Oceanic Methane Biogeochemistry

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1. Introduction

Measurements of dissolved methane in the ocean have been available for only about 50 years. Methane measurements in sediments, where concentrations are millimolar, were first reported in the mid-1950s, while measurements of methane in ocean waters, where concentrations are nanomolar, were first reported in the late 1960s.

Methane is the most abundant hydrocarbon in the atmosphere, where it plays an important role in tropospheric atmospheric chemistry. Further, methane is an important greenhouse gas. Atmospheric time series observations over the past two decades have documented an increase in the atmospheric mixing ratio of methane, and a great deal of activity has focused on the cause and climate consequences of this increase. The ocean contributes a relatively small amount of methane to the global net atmospheric budget, and it cannot be expected to play a role in the contemporary atmospheric methane increase. Our interest in methane in the ocean is understanding the balance between the enormous reported methane additions from continental shelf and slope sediments and the microbial oxidation reactions that must occur in sediments and the water column to produce the low nanomolar concentrations observed in the bulk of the ocean volume.

A number of poorly quantified external sources contribute methane to the ocean water column. The source processes include microbially-mediated diagenesis of sediment organic matter, abiotic production of methane through the serpentinization reaction, a rock/water reaction occurring in hydrothermal systems associated with the midocean ridges and spreading centers, leaks from near-surface petroleum deposits, and decomposition of methane clathrate hydrates. These contributions enter the ocean water column through coastal runoff, by diffusion from organic-rich anoxic sediments, and

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Bill Reeburgh was born and raised in Port Arthur, Texas. He earned a B.S. in Chemistry at the University of Oklahoma in 1961, and M.A. and Ph.D. degrees in Oceanography at The Johns Hopkins University in 1964 and 1967. He was on the faculty of the Institute of Marine Science at the University of Alaska, Fairbanks from 1968 until 1993, when he joined the University of California Irvine as one of the founding faculty of the Program in Geosciences, now the Department of Earth System Science. He was editor of *Global Biogeochemical Cycles* from 1998 to 2004 and was elected AGU Fellow in 2001. His research focus has been on methane geochemistry, particularly documenting the occurrence and extent of anaerobic oxidation of methane, and recent measurements of natural stable isotopes (^{2}H-CH$_4$, ^{13}C-CH$_4$) and radiocarbon (^{14}C-CH$_4$) in methane from anoxic marine sediments and waters.

through seeps, vents, and mud volcanoes emitting methane-rich fluids or methane-rich bubbles. Despite these large and poorly quantified methane additions to the ocean water column, microbially-mediated aerobic and anaerobic oxidation reactions effectively consume the added methane to low nanomolar levels, so that most of the ocean volume is undersaturated with respect to the atmosphere.

Methane is produced within ocean waters at only one location: the nearly ubiquitous surface mixed layer methane maximum, where methane concentrations are ~5 nM, supersaturated with respect to the atmosphere. Methanogenesis is mediated by strict anaerobes, and since the vast majority of the ocean water column contains oxygen, the presence of this methane maximum presents "the ocean methane paradox". Anoxic environments in digestive tracts and leakage from freshly released fecal pellets have been suggested as the major contributor to this enigmatic methane maximum. There is no evidence, even in anoxic basins, of large-scale methanogenesis at other locations in the water column. Curiously, the enigmatic surface mixed layer methane maximum, which also receives contributions from coastal runoff, amounts to about 25% of the ocean source term to the atmosphere in the global methane budget because of its proximity to the atmosphere.

Instead of thinking of an ocean methane cycle, where methane participates in a geochemical cycle involving linked production, utilization, and regeneration reactions, it is more correct to think of the ocean as a large reactor that very effectively oxidizes methane from a wide range of sediment sources. With the exception of the mixed layer methane maximum, the ocean methane is produced in sediments and has a benthic source. Methane is oxidized under anoxic conditions in marine sediments and waters; it is oxidized under oxic conditions at the benthic boundary layer and in the water column.

This paper summarizes the past half-century of ocean methane studies, emphasizing approaches and measurements that have led to the present view of the ocean as a very effective methane consumer or sink fueled by external sources. Since oxidation is so nearly quantitative, aerobic and especially anaerobic methane oxidation rates are summarized and integrated to estimate methane fluxes from the external sources outlined above. This paper also covers recent developments in biomarker molecules, genomics, and benthic communities apparently sustained by methanotrophy, and it outlines fruitful areas for future research.

Recent reviews on global methane biogeochemistry[1−4] emphasize contributions from a number of sources, the use of natural stable and radioisotopes in quantifying and constraining the sources, and processes contributing to the atmospheric methane increase. Reviews of methane geochemistry have emphasized several areas: aquatic environments,[5,6] anaerobic oxidation of methane,[7,8] and recent advances in anaerobic oxidation of methane,[9,10] as well as microbiological aspects of methanogenesis (methane production)[11] and methanotrophy (methane consumption)[12−14] and the role microbial methane consumption plays in controlling methane fluxes to the atmosphere. Methane biogeochemistry is covered in microbial ecology texts,[15] but it has received limited attention in chemical oceanography and marine geochemistry texts[16−20] and reviews.[21]

1.1. Global Methane Budget

Any discussion of oceanic methane biogeochemistry should place the ocean in the context of the global methane budget. A geochemical budget is a flux balance (or a mass balance) that provides a useful means of partitioning and estimating the magnitudes of sources and sinks. Budgets are very useful in exposing our ignorance, but they have no predictive power.

The first global methane budget, a net atmospheric budget, was based on available flux measurements and estimates from a variety of sources.[22,23] The natural radiocarbon (^{14}C) content of atmospheric methane was used to partition the budget between recent biogenic and fossil sources. Oxidation by OH in the troposphere and destruction in the stratosphere were considered sinks.

Time series observations beginning in the late 1970s[24−27] showed that the atmospheric methane mixing ratio was increasing by ~1% year^{-1}, and methane measurements in polar ice cores[28−31] showed that the atmospheric increase started long before it was documented by the atmospheric time series observations. The atmospheric mixing ratio increase and recent field measurements were reviewed by Cicerone and Oremland,[1] who concluded that the atmospheric increase was genuine and proposed a revised methane budget based on new information on sources and sinks. On the basis of a framework of constraints involving the global methane burden, turnover rates, and isotopes, we have high confidence in the total budget, the rate of change, the fraction of modern biogenic methane, and the total source (or sink). How to apportion the individual sources is less certain. By constraining the magnitude of the total, this budget served to limit proliferation of source estimates. Seasonal time series observations at fixed stations were used as a constraint in an inverse model, and several likely global methane budget scenarios were proposed by Fung et al.[32]

1.2. Role of the Ocean in the Global Methane Budget

The role of microbial oxidation in the gross global methane budget is illustrated by Table 1, which is based on Söhngen's[33]

Table 1. Global Net CH_4 Emission (E), Consumption (C), and Gross Production (P), Tg of CH_4 $year^{-1}$ (E + C = P)[f]

source/sink term	E[a]	C[b]	P
animals	80	0	80
wetlands	115	27	142
bogs/tundra (boreal)	35	15	50
swamps/alluvial	80	12	92
rice production	100	477	577
biomass burning	55	0	55
termites	20	24	44
landfills	40	22	62
oceans, freshwaters	10	75.3	85.3
hydrates	5?	5	10
coal production	35	0	35
gas production	40	18	58
venting, flaring	10	0	10
distribution leaks[c]	30	18	48
Total Sources	500[d]		
chemical destruction	−450		
soil consumption	−10	40	40[e]
Total Sinks	−460[d]	688.3	
		Total Production	1188.3

[a] Scenario 7, ref 32. [b] From Table 1, ref 34. [c] Should be considered P. [d] 500 − 460 = 40 Tg CH_4 $year^{-1}$ = annual atmospheric increment (0.9% $year^{-1}$). [e] Soil consumption of atmospheric CH_4 added to the gross budget as an equivalent production term. [f] Reprinted from ref 2, Copyright 2003, with permission from Elsevier.

observation that methane oxidizing processes (methanotrophy) are frequently in close proximity to methane producing processes (methanogenesis). Thus, emission (E) plus consumption (C) equals production (P). The first column of Table 1, emission (E), gives the source categories and well-constrained magnitudes from Fung et al.[32] The second column gives estimates of microbially-mediated methane oxidation (consumption, C) for each of the source terms,[34] and the third column gives the sum, an estimate of global production (P). Although the consumption estimates[34] are conservative, neither the consumption term nor the production term can be constrained by the framework used for the net budget.[1,32] There are several sources where consumption is zero: these are sources where methane is transported directly to the atmosphere with no opportunity for microbial oxidation. We know that methane clathrate hydrates represent an enormous methane reservoir with the potential to be a large source (see section 6.1.3), but so little is known about hydrate contributions that the hydrate term was proposed as a "placeholder" term.[1]

Note that the net global atmospheric budget (E) is the difference between large uncertain numbers and that microbial oxidation accounts for more than half of the estimated methane production. Microbial methane oxidation has the largest influence on the budget *before* emission to the atmosphere, yet it has been largely ignored because of the focus on net emissions. The ocean provides an excellent example of consumption before emission, and it is a small (2%) term in the global methane budget. The ocean term was revisited by Ehhalt[35] and was recently re-evaluated,[36,37] including shelf and estuarine areas. These estimates lie within the range of previous values.[1] The entry for ocean consumption is a conservative estimate based on integrated sediment oxidation applied to shelf areas.[38] One recent estimate[10] is much larger but has no effect on the well-constrained emission estimate. One of the goals of this review is to produce an updated estimate of microbially-mediated methane oxidation.

2. Ocean Methane Measurements

Measurements of oceanic methane lagged those in the atmosphere[2] because of the need to separate dissolved methane from the aqueous phase. Measurements in sediments preceded those in open waters because methane concentrations are 10^3-10^7-fold lower in open waters.

2.1. Water Column

Until the introduction of gas chromatography in the early 1950s, dissolved gas measurements, usually on physiological fluids, were made using manometric[39] and microgasometric[40,41] techniques. Swinnerton and Linnenbom[42] stripped hydrocarbons from solution using a 7 cm diameter chamber fitted with a fine glass frit, and they trapped and concentrated the gases in freeze-out traps. The trapped gases were released by warming and were introduced through a sample loop to a gas chromatograph. A modification[43] of the stripping method eliminated the traps and used carrier gas (He) to quantitatively strip gases directly from liquid samples into a gas chromatograph. A further modification[44] involving use of a sampling valve to ensure uniform liquid sample sizes led to wide application. Central to these modifications was use of a 1 cm diameter stripping chamber equipped with a coarse glass frit. This allowed bubbles of carrier gas to rapidly transit and equilibrate with the liquid sample. The small diameter stripping chamber, combined with the coarse frit, decreased back-pressure, permitted higher flow rates, and resulted in less peak-broadening and tailing than larger diameters. Peak areas were quantified by integration.

The first measurements of natural C_1-C_4 hydrocarbons in individual seawater samples were made using the strip and trap method.[43] The first ocean methane depth distributions were reported by Swinnerton and Linnenbom.[45] Methane depth distributions in anoxic basins were reported by Atkinson and Richards.[46]

2.2. Sediments

Although methane concentrations are much higher in sediments, these measurements involved the additional challenge of extracting gases from semisolid high water content sediment samples. Koyama[47] used CO_2 (generated internally by acidification of marble chips in a gas extraction apparatus) to strip gases from samples of lake sediments into a gas buret. The CO_2 was absorbed with base prior to quantification of the residual gases. Emery and Hoggan[48] produced a sediment/water slurry using a specially-designed fluidizer that allowed addition of water to a sediment core segment, followed by physical mixing to produce the slurry. The fluidized sediment was degassed by introducing it to an evacuated carboy. The extracted gases were measured by mass spectrometry.

Reeburgh used a gas-operated filter press (squeezer)[49] to separate interstitial or pore water from sediment sections, and he introduced the interstitial water directly to a graduated stripping chamber (sampler-stripper),[50] whose dimensions and frit porosity were similar to the Swinnerton et al.[42,43] recommendations. The sampler-strippers contained a small volume of degassed $CrSO_4$ solution to reduce traces of O_2. This ensured that the unresolved $Ar-O_2$ peak contained only Ar, and it permitted measurement of Ar, N_2, and CH_4 on a single sample.[51] The interstitial water sample volume was measured and the sampler-stripper was mounted on a gas chromatograph for stripping and quantification of the gases.[50]

The squeezers were loaded with sediment inside a carrier gas-filled glove bag to avoid atmospheric contamination. Martens[52] devised an "interlock" for loading squeezers that was less cumbersome than glovebags.

2.3. Headspace Measurements

Headspace equilibration is used today for virtually all oceanic methane measurements. McAuliffe allowed dissolved compounds to equilibrate between an aqueous phase and a gas headspace according to Henry's Law, and they used headspace measurements to determine the solubilities of a range of organic compounds[53,54] as well as concentrations in brines.[55] For water samples, serum bottles of known volume are filled and flushed without trapping bubbles and are capped with a crimp-seal serum bottle stopper. A headspace (N_2 or He) of sufficient size to contain >95% of the dissolved methane at equilibrium is introduced to the inverted serum vial using two syringe needles: one to slowly introduce the headspace gas to the top of the inverted bottle and another located near the stopper to remove the displaced water. Following equilibration, the methane concentration of the headspace is measured with gas chromatography. The methane remaining in solution is estimated using seawater methane solubility values.[56,57] Sediment samples, usually collected as lateral subcores with cutoff syringes, are slurried with degassed water, and the headspace is analyzed as with water samples.

An adaptation of the headspace technique involves vacuum−ultrasound (VUS) degassing.[58,59] This extraction technique involves extraction of liter samples and provides sufficient methane for concentration as well as isotopic analysis. Water samples are drawn into a 1 L sample bottle, which is evacuated using a specialized manifold, placed in an ultrasound bath, and pulsed briefly for several minutes. Gases released as fine bubbles are collected in a gas buret and either sampled for analysis or transferred to an evacuated serum vial. Extraction is not quantitative (60% efficient), so uniform extraction conditions are required. Preservatives are not needed prior to analysis.

2.4. Natural Isotopes

Kinetic isotope effects associated with methane production and oxidation lead to changes in the isotopic composition of methane. These isotopic changes in methane samples make it possible to infer origins as well as chemical and physical processes operating on methane. The isotopic composition of methane in natural gases from various origins was compiled by Schoell,[60] and subsequent papers have focused on methane formation[61] and microbial formation and oxidation[62−64] in aquatic and sediment environments. Results from these studies have been presented in C−D diagrams, plots of paired measurements of δ^{13}C-CH_4 (C) vs δ^2H-CH_4 (D), which can be used to infer origins from broad categories, such as thermogenic and bacterial, and to infer trajectories resulting from isotope fractionation due to oxidation[65] and transport.[66]

Stable isotope measurements are performed with mass spectrometers. Results are reported as isotope ratios rather than absolute abundances or atom percentages, so isotope results are expressed in "del" notation[67] as deviations from standards: the PeeDee belemnite (PDB)[68] for ^{13}C and Standard Mean Ocean Water (SMOW)[69] for ^{2}H. Results expressed in del notation are the deviation, expressed in parts per thousand or per mille (‰), of the sample isotope ratio from a standard, where R_{sample} is the $^{13}C/^{12}C$ or the $^2H/^1H$ ratio and

$$\delta = \left\{\frac{R_{sample} - 1}{R_{standard}}\right\} \times 1000 \text{ per mille or ‰} \qquad (1)$$

In del notation, samples that contain less ^{13}C than the standard have negative values and are referred to as isotopically light or depleted. Biogenic or bacterial methane is generally considered to have a δ^{13}C value of less than −50‰,[70] while thermogenic and abiotic methane are isotopically heavier, with δ^{13}C values of greater than −50‰. Methane oxidation involves preferential oxidation of the light isotope, so the residual methane becomes isotopically heavier.

Stable isotopes of methane have been used as natural internal tracers[65,71,72] and, when environments are well-understood, to determine kinetic isotope fractionation factors.[65] Recent kinetic isotope fractionation factors for methane oxidation in well-characterized environments are summarized in Table 3 of Reeburgh.[2]

Mass spectrometry has advanced to a point where compound-specific isotope measurements can be performed by combusting compounds separated by gas chromatography, followed by continuous monitoring of the isotope ratio (GCCIrmMS, gas chromatography−combustion−isotope ratio monitoring mass spectrometry). This technique has the advantage of requiring much smaller samples and no vacuum line preparation.[73,74]

There are few measurements of natural radiocarbon (^{14}C) in environmental methane samples. A limited number of measurements have been performed on large atmospheric samples to partition biogenic and fossil contributions to the atmospheric methane budget.[75,76] Radiocarbon has a radioactive decay half-life of 5730 years, so it is absent from samples containing carbon older than about 8 half-lives. Radiocarbon results are normalized to a standard δ^{13}C value, so reported results show no effects of isotope fractionation. Accelerator Mass Spectrometry (AMS), which measures ^{14}C atoms individually, rather than observing decay events, has high sensitivity and accuracy (0.3% for samples with contemporary levels of ^{14}C) and can utilize very small (~2 μmol of CH_4) methane samples.[77]

3. Oceanic Water Column Methane Distributions

Typical methane depth distributions in ocean waters containing oxygen[78,79] are shown in Figure 1. The methane concentrations are nanomolar throughout the depth distribution and are maximum in the mixed layer above the pycnocline. The mixed layer maximum and supersaturation with respect to the atmosphere have been observed widely.[80−83]

A Pacific Ocean methane section (40° N to 5° S along 165° E), well-removed from coastal influence,[84] is shown in Figure 2. The mixed layer methane maximum is also evident in the section.

Figure 3 shows methane depth distributions in the water columns of the Earth's two largest anoxic basins, the Cariaco Basin[85] and the Black Sea,[86] where methane concentrations in the anoxic water column reach micromolar concentrations.

A large number of underway methane saturation measurements have been reported.[87−89] Seiler and Conrad[90] report continuous measurements of methane saturation in an Atlantic Ocean section from 36° S to 50° N. A recent Pacific

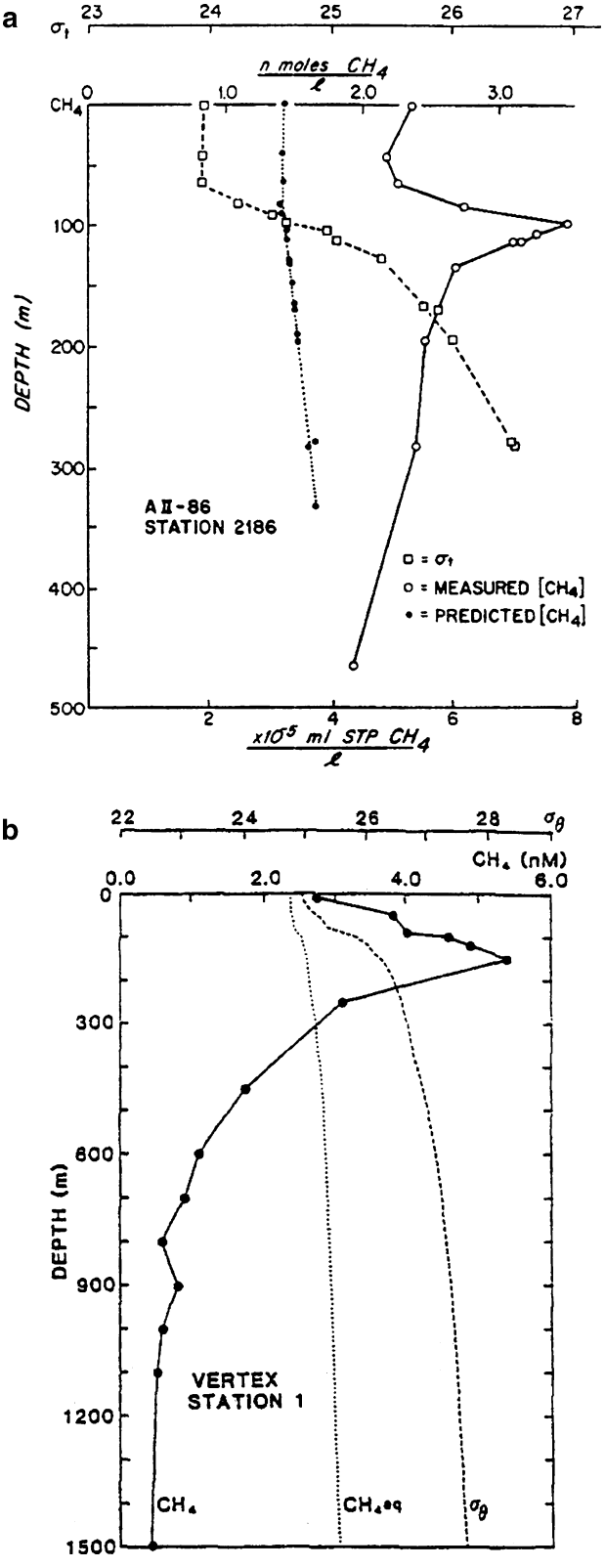

Figure 1. Water column distributions of methane, methane in air-equilibrated water, and density anomaly in the (a) Atlantic and (b) Pacific Oceans. Note the relationship of the methane maximum to the near-surface change in density anomaly (σ_q) or pycnocline. (a) Atlantic Ocean (35.8° N, 122.6° W). Reprinted from ref 78, Copyright 1977, with permission from Elsevier. (b) Pacific Ocean (9.5° N, 107° W). Reprinted from ref 79, Copyright 1995, with permission from Elsevier.

Ocean transect[91] involving sampling at 2° intervals from 27° S to 5° N was consistent with previous work and showed

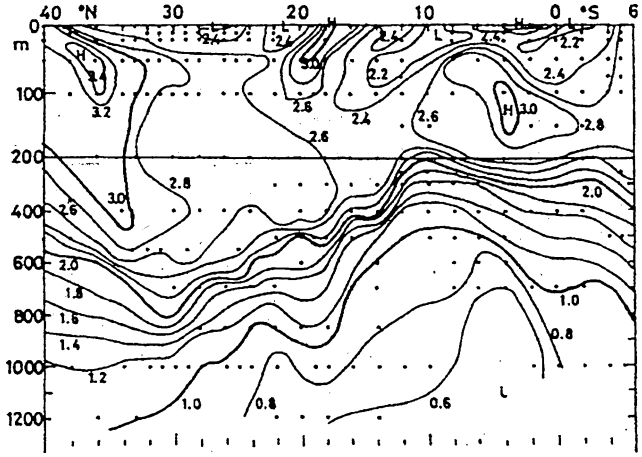

Figure 2. Methane concentration section from 40° N to 5° S along 165° E. Contour interval is 0.2 nM. The mixed layer methane maximum is evident in this section. Reprinted from ref 84, Copyright 1995, with kind permission of Springer Science and Business Media.

that the mixed layer maximum is a consistent feature, except near the equator. Most of these saturation measurements preceded reliable seawater solubility measurements,[56,57] so saturation was assessed by differences in free-air and equilibrator gas-phase concentrations. Methane supersaturation relative to the atmosphere is reported in the open ocean,[78,79,90] on continental shelves,[92,93] near rivers,[88,94,95] and near productive upwelling areas.[96] Surface waters are slightly oversaturated, while deeper waters were in equilibrium or undersaturated with respect to the atmosphere. The reanalysis by Bange et al.[37] resulted in a weighted methane supersaturation of 120% for open ocean waters and several hundred percent for shelf regions. Fluxes of methane across the seawater/atmosphere interface were calculated with a laminar film gas transfer model.[97] The global budget term involved extending these fluxes to the global ocean area.

4. Methane Distributions in Sediments

Methane distributions in marine and freshwater sediments[98] are shown in Figure 4. The key difference between marine and freshwater sediment methane distributions is the concave-up methane distribution and the low-methane surface zone observed in marine sediments.

A schematic diagram of CH_4, SO_4^{2-}, ΣCO_2, and $\delta^{13}C$-CH_4 in an anoxic marine sediment is shown in Figure 5B.[99] This figure is derived from many observations that are summarized in Table 2. Figure 5b shows measurements of CH_4, SO_4^{2-}, $\delta^{13}C$-CO_2, and the methane oxidation rate in Skan Bay sediments.[100] The concave-up distribution with a low-methane surface zone is characteristic of anoxic marine sediments and is due to anaerobic oxidation of methane in a depth interval that coincides with the intersection of the methane and sulfate profiles as well as lack of methanogenesis in the surface sulfate reducing zone. The thickness of the low-methane surface zone, the sulfate/methane transition (SMT) depth, is determined by the organic carbon flux to the sediments.[38] Figure 6 gives examples of Ocean Drilling Project (ODP) methane and sulfate distributions[101] and shows distributions similar to those observed in the upper meter of organic-rich sediments (Figures 4 and 5) expanded over hundreds of meters in ocean sediments. This synthesis provides a global map of the distribution of the low-methane surface zone or SMT, and it identifies two provinces of

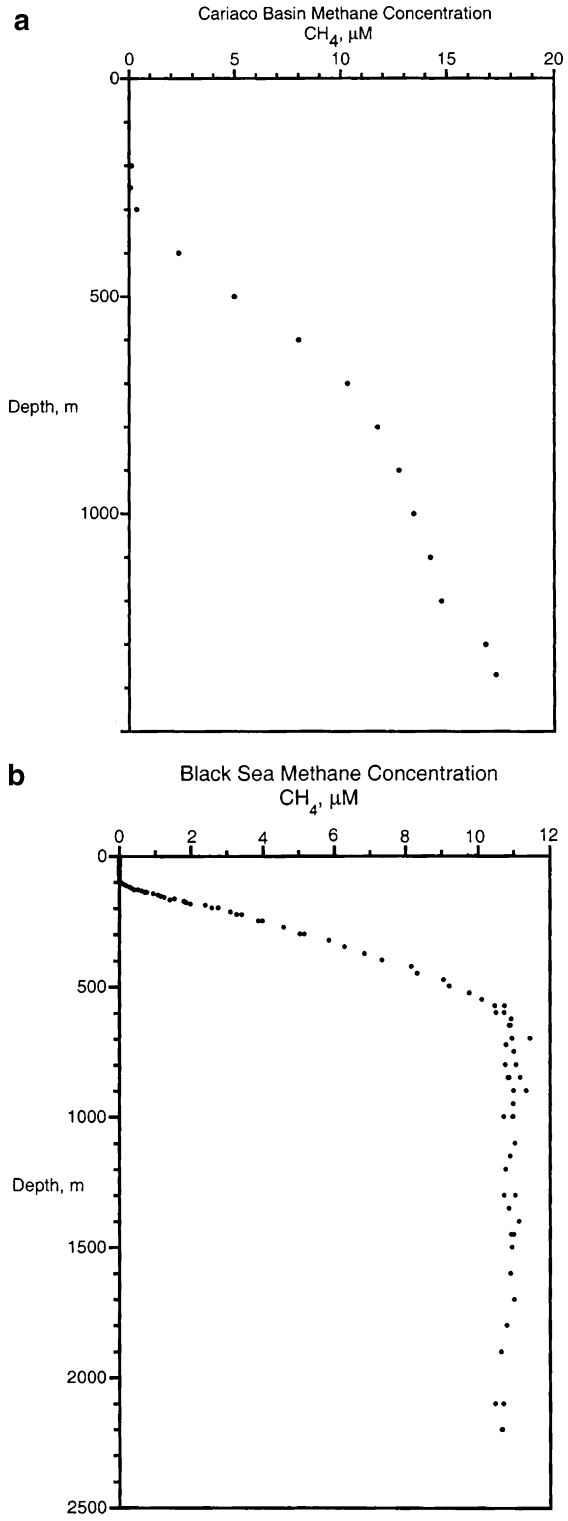

Figure 3. Water column methane distributions in anoxic waters of the Cariaco Basin and the Black Sea. Data from refs 85 and 86.

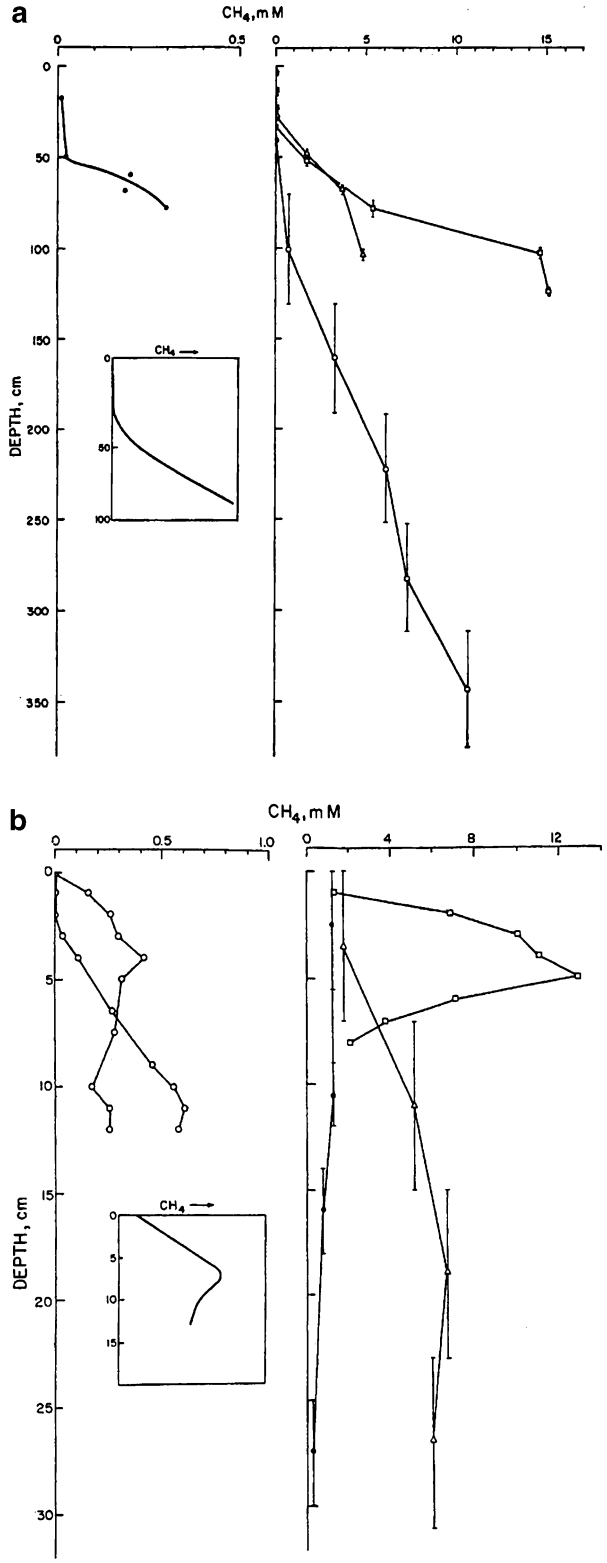

Figure 4. Methane distributions in (a) marine and (b) freshwater sediments. Note the absence of the low-methane concave-up surface zone in freshwater (low SO_4^{2-}) sediments. Reprinted with permission from ref 98. Copyright 1977 by the American Society of Limnology and Oceanography, Inc.

subsurface metabolic activity: one (panel B) located on high carbon flux shelves and slopes, where the low-methane surface zone is evident and high methane concentrations are present in deeper sediments, and a second (panel A) restricted to low carbon flux deep ocean basins, where methane is absent and sulfate is dominant. The distributions shown in panel C account for about one-sixth of the open-ocean sites and contain abundant sulfate and above-background methane concentrations. This occurrence is contrary to the kinetic and thermodynamic constraints on methanogenesis (sections 5.1 and 6.1.1) and was taken as evidence of methanogenesis[101] in sulfate-rich open ocean sediments. These methane concentrations (100 μL L^{-1} or ~4 μM) are *lower* than the methane concentrations encountered in the low-methane surface zones of the environments anoxic sediments that provided early evidence of anaerobic oxidation of methane

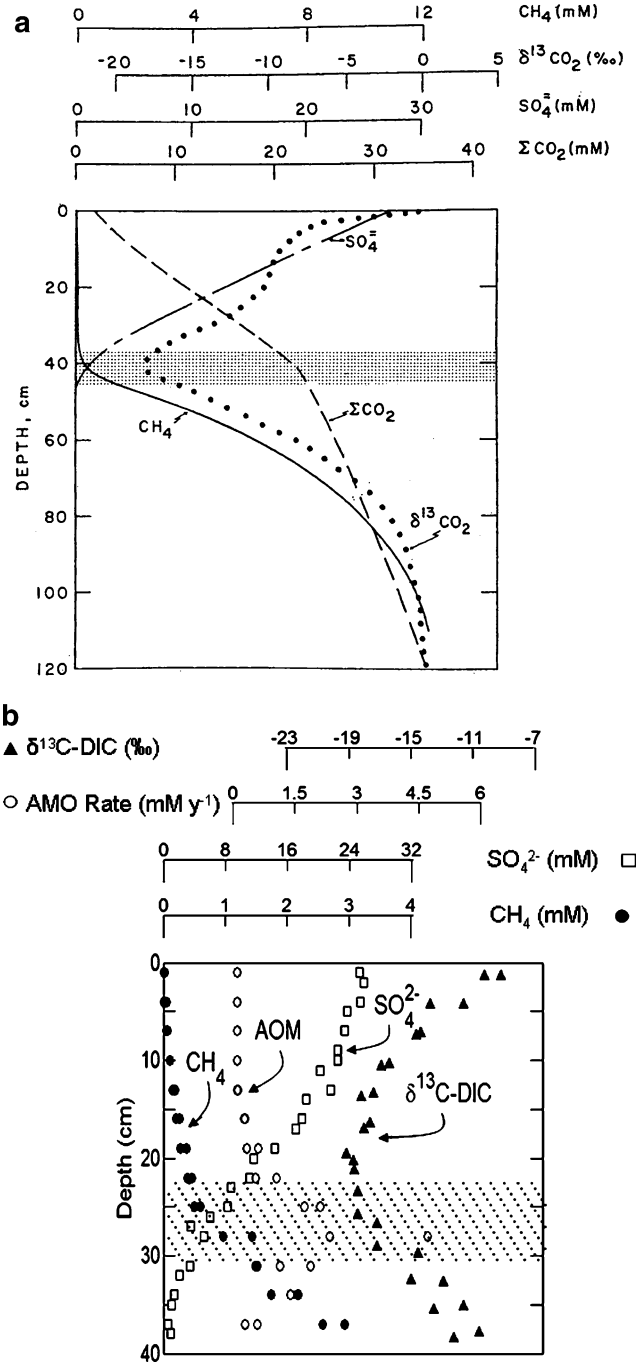

Figure 5. (a) Schematic diagram of methane, SO_4^{2-}, ΣCO_2, and $\delta^{13}C$-CH_4 in an anoxic marine sediment. These distributions have been widely replicated. All distributions show breaks or slope changes in the stippled area, which represents the zone of maximum anaerobic methane oxidation. The distance from the sediment surface to the depth where $SO_4^{2-} = 0$ is known as the sulfate/methane transition (SMT) depth. Reprinted with permission from ref 99. Copyright 1982 Lexington Books. (b) Measured distributions of CH_4, SO_4^{2-}, $\delta^{13}C$-DIC, and the rate of methane oxidation (MOR) in Skan Bay sediments (ref 100). Note that the minimum in $\delta^{13}C$-DIC (product of oxidation of isotopically light CH_4) and the maximum in the methane oxidation rate coincide with the sulfate/methane transition.

(the Cariaco Basin,[85] Santa Barbara Basin,[102] Long Island Sound,[103] Cape Lookout Bight,[104] and Skan Bay[103]), so they are hardly evidence of methanogenesis. The methane present has probably escaped oxidation, as in the above environments, and remains in the sulfate reduction zone, where

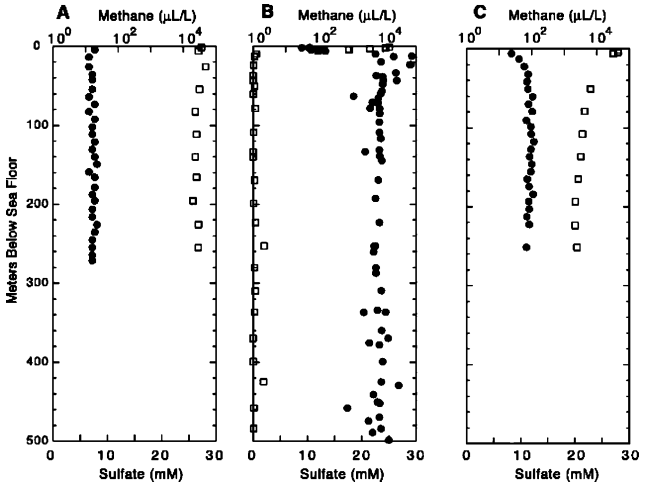

Figure 6. Representative profiles of SO_4^{2-} (open squares) and CH_4 (solid circles) concentrations in Ocean Drilling Project cores from open-ocean and ocean margin sites: (A) open-ocean ODP site 851; (B) ocean margin ODP site 798; (C) open-ocean site 846. These distributions show that the processes depicted in Figure 5 occur on a scale of 10's to 100's of meters at widely distributed locations. Reprinted with permission from *Science* (http://www.aaas.org), ref 101. Copyright 2002 AAAS.

oxidation is less likely. A less likely explanation might be methanogenesis using noncompetitive substrates (section 5.2). The log concentration scale used for methane overemphasizes low concentrations and probably led to overinterpretation of higher sensitivity methane measurements.

5. Water Column Methane Production?

5.1. Thermodynamic, Kinetic, and Physical Constraints on Water Column Methane Production

The reviews by Rudd and Taylor[5] and by Keine[6] take pains to distinguish between marine and freshwater methane geochemistry. This is principally because sulfate, a major constituent in seawater (29 mM), causes profound differences in methane geochemistry in marine systems.[106] This section briefly discusses the thermodynamic, kinetic, and physical constraints that prevent biological and abiotic methane production in the ocean water column. These will be covered in more detail in the discussion in section 6.

Biological production of methane or methanogenesis is the last step in the remineralization of complex organic matter in anaerobic systems.[6] Organic matter degradation involves a sequence of reactions in which complex organic matter is hydrolyzed to monomers and these are fermented to H_2, low-molecular weight fatty acids, alcohols, and methylated compounds. Methanogens require simple molecules as substrate, the most important being H_2 and acetate,[5] and are dependent on the activities of other microorganisms to provide these substrates. The principal biologically mediated reactions for methanogenesis are as follows:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (CO_2 reduction)} \quad (2)$$

and

$$CH_3COOH \rightarrow CO_2 + CH_4 \text{ (acetate fermentation)} \quad (3)$$

Reaction 1 occurs mostly in marine environments because

of acetate depletion by sulfate reducers; reaction 2 is favored in freshwater environments, where acetate is more abundant due to the absence of sulfate reducers.[64]

The thermodynamic energy yield from the oxidation of organic matter coupled to various electron acceptors decreases in the order $O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2$, and these electron acceptors are utilized in the above sequence.[107] Studies in sediments have shown that addition of more energetically favorable electron acceptors results in diversion of the electron flow to the favored electron acceptor.[108−110] Results from anoxic marine sediments indicate that methanogenesis does not occur until sulfate is nearly exhausted and sulfate reduction rates decrease.[103,111] This is not only due to the energy yield constraints above but also because sulfate reducers are very effective in their uptake of H_2 and acetate and are capable of maintaining H_2 and acetate at concentrations too low for methanogens to function.[110] Sulfate reducers thus outcompete methanogens for substrate.

We expect no large-scale methanogenesis in the open ocean water column, primarily because of the presence of O_2. Abundant sulfate, as well as the occurrence of sulfate reduction,[112] also prevent methanogenesis in the water columns of anoxic basins. Almost all of the 29 mM ocean water column sulfate pool must be reduced before conditions favorable for microbial methanogenesis are obtained. The extent of anoxia in natural anoxic basins is surprisingly small: total sulfide (ΣS^{2-}) reaches maximum concentrations of 28 μM in the Cariaco Basin,[46,113] 400 μM in the Black Sea,[114] and 8.4 mM in Framvaren Fjord.[115] Other partially reduced sulfur compounds ($S_2O_3^{2-}$) could also be important, but their concentrations are very small relative to sulfate. These thermodynamic and kinetic grounds effectively eliminate microbial methanogenesis in the ocean water column and require that its source be anoxic sediments, where restricted mobility permits sulfate reduction to a point where methanogenesis is possible.

Abiotic methane production has recently been identified in association with rock/water reactions (the serpentinization reaction) occurring at and near spreading centers (see section 6.1.2). This methane is produced abiotically at temperatures >300 °C from H_2 and CO_2 as seawater circulates through fractured recent crust. Methane plumes with ~50 nM excursions from ambient concentrations have been observed.[116] This methane is clearly produced outside the ocean water column and is transported into the water column by vents.

5.2. Methanogenesis Involving Noncompetitive Substrates

Despite the thermodynamic and kinetic arguments advanced above, methane production can occur in systems involving active sulfate reduction.[6] Stimulation of methane production resulted from additions of methanol, methionine, methylated amines, dimethyl sulfide (DMS), DMDS (dimethyldisulfide), and methane thiol (MSH) in laboratory experiments involving lake, estuarine, and marine sediments.[117−121] Methanol can be produced by bacterial degradation of lignins or pectin, while methylated amines can be produced by decomposition of choline, creatine, and betaine.[117] The production of methane in the presence of active sulfate reduction was interpreted as an example of methanogenesis involving "noncompetitive substrates", because methane was produced without involving the methanogen/sulfate reducer competition. These studies demonstrate turnover and potential pathways, but unfortunately, they provide no information on the importance of methanogenesis involving noncompetitive substrates in the ocean because the ambient concentrations or pool sizes were not measured. There have been suggestions that methanogenesis involving noncompetitive substrates occurs on or within particles[122] and even in oxygenated waters.[123−125]

5.3. Microenvironments and the Ocean Methane Paradox

Since the surface ocean is supersaturated with respect to the atmosphere,[78,79,89] methane must result from addition of high-methane coastal waters or from production in the surface ocean. Coastal additions may account for the supersaturation near coasts,[92−95] but they cannot account for supersaturations observed in the open ocean.[78−84]

Methanogenesis occurs only under strict anoxic conditions,[11] so its occurrence and apparent production in oxic waters to an extent that produces methane supersaturation is termed the "Ocean Methane Paradox".[6] Methanogenic bacteria with the potential to produce methane under anoxic conditions were observed in fish intestines and plankton samples,[126] and anoxic and low-oxygen interiors were observed in marine snow and fecal pellets using oxygen microelectrodes.[127] On the basis of these observations, Sieburth[123] acknowledged earlier suggestions[78,80,92,96] invoking microenvironments and made a case for anoxic microenvironments in ocean particles as the locus for methanogenesis. Viable methanogenic bacteria[128,129] were later found in sinking particulate matter and zooplankton fecal pellets. Particle trap measurements by Karl and Tilbrook[130] provided a mechanism for producing methane and transporting it into the ocean mixed layer. Particle-to-seawater methane fluxes were measured in sediment traps deployed in the ocean mixed layer. Poisoned and unpoisoned collector traps, filled with an autoclaved brine solution to minimize diffusive loss and flushing during recovery, allowed distinguishing methane that entered the traps in association with the particles (poisoned) and methane produced in the traps after particle collection (unpoisoned). The particle traps were equipped with screens to prevent contamination by macrozooplankton. The screens reduced trapping efficiency and excluded large fecal pellets, the most likely loci for methanogenesis, so these particle-to-seawater flux estimates are conservative. Nonetheless, the estimated particle-to-seawater methane fluxes (~40−1400 nmol m^{-2} day^{-1}) are sufficient to produce the methane supersaturations observed in less than a month and to replace the methane in the upper water column in 50 days. Karl and Tilbrook[130] hypothesized that methane is formed in zooplankton guts, enters the sinking particle field as fecal pellets, and is released as the particles are disrupted and exchange with the adjacent water column. Model calculations[131−133] indicate that anoxic conditions cannot persist for long in fecal pellets falling through oxic waters, leading Tilbrook and Karl[79] to conclude that the most favorable conditions for methanogenesis would occur in the digestive tracts of organisms and immediately after defecation. Thus, fecal pellet-derived solutes and gases must be exchanged within a zone close to the formation of the fecal pellets. Mass balance calculations indicate that the methane supersaturations and losses by air/sea exchange can be maintained with net methane production of 2.3 μmol m^{-2} day^{-1} over a 100 m thick surface layer.[130] A recent one-dimensional vertical

advection-diffusion model[134] involving methane release from settling fecal pellets agrees well with the sediment trap data and shows that methane leaking from fecal pellets is sufficient to explain observed open ocean methane concentrations. The model also highlights the importance of methane oxidation, even at specific oxidation rates of 10^{-5} day^{-1}, in shaping the methane concentration profiles. The particle trap results also show that the methane production process is a surface ocean phenomenon; no accumulation of methane was observed at depths below 500 m.

The fecal pellet microenvironment hypothesis provides a good first-order explanation of the mixed layer methane maximum, but a number of questions remain. The mixed layer particle-to-seawater methane flux measurements cover coastal and open ocean conditions, but there are few measurements and seasonal coverage is missing. Isotopically heavy (−42‰ to −45‰) methane has been observed in the subtropical North Pacific and the Sargasso Sea.[122] This could result from isotope fractionation accompanying substantial oxidation. However, methane oxidation rates have not been measured in the ocean mixed layer.

The paradoxical mixed layer methane maximum, resulting from methanogenesis in microenvironments separated by only a hundred microns from impossible thermodynamic and kinetic conditions, contributes to the feature that makes the ocean a small net methane source to the atmosphere because of its proximity to the atmosphere. Paraphrasing Nelson Marshall, Sieburth[123] points out that the slight accumulation of methane in the pycnocline could just be the ashes of a very large fire. For an oxygenated ocean, the "fire" or metabolic process has probably never been larger than present, but the mixed layer methane maximum is a good illustration of how a process occurring at very low rates over vast ocean areas can become an important global biogeochemical budget term.

6. External Water Column Methane Sources

6.1. Production Processes

6.1.1. Diagenesis of Organic Carbon

An estimated 50×10^{15} gC year^{-1} is fixed photosynthetically by phytoplankton in the ocean euphotic zone. The picophytoplankton fraction of this production is degraded by viral lysis and protozoal grazing, while the production by larger phytoplankton is converted into consolidated fecal pellets by mezozooplankton. Globally, an estimated 20% of the primary production sinks from the surface ocean in the form of fecal pellets (ref 20, Table 6.5.1).[135−139] This particulate export flux is highly variable and depends on primary productivity drivers, namely, nutrient supply, water depth and temperature, as well as ecosystem structure.[20] Below 100 m the flux of particulate carbon decreases exponentially so that less than 1% passes a depth of 4000 m.[137] Berner[138] and Hedges and Keil[137] estimate a burial rate of organic carbon in marine sediments of $0.13-0.16 \times 10^{15}$ gC year^{-1}, less than 0.5% of global productivity. About 50% of this organic carbon is deposited on high productivity shelves and slopes. Henrichs and Reeburgh[139] summarized available organic carbon flux data in terms of burial efficiency, the ratio of the burial rate of organic carbon below the zone of active diagenesis to the input rate of organic carbon to the sediment surface, and found that burial efficiency is highest in high sedimentation rate sediments. Methanogenesis amounts to about 0.1% of ocean primary productivity and is most prevalent in high sedimentation rate sediments.

This buried complex organic matter is degraded from complex polymers, to monomers, and finally to acetate and other volatile fatty acids, which serve as the primary substrates for methanogenesis. Emerson and Hedges[140] view our understanding of diagenesis as resting on two pillars: one based on energy yield and thermodynamics, and the second based on kinetics and reaction rates. The degradation of organic matter is governed by a sequence of reactions of electron acceptors that are ordered by free energy yield. The electron acceptors commonly considered important in organic matter degradation include O_2, NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, and organic matter itself. The processes associated with reduction of these electron acceptors are microbially mediated and are referred to as aerobic respiration, denitrification, manganese and iron reduction, sulfate reduction, and, finally, methanogenesis, which occurs by either reduction of carbon dioxide (reaction 2) or fermentation of acetate (reaction 3).

This thermodynamic sequence has been quite successful in explaining the zonation of reactions observed in soils and sediments. Typical half-reactions and reactions using hypothetical organic matter are available in textbooks[141] and other publications.[38,142] While the energy yield determines the sequence of the reactions, the availability (concentration) of the electron acceptors determines the separation between processes as well as the overall system oxidizing capacity. Oxygen and nitrate are present in natural waters in millimolar and micromolar concentrations, and they are rapidly consumed. The oxidizing capacities of Mn(IV) and Fe(III) are difficult to assess. The solubilities of manganese and iron oxides are low in natural waters, so they are probably unimportant, but in sediments and soils they represent a large amount of oxidizing capacity. However, this oxidizing capacity is restricted to the surfaces of particles, and because of rinds and surface coatings, it is probably much smaller than bulk concentrations might suggest. As discussed in section 5.1, the presence of sulfate has a profound influence on the oxidizing capacity of marine sediments as well as methanogenesis. Reeburgh[38] presented a table showing the oxidation capacity of a hypothetical marine sediment saturated with seawater (Table 2 in ref 38). The table shows that sulfate dominates the oxidizing capacity of marine sediments.

Diagenesis in sediments has also been studied using steady-state advection−diffusion−reaction models. The diagenetic models introduced by Berner[143] provide a means of estimating rate constants from measured distributions, provided sedimentation rates, porosities, and tortuosity-corrected diffusivities are available. Independently measured reaction rates can be compared with models, providing a check on the rate measurements[144] and also permitting estimation of isotope fractionation factors.[65] Most of the work on diagenetic modeling has been done on the upper few meters of sediments, and will require extension to greater depths, where the 100−200 mM methane concentrations required for hydrate formation occur.

6.1.2. Hydrothermal Systems and the Serpentinization Reaction

Micromolar concentrations of hydrogen and methane were observed in grab samples of East Pacific Rise hydrothermal fluids.[145] On the basis of the ratio of basalt-derived methane

to helium and the ^{3}He flux, the hydrothermal methane flux from the worldwide ridge system was initially estimated to be 1.6×10^8 m^3 year^{-1} (7.4×10^8 mol year^{-1}). This methane flux was sufficient to replace deep-sea methane in ~30 years, and it implied rapid bacterial oxidation of methane. Further study in the Mariana back-arc spreading center,[146] as well as along the mid-Atlantic ridge,[116] found methane peaks without a corresponding enrichment in ^{3}He, suggesting the methane was supplied by chemical reactions, rather than extraction of gases occluded in basalt. These methane peaks occupied the same depth interval and were presumed to be plumes resulting from introduction of methane by hydrothermal systems.[147] Seawater-induced serpentinization of iron and manganese minerals in ultramafic rocks was proposed as a possible source of this methane.[116] Oxidation of Fe(II) in olivine to Fe(III) in magnetite produces hydrogen, which reacts with CO_2 in the presence of an iron or iron oxide catalyst[116,148] at 300 °C and 500 bar, to abiotically form methane by the Fischer−Tropsch reaction:

$$\underset{\text{(olivine)}}{6[(Mg_{1.5}Fe_{0.5})SiO_4]} + 7H_2O \rightarrow \underset{\text{(serpentine)}}{3[Mg_3Si_2O_5(OH)_4]} + \underset{\text{(magnetite)}}{Fe_3O_4} + H_2 \quad (4)$$

and

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (5)$$

A spectacular example of methane production by serpentinization is provided by the recently discovered Lost City hydrothermal vent system, located in the North Atlantic off the mid-Atlantic ridge system axis.[149,150] This hydrothermal vent field is unusual because it is located on 1.5 Myr crust nearly 15 km from the spreading axis. The fluids are warm (40 to 75 °C), alkaline (pH 9.0−9.8), have elevated hydrogen (0.25−0.4 mM) and methane (0.18−0.28 mM) concentrations, and are emitted to the surrounding waters by massive white carbonate-brucite structures up to 60 m high. The warm fluids could result from exothermic serpentinization reactions.[149] This system was revisited for detailed biological study in 2003, and preliminary analyses show abundant methanogenic as well as methanotrophic populations inside the vents.[151,152] Vent fluid methane isotopic composition ranges from −8.8‰ to −13.6‰, possibly reflecting abiotic production from dissolved inorganic carbon with δ^{13}C values from −8‰ to −2‰. Lost City hydrothermal vent methane contains no radiocarbon.[153]

Unfortunately, no fluid fluxes are available, so the amount of methane supplied by these structures cannot be estimated at this time. Keir et al.[154] observed water column methane anomalies in the rift valley of the Mid-Atlantic Ridge with δ^{13}C values from −15‰ to −10‰. Model calculations indicate that 10^9 mol of CH_4 year^{-1} are released from the Mid-Atlantic Ridge to the open ocean.

6.1.3. Methane Clathrate Hydrate Decomposition

Methane clathrate hydrates are solid nonstoichiometric compounds of methane and water that form under specific *P*/*T* conditions and methane concentrations. Hydrates have been identified in reflection seismic studies as a bottom simulating reflector (BSR), which is thought to coincide with the base of the region where hydrate is thermodynamically stable. Hydrates occur along continental margins at depths

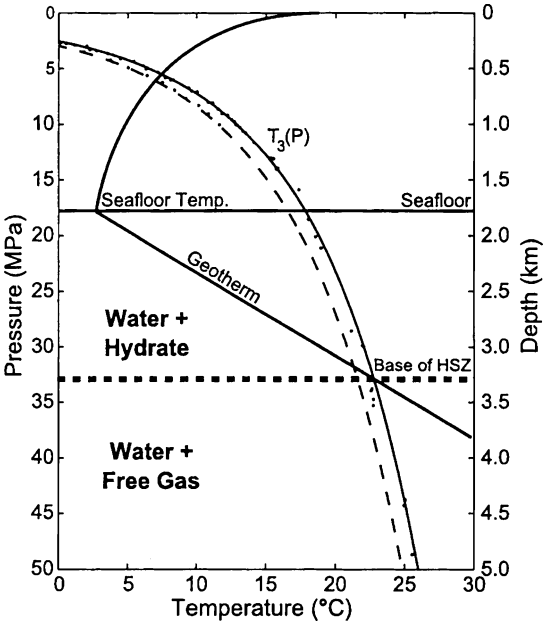

Figure 7. Schematic drawing of the temperature for hydrate stability, T_3(P), through the ocean and sediments. Experimental data fits for T_3(P) are shown for pure water (dashed line) and seawater (solid line). The base of the hydrate stability zone (HSZ) is defined by the intersection of the geotherm and T_3(P). Reprinted from ref 157, Copyright 2004, with permission from Elsevier.

of 600−3000 m and represent an enormous methane reservoir. A "consensus value" of 10 000 Gt C reported in 1991[155] was revised downward to 500−2500 Gt,[156] and a recent model-derived inventory reports values of 3000 Gt in clathrate and 2000 Gt in methane bubbles.[157] For perspective, 10 000 Gt of C is about twice the amount of all fossil fuels on Earth and 3000 times the amount of methane in the atmosphere. Hydrates have attracted attention as a possible future energy source, as a submarine geological hazard, and as a factor in climate change. Several reviews have covered hydrate structure and stability fields, occurrence in nature, and possible future changes.[158−163] Our concerns here are how much methane they contribute to the present ocean water column (the dissociation/dissolution rate) as well as insights into the time scales of formation and decomposition.

Figure 7 is a schematic phase diagram, which shows the temperature for clathrate stability, T_3(P), for pure water and seawater.[157] The presence of salt decreases the T_3(P) by approximately 1.5 °C.[164] Dickens[165] emphasized that since clathrates occur in the hydrate stability zone (HSZ), they must be a dynamic reservoir, forming at the bottom of the HSZ and decomposing at the top.

Davie and Buffett[166] point out that the persistence of hydrates requires a continual supply of methane and that hydrates are absent near the sea floor because methane oxidation makes it impossible to sustain the high methane concentrations (100−200 mM) needed for hydrate stability.

What is the origin of the methane trapped in hydrates? Composition and stable isotope measurements on hydrate methane indicate that it has a biogenic origin.[167] The gases are usually >99% methane, with δ^{13}C values ranging from −56‰ to −73‰. Hydrates from the Gulf of Mexico and the Caspian Sea are believed to contain a mixture of biogenic and thermal methane; they have a smaller proportion (21−97%) of methane, contain C_2−C_4 hydrocarbons, and have heavier δ^{13}C values (−29‰ to −57‰).[167] Stable isotope measurements (δ^{13}C and δ^2H) on Hydrate Ridge hydrates

indicated the methane is formed by CO_2 reduction, and the absence of ^{14}C indicated that there are no contributions of recent carbon to the hydrate carbon pool.[168] The absence of radiocarbon cannot be interpreted as a hydrate age but as an indication that the methane trapped in the hydrate is fossil.

Stable carbon isotope records in ODP (Ocean Drilling Program) cores show an excursion in the Late Paleocene Thermal Maximum (50 million years ago) that suggests release of a large quantity of isotopically light carbon.[169] Methane was implicated because of its characteristic light isotopic signature. Isotopically light benthic and planktonic foraminifera have been located in an ODP core from the Santa Barbara Basin. A connection between the termination of the last glaciation and these isotopically light foraminifera has led to the "Clathrate Gun Hypothesis", which holds that the isotopically light foraminifera could have resulted from a release of methane large enough to have terminated the last glaciation.[170]

The Clathrate Gun Hypothesis has stimulated a debate and research aimed at testing the hypothesis. Variations in the isotopic composition of the biomarker diplopterol, a hopanoid synthesized by aerobic methanotrophs,[171] suggest large releases of methane on a regional scale. Several recent studies challenge the hypothesis, namely, the finding that warming and methane increases recorded in polar ice cores *preceded* the events recorded in the Santa Barbara Basin foraminifera, so a hydrate release could not have initiated the end of the last glacial period.[172] A report that organic carbon in sediments adjacent to the foraminifera shows no isotope excursion[173] raises further questions, as does a recent report that the δ^2H content of ice core methane from the appropriate time interval is more similar to that of wetland methane than to that of marine methane.[174]

The methane contribution from methane clathrate hydrate dissolution/decomposition is an important unknown in the global methane budget. We know that hydrates are a dynamic reservoir, and the basal rate of decomposition is an important unknown. Direct measurements of the rate of hydrate dissolution are a challenge but were made in a novel experiment that involved *in situ* observations of the decomposition of cylindrical test specimens of laboratory-synthesized methane and CO_2 hydrate on the sea floor.[175] These measurements were conducted at P/T conditions that lie within the hydrate stability zone, but they were performed in a variable flow field under undersaturated conditions. Since natural hydrates are located within a sediment matrix where diffusion dominates and are presumably surrounded by CH_4-saturated fluids, the reported decomposition rate of 0.37 ± 0.03 mmol of CH_4 m^{-2} s^{-1} ($11670 \pm$ mol of CH_4 m^{-2} $year^{-1}$) probably represents an upper limit. This measurement can be compared with a recent estimate of basin-wide methane inputs from seeps to the Black Sea.[176] Assuming that all Black Sea seep fluxes result from decomposing hydrates (which may overestimate the hydrate contribution), the estimated hydrate decomposition rate is $0.53-0.84$ mol of CH_4 m^{-2} $year^{-1}$, or 10^5-fold smaller. Experimental observations of hydrate decomposition rates under near-natural conditions, as well as realistic models, are needed to resolve this question.

A series of models that reproduce data from ODP cores have been developed over the past decade and have led to major advances in our understanding of hydrates. These models provide important insights into the formation of hydrates,[177−180] the methane source[166,181,182] and methane concentration constraints,[183] ocean methane inventories,[157] and the sensitivity of these inventories to oceanographic conditions and climate forcing.[157,184] The methane inventory is very sensitive to temperature changes; a 1.5 °C temperature change results in a 2-fold methane inventory change, while a 3 °C increase results in an 85% decrease.[157,184] Modest deep ocean oxygen changes of 40 μM result in factor of 2 changes in the methane inventory, and a 50% increase in primary production also doubles the inventory. Changes in sea level have a small effect. A 100 m drop in sea level reduces the thickness of the hydrate stability zone by less than 10 m and results in a 3% decrease in the clathrate inventory.[184]

At Hydrate Ridge, in the Gulf of Mexico, and on the Angola slope, hydrates occur a few centimeters below the sea floor. Hydrate outcrops at the sea floor[185,186] have been reported, and evidence of extensive methane oxidation is present in Hydrate Ridge sediments and surrounding waters,[187] but outside of the placeholder term, there are no estimates of hydrate contributions.

6.2. Transport Processes: Scope and Scale

6.2.1. Coastal Contributions

There are only a few studies of coastal methane contributions to the ocean, so the processes transporting methane to the ocean water column are not well quantified. Bange et al.[37] summarized recent ocean studies and concluded that coastal sources contribute about 75% of global oceanic methane emissions to the atmosphere, but they proposed no changes to the global budget since the new estimate lay within the range of earlier estimates.[1] A number of methane saturation measurements in rivers have been reported, covering large rivers like the Amazon[188] and Orinoco,[189] as well as rivers with pristine drainages,[190] and those with agricultural[94,141] and urban drainages.[95,192−194] Methane oxidation rates were measured in several of these studies,[95,191,194] but oxidation was found to be a minor sink compared with diffusive flux across the river/atmosphere interface.

Methane distributions on continental shelves frequently have two or more maxima: one associated with the bottom of the euphoic zone,[92] probably associated with a zooplankton fecal pellet source, and the other, well below the euphotic zone and separated from the sediments,[73,93] suggesting an advective source from continental shelf sediments. Methane oxidation rate measurements in these midwater methane maxima[73,193,196] indicate turnover times of months, rather than years, as found for most of the ocean water column.

The Eastern Tropical North Pacific (ETNP), an area located off the Pacific coast of Mexico, is fueled by coastal upwelling and is known for its oxygen minimum zone, which extends almost to the Hawaiian Islands.[83,197] It also contains the largest dissolved methane reservoir in the ocean. Stable isotope measurements suggest that methane in the upper part of the 600 m thick high-methane zone of the ETNP is associated with locally produced sinking particulate material. The deeper part of the methane pool was suggested,[197] and recently confirmed,[198] to have a coastal source. The methane source represents depth intervals of the open-margin sediments where the anoxic waters intersect the bottom. No methane oxidation rate measurements have been conducted here. Coastal upwelling has also been associated with high water column methane off Walvis Bay[96] and the Oregon coast.[199,200] Hovland and Judd[201] have documented crater-

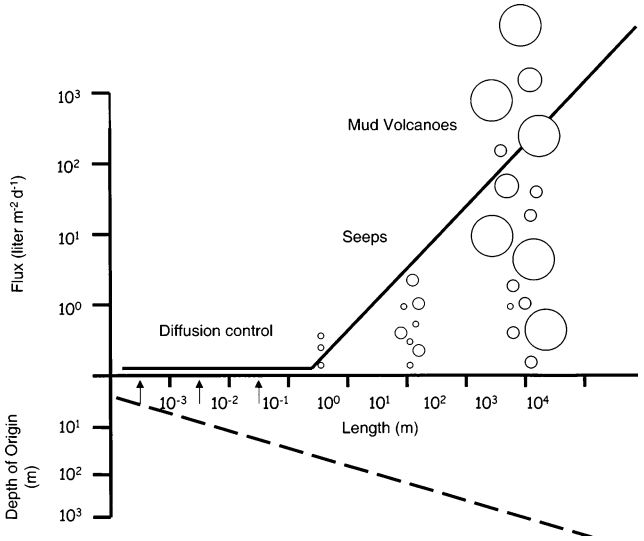

Figure 8. Schematic diagram showing the length, depth, and flux scales of methane additions from a range of sources to the ocean water column.

like features on continental shelves throughout the world ocean, but measurements of methane release are few.

6.2.2. Seeps and Vents

Figure 8 is a schematic diagram showing the range of methane flux to the ocean water column from a variety of sources, the lateral size-scale of the sources, and an indication of the depth of origin of the methane.

The left-hand side of the diagram illustrates diffusion-controlled coastal sediments, where methane formed below the sulfate/methane transition is subjected to anaerobic methane oxidation, so that only a small amount escapes to the water column. The middle of the diagram illustrates seeps, where methane from scarps, fractures, and decomposing hydrates is introduced in fluids and as gas streams. This methane has a deeper origin, and fluxes are high enough to overwhelm sediment oxidation processes. Methane reaches the ocean surface in only a few examples. The right-hand side of the diagram illustrates methane contributions by large seeps and mud volcanoes. Mud volcanoes are large, rimmed features with kilometer-scale diameters that are fed by deep gas accumulations and hydrates. Emission magnitude, and especially variability, increases from left to right, with diffusion and small seeps being relatively constant and with larger seeps and mud volcanoes showing highly episodic behavior. Direct measurements on all but the smallest methane-emitting features are absent, so the diagram is based on only a few measurements. As mentioned earlier (section 1.1: Global Methane Budget), the natural radiocarbon content of atmospheric methane was used to partition the atmospheric methane budget between recent biogenic and fossil sources. Finding large enough fossil methane sources has been a problem with the atmospheric budget, so most studies of vents and seeps emphasize additions to the atmosphere rather than the ocean water column.

Perhaps the best estimates of seep emission are from the Santa Barbara Channel and the Black Sea, where seeps have received more attention than other locations. Hornafius et al.[202] used acoustic data to estimate a mean methane emission rate for the Coal Oil Point seep field of 28 g of CH_4 m^{-2} $year^{-1}$. The amount of methane released within the Santa Barbara Basin is believed to rank within the top 1−0.1% of natural seeps. Dimitrov[203] estimated methane flux from the Black Sea shelf by estimating seep numbers and binning them into flux classes with emission rates ranging from 0.4 to 3.5 L min^{-1}. The amount of methane that dissolved during ascent to the water surface was estimated and applied as a correction to the atmospheric flux. Dimitrov concluded that between 0.03 and 0.15 Tg of methane enters the atmosphere from this area. Measurements of natural radiocarbon in semienclosed anoxic basins have been used to make basin-wide estimates of seep contributions to the Black Sea and the Cariaco Basin.[176,204] The bulk of this seep-derived methane is oxidized by microbes in the water column so that only a small amount escapes to the atmosphere.

6.2.3. Mud Volcanoes

Dimitrov[205] provides a useful description of the structure of inland and submarine mud volcanoes. Mud volcanoes are aligned around subduction zones and orogenic belts with thick, rapidly deposited clays and sediment overpressuring due to hydrocarbon formation. Gas hydrates are often associated with deep-water mud volcanoes.[206] Geographic inventories of mud volcano occurrences are presented by Dimitrov[205] and Milkov.[206] Milkov pointed out that most mud volcanoes are submarine and estimated that there are 10^3 to 10^5 worldwide.

Dimitrov[205] estimates that 10.3−12.6 Tg of CH_4 $year^{-1}$ enter the atmosphere by quiescent and eruptive activity. Most of the methane emitted from submarine mud volcanoes deeper than 75 m, particularly during quiescent periods, dissolves before it reaches the atmosphere. Milkov et al.[207] estimate that 5000 submarine mud volcanoes release 13 Tg $year^{-1}$ during quiescent periods and 14 Tg $year^{-1}$ during eruptions, and that most of this remains in the ocean. Etiope and Milkov[208,209] estimate the atmospheric flux from mud volcanoes as 6−9 Tg CH_4 $year^{-1}$. Eruptive activity is infrequent, but spectacular. Dimitrov[205] describes reports of 100−500 m tall flaming pillars that burn for several days. The most recent summary of methane released from geological sources is presented by Kvenvolden and Rogers,[210] who estimate the atmospheric contribution of seeps, mud volcanoes, and miscellaneous sources at 45 Tg of CH_4 $year^{-1}$.

The Håkon Mosby mud volcano, located in the Norwegian Sea at a depth of ∼1200 m, was recently studied by an international interdisciplinary team using a remotely operated vehicle and instruments measuring *in situ* microprofiles[211] to study habitats and their relationship to fluid flow and composition.[212] Previous work[213] reported concentric zonation of sea floor morphology as well as geochemical and biological processes related to ejection of sediment, water, and methane from the mud volcano crater. Total methane release was estimated to be $2.0-6.4 \times 10^8$ g of CH_4 $year^{-1}$.[214] Some 40% of the total methane was consumed by aerobic (1−3%) and anaerobic (37%) processes. The methane that escapes the Håkon Mosby mud volcano rises to form a plume whose carbon isotope signature is identical to the source methane, suggesting no oxidation.[215] The recent expedition found that the flow in the center of the crater was high and depleted in oxidants, so that aerobic methane oxidation in the surface centimeter of the sediments was the major process.[212] Lower flow resulted in *Beggiatoa* mats associated with a previously undescribed clade of archaea, ANME-3. Dense colonies of siboglinid tubeworms were associated with the lowest flows on the hummocky perimeter.

Methane-utilizing communities are discussed further in section 8.3.

7. Microbially-Mediated Oxidation of Ocean Methane

7.1. Aerobic Oxidation of Methane

There have been few measurements of methane oxidation rates in oxic ocean waters. The first estimates were made by Scranton and Brewer,[78] who related apparent methane utilization, the difference between actual and air-saturated values, and water mass ages determined with $^3H/^3He$ and ^{14}C to determine methane oxidation rates in open ocean waters. They found that methane oxidation is rapid (0.15 nM year^{-1}) for the first decade and decreases to rates of 10^{-4} nM year^{-1} for waters older than about 150 years. Ward and co-workers[216−219] used ^{14}C-CH_4 as tracer and determined methane oxidation rates in Cariaco Basin and Saanich Inlet and methane maxima in the Southern California bight. Addition of ^{14}C-CH_4 tracer increases the ambient CH_4 pool size, so it was necessary to perform rate measurements at several levels of tracer addition and to correct back to *in situ* concentrations.[216,218] The highest fractional turnover rates for aerobic methane oxidation (0.15 day^{-1}) observed to date were made using ^{14}C-CH_4 tracer in deep-sea plumes generated by a vent field on the Juan de Fuca Ridge.[220] Valentine et al.[196] used ^3H-CH_4, which has a much higher specific activity than ^{14}C-CH_4, as tracer and determined methane oxidation rates at a number of stations in the Eel River basin. The specific activity of ^3H-CH_4 has the potential to be over 500-fold higher than that of ^{14}C-CH_4. The product ^3H_2O is easily purified at sea and required only stripping to remove the unreacted ^3H-CH_4 tracer. Rehder et al.[221] combined concentration measurements of methane and CFC-11 with the input function of CFC-11 to determine a time scale for methane oxidation in the North Atlantic of about 50 years. CFC-11 is not oxidized in oxic seawater and serves as a conservative tracer.

Open ocean water column methane oxidation rates are generally viewed as being quite low, but fractional turnover rates of days[220] and months[196,219] have been observed in maxima with methane concentrations of ∼20 nM. De Angelis et al.[222] measured the effect of hydrostatic pressure on microbial methane oxidizing activity, and they observed rate increases of 21−62% at elevated (∼200 atm) pressure. There are very few measurements of open ocean methane oxidation rates using tracers, so our understanding of the kinetics of microbial methane oxidation in the oxic ocean, particularly in subsurface maxima and plumes, is poor.

7.2. Anaerobic Oxidation of Methane

Anaerobic methane oxidation (AMO) is an old, controversial subject that has experienced a recent renaissance in activity (and a name change to anaerobic oxidation of methane (AOM) as well)[223] following application of new observation and sampling technology (remotely operated vehicles (ROVs), submersibles) and an array of new molecular and molecular genetic tools. Because the subject was so controversial, and because it occurred below the sediment surface where it was "invisible", the early measurements of methane concentration, methane oxidation rate, sulfate reduction rate, and stable isotope distributions were replicated extensively in a wide variety of environments. Table 2 updates previous summaries[144,224] to include studies on anaerobic oxidation of methane to date. A number of independent approaches involving diagenetic modeling of measured profiles, radiotracer measurements of reaction rates, thermodynamic calculations, stable isotope measurements, and laboratory inhibition and incubation experiments combine to make a compelling geochemical case for anaerobic oxidation of methane. Anaerobic oxidation of methane was initially regarded as a curiosity restricted to diffusion-controlled anoxic sediments, but studies over the past 5 years demonstrate clearly that AOM is a major geochemical process that functions as an important sink in oceanic methane geochemistry. The earliest points of the AOM controversy, isolation of the responsible organism and demonstration of the biochemical pathway, have not been answered.

7.2.1. Early Observations and the Methane/Sulfate Connection

Thermodynamic calculations on systems with coexisting sulfate and methane showed that free-energy changes were small, but suggested that anaerobic oxidation of methane might be possible at elevated temperatures.[225] Methane oxidation rate measurements on waters from the Carrizo (TX) formation using sulfate-reducing bacteria and ^{14}C-CH_4 tracer showed that methane oxidation occurred at "low rates",[226] and studies in anoxic ocean sediments showed that methane could not serve as the sole substrate for sulfate reducers.[227]

Three papers[85,102,103] are frequently cited as early reports of anaerobic methane oxidation. Research prior to these papers is usually not mentioned, but it provided a necessary basis for these papers. First, measurements of sediment methane distributions consistently showed concave-up low-methane surface zones[49,50] and raised the question, "What processes control the methane distribution?"[51] On the basis of measurements in Chesapeake Bay, Reeburgh[51] suggested that the concave-up low-methane surface zone might be caused by addition of O_2 by the irrigating activities of benthic fauna. Differences in methane distributions in marine and freshwater sediments[98] as well as time series incubations in sealed canning jars (Mason jar experiments)[228] established relationships between methane concentrations, sulfate concentrations, sulfate reduction, methanogenesis, and possibly methane oxidation.

The Barnes and Goldberg[102] study was conducted in the Santa Barbara Basin, an intermittently anoxic California Borderland basin, and involved a diagenetic model of sediment methane only. The Martens and Berner[103] study focused on near-shore sediments of Long Island Sound and involved field measurements as well as laboratory incubations. Martens and Berner advanced four alternative hypotheses to explain their time series incubations and depth distributions and to guide future work:[228] (a) methane is produced throughout the sediment column but is consumed by sulfate-reducing bacteria; (b) methane is produced only in the absence of dissolved sulfate, and the coexistence of sulfate and methane is due to interdiffusion; (c) methane is produced only in the absence of sulfate but, as in hypothesis a, is consumed by sulfate-reducing bacteria; and (d) methane is produced to a limited extent in the presence of sulfate-reducing bacteria but is not utilized by them. On the basis of their measurements, Martens and Berner[228] favored hypotheses b and d.

The Reeburgh study[85] was conducted in the Cariaco Basin and involved methane concentration measurements in the

Table 2. Summary of Anaerobic Oxidation of Methane Studies

location	study date(s)	water column	sediment	sulfate/methane transition depth	observations reported, ref
			Atlantic Ocean, W		
Chesapeake Bay (MD)	1966, 1967	−	+	30 cm	CH_4, Ar, N_2 profiles[51]
Long Island Sound (CT)	1974, 1977	−	+	20−60 cm	CH_4, SO_4^{2-} profiles, jar experiments[52,103] diagenetic model[252]
Cape Lookout Bight (NC)	1976−	−	+	<10 cm (S)	CH_4, SO_4^{2-} profiles, SRR[a] [104,253]
				25 cm (W)	CH_4 fluxes [254]
					org C budget, diagenetic model[255]
White Oak Estuary (NC)	1975	−	+	20 cm	CH_4, SO_4^{2-} profiles[230]
Blake Ridge ODP Leg 164	1995	−	+	21.2 m	CH_4, SO_4^{2-} profiles, $\delta^{13}CH_4$, SRR, MOR[b] [256]
Gulf of Mexico	1977	−	+		CH_4, SO_4^{2-} profiles, diagenetic model[257]
	1979	+	+		CH_4, $\delta^{13}CH_4$ (Orca Basin)[258]
	2001−2004	−	+		CH_4, SO_4^{2-} profiles, SRR, MOR adjacent hydrate mounds [259]
		-	+		CH_4, SO_4^{2-} profiles, SRR, MOR, biomarkers, AMNE-1, ANME-2[260]
Cariaco Basin (VE)	1976	+	+	60 cm	CH_4 profiles, advection-diffusion model[85]
	1986	+	−		anaerobic CH_4 oxidation rates (^{14}C-CH_4 tracer)[216]
	1988	+	−		CH_4 profiles, time-dependent box model[248]
	2005	+	+		CH_4 stable isotope, natural ^{14}C-CH_4 profiles, time-dep box model[204]
Amazon Shelf (BR)	1995	−	+	500−800 cm	CH_4, SO_4^{2-}, ΣCO_2 profiles, $\delta^{13}CO_2$ [261,262]
W. Argentine Basin	1999−2000	−	+	4−5 m	CH_4, SO_4^{2-}, H_2S profiles, SRR[263]
			Atlantic Ocean, E		
Håkon Mosby Mud Volcano	1990−2003	+	−		CH_4 plumes[213]
		+	+		SRR, MOR[264]
			+	0−3 cm	ROV observations, microprofiles, fluxes, FISH (ANME-3)[211,212]
Framvaren (NO)	1981	−	+		incubations of anoxic water[265]
Kysing Fjord (DK)	1979−80	−	+	~18 cm	CH_4, SO_4^{2-}, SRR, MOR profiles[266]
Kattegat/Skagerrak (DK)	1981	−	+	90−140 cm	CH_4, SO_4^{2-}, SRR, MOR profiles[241]
Ekernförde Bay (FRG)	1993, 1994	−	+	150 cm	CH_4, SO_4^{2-}, profiles[267]
		−	+	40 cm	CH_4, SO_4^{2-}, ΣCO_2, δ^2H-CH_4, δ^{13}C-CH_4. Isotope fractionation αC, αH[247]
Black Sea	1998	+	+	10 cm	CH_4, MOR (^{14}C-CH_4, ^{3}H-CH_4), δ^2H-CH_4, δ^{13}C-CH_4,[83] SRR,[86,112] biomarkers[218,219]
	1997	−	+	160−260 cm	CH_4, SO_4^{2-}, SRR[269]
	2001	−	+		submersible collections from vents, microbial structures. AOM, SR potential, lipid biomarkers, δ^{13}C-CH_4, FISH[270]
	2004	−	+		CH_4, δ^{13}C-CH_4, SO_4^{2-}, SRR, FISH (ANME-1) adj. microbial mat.[271]
	2005	+	+		biomarker,[272,273] authigenic carbonate studies[2244]
	2001	+	−		CH_4, δ^2H-CH_4, δ^{13}C-CH_4, natural ^{14}C-CH_4[176]
	2003	+	−		CH_4, MOR (^{3}H-CH_4), $\delta^{13}CH_4$, ^{4}He, Ne, FISH, bacterial abundance[275,276]
Namibian Coast	1996	−	+	3−10 m	CH_4, SO_4^{2-}, H_2S, alk, nutrient profiles[277]
			+	3−6 m	CH_4, SO_4^{2-}, H_2S, SRR[278]
			Pacific Ocean		
Skan Bay (AK)	1978−2004	+	−	30 cm	CH_4, SRR, MOR[104] ^{13}C isotope budget (CH_4, DIC, DOC, PIC, POC),[65,100,144] acetate, acetate turnover,[279] MoO_4^{2-}, BES inhibition expts,[237] ^{210}Pb, ^{137}Cs sed rates,[280] isotope fractionation factors, αC, αH,[65] natural ^{14}C-CH_4 [281]
Saanich Inlet (BC)	1977−	+	+	20 cm	SO_4^{2-}, H_2S, Fe, alkalinity, major cations[231]
	1977−1978	−	+	15 cm	SO_4^{2-}, SRR,[241] CH_4, MOR[240]
		−	+		coupled SO_4^{2-} red./CH_4 oxid. model[232]
	1986	+	−		CH_4, MOR (^{14}C-CH_4 tracer) [217]
Hydrate Ridge (OR)	2002	+	+	3 cm	SO_4^{2-}, SRR, ^{13}C-depleted biomarkers, FISH,[282,283] AOM, [284,285] AOM/SRR coupling, *in vitro* growth[286]
Eel River Basin (CA)		−	+		^{13}C-depleted biomarkers, anaerobic CH_4 oxidizing activity, 16S rRNA[287]
		−	+		CH_4, SO_4^{2-}, FISH[288,289]
		+	−		water column (aerobic) CH_4 oxidation rates (^{3}H-CH_4 tracer) [196]
Santa Barbara Basin (CA)	1973, 1974	−	+	200−250 cm	CH_4, diagenetic model[102]
	1977	−	+		CH_4, CH_4 production,[290] CH_4 production and oxidation [291]
Guaymas Basin (MEX)	1998	−	+		^{13}C-depleted biomarkers, ANME-1, ANME-2[292]
Chilean Margin	2001	+	−	210−350	CH_4, SO_4^{2-}, SRR, MOR, δ^{13}C of TIC, DIC [293]

Table 2. (Continued)

location	study date(s)	water column	sediment	sulfate/methane transition depth	observations reported, ref
			Salt Lakes		
Big Soda Lake (NV)	1982−1984	+	−		CH_4, δ^{13}C-CH_4, CH_4 production, MOR profiles,[294] SO_4^{2-}, SRR profiles [295]
Mono Lake (CA)	1986	+	+	50 cm	CH_4, δ^2H-CH_4, δ^{13}C-CH_4, Δ^{14}C-CH_4, CH_4 production, MOR, SO_4^{2-}, SRR[296]
			Deep Biosphere		
ODP biogeochemistry legs					
DSDP leg 1 through ODP leg 182		−	+		ref 101
ODP biogeochemistry leg Peru leg 201		−	+		ref 297

[a] SRR = sulfate reduction rate. [b] MOR = methane oxidation rate. [c] FISH = fluorescent *in situ* hybridization.

sediments as well as the overlying permanently anoxic water column.[85] The methane distribution in the sediments showed the familiar concave-up methane distribution in the low-methane surface zone. Since the overlying waters were anoxic and benthic fauna are absent, bioturbation and addition of oxygen could be eliminated as possible causes of the low-methane surface zone. Further, fitting the water column methane distribution with a vertical advection−diffusion model[113,229] showed that methane in the anoxic water column was nonconservative (not governed by physical mixing alone) and that it was clearly being consumed in an anoxic environment. These results supported hypothesis c[228] and suggested that a general process might be responsible for the methane distributions observed in all marine sediments.

Diagenetic models[143] were applied to methane and sulfate sediment distributions from a variety of environments (Long Island Sound, Skan Bay, Saanich Inlet, Skan Bay).[38,144,230−232] The diagenetic models provided a useful framework for both interpreting the depth distributions and pointing the way to future measurements. For example, reaction rates and depth distributions predicted by diagenetic models could be confirmed with measurements, and this stimulated direct measurements of methane oxidation and sulfate reduction rates. However, the emphasis on diagenetic models, which can only be applied in diffusion-controlled sediments, led to the incorrect view that anaerobic oxidation of methane was restricted to quiescent anoxic muds.

7.2.2. Rate Measurements

In order to compare measured rates with modeled rates, the measured rates must be environmentally realistic. This requires working with systems that are minimally disturbed, ensuring that true tracer experiments (pool size changes by <1%) are performed, and conducting incubations under realistic temperatures. Adding tracer in quantities large enough to stimulate the reactions being studied results in measurements of "potential", which cannot be compared with models.

Jørgensen[233−235] described measurements of the rate of sulfate reduction in anoxic sediments using $^{35}SO_4^{2-}$ as tracer. The radiochemical $^{35}SO_4^{2-}$ can be obtained carrier-free, so specific activity modifications are of no concern over the range of sulfate concentrations encountered in marine sediments. Sulfate reduction was a well-known process, and the ability to measure rates of sulfate reduction was welcomed as a major advance that stimulated studies of rates of microbially-mediated reactions in sediments. Tracer was injected at intervals in intact sediment cores, and following incubation, ΣS^{2-} and the product $^{35}S^{2-}$ were recovered by extraction in an acidic Cr(II) solution before counting. The most common field tracer measurement in the 1970s was the rate of water column photosynthesis (primary production, $H^{14}CO_3^-$ tracer), and many workers believed that homogenization of the tracer before incubation was required for *all* tracer studies. The Jørgensen papers made an important point, central to sediment studies, that was not widely appreciated at the time: *it is not necessary to homogenize the tracer, provided the system analyzed contains all of the added tracer*. Rate measurements involving ^{14}C-CH_4 would have been impossible if homogenization were required.

Studies using ^{14}C-CH_4 in whole-lake experiments[236] suggested that methane oxidation rates in marine sediment were feasible, so Jørgensen's $^{35}SO_4^{2-}$ sediment techniques were extended to methane in marine sediments by Reeburgh,[105] using ^{14}C-CH_4 as tracer and techniques identical to those of Jørgensen. Reeburgh studied intact sediments with millimolar methane concentrations using segmented plastic core-liners. Each core segment contained a silicone rubber septum that permitted injection of the ^{14}C-CH_4 tracer into the center of the segment. Following incubation, the segmented core was dismantled by inserting metal shims between the segments, and each segment was emptied into a canning jar whose lid was fitted with a gas inlet and outlet and a port for adding degassed water to form a slurry. The slurry was stripped in two stages: First, the sediment slurry was made basic with NaOH and the unreacted ^{14}C-CH_4 tracer was removed, oxidized, and trapped for counting. Following stripping at high pH, the sample was made acidic and the product of methane oxidation, $^{14}CO_2$, was stripped and trapped in a phenethylamine-based scintillation cocktail. It was necessary to remove the H_2S released by acidification with a $CuSO_4$-on-Celite trap prior to trapping the $^{14}CO_2$, as H_2S is a potent quencher in scintillation counting. The depth resolution of these measurements was coarse (3−5 cm), but the rates agreed with diagenetic models and methane oxidation and sulfate reduction rates showed overlapping rate maxima. The depth resolution of the rate measurements was improved by using lateral subcores collected with glass syringes that allowed headspace-free incubation,[237] and a means of removing small amounts of ^{14}CO contamination was described.[238] The original methane oxidation rate measurements in sediments were viewed as reckless by microbiologists, as they involved adding a potential substrate to a complex natural system without controls and without fully understanding the consequences. Methane oxidation rate and sulfate reduction

rate depth distributions were replicated in Saanich Inlet[239,240] and Kategatt/Skagerrak sediments.[241]

Extending methane oxidation rate measurements to water column environments, where methane concentrations are nanomolar, requires attention to the specific activity, which governs the amount of methane added with the tracer. The first ocean water column tracer measurements of methane oxidation were made by Ward et al.,[216] who recognized that measurements at nanomolar methane levels would be affected by addition of a tracer. Ward et al.[216,218] measured rates at several levels of tracer addition and used the linear relationship that resulted to extrapolate back to *in situ* concentrations. Sandbeck and Reeburgh[242] synthesized tritium-labeled methane (^{3}H-CH$_4$), which, because of its much shorter half-life and 500-fold higher specific activity, can be used without affecting the ambient water column methane pool size, and applied it to water column determinations of AOM rate. Parallel determinations of the rate of anaerobic oxidation of methane in the Black Sea water column were performed using ^{14}C-CH$_4$ and ^{3}H-CH$_4$ tracers, and the determinations agreed within a factor of 2.[86] Large-scale methanogenesis in the Black Sea water column can be eliminated on thermodynamic and kinetic grounds,[7,112,243] so these rates are a direct measure of net methane oxidation. The Cariaco Basin and the Black Sea are the only water column environments where measurements of the rate of anaerobic oxidation have been performed, and in both environments, AOM was clearly the major methane sink.

There are several instances of rate measurements that are not environmentally realistic. Griffiths et al.[244] replaced the methane inventory of Bering Sea water column samples with a standard quantity of gas containing ^{14}C-CH$_4$ and termed these measurements "relative methane oxidation rates". The difference between the rates of methanogenesis and methane oxidation was used to estimate net methane consumption in the Black Sea. Assuming the methane is produced by both CO_2 reduction and acetate fermentation, Ivanov et al.[245] estimated the rate of methanogenesis with experiments using $^{14}CO_2$ and ^{14}C-labeled acetate to determine the turnover of these tracers to methane. The rate of methane oxidation was measured using ^{14}C-CH$_4$ as tracer. The difference between methanogenesis and methane oxidation yielded a net methane oxidation rate for the Black Sea similar in magnitude to the basin-wide rate reported by Reeburgh et al.[86] Ivanov et al.[245] did not consider the specific activity and pool size effects discussed above. Regarding the measurements of CO_2 turnover to methane, the tracer is swamped or diluted beyond utility by the large seawater dissolved inorganic carbon (DIC) pool. Regarding measurements of acetate turnover to methane, ambient acetate concentrations are so low that addition of the tracer overwhelmed the acetate pool and likely led to enhanced rates. These measurements are not geochemically realistic, and they are best viewed as measurements of potential methanogenesis and methane oxidation; their agreement with the Reeburgh et al.[86] result can only be fortuitous.

7.2.3. Natural Isotope Studies

Stable carbon isotope measurements of methane and CO_2 in sediments have been reported in a number of marine and salt lake environments.[61,70,71,246] These results were extended by measurement of a stable isotope budget in sediments of Skan Bay.[65,100] This stable isotope budget involved overdetermining the Skan Bay system by measuring δ^{13}C in five carbon pools: (a) methane, (b) dissolved inorganic carbon (DIC), (c) dissolved organic carbon (DOC), (d) particulate inorganic carbon (PIC), and (e) particulate organic carbon (POC). The approach was to use the characteristic light isotopic signature of methane as an internal tracer to observe isotopic "pushes" and "pulls" between pools driven by anaerobic methane oxidation. These measurements were performed on 3-cm thick sediment segments from three subcores collected from a single box core. The core segments were sliced, placed in steel cans under an N_2 atmosphere, sealed, and frozen until analysis. The study involved neither additions nor incubations and considered the isotope distributions as a snapshot of what was occurring naturally in an undisturbed sediment interval. The DIC and methane pools showed the largest isotope changes. Oxidation of isotopically light methane to CO_2 resulted in an equivalent shift of the isotopic composition of the DIC pool, producing a δ^{13}C-CO_2 minimum (see Figure 5) that occurred at the same depth as changes in the sulfate and methane distributions. The remaining methane became isotopically heavier above the methane/sulfate transition, reflecting the fact that methane containing the light isotope was preferentially oxidized. Combined with parallel rate measurements and a diagenetic model, these measurements were used to estimate kinetic isotope fractionation factors, α_C ($=1.0088 \pm 0.0013$) and α_H ($=1.157 \pm 0.023$), associated with anaerobic oxidation of methane.[65] A similar study in Eckernförde Bay[247] yielded fractionation factors that agreed within experimental error. Curiously, these seemingly arcane isotope measurements on canned sediment samples provided the key evidence that convinced microbiologists of the existence of anaerobic oxidation of methane, and the controversy over anaerobic oxidation of methane ended.

Recent measurements of natural isotope distributions in waters and sediments of the Cariaco Basin and the Black Sea have provided unexpected insights into methane geochemistry in these environments. The Cariaco Basin was an early focus in studies of anaerobic methane oxidation,[85,216] and time series measurements of methane documented a methane increase. Finding that the Cariaco Basin water column was not in steady state led to development of a time-dependent box model to describe methane distributions.[248,249] Measurements in the Black Sea consisted of a detailed water column methane concentration profile, water column oxidation rates, and distributions in sediments. A budget based on sinks was produced from this data that included evasion to the atmosphere, water column oxidation, oxidation by abyssal sediments, and outflow at the Bosporus. Anaerobic oxidation of methane in the water column was the largest term by a factor of over 70. Only 15% of the methane source needed to maintain the steady-state Black Sea methane distribution could be identified. Distributions of methane concentration, δ^{13}C-CH$_4$, and methane oxidation rate were uniform in waters below 600 m.[86,250] Reports of extensive seeps, hydrate deposits, and mud volcanoes along the northern margin appeared after 1991 and were suspected as the source of the "missing" 85% of the methane source. The methane emitted from these seeps was expected to be of hydrate or thermogenic origin and was expected to contain little or no radiocarbon, so measurements of natural ^{14}C-CH$_4$ were proposed. Reliable determination of the anticipated low radiocarbon levels required attention to blanks and backgrounds.[77] The variety of seeps suggested multiple origins for methane in the Black Sea, so a second study involving the Cariaco Basin was proposed. Temperatures in the Cariaco

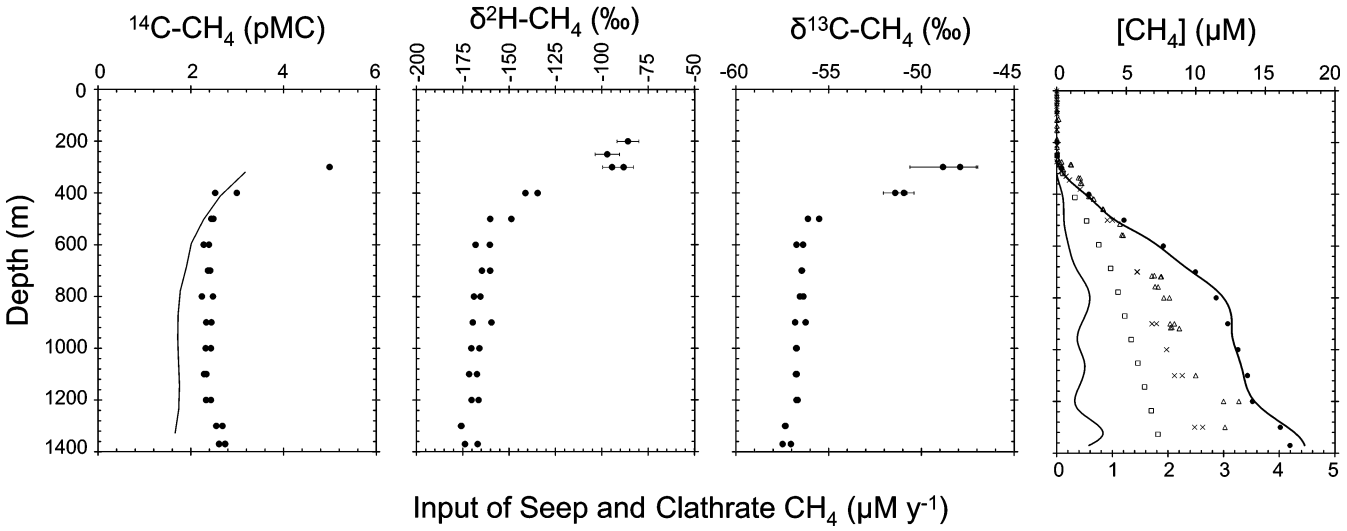

Figure 9. Cariaco Basin water column ^{14}C-CH$_4$, δ^2H-CH$_4$, and δ^{13}C-CH$_4$ versus depth and model-derived depth distribution of seep methane additions: (a) ^{14}C-CH$_4$ (ref 204); (b) δ^2H-CH$_4$ (ref 251); (c) δ^{13}C-CH$_4$ (ref 204); (d) depth distribution of seep methane inputs (ref 181). Adapted from refs 204 and 251 with permission. Copyright 2005, 2006 American Geophysical Union.

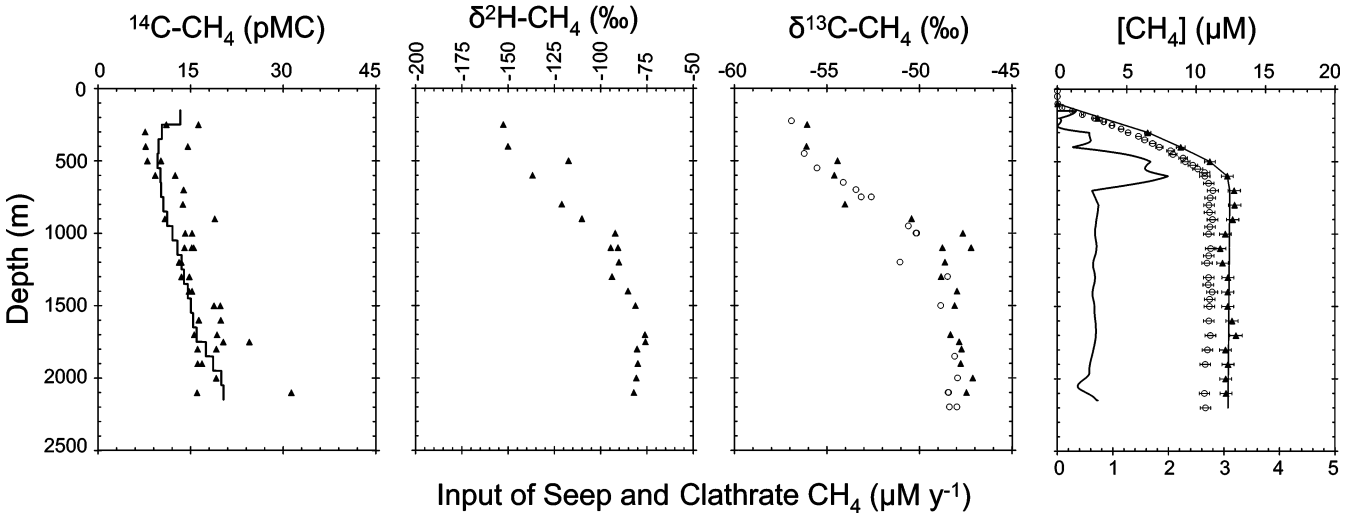

Figure 10. Black Sea water column ^{14}C-CH$_4$, δ^2H-CH$_4$, and δ^{13}C-CH$_4$ versus depth and model-derived depth distribution of seep methane additions: (a) ^{14}C-CH$_4$ (ref 176); (b) δ^2H-CH$_4$ (ref 251); (c) δ^{13}C-CH$_4$ (circles, July 1988; triangles, May 2001; samples, refs 250 and 251); (d) depth distribution of seep methane inputs (ref 176). Adapted from ref 176, Copyright 2005, with permission from Elsevier. Adapted from ref 251 with permission. Copyright 2006 American Geophysical Union.

Basin are too high for hydrate stability, and there were no reports of seeps, so the Cariaco Basin was regarded as a "control" environment with a single (sediment diagenesis) methane source.

Figure 9 shows methane isotope distributions in the Cariaco Basin as well as a panel showing the depth distribution of seep inputs. This same panel shows that the Cariaco Basin water column methane concentration has approximately doubled over the past 30 years. The increase appears to be related to a 1967 earthquake whose epicenter was in the Caribbean Sea. A time-dependent box model indicates that oxidation will increase and that Cariaco Basin water column concentrations will reach steady state by 2065.[204] Cariaco Basin sediments have ^{14}C-CH$_4$ levels that are consistent with diagenesis of particles fixed in the photic zone, so methane in the sediments and mtehane in the water column clearly have different sources.

Figure 10 shows isotope distributions in the Black Sea as well as a panel showing the depth distribution of seep inputs. Two sets of δ^{13}C-CH$_4$ measurements taken 13 years apart and at different locations are indistinguishable, suggesting that the Black Sea is in steady state with respect to methane.[176,251] The methane concentrations, methane oxidation rates, and δ^{13}C-CH$_4$ distributions are uniform below 1000 meters, leading to the suggestion that methane is being added as rapidly as it is being consumed in this depth interval.[250]

Kessler, Reeburgh, and Tyler[251] compared the stable isotope and methane concentration distributions in the Cariaco Basin and the Black Sea. Between-basin differences in the deep parts of the basins are large, 9‰ for δ^{13}C-CH$_4$ and 83‰ for δ^2H-CH$_4$, and the stable isotope distributions are mirror-images of one another. The methane concentration distributions are controlled by the depth distribution of seep inputs. The isotope distributions are controlled by isotope fractionation resulting from anaerobic oxidation of methane under open-system non-steady-state conditions in the Cariaco Basin and open-system steady-state conditions in the Black Sea. Carbon and hydrogen isotope fractionation in the Black Sea water column agrees well with the kinetic isotope fractionation factors determined in Skan Bay[65] and Eckernförde Bay[247] sediments.

7.2.4. Reaction and Mechanism

Early studies of anaerobic oxidation of methane[85,102,103] proposed the following net reaction as governing the process:

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \quad (6)$$

Free-energy calculations using representative environmental concentrations indicate that the free-energy yield is ~25 kJ mol^{-1} of CH_4 oxidized, a value below the commonly accepted biological energy quantum (~20 kJ mol^{-1} $organism^{-1}$).[298] Zehnder and Brock[299,300] suggested that reverse methanogenesis might be responsible for AOM, and they demonstrated that small amounts of ^{14}C-CH_4 appeared under high methane concentrations and extreme reducing conditions in the presence of $^{14}CO_2$ tracer. Net methane oxidation is the rule rather than the exception in natural systems, so these studies were puzzling to field workers. Alperin and Reeburgh[237] performed an inhibition experiment on slurried Skan Bay sediments which involved using 2-bromoethanesulfonic acid (BES), an inhibitor of methanogenesis and methane oxidation by methanogens, molybdate, an inhibitor of sulfate reduction, and fluoroacetate, an inhibitor of acetate utilization. These experiments were conducted on intact and slurried sediments using ^{14}C-CH_4 and $^{35}SO_4^{2-}$ tracers. Methane oxidation was not inhibited by BES, molybdate, or fluoroacetate. The experimental results were consistent with two possibilities: that methane oxidation is mediated either by an unknown methane oxidizer or by a consortium involving an unknown methane oxidizer and a sulfate-reducing bacteria. Reaction rates were much lower in the slurries than in the intact sediments. Hoehler et al.[7] also used inhibitors and extended the idea of a consortium, demonstrating that "reverse methanogenesis" according to the reaction

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (7)$$

was possible when H_2 concentrations were maintained below 0.29 nM. Thus, sulfate-reducers, well-known for their ability to outcompete methanogens for H_2, serve as the means of maintaining H_2 at low concentrations, and anaerobic methane oxidation occurs at the methane/sulfate transition. Above the methane/sulfate transition, methanogens cannot compete for H_2, and below the transition, there is too little sulfate to sustain the sulfate-reducers. This mechanism was attractive for several reasons: it involved no new organism, was consistent with all previous studies, and offered an explanation for puzzling results from previous inhibition experiments. The "reverse methanogenesis hypothesis" was tested in the laboratory by Valentine and co-workers,[301,302] who designed an apparatus that could maintain pure cultures of methanogens under low and known H_2 partial pressures. However, none of the five methanogen strains tested demonstrated sustained H_2 production, which would be expected if reverse methanogenesis were occurring. Reverse methanogenesis is suggested as the mechanism for anaerobic methane oxidation by the genomics community.[303,304]

Valentine and Reeburgh[9] explored alternative mechanisms consistent with previous observations that also allowed for greater thermodynamic energy yields. One involves formation of acetate and H_2 from methane:

Mechanism I

$$2CH_4 + 2H_2O \rightarrow CH_3COOH + 4H_2 \quad (MO) \quad (8)$$

$$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O \quad (SR) \quad (9)$$

$$CH_3COOH + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- + H^+ \quad (SR) \quad (10)$$

$$2CH_4 + 2SO_4^{2-} \rightarrow 2HCO_3^- + 2HS^- + 2H_2O \quad (Net) \quad (11)$$

$$\Delta G = -50.7 \text{ kJ}$$

And the other[7,272] involves a reversal of acetoclastic methanogenesis:

Mechanism II

$$CH_4 + HCO_3^- \rightarrow CH_3COO^- + H_2O \quad (MO) \quad (12)$$

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^- \quad (SR) \quad (13)$$

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (Net) \quad (14)$$

$$\Delta G = -25.4 \text{ kJ}$$

Valentine and Reeburgh favored mechanism I (reactions 8−11), as it provides more energy for each organism involved and may explain isotopically light lipids in sulfate-reducers. Both mechanisms can be tested experimentally, as the light isotopic signature of methane would be reflected in acetate. Under most conditions, however, acetate turns over so rapidly that sampling quantities of acetate sufficient for an isotopic measurement will be difficult. The high sensitivity of accelerator mass spectrometry offers a possible means of determining radiocarbon in micromolar acetate concentrations.

Microbes capable of oxidizing methane anaerobically with nitrate have been reported recently.[305,306] These organisms were recovered from a drainage ditch rich with nitrate from agricultural runoff. Suitable conditions for these organisms probably do not exist in the ocean but could be present in soils.

7.2.5. Isotopically Light Carbonates

Anaerobic oxidation of methane produces another distinctive product: isotopically light calcium carbonate. Anaerobic oxidation of methane according to the reaction

$$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O \quad (15)$$

results in an alkalinity increase, favoring precipitation of calcium carbonate, so that

$$CH_4 + SO_4^{2-} + Ca^{2+} \rightarrow CaCO_3\downarrow + H_2S + H_2O \quad (16)$$

while aerobic oxidation of methane,

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (17)$$

results in an increase in acidity, favoring carbonate dissolution. Isotopically light carbonates have been observed as carbonate cements,[307−309] veins,[310] structures,[270,244,311] limestone-shale sequences,[312] and crusts.[283,313] All result from precipitation resulting from alkalinity increases associated with anaerobic oxidation of methane, and all contain isotopically

light carbon as a result of precipitation of some methane-derived HCO_3^-. Isotopically light biomarkers have been recovered from Black Sea carbonates, further supporting the connection with anaerobic oxidation of methane.[274]

8. New Tools and Recent Developments

The introduction and improvement of remotely operated vehicles (ROVs) and submersibles over the last two decades has revolutionized studies of the sea floor. In particular, these devices have allowed visual inspection and refined sampling of cold seeps, where methane-rich waters are advected upward through the sediments of geologically active and passive continental margins. New biomarker and culture-independent phylogenetic techniques[282,287,289,314] applied in higher methane flux environments[270,283] as well as successful laboratory studies *in vitro*[286,315] and in continuous-flow bioreactors[316] have led to a renaissance in studies of anaerobic methane oxidation. These studies have played a major role in raising and broadening our awareness of the extent and importance of the anaerobic oxidation of methane. Oremland and co-workers[317] emphasize that these studies build on some 40 years of intensive research on methanogens, methanotrophs, and the marine geochemistry of methane. Absent any previous knowledge of anaerobic oxidation of methane, the methane-oxidizing communities observed solely with a community genomics approach would seem to be aggregations of normally functioning methanogens.

8.1. Biomarkers

Molecular biological markers or biomarkers are natural products, usually lipid cell wall constituents, whose biosynthetic origin is known or can be determined. To be used as proxies in modern as well as ancient geochemical samples, biomarkers should have high taxonomic specificity and be recalcitrant enough to have high potential for preservation.[318] Compound-specific isotope analysis has revolutionized biomarker research by providing information on the origin of compounds and isotope fractionation during assimilation and biosynthesis. The feasibility of compound specific isotope analysis was demonstrated in 1978.[319] Subsequent improvements have led to the application of this tool to a wide range of geochemical questions.[320] Presently, multiple isotope ratios (C, H, O, N)[321] and natural radiocarbon[322] can be determined on single compounds.

Two recent reviews[9,10] summarize work on archaeal biomarkers up to 2002. One of the first described and perhaps the most specific archaeal biomarker of anaerobic methanotrophy is crocetane, 2,1,11,5-tetramethylhexadecane, an isomer of phytane, which was isolated from the previously observed methane/sulfate transition[241] in Kattegat sediment samples.[326] This Kattegat crocetane had a $\delta^{13}C$ value of $-90 \pm 10‰$. A number of candidate biomarkers for both methanogenic archaea as well as bacteria have been identified with compound specific isotope analysis in cold seep environments.[171,262,284,287,324−327] Recent work shows that membrane lipids from two archaeal clusters, ANME-1 and ANME-2, can be distinguished,[328] providing a tool for study of recent and fossil methane environments. Archaea-specific ether bound cyclic biphytanes associated with particulate matter in the anoxic Black Sea water column[268,273,329] occur in the deeper parts of the anoxic water column but are not preserved in sediments. Measurements of diplopterol in Santa Barbara Basin sediments offer support for biological incorporation of regional scale methane releases.[171] The isotopic composition of diplopterol, a hopanoid synthesized by aerobic bacteria, including methanotrophs, shows variations consistent with excursions in the carbon isotopic record of planktonic foraminifera.

Anaerobic methane oxidizers have been difficult to culture and are notoriously slow-growing, so there are only a small number of recent reports of successful laboratory[286,330] and mesocosm[315,331] cultivation. Thus, controlled experiments aimed at determining which biomarkers best reflect AOM have been difficult. A recent study[332] involving *in vitro* labeling (^{13}C-enriched CH_4) of a methane-oxidizing Black Sea microbial mat[273] showed remarkable differences in individual archaeal and bacterial lipids. Similar studies are needed to better understand the specificity and origin of archaeal and bacterial biomarkers associated with AOM.

Isotopically light biomarkers have proved particularly important in identifying the presence of the archaeal and bacterial members of the consortia believed to be responsible for anaerobic methane oxidation. Initially regarded as a "smoking gun" for anaerobic oxidation of methane because their light isotopic signature suggested anabolism of isotopically light methane carbon by the source biota, biomarkers have been combined with FISH (fluorescent in situ hybridization) experiments to become the primary evidence or "golden standard" for identifying the presence of anaerobic methane oxidation.[314] This is particularly so in and adjacent to seeps, where (1) performing reliable direct rate measurements using tracers and (2) obtaining methane distributions suitable for diagenetic modeling are both impossible. We would likely be completely unaware of anaerobic methane oxidation in these seep areas without biomarker and FISH studies. Thus, isotopically light biomarkers and gene probes have played a major role in raising and broadening our awareness of the extent of anaerobic oxidation of methane.

8.2. Physiological and Culture-Independent Phylogenetic Studies

Using small-subunit ribosomal RNA sequences (16S rRNA) from a methane seep in the Eel River Basin, Hinrichs and co-workers[287] found a mixture of bacteria and archaea. The archaea consisted of a novel group, ANME-1, peripherally related to *Methanosarcinales*, and a novel species of *Methanosarcinales*. Boetius et al.[282] used specific fluorescently labeled 16S rRNA-targeted oligonucleotide probes as "phylogenetic stains" (FISH, fluorescent in situ hydridization) to visualize aggregates of archaeal cells (ANME-2) surrounded by sulfate-reducing bacteria. Secondary ion mass spectrometry (SIMS) was used on FISH-visualized targets (FISH/SIMS)[314] to show that the archaea located in the interior of the aggregates were isotopically light, consistent with the hypothesis that the archaea were mediating anaerobic oxidation of methane. Orphan et al.[288,289] showed that distinct multiple groups, ANME-1 and ANME-2, were located at methane seeps and mediated the anaerobic oxidation of methane. At her study sites, the ANME-1 group existed as monospecific aggregates and individual cells, while the ANME-2 cells were present in aggregates associated with *Desulfosarcina*. However, at gas seeps in the Black Sea, ANME-1 cells in consortia with sulfate-reducing bacteria of the *Desulfosarcina* cluster form large methanotrophic mats.[270] Nauhaus and co-workers successfully enriched anaerobic methane oxidizers *in vitro*[286] and showed that the ANME-2 dominated community showed higher cell-specific AOM

rates and was more tolerant of low temperatures than the ANME-1 cells.[330] A new previously undescribed clade of archaea, ANME-3, was associated with *Beggiatoa* mats in Håkon Mosby mud volcano sediments.[212] Long-term *in vitro* incubations with a continuous supply of methane and sulfate resulted in a doubling time of approximately 7 months and growth of ANME-2/*Desulfosarcina*/*Desulfococcus* clusters with the same morphology as those present in the original sediment innoculum.[315] Hallam and co-workers[303] used environmental genomic techniques on an enrichment of natural anaerobic methanotrophs to show that nearly all genes associated with methane production are present and associated with ANME-1 and ANME-2 organisms. A major finding in this regard is the high abundance of a distinct nickel compound in the Black Sea methanotrophic mats formed by ANME-1, which is related to the nickel cofactor of methylcoenzyme M reductase, the terminal enzyme of methanogenesis.[332] As mentioned earlier, five strains of methanogens exhibited no sign of reverse methanogenesis under low H_2 conditions in a specially designed apparatus,[301,302] so whether the genes are expressed becomes a key issue.

Girguis et al.[316] developed a continuous-flow bioreactor, the anaerobic methane incubation system (AMIS), that simulated *in situ* conditions and supported the metabolism and growth of anaerobic methanotrophic archaea. The ANME-1 and ANME-2 organisms differed in their response to pore water flow rates;[331] the ANME-2 cells had the highest specific growth rates under low-flow conditions, while the ANME-1 cells had the highest specific growth rates under high flow conditions, corroborating field observations. These continuous flow bioreactors offer the potential for determining the reaction mechanisms as well as determining species-specific isotope fractionation factors.

These culture-independent studies have been applied in hydrothermally active sediments of the Guaymas Basin.[292] This work demonstrated that relatives of the AMNE-1 and ANME-2 organisms were present, and emphasized the high diversity among communities capable of anaerobic oxidation of methane. Recent results from Ocean Drilling Program Legs 201 and 204 at Hydrate Ridge and the Peru Margin[334,335] showed that known methanotrophic archaea were not detectable but that representatives of the Deep-Sea Archaeal Group were the dominant phylotype associated with methane hydrates. Known methanotrophic archaea were also absent from Leg 201 (Peru) sediments,[335] and methane oxidation appeared to be mediated by Marine Benthic Group B and the Miscellaneous Crenarchaeotal Group. Community turnover times of 100−2000 years and maintenance energies orders of magnitude lower than minima from laboratory observations were suggested.

8.3. Methane-Utilizing Communities

Levin reviewed the ecology of cold seep sediments[336] and has presented isotopic evidence of chemosynthetic nutrition (anaerobic methane oxidation, aerobic oxidation of sulfide),[337] as well as evidence that spatial distributions and community structure are related to flow rates or methane supply.[338,339] Studies at Hydrate Ridge[285,339−341] have shown that distinct chemosynthetic communities are arranged according to methane flux, as shown schematically in Figure 11. Mats of *Beggiatoa*, a sulfide-oxidizing bacterium, are present at the highest methane efflux and anaerobic oxidation rates (99 mmol m^{-2} d^{-1}), clams of the genus *Calyptogena* function in AOM rates of 56 mmol m^{-2} d^{-1}, and bivalves

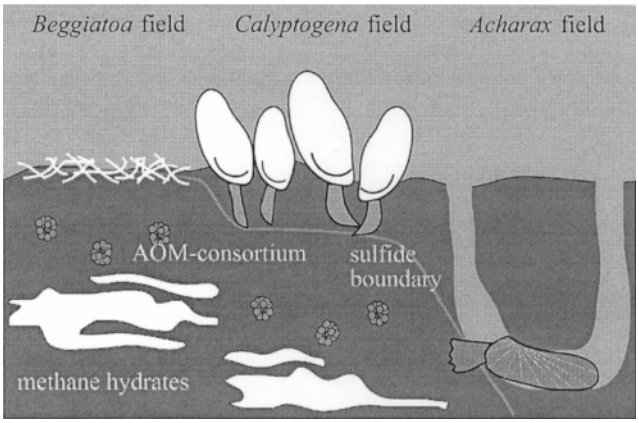

Figure 11. Schematic diagram showing the relationship of the depth of the sediment sulfide boundary to benthic bacterial mats and clam beds. Reprinted with permission from ref 285. Copyright 2003 Inter-Research.

of the genus *Acharax* reside within the sediments where the methane/sulfate transition is deeper and methane fluxes and oxidation rates are much lower (2.1 mmol m^{-2} d^{-1}). *Calyptogena* and *Acharax* metabolism is based on sulfide-oxidizing bacteria, which are harbored in their gill tissues.[342] These mollusks penetrate the reduced sediments with their feet to take up sulfide produced by anaerobic oxidation of methane, and the sulfide is oxidized in the gills by commensal sulfide-oxidizing bacteria.[343] The efficiency of methane oxidation ranges from 66% in the *Beggiatoa* mats to 83% in the clam sites, so a fraction of the advective methane flux escapes to the ocean, where it creates a local oxygen demand.[343] While sulfide-oxidizing benthic fauna are most common, organisms that oxidize methane directly have been observed.[344,345] High concentrations of dissolved organic carbon observed in seep fluids from Hydrate Ridge raise the possibility that dissolved organic carbon may be an important additional energy and carbon source to "methane seep" communities.[346]

Sea floor oxygen minimum zones typically occur at depths between 200 and 1000 m, where midwater oxygen minimum zones (O_2 < 0.5 mL L^{-1}) intersect the continental margin. The extent of naturally occurring hypoxic sediments has been estimated as 10^6 km^2.[347] Benthic organisms adapt to hypoxia,[348] organic matter oxidation is decreased,[349] and burial of organic matter is enhanced in these sediments.[350]

9. Summary of Ocean Methane Sources and Sinks

Table 3 is intended as a compilation of recent estimates of ocean methane sources and sinks, methane standing stock, and turnover times derived from a handful of rate measurements. Since the entries are uncertain and also because there is a strong possibility of "double counting" both sources and sinks, no attempt is made to interpret the table entries. Ocean volumes and the areas of various ocean depth intervals are from Menard and Smith.[351]

Under "Sources", Table 3 considers fecal pellet disaggregation, escape from benthic methane-oxidizing communities, shelf additions, mud volcanoes, inputs from serpentinization, and inputs from hydrate dissociation. The magnitudes of the shelf addition and mud volcano entries were specifically identified as additions to the water column, not the atmosphere. These additions can dissolve, be oxidized, or be sequestered as hydrates before they reach the sediment/water

Table 3. Summary of Ocean Methane Sources, Sinks, Standing Stocks, and Specific Turnover Rates

SOURCES

A. Fecal Pellet Disaggregation[79,130]	
($2.3\ \mu$mol m^{-2} day^{-1}) × ocean area excluding adjacent seas (3.26×10^8 km^2)	
2.74×10^{11} mol $year^{-1}$ =	4.38 Tg $year^{-1}$
B. Escape from Methane-Utilizing Communities[285,340,341]	
(See SINKS C below for consumption estimate)	
Beggiatoa (less than 50% escapes)	3.99 Tg $year^{-1}$
Calyptogena (less than 15% escapes)	0.66 Tg $year^{-1}$
Acharax (none escapes)	0
C. Shelf Additions	
(ref 353) ("passes through shelf seabed")	8−65 Tg $year^{-1}$
(ref 210)	20 Tg $year^{-1}$
	35 Tg $year^{-1}$
D. Mud Volcanoes[205,209]	
during quiescent periods	13 Tg $year^{-1}$
during eruptions	14 Tg $year^{-1}$
total	27 Tg $year^{-1}$
(added to water column, but subject to dissolution, sequestration as hydrates, and oxidation)	
E. Mid-Ocean Ridges, Serpentinization[154]	
escape from Mid-Atlantic Ridge	10^9 mol $year^{-1}$
increase 5-fold for world mid-ocean ridge system	5×10^9 mol $year^{-1}$
	0.08 Tg $year^{-1}$
F. Hydrate Dissociation	
Black Sea[176]	0.53−0.84 mol m^{-2} $year^{-1}$
Eel River basin[96]	5.2 mmol m^{-2} $year^{-1}$

SINKS AND ANAEROBIC OXIDATION OF METHANE

A. Deep Biosphere, Ocean Margins (ref 101)

ocean margin sites	SO_4^{-2} flux to subsurface (mol cm^{-2} $year^{-1}$)	% due to AOM	over 0−4 km ocean area (Tg $year^{-1}$)
798B Japan Sea	4.2×10^{-6}	80	9.42×10^3
681 C Peru Margin	8.1×10^{-7}	85	1.81×10^3
1175 Nankai Trough	1.3×10^{-6}	43	1.48×10^3
(ocean area: 0−4 km = 165.57×10^6 km^2)			

B. Anaerobic Methane Oxidation near the Sediment Surface[10]

depth interval	10^{12} mol $year^{-1}$	Tg $year^{-1}$
inner shelf (0−50 m)	4.6	73.6
outer shelf (50−200 m)	4.0	64.0
upper margin (200−1000 m)	3.5	56.0
lower margin (1000−4000)	6.9	110.4
sediment total		304
seeps	4.9	78.4
total		382.4

C. Consumption by Methane-Utilizing Communities[209,259,285,341]

Measured Consumption[285]	(mol m^{-2} $year^{-1}$)	(Tg $year^{-1}$)
Beggiatoa	36.1	
Calyptogena	20	
Acharax	2.1	
Consider ocean area within 0.2−4 km depth interval (1.38×10^8 km^2) and 0.1% coverage:		
Extended Consumption		
Beggiatoa	4.98×10^{12}	7.97
Calyptogena	2.76×10^{12}	4.42
Acharax	1×10^{11}	1.70

D. Oxidation in Anoxic Water Columns

Cariaco Basin[204]	
$^{14}CH_4$ budget	0.25−0.28 Tg $year^{-1}$
(0.01 Tg $year^{-1}$ oxidized, balance results in water column concentration increase)	
Black Sea[176]	
$^{14}CH_4$ budget	3.6−4.28 Tg $year^{-1}$
(time-dependent model)	4.95−5.65 Tg $year^{-1}$
(Black Sea is in steady state: additions = oxidation)	

E. Evasion to Atmosphere

ref 37	11−18 Tg $year^{-1}$

METHANE STANDING STOCK OR BURDEN

open ocean (2 nM × ocean volume (1.35×10^9 km^3)) =	43.2 Tg
Black Sea[176]	96 Tg
Cariaco Basin[204]	7×10^{-4} Tg
Eastern Tropical North Pacific[197]	∼0.3 Tg

SPECIFIC TURNOVER RATES (AEROBIC)

ref 78	"apparent methane utilization" 0.15 to 10^{-4} nM $year^{-1}$
ref 94	^{14}C-CH_4 tracer; detection limit 0.005 nM h^{-1}; specific oxidation rates range from 0.01 to 0.15 day^{-1}
ref 92	^{14}C-CH_4 tracer; 0.01−0.06 day^{-1}
ref 96	^{3}H-CH_4 tracer; 0.67 $year^{-1}$
ref 221	modeled CFC-11, CH_4 measurements; 0.02 $year^{-1}$
ref 154	model result; 0.05 $year^{-1}$

interface. The global additions from submarine mud volcanoes are very uncertain because the number of mud volcanoes as well as their gas release is unknown. Additions from dissociating gas hydrates are also uncertain and are especially susceptible to double counting since this flux appears to support methane-utilizing communities. Fluxes estimated from the Black Sea budget and integrated Eel River Basin water column oxidation rates are shown.

Under "Sinks", Table 3 distinguishes between methane oxidized deep in sediments, methane oxidized near the surface of sediments, methane oxidized by methane-utilizing benthic communities, and methane introduced to and oxidized in the water columns of anoxic basins. Table 3 builds on two previous estimates of the extent of anaerobic methane oxidation in sediments. The first estimate[38,139] applied an average of depth-integrated measurements of anaerobic methane oxidation in diffusion-controlled systems to the ocean continental shelf area. This estimate was made before the discovery of vents and advective fluxes to the ocean, and it was based on only a few environments. The resulting 70 Tg year^{-1} estimate is of historical interest and can only be considered a conservative end-member. The recent AOM estimate of Hinrichs and Boetius,[10] 304 Tg year^{-1}, uses a similar approach, multiplying averaged and depth-integrated methane oxidation rates by areas of four depth intervals. The increase in the number of observations considered in summaries of 1983,[38] 2002,[10] and this paper (Table 2) gives an indication of the attention AOM has received. Given the uncertainty in seep fluxes, the actual consumption flux could easily be larger. For benthic methane-utilizing communities (C), the measurements reported for Hydrate Ridge[285,341] are used in Table 3 because they also provide information on methane escaping these communities. Similar communities have been observed in the Gulf of Mexico[259] and adjacent Costa Rican mud extrusions.[352] We have very little information on the areal extent of these methane-utilizing communities, so an areal coverage of 0.1% was used to scale-up the observations. The entries under A, B, and C represent the quantity of methane that is intercepted *before* it enters the ocean water column; it is removed and never becomes part of the water column methane inventory. The term for evasion to the atmosphere is from a recent comprehensive study.[37]

Table 3 also presents methane standing stocks for the open ocean and two well-studied anoxic basins. Dividing the open ocean standing stock by estimated methane fluxes from mud volcanoes (27 Tg year^{-1}) and shelf additions (20 Tg year^{-1}) gives an estimated residence time based on additions of between 2 and 3 years. The reciprocal of measured and modeled specific turnover rates for the deep ocean (0.01−0.02 year^{-1}) gives a residence time based on removal of 50−100 years, a factor of over 10 and almost 100 lower. Reconciling these large differences in turnover rates on the basis of additions and removals, as well as showing how they result in the nanomolar methane concentrations observed in the ocean are the principal tasks of future work. The following section outlines future work aimed at addressing this mismatch.

10. Summary

This review shows that thermodynamic and kinetic constraints largely prevent large-scale methanogenesis in the open ocean water column. One example of open-ocean methanogenesis involves anoxic digestive tracts and fecal pellet microenvironments; methane released during fecal pellet disaggregation results in the mixed-layer methane maximum. However, the bulk of the methane in the ocean is added by coastal runoff, seeps, hydrothermal vents, decomposing hydrates, and mud volcanoes. Since methane is present in the open ocean at nanomolar concentrations, and since the flux to the atmosphere is small, the ultimate fate of ocean methane additions must be oxidation within the ocean. As indicated in the Introduction and highlighted in Table 3, sources of methane to the ocean water column are poorly quantified. There are only a small number of direct water column methane oxidation rates, so sinks are also poorly quantified. We know that methane oxidation rates are sensitive to ambient methane concentrations, but we have no information on reaction kinetics and only one report of the effect of pressure on methane oxidation.[223]

Our perspective on methane sources and the extent of methane oxidation has been changed dramatically by new techniques involving gene probes, determination of isotopically depleted biomarkers, and recent ^{14}C-CH_4 measurements showing that methane geochemistry in anoxic basins is dominated by seeps providing fossil methane. The role of anaerobic oxidation of methane has changed from a controversial curiosity to a major sink in anoxic basins and sediments.

11. Future Work

11.1. Natural ^{14}C Measurements on Ocean Water Column Methane

The recent measurements demonstrating that fossil methane from seeps is the major methane source to the Cariaco Basin and the Black Sea,[176,204] radiocarbon measurements on methane hydrates,[168] and observations of methane-utilizing benthic communities[285] suggest that the fossil methane source to the ocean may be much larger than expected. The magnitudes of the vent and mud volcano sources, both fossil methane sources, make this a first-order problem with direct bearing on methane geochemistry as well as the role of the methane subcycle in the ocean CO_2 budget.[354] As a first step, the fossil methane contribution can be evaluated with measurements of natural ^{14}C-CH_4 in the coastal and open ocean water columns. The nanomolar methane background in the ocean results from extensive oxidation and extensive isotope fractionation can be expected, but ^{14}C-CH_4 measurements are normalized to the same $\delta^{13}C$ value and are unaffected by the extent of oxidation. Measurements of natural ^{14}C-CH_4 will be challenging because of the nanomolar methane concentrations, as well as the requirement for low blanks and backgrounds. Even with the high sensitivity of AMS, samples of at least 10^3 L will be required to perform reliable analyses. Samples of 250 L have been extracted previously[355] for measurements of ^{85}Kr. Provided low ^{14}C blanks and background values can be obtained, it may be possible to employ commercially available membrane gas exchange technology to extract enough methane for ^{14}C measurement by AMS.

11.2. Oxidation Rate Measurements

Through most of the brief history of oceanic methane geochemistry studies, the prevailing view has been that observed methane concentrations in the ocean represent a balance between methanogenesis (methane production) and methanotrophy (methane oxidation). A very small number

of direct methane oxidation rate measurements have led to our present view of the importance of methanotrophy. There are several reasons for this situation. Methane oxidation rate measurements do not lend themselves to a "kill and store" approach, and they must be performed at sea. The regulatory environment also plays a role in this situation; rate measurements using radioisotope tracers can only be performed in isolated isotope vans, and these require large ships and major expeditions. International shipment of radiosotopes is possible, but very difficult.

This situation could be improved by development of a technique using accelerator mass spectrometry (AMS) technology to determine increases in $^{14}CO_2$ resulting from incubating samples spiked with highly diluted ^{14}C-CH_4 tracer. This approach builds on and extends recent biomedical and terrestrial studies involving pulse−chase experiments with $^{14}CO_2$- and ^{14}C-labeled compounds diluted to levels that do not require handling as radioactive waste ($\leq$50 nCi/g or 1.85 Bq/g, 10 CFR.20.2005).[356] This approach takes advantage of the high sensitivity and accuracy (0.3% of modern) of accelerator mass spectrometry, which measures ^{14}C atoms individually rather than observing decay events by counting. Calculations indicate that these rate measurements are feasible in anoxic basins such as the Black Sea and Cariaco Basin with nominal oxidation rates of 0.4 nM day^{-1} and micromolar methane concentrations. Use of tracers with activities of less than 50 nCi/g would simplify shipping and should permit wider application of these measurements in remote locations. Whether methane oxidation is a barophilic process should be confirmed to determine whether oxidation rate measurements will require *in situ* measurements[357] or incubation of samples from plumes[358] at *in situ* pressures to avoid large biases.

11.3. Mixed Layer Maximum

Processes in the surface methane maximum, particularly the fate of methane as it is transported from the subsurface maximum to a point where it can evade to the atmosphere, remain a key question. Initial approaches should involve methane oxidation rate measurements (^3H-CH_4 tracer) combined with parallel measurements of a natural conservative gas tracer with a similar removal time scale, such as ^{222}Rn. We have the ability to make both measurements at concentrations encountered in the surface mixed layer of the ocean.

A recent report of acoustical detection of gas release by Atlantic and Pacific herring[359] should be examined as a potential methane source. Wild-caught captive herring produce distinctive bursts of pulses, fast repetitive tick (FRT) sounds, which have been associated by video analysis with bubble expulsion from the anal duct. Gulped air was excluded as a possibility, and whether the expelled gas originates in the gut or the swim bladder is not known. Methane could be present in either case, much as it is present in respired air from ruminants.

Measurements of natural ^{14}C-CH_4 also have the potential to discriminate between and possibly quantify fecal pellet and coastal seep methane contributions. A careful study in the Eastern Tropical North Pacific, where fecal pellet contributions (modern?), coastal seep contributions (modern to fossil?), and open ocean (fossil?) conditions occur at a single station,[197] would be invaluable.

11.4. Methane-Consuming Benthic Communities

Observations of methane fluxes around *Beggiatoa* mats and *Calyptogena* clam beds show that these communities exist within fairly narrow methane flux ranges. These communities function by oxidizing sulfide that is produced by anaerobic oxidation of methane. High methane fluxes result in a shallow methane/sulfate transition depth and favor the occurrence of *Beggiatoa* mats and *Calyptogena* clam beds. These observations are based on relatively new ROV and submersible technologies, and they have naturally attracted attention as individual sites. We need to understand the distribution and areal extent of these communities well enough to scale-up and make realistic methane oxidation and flux estimates. We also need to understand methane leakage from these communities into the water column as well as the role of elevated dissolved organic carbon reported recently in Hydrate Ridge vents supporting benthic methanotrophic communities.[346]

11.5. Hydrate Dissociation

One key piece of missing information, central to understanding oceanic methane biogeochemistry, is the distribution as well as the basal rate of methane clathrate hydrate decomposition. Methane hydrates are a dynamic reservoir, and their decomposition is believed to be an important source of methane emissions from convergent margins. Direct observations under *in situ* conditions in methane-saturated sediments may be possible in the laboratory or field using ROVs. Recent studies of natural stable isotope distributions show that isotope fractionation accompanying oxidation is so large that it is impossible to assess fluxes. It is difficult to distinguish hydrate methane from thermogenic or petroleum-derived methane with measurements of ^{14}C-CH_4. Direct measurements of hydrate dissociation rates are very difficult, so it appears that the most viable approach to estimating the basal hydrate decomposition rate lies in the continued development of heat transfer models.

11.6. Molecular Genetics, Reaction Mechanism, and Biomarkers

Reports of the application of biomarker and genomic techniques (FISH) have become so widespread as documentation of the existence of anaerobic oxidation of methane that they give the impression of being applied almost like litmus paper. These powerful, specific tools document the presence of communities capable of anaerobically oxidizing methane, but they provide no rate information. Fundamental questions remain, though. For example, the spectacular photomicrographs of aggregates of archaea surrounded by sulfate reducers[282] are comforting because such close proximity would facilitate interspecies transfer, an important, but unknown part of this consortium. But what about the archaea *inside* these aggregates? What is their substrate, and how is it supplied through a gauntlet of sulfate reducers? Why do the ANME-2 organisms occur in aggregates, while the ANME-1 organisms are solitary or mat-forming? What role do the ANME-3 organisms play? Is it a question of physiological differences or methane supply, or both? Finally, since the application of these techniques has become so widespread, the recent paper by Oremland and co-workers[317] should be required reading. This thoughtful paper emphasizes that genomic techniques do not provide all of the answers and that parallel geochemical and microbiological evidence is also needed. Absent any previous knowledge of anaerobic oxidation of methane, the methane-oxidizing communities observed solely with a community genomics approach would

seem to be aggregations of normally functioning methanogens. For example, a recent genomic study[303] "proved" that "reverse methanogenesis" was the mechanism for AOM because the genome investigated contained sequences indicating enzymes common to methanogens. This work, however, failed to consider laboratory work showing the inability to induce reverse methanogenesis (H_2 production) in studies of five selected methanogen cultures under known and carefully controlled low H_2 partial pressures.[301,302] Knowing the genome alone is fine, but a key question is whether it is expressed. Microbes capable of anaerobically oxidizing methane have not been isolated, but enrichments have been grown *in vitro* and in continuous-flow bioreactors, and these should facilitate studies aimed at determining the elusive mechanism.

Accelerator mass spectrometry technology could also play a role in elucidating the reaction mechanism for AOM by determining whether acetate is an intermediate in anaerobic oxidation of methane (section 7.2.4). Both of the mechanisms proposed[9] can be tested experimentally, as the light isotopic signature of methane would be reflected in acetate. Under natural conditions, however, acetate turns over so rapidly that sampling quantities of acetate sufficient for analysis is difficult. Analysis of labeled acetate following tracer additions of ^{14}C-CH_4 would be difficult with conventional counting, but the high sensitivity of accelerator mass spectrometry offers a possible means of determining radiocarbon resulting from methane oxidation in micromolar acetate concentrations.

Measurements of ^{13}C-depleted biomarker molecules are also approaching litmus paper status as evidence of the presence of AOM. In particular, they have been regarded as a "smoking gun" and have been cited as proof that methane, which was characteristically depleted in ^{13}C (high negative $\delta^{13}C$ values), is the substrate for the organisms that synthesize the biomarkers. This is probably true, but isotopically light methane is a sufficient condition, not a necessary *and* sufficient condition, for synthesis of ^{13}C-depleted biomarkers. Methanogenesis by noncompetitive substrates could change the interpretation dramatically. The recent papers by Alperin and Hoehler[360,361] also deserve a place on the required reading list. Laboratory studies with isotopically heavy methane as substrate, similar to the recent work by Blumenberg and coworkers,[332] should continue when opportunities arise.

11.7. Sensors

The early studies of methane plumes observed near spreading centers and mud volcanoes were documented by samples taken from bottle casts—samples collected by essentially "flying blind". More recent studies use remotely operated vehicles to guide and perform sampling. A rapid-response sensor capable of analyzing methane *in situ* at the ≤ 5 nM level would be invaluable in documenting the presence and fate of methane emitted from hydrothermal plumes and mud volcanoes. Commercial methane sensors are available, but they involve membranes and have slow response as well as long recovery times following encounters with high methane concentrations. It may be possible to employ an *in situ* equilibration system or a device involving immobilized enzymes to develop rapid-response, high-sensitivity methane sensors. We presume that methane from plumes is rapidly oxidized,[173,191] but one study of the Håkon Mosby mud volcano documents physical dilution with undetectable oxidation.[215]

11.8. Mud Volcanoes

So little is known about the numbers of mud volcanoes, that they fall more under the purview of geophysical surveys than methane geochemistry. Enumerating mud volcanoes will require extensive seismic surveys. Once located, monitoring methane emission from representative mud volcanoes should involve long-term deployment of *in situ* instruments: initially, temperature sensors and, possibly, flow sensors. *In situ* microprofilers have been deployed[211] and will play a central role in future work. Approaches employing atmospheric measurements that allow budgets and partitioning of emissions should be used when possible. A recent example of this approach applied to a blowout in the Santa Barbara Basin is given by Leifer et al.[362]

12. Acknowledgments

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13. Note Added in Proof

A recent study (Karl, D. M.; Beversdorf, L.; Björkman, K.; Church, M.; DeLong, E. F. Aerobic Production of Methane in the Sea, submitted) provides new information on the mixed layer methane maximum (section 5.2 Methanogenesis Involving Noncompetitive Substrates and section 5.3 Microenvironments and the Ocean Methane Paradox). This work documents aerobic production of methane by a novel unrecognized pathway, decomposition of methylphosphonate. Phosphonates contain a carbon-phosphorus (C-P) bond, rather than the more common carbon-oxygen-phosphorus (C-O-P) bond. When methylphosphonate is used as a phosphorus source in phosphate-stressed habitats, principally the tropical ocean mixed layer, methane is quantitatively released. The ocean methane paradox could be resolved if methylphosphonate supplied only 1−2% of the daily organic phosphorus flux.

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