations and magnitudes of the rate maxima accord with model predictions. The results from several investigations, which are summarized in Table 6.5, agree well.

6.3.5 Stable carbon isotope distributions

The advantages of using stable isotopes as tracers in natural systems result from the fact that they require no additions, incubations or controls, and avoid the uncertainties introduced by each of these manipulations. Biogenic methane has a characteristic light (−60‰ to −100‰) stable carbon isotope signature, while the dissolved inorganic carbon (DIC) is much heavier isotopically (0‰ to −5‰); this large isotopic difference may be used to quantify additions of methane-derived CO_2. Figures 6.5 and 6.6 show characteristic features in the stable isotope distributions that result from anaerobic methane oxidation. Figure 6.5 shows a minimum of $\delta^{13}CO_2$,

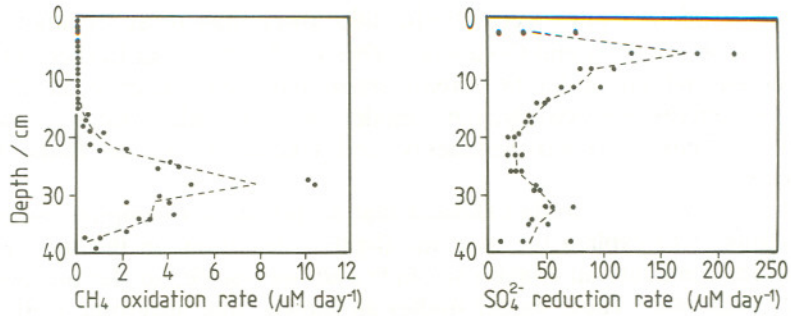

Figure 6.4 Depth distributions of measured anaerobic methane oxidation and sulphate reduction rates in Skan Bay sediments. Note the subsurface maximum in sulphate reduction rate as well as the maximum in methane oxidation coincident with the second subsurface maximum sulphate reduction rate. The coincident maxima in rates have been observed in other environments and are the strongest evidence to date for a link between anaerobic methane oxidation and sulphate reduction. Adapted from Alperin and Reeburgh (1985)

Table 6.5 Integrated anaerobic methane oxidation rates

Location and depth	Integration depth of sediments	Oxidation rate (mol $cm^{-2}a^{-1}$)	Study
Skan Bay (65 m)	25 cm	27.0	Alperin and Reeburg, 1984
Kattegat (65 m)	172 cm	30.3	Iversen and Jørgensen, 1985
Skagerrak (200 m)	112 cm	42.3	
Saanich Inlet (225 m) (measured)	27 cm	71.3 25.8 40.9	Devol, 1983
		Average 45.9	
Saanich Inlet (225 m) (modelled)	27 cm	95.5 90.2 139.3	Devol, 1983
		Average 108.4	

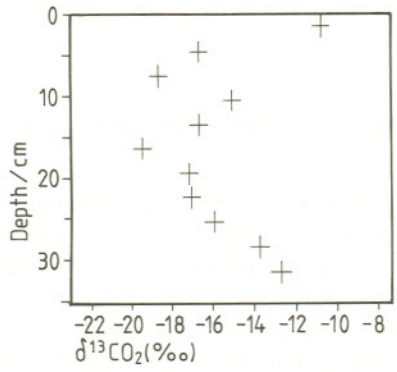

Figure 6.5 Depth distribution of $\delta^{13}CO_2$ in Skan Bay sediment. Note the subsurface minimum, which corresponds to the subsurface methane oxidation rate maximum in Figure 6.4. Adapted from Alperin and Reeburgh (1984)

similar to the minimum in CH_4 concentration shown schematically in Figure 6.3. This minimum is caused by oxidation of isotopically light methane in the methane oxidizing zone, which results in a localized input of isotopically light, methane-derived CO_2. Figure 6.6 shows the depth distribution of $\delta^{13}CH_4$ in the same samples as used to obtain the data shown in Figure 6.5. This distribution shows the residual methane becoming progressively heavier in line with the preferential oxidation of lighter methane in the sediments. These data, fitted to a Rayleigh distillation model, yielded a fractionation factor of 1.004. A mixing model involving conservation of mass and stable isotopes was presented in Alperin and Reeburgh (1984) and gave results

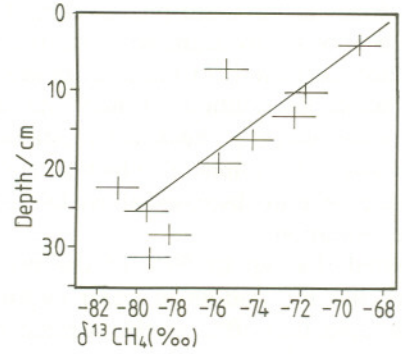

Figure 6.6 Depth distribution of $\delta^{13}CH_4$ in Skan Bay sediments showing sample depth intervals and standard error bars. This diagram shows residual methane becoming isotopically heavier as the lighter fraction is preferentially oxidized in surface sediments. A Rayleigh distillation model applied to the data yields a fractionation factor of 1.004. Adapted from Alperin and Reeburgh (1984)

that agreed with those from both diagenetic models and from direct rate measurements.

6.3.6 Importance of anaerobic methane oxidation in global methane and sulphur cycles

Anaerobic methane oxidation and sulphate reduction occur in the same environments—high organic carbon content coastal and shelf sediments. Attempts to determine what fraction of anaerobic methane oxidation can be accounted for by sulphate reduction have involved modelling as well as direct rate measurements of anaerobic methane oxidation and sulphate reduction. The integrated anaerobic methane oxidation during the process of sulphate reduction in the sediments, derived from model calculations, ranges from 30 to 50% (Reeburgh, 1982) to a high of 70% (Murray *et al.*, 1978) of total consumption of organic carbon. Depth integrations of direct rate measurements give a somewhat different picture, with methane oxidation accounting for 23 to 40% of the total sulphate reduction in Saanich Inlet, USA and 12% in Skan Bay sediments (Devol *et al.*, 1984). Iversen and Jørgensen (1985) showed this same ratio was 10% in Kattegat and Skagerrak sediments.

The measurements listed in Table 6.5 may be used to obtain a preliminary estimate of the importance of anaerobic methane oxidation in marine sediments to the global atmospheric methane budget. Depth-integrated anaerobic methane oxidation rate measurements are multiplied by the areas of estuaries and continental shelves; the two environments where anaerobic methane oxidation is known to be important. These areas have been tabulated by Sheppard *et al.* (1982) as part of a global compilation of methane sources and fluxes to the atmosphere. Table 6.6 shows the results of this estimate, which is probably high, since continental shelf sediments are not likely to produce methane over their entire area. Although there is no information on global distribution of methane in continental shelf sediments, these estimates may be checked by estimating the amount of primary production oxidized by sulphate reduction and using the methane oxidation: sulphate reduction ratio discussed above to estimate the importance of anaerobic methane oxidation.

Suess (1980) estimated that up to 50% of the primary production on continental shelves reaches the bottom in water depths of 100–200 m and Jørgensen (1983) estimated that 50% of the organic matter oxidation on shelves is carried out by sulphate reduction. Assuming a conservative continental shelf primary production rate of 100 g (C) $m^{-2}a^{-1}$ and a methane oxidation: sulphate reduction ratio of 0.1, the anaerobic methane oxidation rate is 2.5 g (C) m^{-2} a^{-1}. Extended to the area of estuaries and shelves, 28×10^{12} m^2, this rate yields 70 Tg (C) a^{-1}, which agrees reasonably with

Table 6.6 Global importance of anaerobic methane oxidation

Measured Rates (Table 6.6) = 27 to 46 mol cm^{-2} a^{-1}	
Environment areas	Methane consumption (Tg a^{-1})
Estuaries ($1.4 \times 10^{12} m^2$)	6–10
Continental shelves ($26.6 \times 10^{12} m^2$)	115–195
	121–205

the estimates derived from rate measurements.

The amount of reduced sulphur buried in marine sediments annually is 111.4 Tg (S) a^{-1} (Volkov and Rosanov, 1983; Ivanov, 1983). This number does not include the much larger amount of reduced sulphur that is re-oxidized at the sediments–water interface and made available for further sulphate reduction. The total sulphate reduction associated with primary production of 100 g (C) m^{-2} a^{-1} is 25 g (C) m^{-2} a^{-1}, or in terms of S (2 : 1 C : S stoichiometry), 33 g (S) m^{-2} a^{-1}. Extending this rate to the area of estuaries and shelves yields 900 Tg (S) a^{-1}. This estimate is somewhat higher than the 400–600 Tg (S) a^{-1} reported by Andreae and Galbally (1985). Methane oxidation would thus be responsible for 10% of the estimated total sulphate reduction, or 40–90 Tg (S) a^{-1}.

6.3.7 Evidence for a link between anaerobic methane oxidation and sulphate reduction

Evidence linking anaerobic methane oxidation and sulphate reduction comes from several sources. Coincident slope changes in the profiles of sulphate, methane, total carbon dioxide and $\delta^{13}CO_2$ (Figure 6.3) have been cited as evidence for a possible link (Reeburgh, 1982). Differences in methane distributions in freshwater and marine environments (Reeburgh and Heggie, 1977) also suggest the involvement of sulphate. The concave methane distribution observed in marine systems are not observed in low sulphate freshwater systems; linear methane profiles are observed in these systems, suggesting that methane produced in freshwater sediments diffuses into the water rather than being consumed within the sediments as in marine environments. Thermodynamic arguments also suggest that oxidation of methane by sulphate is possible at *in situ* concentrations (Martens and Berner, 1977). The quantitative dominance of sulphate reduction in marine sedimentary environments suggests that it is one of the few processes with sufficient oxidizing capacity to oxidize large quantities of methane (Reeburgh, 1983). The coincident maxima in measured methane oxidation and sulphate

reduction rates that have been observed by Devol *et al.* (1984), Iversen and Jørgensen (1985) and Alperin and Reeburgh (1985) are perhaps the strongest evidence for a link between anaerobic methane oxidation and sulphate reduction.

6.3.8 Possible mechanisms for anaerobic methane oxidation and future work

It is not possible to determine from the above evidence whether the link between methane oxidation and sulphate reduction is direct or indirect. Experiments using specific inhibitors were conducted recently (Alperin and Reeburgh, 1985) to determine whether there is a direct couple between the two processes and also to narrow the range of possible organisms capable of mediating anaerobic methane oxidation. The organisms considered capable of mediating anaerobic methane oxidation are methanogens, sulphate reducers, an unknown organism or a consortium involving sulphate reducers. Methanogens have been observed to produce and consume methane (Zehnder and Brock, 1979; 1980), although net consumption has not been demonstrated. Sulphate reducers have been shown to oxidize methane; additional electron acceptors must be present (Iversen, 1984) and net methane consumption has not been demonstrated.

The Alperin and Reeburgh (1985) study was conducted on intact sediments and slurries from the anaerobic methane oxidation maximum in Skan Bay sediments. Sediments were injected with molybdate, an inhibitor of sulphate reduction, 2-bromoethanesulphonic acid (BES), an inhibitor of methanogenesis and methane oxidation (Zehnder and Brock, 1979) and fluoroacetate, an inhibitor of acetate oxidation; both sulphate reduction and methane oxidation rates were measured on sediments with each treatment. The results showed no inhibition of methane oxidation with any of the inhibitors; sulphate reduction was only inhibited by molybdate. The inhibition experiment results eliminate methanogens as responsible for anaerobic methane oxidation. The results also eliminate normal sulphate reducers as being directly responsible for anaerobic methane oxidation, although it is possible that the observed anaerobic methane oxidation could have been mediated by the 1–2% of sulphate reducers that were not inhibited in the experiment or by a small number of atypical organisms.

The results are consistent with two possibilities: anaerobic methane oxidation may be conducted by unknown organisms using iron or manganese oxides or reduced sulphur compounds (S (0) to S (IV)) as electron acceptors, or by a consortium involving an unknown organism and a sulphur-reducer which uses hydrogen as the coupling substrate. Simulation experiments will be necessary to confirm these possibilities.

6.4 QUANTITATIVE EVALUATION OF BIOGENIC METHANE GENERATION AND OXIDATION IN OCEANIC SEDIMENTS*

The problem of methane genesis and development of methods for determining the rates of its formation, accumulation and oxidation in modern sediments of the world ocean has recently acquired a more applied significance. This has been primarily connected with the utilization of geochemical means of prospecting for oil and gas deposits in sedimentary rocks beneath the oceans. These investigations are no less important for comprehending the conditions favouring the formation of crystallohydrate gas fields which presently occur in young oceanic sediments (Makagon *et al.*, 1983; Claypool and Kaplan, 1974; Trofimuk *et al.*, 1975; Geodakyan *et al.*, 1979; Galimov and Kodina, 1982).

Rather abundant isotopic-geochemical evidence characterizing the $\delta^{13}C$ value of methane in the subsurface horizons of reduced bottom sediments of the Black, Bering and Baltic Seas and the Gulf of California (Table 6.7), suggests that the bulk of methane in these sediments is of a biogenic origin. The methane is characterized by an extremely light isotopic composition of carbon ($\delta^{13}C$ values vary from -60.0 to $-82.0‰$).

A similar isotopic composition of methane is peculiar also to most samples taken and analysed in the course of the work on the deep sea drilling project in sedimentary rocks to a depth of 1000–1600 m under the oceanic floor (Table 6.8). During microbial methanogenesis in bottom sediments of oceans, the bulk of methane is formed at the expense of carbon dioxide reduction (Belyaev and Finkelstein, 1976; Ivanov, 1979; Belyaev *et al.*, 1980; Lein *et al.*, 1981). This process not only enriches methane with isotopically light ^{12}C but also enriches the residual carbon dioxide with ^{13}C (Ivanov, 1979).

In the light of these data, of particular interest is the fact that, in many cases listed in Tables 6.7 and 6.8 the isotopically light methane is present together with carbon dioxide enriched in ^{13}C, as compared to the $\delta^{13}C$ value of inorganic carbon dissolved in oceanic water.

A principal scheme of biogeochemical processes resulting in methanogenesis under anaerobic conditions is given in Figure 6.7. It is seen that, in its geochemical essence, the microbial methanogenesis, alongside microbial sulphate reduction, is one of the final steps of the multi-stage process of organic matter decomposition under anaerobic conditions.

As seen from this scheme, there are two basic processes of microbial methanogenesis: methane formation from methyl groups of low molecular weight fatty acids, primarily acetate, and biogenic CO_2 reduction by hydrogen which is also one of the key intermediates in the anaerobic decomposition of organic matter.

*M.V. Ivanov and A.Yu. Lein.

Table 6.7 Isotopic composition ($\delta^{13}C$, ‰) of methane and carbon dioxide in upper horizons of reduced sediments of the Black, Baltic and Bering Seas and the Gulf of California

Sampling site, No. station	Depth of sea (m)	Horizon of silt sampling (cm)	$\delta^{13}C$-CH_4 (‰)	$\delta^{13}C$-CO_2 (‰)	Reference
Black Sea					
1. 113b	8	115–162	−64	−17	Alexeev and Lebedev, 1975
2. DSDP 380-1-6	9	115	−70	—	Hunt and Whelan, 1978
3. 114a	15	144–209	−60	−12	Alexeev and Lebedev, 1975
4. DSDP 379A-4-5	33	54	−66	—	Hunt and Whelan, 1978
5. DSDP 381-6-4	52	31	−72	—	Hunt and Whelan, 1978
6. 590	66	100–120	−82	—	Ivanov *et al.*, 1983
7. 564	68	140–160	−78	—	Ivanov *et al*, 1983
8. DSDP 381-17-6	151	63	−63	—	Hunt and Whelan, 1978
9. DSDP 380A-8-5	406	116	−65	—	Hunt and Whelan, 1978
10. DSDP 379A-45-4	412	100	−66	—	Hunt and Whelan, 1978
11. 109	440	160–200	−62	+9	Alexeev and Lebedev, 1975
12. DSDP 381-51-3	469	50	−67	—	Hunt and Whelan, 1978
13. DSDP 379A-67-2	608	77	−65	—	Hunt and Whelan, 1978
14. DSDP 380A-46-4	756	76	−63	—	Hunt and Whelan, 1978
15. DSDP 380A-792	1066	0	−65	—	Hunt and Whelan, 1978
Baltic Sea					
16. 2679	78	40–75	−64	−23	Lein *et al.*, 1982
Bering Sea					
17. Scan Bay	—	0–35	from −70 to −80 (10 tests)	from −11 to −20 (11 tests)	Reeburgh, 1983
Gulf of California					
18. South Guaymos depression	—	0–300	−76	from +2 to −16	Claypool and Kaplan, 1974

Table 6.8 Isotopic composition of methane and carbon dioxide ($\delta^{13}C$, ‰) in drilled wells of deep water oceanic sediments (DSDP)

Drilling site No. Drilled well (DSDP)	Depth of sea (m)	Thickness of drilled sediments, (m)	$\delta^{13}C$,‰		Reference
			CH_4	CO_2	
The Atlantic Ocean					
Maroc depression					
1. 415	2817	220	−71	—	Galimov and Kodina, 1982
2. 415A	2817	1042	−61 to −71	—	
3. 416	4203	1624	−82	—	Galimov and Tchinenov, 1978
4. Blake-Outer-Ridge 533		400	−66 to −94	−4 to −25	Galimov and Kvenvolden, 1982
5. Blake-Babama Ridge	—	700	−70 to −90	+3 to −28	Claypool and Kaplan, 1974
6. Cariaco Trench		180	−60 to −80	+10 to −20	
The Pacific Ocean					
7. Axtoria Fan	—	800	−70 to −80	0 to −20	Claypool and Kaplan, 1974
8. Aleutian depression 180	—	450	−75 to −80	+5 to −20	
Gulf of California					
9. 474	3023	14	−75	—	
10. 474A	3023	529	−40 to −60	—	Galimov and Kodina, 1982
11. 477	2003	182	−40 to −44	−11 to −16	
12. 478	1889	309	−62 to −80	−6 to −9	
	747	435	−52 to −62	+1 to −10	
13. 479					
14. 480	—	119	−67	−4	
15. 481A	1998	−55 to	−7 to		
	159	−77	−12		

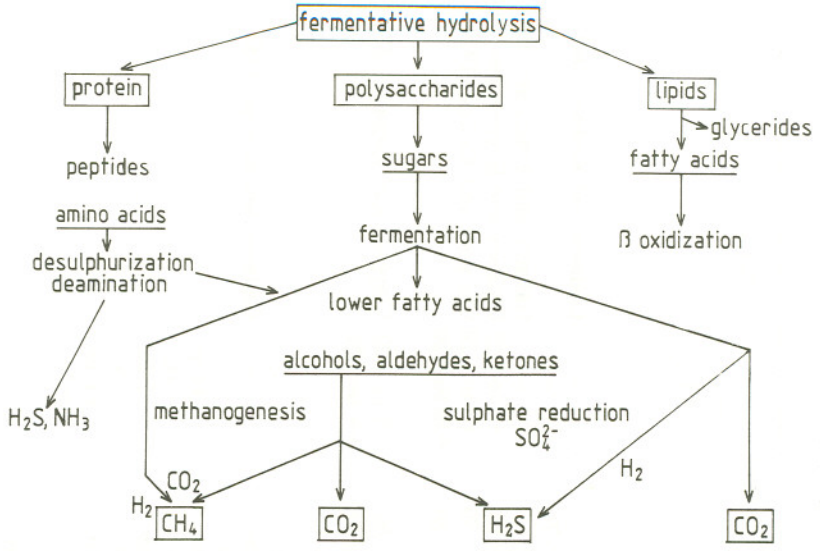

Figure 6.7 Scheme for the anaerobic degradation of organic matter in bottom sediments of seas and oceans

These two functions are found in the overwhelming majority of methanogenic bacteria studied hitherto, though the range of organic compounds known, i.e. substrates for microbial methanogenesis, has greatly broadened recently at the expense of methanol and compounds of a methylamine type.

The rest of this section reviews the quantitative data on microbial methanogenesis and oxidation of methane in oceanic sediments. The methods employed are described in detail in numerous reports (Belyaev and Ivanov, 1975; Ivanov *et al.*, 1976; Lein, 1978; Belyaev *et al.*, 1980; Lein *et al.*, 1982).

Starting from 1973, these investigations included the following regions of the world ocean:

(a) The sub-equatorial part of the Pacific Ocean in the cross-section from Wake Atoll to Mexico touching the Gulf of California, the Southern Pacific including the Tasman Sea in the cross-section from New Zealand to Lima (Peru) including the Peruvian–Chilean trench.
(b) The South-China and Bering Seas.
(c) The Indian Ocean; during three expeditions basic investigations were carried out in the Arabian Sea, Gulf of Persia and Aden, and near the East Africa shores from the Somalia horn to Maputu.
(d) The Black, Baltic and Caspian Seas.

The results obtained showed rather a wide distribution of methanogenic bacteria in the upper horizons of reduced sediments of the world ocean. Their maximal quantities (up to 1000 cells per gram silt) were found in bottom sediments of continental seas surrounding the Soviet Union: Baltic, Black and Caspian. They are also present in the most samples of silt sediments of marginal seas (Bering and South-China) and sediments of the Gulf of California, Persia and Aden. Referring to oceanic sediments proper, methanogenic bacteria were found in samples of moderately and highly reduced sediments along the east coast of Africa and the sediments of the Peruvian–Chilean trench and the Pacific Ocean near the west coast of Mexico.

However, none of these bacteria were found in the red clay samples taken in the trans-Pacific cross-section along 19°N latitude and in the cross-section from New Zealand to Peru. The same results were obtained in the analysis of deep-water carbonate-clayish sediments from the northwest part of the Indian Ocean and oxidized sediments from the Tasman Sea.

We focused our attention on obtaining materials that quantitatively characterized the intensity of microbial methanogenesis using labelled $^{14}CO_2$ and $^{14}CH_3COOH$. Labelled compounds were injected in silt columns and the intensity of methanogenesis was calculated from the quantity of $^{14}CH_4$ generated in a sample.

A typical profile of the methanogenic activity in the sediment cores is given in Figure 6.8. As seen from these data, methanogenesis occurs throughout the reduced sediments under study from the subsurface horizons to a depth of more than 2 m. In many cases a clear-cut maximum of methanogenesis is observed in upper centimetres of reduced silts (Figure 6.8), i.e. methanogenesis occurs in horizons of sediments characterized by high activity of sulphate-reducing bacteria. No inhibition of the activity of methanogen by sulphates of porewaters or by hydrogen sulphide is observed.

The data on the intensity of methanogenesis in the upper horizons of sediments (to a depth of 2–3 m) are given in Table 6.9 which shows wide variations in sea and oceanic sediments—from dozens of milligrams to fractions of a milligram carbon per kilogram of wet silt per day. Maximal values are peculiar to sediments of the North and especially Baltic Seas, while minimal ones are characteristic of coastal sediments of the Indian (Arabian Sea and Somali depression) and Pacific Oceans (South-China Sea, Peruvian cross-section).

Rather intensive methanogenesis was observed in the bottom sediments in the west part of the Black Sea and deep-water sediments of the Bering Sea (Table 6.9). Comparatively low intensity of methanogenesis in sediments of the Gulfs of California, Persia and Oman, rich in organic matter, may be explained by the inadequate attention to sampling from the uppermost horizons of these sediments (Belyaev and Finkelstein, 1976; Ivanov *et al.*,

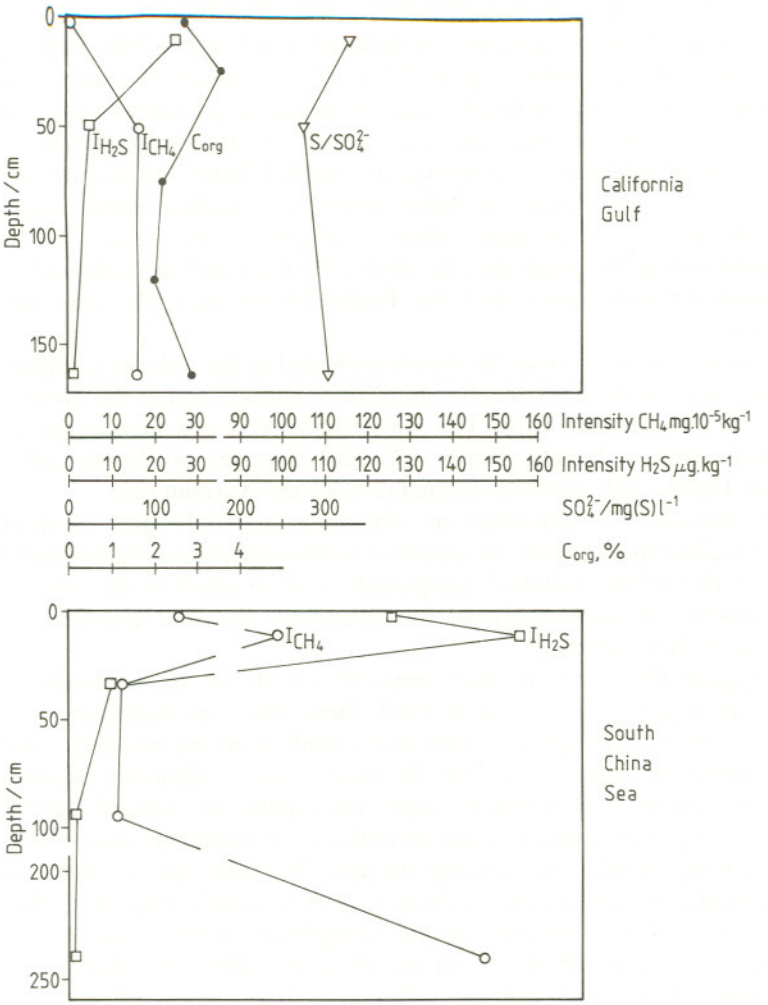

Figure 6.8 Distribution of the intensity of methanogenesis (I_{CH_4}), sulphate reduction (I_{H_2S}), content of sulphate sulphur (S/SO_4^{2-}) in porewater and C_{org} (% or dry weight) in cores in cores of reduced bottom sediments

1980). However, as became evident from further investigations, the highest methanogenic intensities were observed in the upper horizons (Figure 6.9).

Using two radioactively labelled compounds—carbon dioxide and acetate—we managed to show that in the overwhelming majority of sediments studied, the bulk of the methane was formed at the expense of carbon dioxide reduction (Table 6.9). This conclusion is important in interpreting pathways of anaerobic decomposition of organic matter in sediments (Figure 6.7),

Table 6.9 Intensity (mg 10^{-6} per kg wet silt per day) and productivity (mg m^{-3} (top metre) per day) of microbial methanogenesis in bottom sediments of seas and coeans, as well as the fraction of methane generated from carbon dioxide

Sampling site and number of analysed cores	Intensity of CH_4 formation	Productivity of CH_4 formation	Fraction of CH_4 from CO_2 %	References
I. *Basin of the Atlantic Ocean*				
Baltic Sea (7 cores)	200–11600	200–21000	56–99	Lein *et al.*, 1982
North Sea	10–1200	—	the bulk	Senior *et al.*, 1982
Black Sea, west part (8 cores)	0.5–220	7–68	70	Ivanov *et al.*, 1983
II. *Basin of the Pacific Ocean*				
Bering Sea (10 cores)	6–680	2–195	the bulk	Gorlatov, 1984
Gulf of California (4 cores)	0.1–3.0	3–5	86–99	Belyaev and Finkelstein, 1976
Peruvian profile (6 cores)	0.1–34	2–25	the bulk	Laurinavitchus *et al.*, 1981
South-China Sea (7 cores)	0.3–22	1–22	the bulk	Laurinavitchus *et al.*, 1981
III. Basin of the Indian Ocean				
Arabian Sea (4 cores)	2–50	6–63	the bulk	Ivanov *et al.*, 1980
Gulf of Oman (4 cores)	1–25	5–72	74–98	
Gulf of Persia (1 core)	4	—	83	
Somalian depression (1 core)	2–4	—	95–100	

and, as will be shown later, is in good agreement with isotope-geochemical data.

Table 6.9 also contains values of the biogenic methane production per square metre in a metre section of silt sediments calculated taking the results of all measurements of intensities down the sediment core from 0 to 100 cm into account. These data, corrected for microbial methane oxidation, can be employed to calculate the potential methanogenic activity of bottom sediments in various regions of the world ocean and thus forecast the possible formation of geologically young deposits of gaseous hydrocarbons in marine sediments.

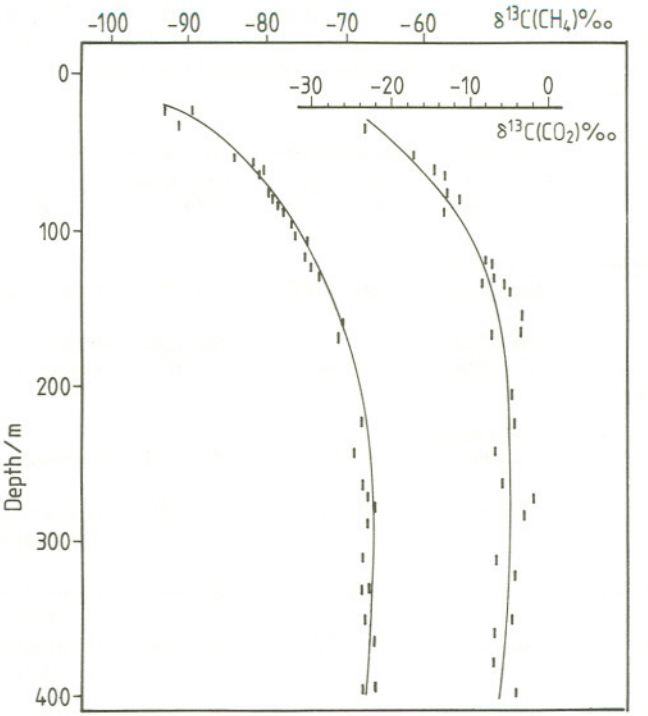

Figure 6.9 Simultaneous weighting of the isotopic composition ($\delta^{13}C$,) of methane and carbon dioxide along the seciton of well No. 533 drilled in Project DSDP in the Atlantic Ocean (Galimov and Kvenvolden, 1982)

It might be best to point out that, simultaneous with research into the intensity of methane formation and oxidation, the intensity of sulphate reduction in the same samples was also studied. This thus allowed us to show that sulphate reduction is the main mechanism of uptake of the low molecular weight organic compounds formed during anaerobic decomposition of organic matter in upper horizons of sea sediments (Ivanov, 1979; Belyaev *et al.*, 1980; Lein *et al.*, 1982). However, the intensity of sulphate reduction drops significantly in deeper parts of the silt mass (Figure 6.8), as do amounts of sulphate sulphur, while the relative contribution of methanogenesis to the transformation of organic matter increases markedly.

Based on isotope-geochemical evidence (changes in $\delta^{13}C$ values of methane and CO_2 in the mass of oceanic sediments (Figure 6.9)) one can assume that methanogenesis, at least that due to CO_2 reduction, continues down to a considerable depth.

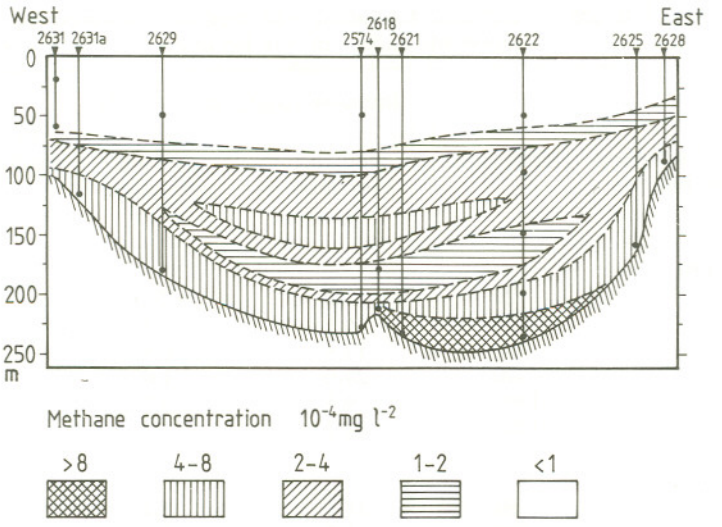

Figure 6.10 Content of dissolved methane in the Gotland depression (Trotzuk *et al.*, 1984)

This is confirmed by simultaneously weighting the isotopic composition of both the substrate for methanogenesis (carbon dioxide) and the product (methane) (Figure 6.9).

The impact of anaerobic oxidation of methane on the character of its distribution in the upper horizons of marine sediments was considered in sufficient detail in the earlier section by Reeburgh (Section 6.3). Here we wish only to supplement his data with recent findings on the rate of methane oxidation in marine sediments.

Probably the most popular explanation for anaerobic oxidation of methane has been the one maintaining that, in the uppermost layers of the sediment, bacterial methanogenesis does not occur. This is because either conditions are insufficiently anaerobic or sulphate-reducing bacteria compete for organic matter and hydrogen more effectively than methanogenic bacteria. As shown above (Figure 6.8) this point of view has not been confirmed by new data: maximum intensity of methanogenesis is observed, in many cases, in zones of active sulphate reduction in sediments.

Two other hypotheses explain a sharp decrease in the methane content in subsurface horizons of bottom sediments either by the loss of methane from bottom sediments to the water mass or by its anaerobic oxidation in sediments. The geochemical data being reported here support both mechanisms. The validity of the migration theory is strengthened by numerous observations of the increased dissolved methane content in bottom water in contact with reduced sediments (Figure 6.10).

Table 6.10 Balance of methane formation and methane oxidation processes in sediments under $1m^2$ for 1m layer

Place of sampling (station number)	Depth (m)	Intensity ($\mu g(C)\ m^{-2}\ day^{-1}$)		Portion of oxidized CH_4, %
		methane formation	methane oxidation	
Black Sea				
555	22	11.2	6.22.9	55
559	26	6.9	2.7	42
568	86	13.4	6.5	20
580	340	28.0	1.0	23
546	1400	9.5	3.7	11
545	1700	68.2		5
Bering Sea				
Pp	89	14.1	2.4	17
26	300	21.2	4.6	22
9	870	23.2	4.9	21
22	1200	28.2	4.1	15
1	1320	18.3	1.4	8
27	3350	109.7	2.8	3
1p	3000	115.6	6.4	6
6	3650	256.6	10.3	4
28	3850	290.0	10.8	4
32	3850	301.5	4.3	2

Simultaneous with the accumulation of results from experiments with $^{14}CH_4$ added to water and silt samples from anaerobic zones of lakes (Laurinavitchus *et al.*, 1981) and from reduced marine sediments, data also appear on the scale of methane oxidation in such ecosystems. Given the initial methane content of an analysed sample and the distribution of radioactivity between methane introduced to the biomass of methane-oxidizing bacteria, carbon dioxide released and the other products of $^{14}CH_4$ oxidation, it is possible to calculate the intensity of methane oxidation during the experiment.

Table 6.10, contains our own data characterizing the intensity of methane oxidation in upper horizons of the Black (Ivanov *et al.*, 1983) and Bering Seas. As with the case of methanogenesis (Table 6.9) all figures have been scaled to a cubic metre of sediment in order to have comparable values. Table 6.10 also presents data on methanogenesis obtained at the same stations. The comparison between the activities of these two key processes of the methane cycle in bottom sediments of seas shows that a substantial

part of newly formed microbial methane (up to 40–55%) may be oxidized within the sediments. In two regimes (sediments of Black and Bering Seas) the maximal part of biogenic methane is oxidized in shallow sediments of the shelf and the upper part of the continental slope.

In deep-water sediments (below 1000 m), characterized by a higher productivity of methanogenesis (Table 6.10), no more than 10% of newly formed methane is oxidized, making conditions more favourable for large accumulations.

In ten years of investigations carried out in the laboratory for Biogeochemistry (Institute of Biochemistry and Physiology of Microorganisms, USSR Academy of Sciences), we have developed quantitative methods for evaluating the intensities of microbial formation and oxidation of methane. Using these methods we have shown that such processes play an important role in final stages of mineralization of organic matter in sediments of different regions of the world ocean.

The data obtained show that the present methane generation and oxidation in sediments have considerable effect on sediment geochemistry and the isotopic composition of low molecular weight organic compounds. Therefore all the biogeochemical problems of methanogenesis in sediments can only be solved after accounting for a considerable microbial contribution.

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