The Biogeochemical Methane Cycle

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Michael J. Whiticar

Contents

Abstract

Methane, the simplest alkane, is one of the most important and abundant carbon molecules on Earth. It is a major supply of energy, a chemical feedstock, and a potent greenhouse gas. Aside from thermogenic, pyrogenic, and abiotic sources, methane is primarily formed in the Earth's surface by a variety of microbial processes, i.e., methanogenesis. These processes utilize a range of pathways that involve small carbon-bearing molecules, e.g., CO_2, acetate, etc. Methanogens are active in widely diverse anaerobic environments, e.g., rocks, soils, sediments, lakes, oceans, and animals, and cover a wide ecological habitats extending from

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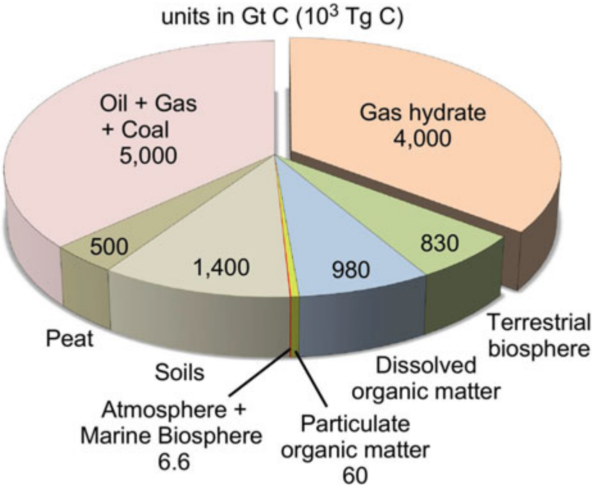
−1 °C to 122 °C, pH 5 to 11, and salinities up to 100 g/L. The biogeochemical methane cycle also includes the microbial oxidation of methane, both by aerobic and anaerobic organisms and consortia, of which some pathways remain uncertain. Together with chemical oxidation, these microbial "biofilters" of methane are critical in controlling methane distributions. A variety of tools, including biomarker molecules, stable isotopes, and molecular gene sequencing, can characterize these formation and consumption pathways. This has lead to a more robust understanding of methane occurences, abundances, reservoirs, fluxes, and budgets over the past century.

1 Introduction

Methane, named by the German chemist August Wilhelm von Hofmann (1866), is chemically the most reduced form of carbon, i.e., the antithesis of carbon dioxide (CO_2), and the most oxidized form. As a result, methane readily combusts in today's oxygenated Earth atmosphere. Benjamin Franklin apparently reported this in 1774 (Priestley 1775; Heilbron 1976), but Alessandro Volta (1777) is generally credited with the chemical identification of CH_4 after recovering gas by stirring the sediments at Lake Maggiore, Italy (Fig. 1). Early investigators of methane formation also include MacBride (1764), who addressed fermentation reactions, and Jameson (1800), who looked at processes of anaerobic peat and torf environments. Hoppe-Seyler (1876) is one of the first to investigate methanogenesis in cultures amended with acetate, while Omelianski (1904), Söhngen (1906), Coolhass (1928), Barker (1936a, b), etc. provided the first descriptions of various methanogens.

Fig. 1 Discovery of methane gases in Italian swamps by Volte (1777)

Fig. 2 Pie diagram showing the relative sizes of the major organic carbon pools



Our interests in methane are largely driven by its energy potential and by our concern for changes to the atmospheric radiative balance and changing climate. The oxidation of CH_4 to CO_2 through biological and photochemical processes, and our combustion of methane for energy, are important contributors to the increase in the tropospheric CO_2 budget (~0.016 Wm^{-2}, IPCC). However, the emission of CH_4 into the troposphere of ~550 to 600 Tg CH_4 $year^{-1}$ (Prather et al. 2012; Kirschke et al. 2013; Saunois et al. 2016) has resulted in ~0.57 Wm^{-2} total radiative forcing by CH_4 since preindustrial times (Myhre et al. 2013). The global warming potential (GWP relative to CO_2 of ~28 and 84 over 100- and 20-year lifetimes, respectively) emphasizes the relative impact of CH_4 compared to CO_2.

Methane (CH_4) is the most simple and stable of the *n*-alkanes with the strongest C–H bond strength, i.e., dissociation energy of +439 kJ mol^{-1} (Thauer and Shima 2008). Methane is also the most abundant organic molecule on Earth, even though we actually do not know the total amount of methane present. In the lithosphere, the majority of this methane is contained in methane hydrates, in particular marine gas clathrates. Recent estimates of methane in hydrates vary, with probable values from ~5–36 × 10^5 Tg CH_4 (~1 to 5 × 10^{15} m^3 CH_4, e.g., Milkov 2005; Boswell and Collett 2011; Wallmann et al. 2012), dropping from the earlier "consensus value" of 150 × 10^5 Tg CH_4 (21 × 10^{15} m^3, Kvenvolden 1999) to the current number of ~36 × 10^5 Tg CH_4 (~5 × 10^{15} m^3). Despite the uncertainty in the amount of methane stored in hydrates, it eclipses the global proven (recoverable) natural gas reserves of 1.4 × 10^5 Tg CH_4 (~0.2 × 10^{15} m^3, e.g., CIA 2017; BP 2017). In fact, the amount of carbon in methane hydrates is likely even greater than the summation of all soils, sediments, and dissolved organic carbon and is about the same as the combination of the known oil, natural gas, and coal reserves (Fig. 2). For comparison, the 2019 tropospheric methane mixing ratio of ~1864 ppm (Dlugokencky 2019) translates to a methane burden calculation of 0.0485 × 10^5 Tg CH_4 (IPCC 2013) or ~740 times less than contained in methane hydrates. Methane dissolved in the ocean is estimated to be ~43 Tg CH_4 (Reeburgh 2007) or 84,000 times less than the CH_4 in hydrates. Massive releases of methane from hydrates to the atmosphere have been implicated in Paleocene-Eocene Thermal Maximum, 55 mya (Dickens et al. 1995), and, questionably, the late Quaternary abrupt millennial-scale warming and climate change (Kennett et al. 2003). Destabilization of Neoproterozoic hydrates may, arguably, also have influenced both the pre- and post-snowball Earth carbon systems (Halverson et al. 2002; Kennedy et al. 2001). These catastrophic releases assume that it is predominantly microbial gas that is dissociating from massive methane hydrate deposits. This methane has a diagnostic carbon and hydrogen isotope signature (see Eq. 6), i.e., ^{13}C-depleted methane of $\delta^{13}CH_4 \sim -67$ ‰ versus VPDB and δ^2H-$CH_4 \sim -190$ ‰ versus VSMOW (Figs. 3 and 4).

The majority of methane on Earth is generated from accumulated organic matter through various processes, including microbial, thermogenic, and pyrogenic mechanisms. This methane formation from organic matter is augmented by lesser amounts of abiotic methane formation (e.g., Etiope 2015). It has been estimated that approximately 0.1% of the solar radiation reaching surface of the Earth (3.4×10^6 EJ year^{-1}) is transferred into biomass (~150 Gt year^{-1}, Thomson 1852; Monteith 1972; Lieth 1973) and that ~1% of the primary productivity or about 1.5 Gt is ultimately converted to CH_4 (Thauer 1998; Reeburgh 2003). This transfer ratio does depend on the environment. For example, the conversion to CH_4 in wetlands ranges from 2% to

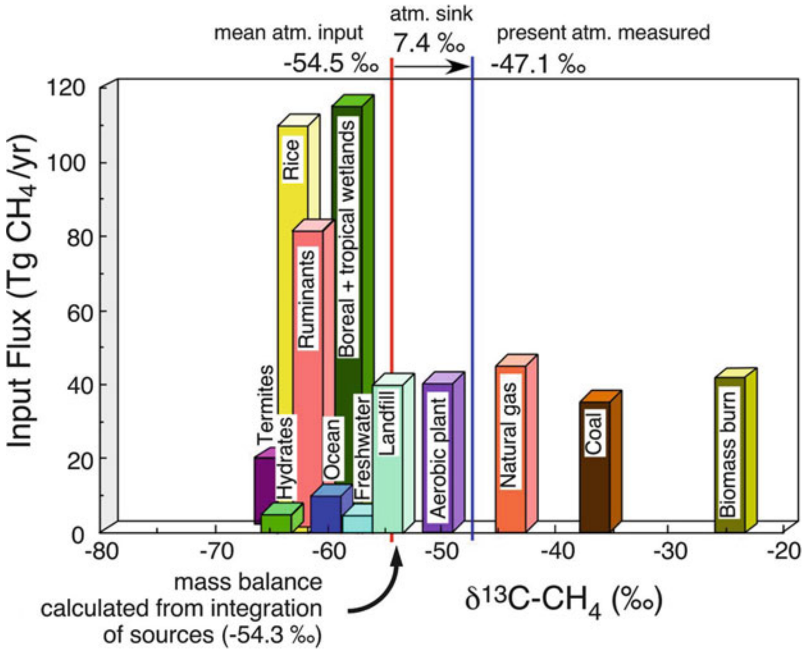


Fig. 3 Mean methane carbon stable isotope ratio of primary sources of methane flux (Tg/year) to the atmosphere. The integrated δ^{13}C-CH_4 input signal from the sources and the combined isotope shift due to methane oxidation and present-day δ^{13}C-CH_4 value are also shown. (From Whiticar and Schaefer 2007)

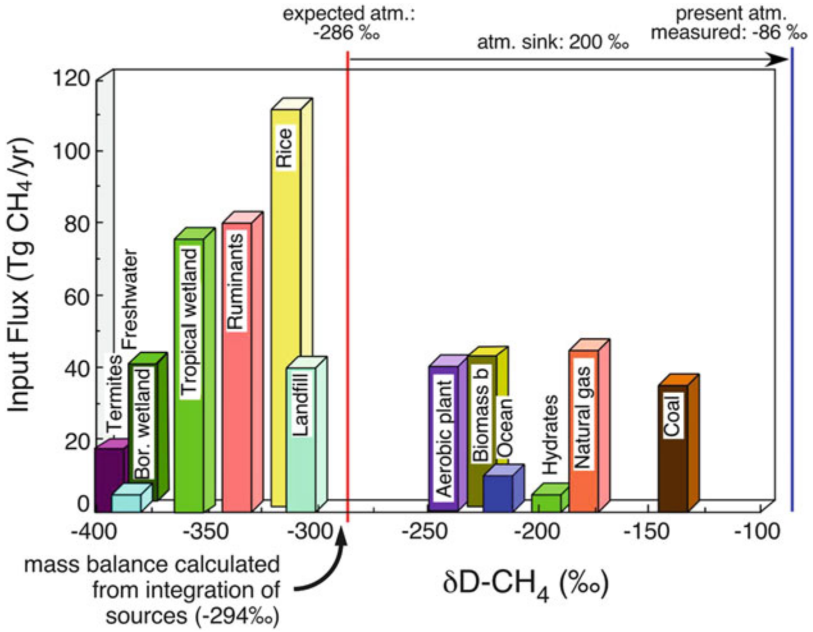


Fig. 4 Mean methane hydrogen stable isotope ratio of primary sources of methane flux (Tg/year) to the atmosphere. The integrated δ^2H-CH_4 input signal from the sources and the combined isotope shift due to methane oxidation and present-day δ^2H-CH_4 value are also shown. (From Whiticar and Schaefer 2007)

10% of the local primary productivity (Aselmann and Crutzen 1989; Sebacher et al. 1986; Moore and Knowles 1990; Pulliam 1993). Of this total methane generation, about 40% or 582 Tg CH_4 year^{-1} (Denman et al. 2007) reaches the troposphere, while most of the remainder is oxidized. This microbial methane source compares with the smaller flux of geologically sourced gas (“geogas”), i.e., methane without ^{14}C, reaching the atmosphere (~10% or ~42–64 Tg CH_4 year^{-1}, Etiope et al. 2008; Schaefer and Whiticar 2008).

Although assessing the magnitudes of the various methane reservoirs is important, it is also important to know how and how much methane moves between these reservoirs and the processes of formation and destruction of methane. A critical aspect of this is accurate characterization of the biogeochemistry of methane, the focus of this chapter.

2 Biogeochemical Process of Microbial Methane Formation

The remineralization sequence of organic matter follows distinct stages, as is shown schematically in Fig. 5. These generally occupy separate horizons or diagenetic zones as illustrated in Fig. 6. Hydrolytic microflora, which operate aerobically, anaerobically, or facultatively, break down complex organic molecules by hydrolysis

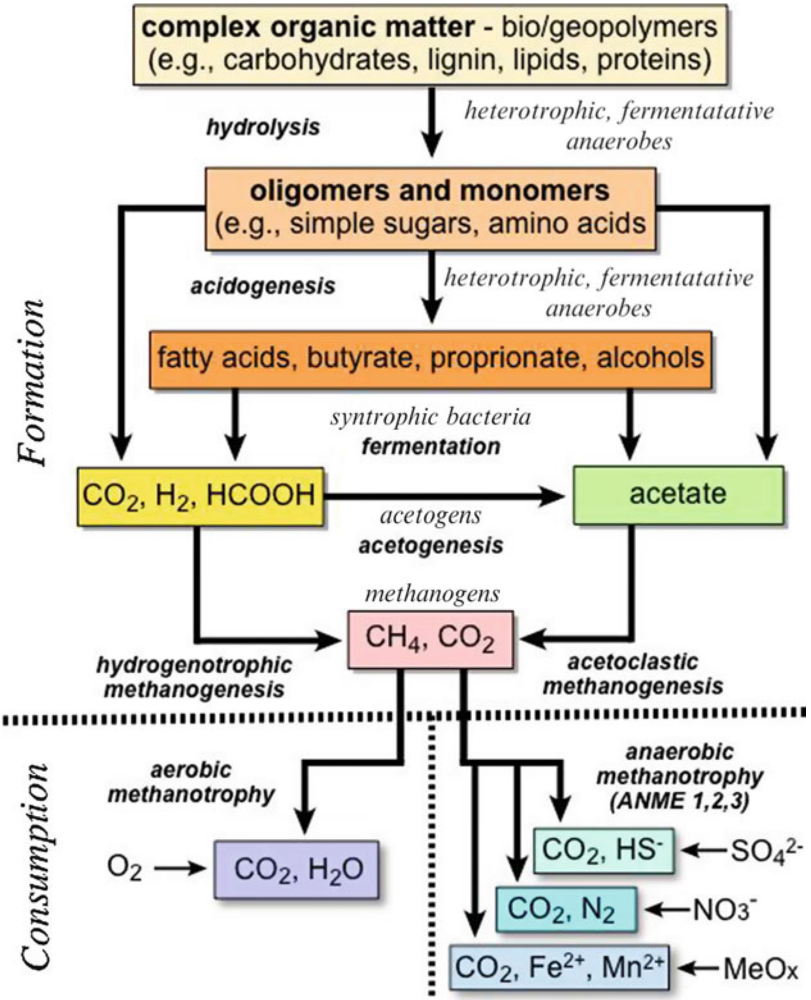


Fig. 5 Schematic of the basic remineralization sequence for organic matter as it is ultimately transformed from complex to progressively simpler organic molecules, then into methane by methanogenic processes and even consumed by aerobic or anaerobic methanotrophy. Note non-competitive substrates have not been depicted for the sake of clarity

to monomers, e.g., sugars, volatile, short-chained fatty acids, and amino acids. Acidogenesis by anaerobic or facultative fermentative microflora further degrades these monomeric and intermediate compounds to fatty acids and alcohols, etc. Subsequently, these compounds can be fermented by syntrophic or homoacetogenic bacteria to precursor substrates, such as acetate or $H_2 + CO_2$, for acetoclastic and hydrogenotrophic methanogens. Methanogenesis involves a specialized microflora that requires strict anaerobic conditions with low oxydo-reduction potentials ($Eh < -200$ mV, e.g., Thauer et al. 1977; Zinder 1993).

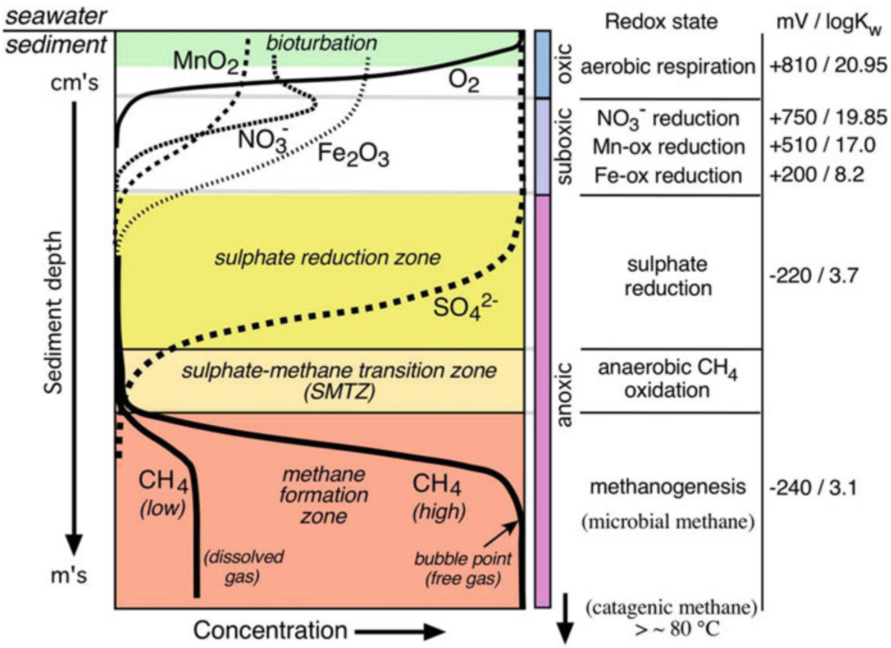


Fig. 6 Schematic representation of diagenetic depth/redox zonation in marine sediments with the corresponding compound depth distributions. Redox potentials (mV) and log K_w's for CH_2O oxidation and TEAs along the redox ladder (standard conditions) are shown to the right (Stigliani 1988; Sikora et al. 2017). The bioturbation, sulfate reduction (SRZ), and sulfate-methane transition (SMTZ) zones are indicated in the figure

This anaerobic digestion of organic matter essentially involves heterotrophic bacteria converting larger organic bio−/geopolymers into small molecules, such as acetate, CO_2, or substances containing a methyl group, that methanogens can utilize (e.g., Liu and Whitman 2008). This remineralization of organic matter to methane operates sympathetically with the remineralization free energy levels shown in Fig. 6.

Over the past century, since the isolation of a methanogen from mud by Stephenson and Strickland (1933) and the identification in the 1960s of archaea-specific lipids (e.g., Kates 1966), considerable progress has been made in understanding the biogeochemistry of methane. Certainly, critical was the definition of the domain Archaea as a distinct phylogenetic group using molecular biology with small rRNAs (e.g., Woese and Fox 1977). This phylogenetic system reclassified methanogens as Euryarchaeota from the original bacteria designation and also as distinct from eukaryotes (Woese et al. 1990). Currently, there are 26 methanogenic genera and over 110 known species of methanogens (NCBI 2017), and they are cosmopolitan with respect to environmental conditions, including many extremophiles (e.g., Bürgmann 2011; Plasencia et al. 2011). Initially, all methanogens were classified into the archaeal phylum Euryarchaeota. Recently, they were subdivided into the seven orders: *Methanobacteriales*, *Methanococcales*, *Methanomicrobiales*, *Methanosarcinales*, *Methanocellales*, *Methanopyrales*, and *Methanomassiliicoccales* (e.g., Hedderich and Whitman 2013). Methanogens are also divided as to whether or not they have cytochromes (Thauer et al. 2008) or into the five groups based on the substrate they utilize, i.e., hydrogenotrophs, acetotrophs, methylotrophs, formatotrophs, or alcoholotrophs (Garcia et al. 2000; Le Mer and Roger 2001).

Methanogens are the microbial fermentative stage in largely, but not exclusively, anaerobic environments that convert single-carbon compounds into the catabolic end-product methane. The two most commonly described pathways are (1) hydrogenotrophic methanogenesis (Eq. 1), which involves the utilization of inorganic carbon dioxide, and (2) acetoclastic methanogenesis (Eq. 2), which uses acetate as the terminal electron acceptor ("TEA") by dismutation (Fig. 5) (e.g., Barker and Buswell 1956; Zeikus 1977; Mah et al. 1977; Weimer and Zeikus 1978; Weiss and Thauer 1993; Demirel and Scherer 2008):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{1}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{2}$$

The former (also referred to in the early literature as "carbonate reduction methanogenesis") is thought to be the ancestral methanogenic form (Bapteste et al. 2005). The relative contributions of these two pathways generally depend on the abundance of either H_2-oxidizing CO_2-reducing acetogenic species (Kotelnikova and Pedersen 1998) or acetate-oxidizing H_2-producing anaerobes (Zinder and Koch 1984), respectively.

A third, general methanogenic pathway is methylotrophic methanogenesis (e.g., Thauer et al. 2008; Lang et al. 2015). In this case, simple C1-bearing compounds, such as methanol, methylamines, and methylsulfides, can serve as substrates for methanogens, often termed as "noncompetitive substrates" (e.g., King et al. 1983; Oremland 1988; Kuivila et al. 1989; Table 1). Methylotrophic methanogenesis can follow either the hydrogen-dependent or hydrogen-independent pathways, using coenzyme M or B, respectively (Keltjens and Vogels 1993; Sikora et al. 2017; Lackner et al. 2018). Some methanogens can utilize carbon monoxide, but growth is very slow (e.g., Fischer et al. 1931; Daniels et al. 1977; Rother and Metcalf 2004; Diender et al. 2015). Acetoclastic methanogenesis (sometimes in the literature referred as "methyl-type fermentation") comprises roughly 2/3 of the microbial methane (estimated range is 50–90%) (e.g., Huser et al. 1982; Ferry 1992; Conrad and Klose 1999; Le Mer and Roger 2001; Kotsyurbenko et al. 2004; Valentine et al. 2004; Goevert and Conrad 2009).

In addition, methanogens can operate in a range of syntrophic relationships with other organisms thereby accessing a wider range of precursor compounds, such as sugars, fatty acids, ketones, and alcohols, that can result in methane formation (e.g., Barker 1936a, b); Schnellen 1947; Bryant et al. 1967; Tatton et al. 1989; Schink 1997; Hattori 2008; Wrede et al. 2012). For example, Schink (1997) described how the *Methanobacillus omelianskii* culture with strains S and M.o.H. use interspecies

Table 1 Common methanogenic substrates ([1]competitive hydrogenotrophic, [2]competitive acetoclastic, [3]noncompetitive substrates, [4]involves syntrophy). Free energies ($\Delta G°$) are at standard state and pH = 7, but $\Delta G°$ will vary in nature with actual activities of the reactants and environmental conditions. (After Rother and Metcalf 2004; Whitman et al. 2006; Liu and Whitman 2008)

Substrates	Representative reactions	$\Delta G°$ (kJ mol^{-1} of CH_4)
Carbon dioxide + hydrogen gas[1]	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	−131
Acetate[2] (acetic acid)[1]+ proton	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	−36
Formate[3]	$4HCOO^- \rightarrow CH_4 + 3CO_2 + 2H_2O$	−130
Methanol[3] + hydrogen gas	$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	−113
Methanol[3] (hydrogen independent)	$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$	−105
Ethanol[3,4]/(1-propanol[3,4] and 1-butanol[2,4]) + carbon dioxide	$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COO^- + 2H^+$	−112
Carbon monoxide + water	$4CO + 5H_2O \rightarrow CH_4 + 3HCO_3^- + 3H^+$	−196
Methylamine[3] + water	$4CH_3NH_3^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+$	−75
Dimethylamine[3] + water	$2(CH_3)_2NH_2^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 2NH_4^+$	−73
Trimethylamine[3] + water	$4(CH_3)_3NH^+ + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_4^+$	−74
Dimethylsulfide[3] + water	$2(CH_3)_2S + 2H_2O \rightarrow 3CH_4 + CO_2 + H_2S$	−74

hydrogen transfer to syntrophically convert ethanol to methane and acetate by the following reactions (Eqs. 3, 4, and 5):

$$\text{Strain S}: 2CH_3CH_2OH + 2H_2O \rightarrow 2CH_3COO^- + 2H^+ + 4H_2 \left(\Delta G^{\circ} = +19\ \text{kJ}\ 2\ \text{mol}^{-1}\ \text{ethanol}\right), \tag{3}$$

$$\text{Strain M.o.H.}: CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \left(\Delta G^{\circ} = -131\ \text{kJ}\ \text{mol}^{-1}\ \text{methane}\right), \tag{4}$$

and the overall reaction

$$2CH_3CH_2OH + CO_2 \rightarrow 2CH_3COO^- + 2H^+ + CH_4 \left(\Delta G^{\circ} = -112\ \text{kJ}\ \text{mol}^{-1}\ \text{methane}\right). \tag{5}$$

Methanogenic archaea produce organic biomarker compounds that can be used as specific molecular indicators of these organisms. When preserved in certain settings, such as sediments and soils, these archaeal biomarkers may potentially offer time records of environmental conditions. For example, archaea use irregular, acyclic isoprenoids as structural compounds for their membranes. These diagnostic compounds, including 2, 6, 10, 15, 19-pentamethylicosenes (PMIs), have been related to methanogens (e.g., Tornabene et al. 1979; Brassell et al. 1981; Sinninghe Damsté et al. 1997) and anaerobic methanotrophs (e.g., Elvert et al. 1999; Thiel et al. 1999).

Archaea also synthesize polar membrane lipids that may in some cases be distinctive from bacteria, such as certain glycerol dialkyl diether (DGDs), such as archaeol and hydroxyarchaeol, glycerol dialkyl glycerol tetraether (GDGT), and glycerol-dialkyl-nonitol tetraether (GDNT) lipids, e.g., where isoprenoids are ether-bound to glycerol to make the lipid's hydrophobic end (Kates et al. 1963; De Rosa and Gambacorta 1988). Initially, some of these isopranyl glycerol ethers were postulated to be related only to extremophiles, but they are now known to be commonly synthesized by other archaeal groups and occur in a broad range of environments, such as marine and lacustrine sediments (e.g., Michaelis and Albrecht 1979; Chappe et al. 1982). Subsequently, investigators identified various forms of GDGTs, including non-isoprenoid GDGTs, those with 0 to 8 cyclopentane moieties, crenarchaeol, and those with branched carbon skeletons (e.g., Sinninghe Damsté et al. 2000, 2002). GDGTs with methylated isoprenoid chains have been found in *Methanothermobacter thermautotrophicus* (Knappy 2010), but the assignment is not necessarily exclusive to this methanogen. The occurrence of GDGTs in both archaea and possibly their emerging presence in bacteria and a multitude of environments, including methanotrophy, makes the use of these compounds as biomarkers for methanogens increasingly more complicated and less specific than initially hoped (e.g., Schouten et al. 2012; Naeher et al. 2014).

The stable carbon and hydrogen isotopes of methane ($^{13}C/^{12}C$ and $^{2}H/^{1}H$ also denoted D/H) are helpful parameters to differentiate methanogenic pathways, such as hydrogenotrophic methanogenesis from those involving preformed substrates, e.g., acetate, formate, methylamines, etc. (Whiticar 1999; Hornibrook et al. 1997; Valentine et al. 2004; Londry et al. 2008). Stable isotopes are also useful to distinguish microbial methane from other sources, such as thermogenic, geothermal, and abiogenic (Lyon and Hulston 1984; Schoell 1988; Whiticar 1994; Etiope and Sherwood Lollar 2013). Stable isotope ratios in natural sciences are typically expressed for convenience in the standard delta notation (δ) as the deviation in ‰ from a standard, e.g., $\delta^{13}C\text{-}CH_4$ (sometimes shortened to $\delta^{13}CH_4$) and $\delta^{2}H\text{-}CH_4$ (also written as $\delta D\text{-}CH_4$), i.e., Eq. 6:

$$\delta_x(‰) = \left(\frac{R_x - R_{std}}{R_{std}}\right)\cdot 1000, \tag{6}$$

where R is the isotope ratio, for example, the $^{13}C/^{12}C$ or $^{2}H/^{1}H$ of the sample "x" and isotope reference standard "std" (generally VPDB for carbon and VSMOW for hydrogen, e.g., Verkouteren and Klinedinst 2004).

The magnitude of the isotope effect that partitions the isotopes between phases (A and B) is quantified as the fractionation factor (α_{A-B}):

$$\alpha_{A-B} = \alpha_B^A = \left(\frac{R_A}{R_B}\right), \tag{7}$$

which can be rewritten in δ notation as

$$\alpha_{A-B} = \frac{\delta_A + 1000}{\delta_B + 1000}. \tag{8}$$

For simplification, some authors prefer enrichment factors (ε) that recast α_{A-B} as

$$\varepsilon_{A-B} \approx 10^3 \, ln \, \alpha_{A-B} \approx 10^3(\alpha_{A-B} - 1). \tag{9}$$

The enrichment factor (ε) is approximately the same as the isotope separation provided the differences are small, i.e., typically <25 ‰, so

$$\varepsilon_{\mathrm{CO2-CH4}} \approx \delta^{13}\mathrm{CO}_2 - \delta^{13}\mathrm{CH}_4. \tag{10}$$

It should be noted that methanogenesis, especially hydrogenotrophic methanogenesis, can have $\delta^{13}\mathrm{CO}_2 - \delta^{13}\mathrm{CH}_4. > 25$ ‰, so $\alpha_{\mathrm{CO2\ -\ CH4}}$ is preferred for rigorous calculations of isotope separation.

The stable C- and H-isotope signatures of the different methane sources can be shown by cross-plotting δ^{13}C-CH$_4$ versus δ^2H-CH$_4$ (CD plot, Fig. 7, after Whiticar 1999). In general, the combination of the C- and H isotopes give signatures for hydrogenotrophic methanogenesis (HM) that can be distinguished from acetoclastic

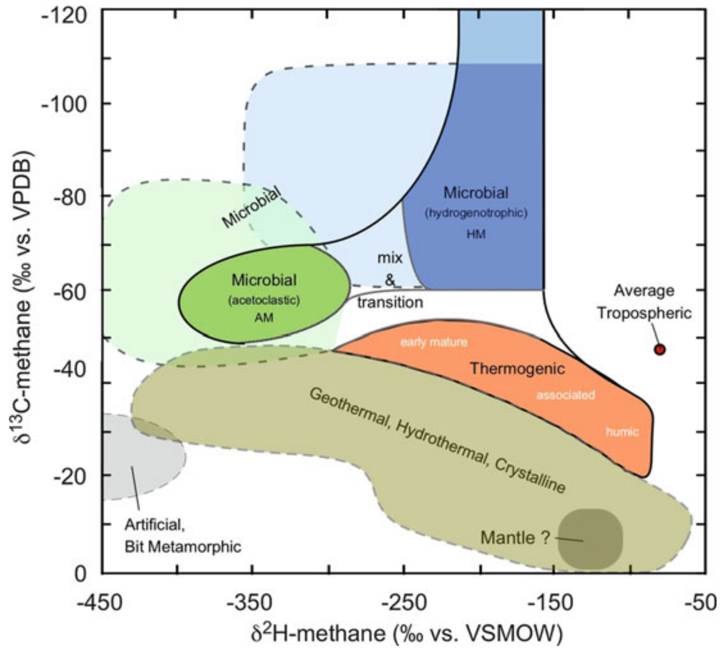


Fig. 7 Carbon and hydrogen stable isotope (CD) plot to isotopically characterize various sources of biotic and abiotic methane. (After Whiticar 1999)

methanogenesis (AM). In addition to the microbial methane, Fig. 7 also shows the typical isotope regions for thermogenic, hydrothermal, and abiogenic gases and how they also can be distinguished from microbial methane. Although other papers have reversed the axes of the CD plot (e.g., Schoell 1980; Etiope and Sherwood Lollar 2013), my historical rationale for plotting $\delta^{13}C\text{-}CH_4$ on the ordinate axis and increasing upward with ^{12}C-enriched values (e.g., Whiticar et al. 1986) is to help illustrate the typical, vertically downward depth trend of diagenesis to catagenesis observed in nature, e.g., normally encountered during drilling of a well. It should also be noted that Fig. 7 is an empirical diagram, whereby the fields are delineated by "primary gases," i.e., those thought to be representative of the gas types and not "secondary gases," which may have been influenced by mixing or alteration processes. Milkov and Etiope (2018) sorted the C- and H-isotope data on over 20,000 natural gases as microbial, thermogenic, and abiotic. Their classified data on the CD plot, shown in Fig. 8, shows general agreement with the established fields in Fig. 7, although the assignments to specific gas types or whether or not the gas is "primary" remains subjective.

Several processes can shift the typical isotope signature for microbial gases in addition to the type of methanogenic pathway. These include variations in the carbon and hydrogen ratios of the precursor materials (shown by the heavy dashed box in Fig. 9). There are also secondary effects, such as mixing of methane from different

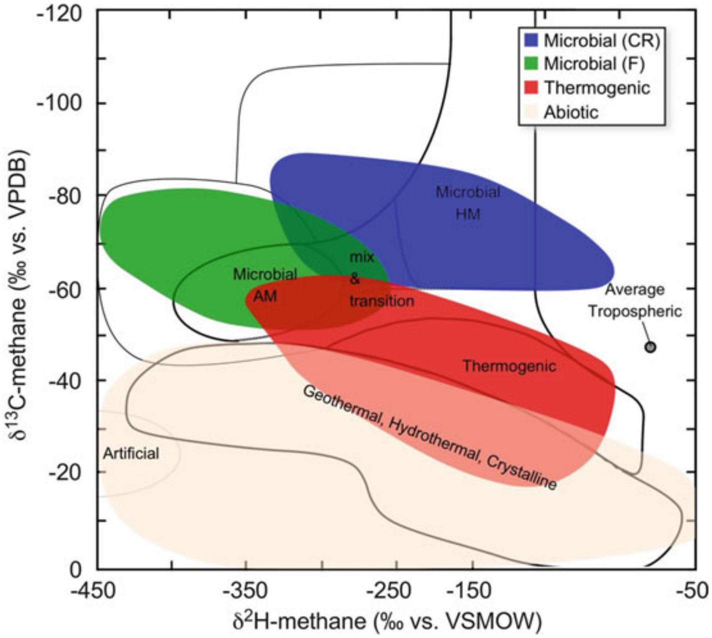


Fig. 8 Extension of carbon and hydrogen stable isotope plot of Whiticar (1999) (shown in outline) using the >20,000 data points from Milkov and Etiope (2018) to delineate biotic and abiotic methane types

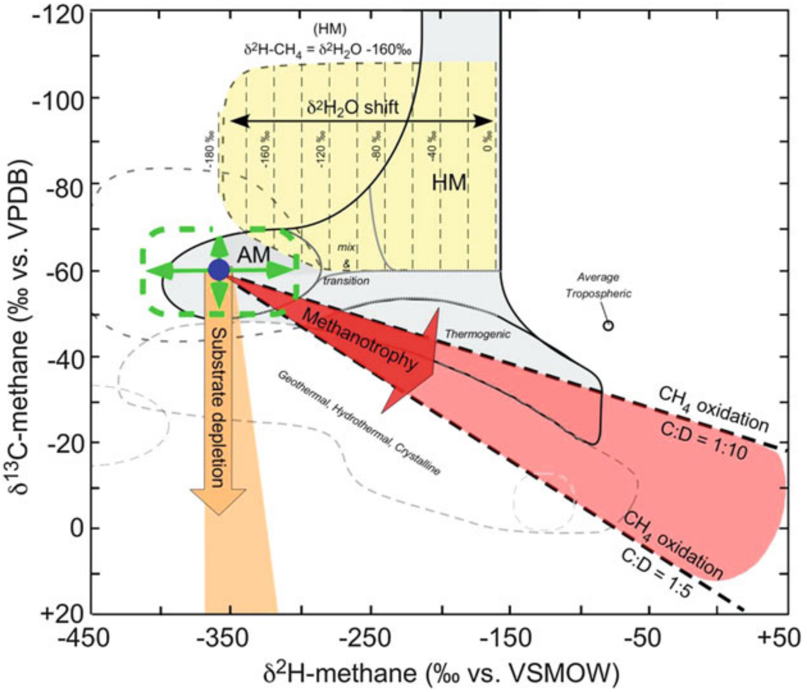
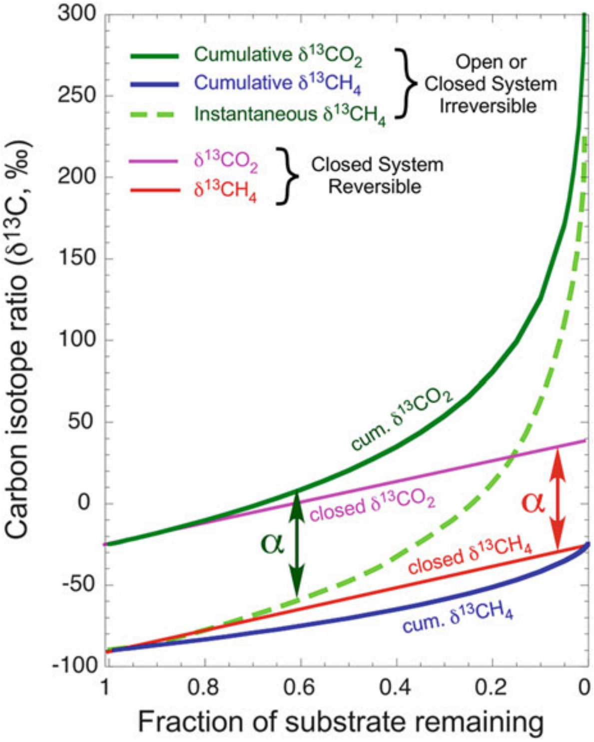


Fig. 9 Potential shifts in carbon and hydrogen stable isotope ratios for methane due to variations in precursor substrates (heavy dash and arrows), precursor δ^2H-water (grid), and due to secondary effects, such as substrate depletion and methane oxidation. (After Whiticar 1999)

microbial pathways and with nonmicrobial methane, or methane oxidation, that create diagnostic shifts in δ^{13}C-CH_4 versus δ^2H-CH_4 values from unaltered methane signatures. The utilization of the carbon substrates, e.g., CO_2 or acetate, etc., by methanogens is associated with isotope effects that usually deplete the lighter isotopologue (e.g., $^{12}CO_2$) in the substrate pool at a higher rate than the heavier isotopologue (e.g., $^{13}CO_2$). As the substrate pool is consumed, the remaining carbon becomes increasingly ^{13}C-enriched, generally following a Rayleigh relationship (Rayleigh 1896; Claypool and Kaplan 1974; Mahieu et al. 2006). This relationship depends on system conditions, such as open versus closed and reversible versus irreversible reactions as shown in Fig. 10 (e.g., Mariotti et al. 1981; Rooney et al. 1995; Hayes 2001). Because the pool of precursor hydrogen (water) is typically very much larger compared with the amount of hydrogen in methane, generally no hydrogen depletion effect is observed. The carbon shift due to substrate depletion is illustrated in CD plot in Fig. 9.

The magnitudes of kinetic isotope effects (KIE) are generally dependent on temperature, i.e., KIE decreases as temperature increases. This relationship of KIE on temperature was observed for field and culture data of methanogenesis over the temperature range of −1.3 °C to 110 °C with $\varepsilon_{CO2-CH4}$ decreasing from 9 to ~3.5

Fig. 10 Rayleigh approximated shifts in carbon stable isotope ratios of reactants (CO_2) and products (CH_4, dashed = instantaneous, solid = cumulative) for open, closed, reversible, and irreversible systems. (After Rooney et al. 1995; Hayes 2001)



(Fig. 11, Whiticar et al. 1986; Botz et al. 1996; Whiticar 1999; Fey et al. 2004). In contrast, culture experiments with various substrates by Penger et al. (2014) did not observe any change in ε_C over the range of 25–68 °C, so this question of temperature sensitivity is not yet fully resolved and that in some cases the influence of temperature on KIE may be masked by other factors.

The $\delta^2H\text{-}H_2O$ of the formation water from which the methanogens directly or indirectly derive their hydrogen determines the $\delta^2H\text{-}CH_4$ value along with distinguishing the methanogenic pathway (Schoell 1980; Whiticar et al. 1986; Balabane et al. 1987). Figure 12 shows the expected relationship between the formation water $\delta^2H\text{-}H_2O$ and the $\delta^2H\text{-}CH_4$ for both hydrogenotrophic methanogenesis (HM) and acetoclastic methanogenesis (AM). The relationships are defined as

$$\delta^2H_{CH4} = m{\cdot}\delta^2H_{H2O} - \beta, \tag{11}$$

where m, the slope, is 1.0 for HM and 0.25 for AM depending on the direct versus indirect (intact hydrogen transfer) (Daniels et al. 1980). The offset, β, is determined empirically from natural and culture samples to be around −160 to −180 ‰ for HM and ~ −325 ‰ for AM (Whiticar 1999). Mixtures between the HM and AM processes are commonly found, e.g., Waldron et al. (1999) reported values of

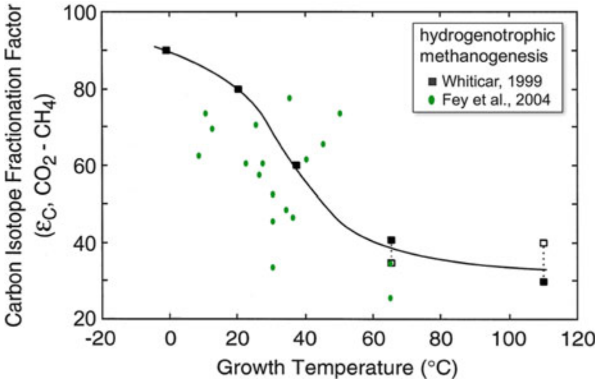


Fig. 11 Dependence of $\varepsilon_{\mathrm{C}\,(\mathrm{CO2\text{-}CH4})}$ on growth temperature. (After Whiticar 1999; Fey et al. 2004)

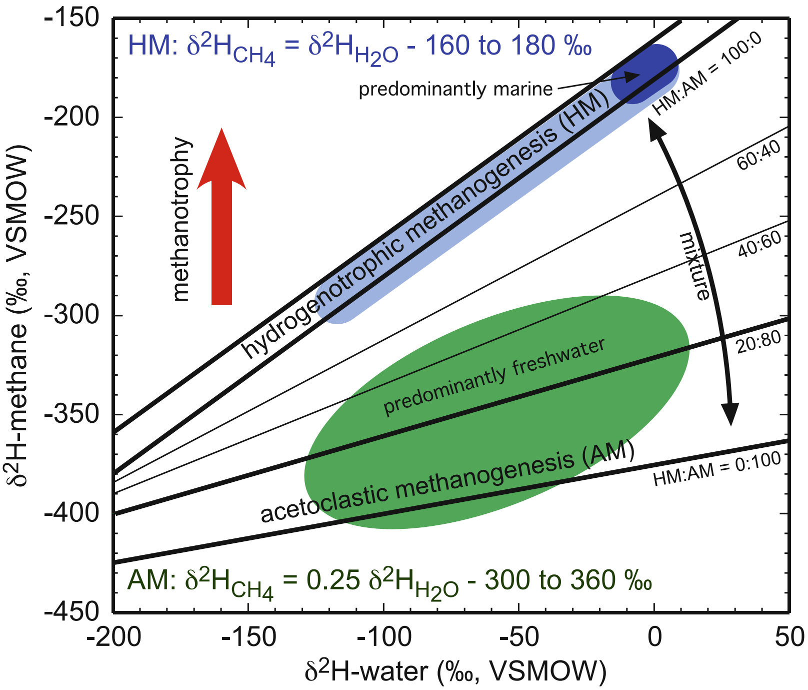


Fig. 12 Dependence of the δ^2H-CH_4 for the HM and AM pathways on the associated formation water δ^2H-H_2O. Mixing slopes between HM and AM and the direction for methanotrophy are shown. The wider range in the predominantly freshwater environments region is largely related to mixtures of AM and HM pathways. The approximate trajectory for methane oxidation is also indicated. (After Whiticar 1999)

0.675 for m and −284 ‰ for ß (Eq. 11) from freshwater wetlands with δ^2H-H_2O values ranging from −130 ‰ to +10 ‰. The consequence of the dependency of δ^2H-CH_4 on δ^2H-H_2O is illustrated for HM in Fig. 9. The shift in δ^2H-CH_4, as

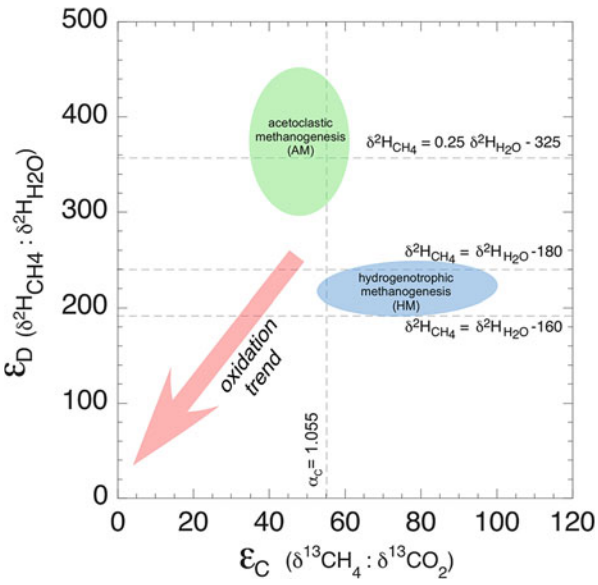


Fig. 13 Differentiation of hydrogenotrophic (HM) and acetoclastic (AM) methanogenic pathways based on carbon (δ^{13}C-CO$_2$ and δ^{13}C-CH$_4$,) and hydrogen (δ^2H-H$_2$O and δ^2H-CH$_4$) isotope separations, respectively, $\varepsilon_{C(CO2\text{-}CH4)}$ and $\varepsilon_{D(H2O\text{-}CH4)}$. The approximate ε_C, ε_D. slope for methane oxidation is also indicated

shown, can be dramatic especially for environments with isotopically light formation water, e.g., high-latitude regions. The original HM region in Fig. 7 was largely defined for marine environments (δ^2H-H$_2$O ~0 ‰) and must be corrected for the actual δ^2H-H$_2$O utilized by the methanogens. The different dependence of δ^2H-CH$_4$ on δ^2H-H$_2$O for hydrogenotrophic and acetoclastic methanogenic pathways can also be expressed in terms of $\varepsilon_{D\ (H2O\text{-}CH4)}$ (Eq. 9). The former (HM) typically has $\varepsilon_{D\ (H2O\text{-}CH4)}$ around 160–200, while AM is larger from ~300 to 450 (Fig. 13).

There can also be a carbon isotope relationship between CO$_2$ and CH$_4$, which can be exploited to further distinguish between various methane pathways and types. The delineation of HM and AM methanogenic pathways is based on their distinctive separations between δ^{13}CO$_2$ and δ^{13}CH$_4$ ($\varepsilon_{C(CO2\text{-}CH4)}$). This approach is valid only if there is a direct microbial relationship between CO$_2$ and CH$_4$ (coexisting pairs) in the gas measured, i.e., the microbial processes essentially modulate the δ^{13}CO$_2$ and δ^{13}CH$_4$. In cases where CO$_2$ or CH$_4$ are not coupled, e.g., admixture of allochthonous CO$_2$ or CH$_4$, such as additions of unrelated thermogenic CH$_4$ or inorganic CO$_2$, then the use of this CO$_2$–CH$_4$ coexisting pair relationship can be compromised. An alternative approach is to compare the δ^{13}C of the precursor organic substrate with δ^{13}CH$_4$ (e.g., Summons et al. 1998). Figure 14 illustrates the empirically defined regions of $\varepsilon_{C(CO2\text{-}CH4)}$ for HM and AM pathways together with those for thermogenic gas and atmospheric methane. The general trend for CH$_4$ oxidation and CO$_2$ evolution is also depicted, although the magnitude and slope depend on degree of consumption and the TEA involved, e.g., O$_2$ or SO$_4^{2-}$ (Coleman et al. 1981; Whiticar 1999). Although a $\varepsilon_{C(CO2\text{-}CH4)}$ of ~55 has been used in the past to demarcate AM from HM (Fig. 14), this is not a robust measure, and there are examples where this is clearly violated. A more robust approach to demarcate AM

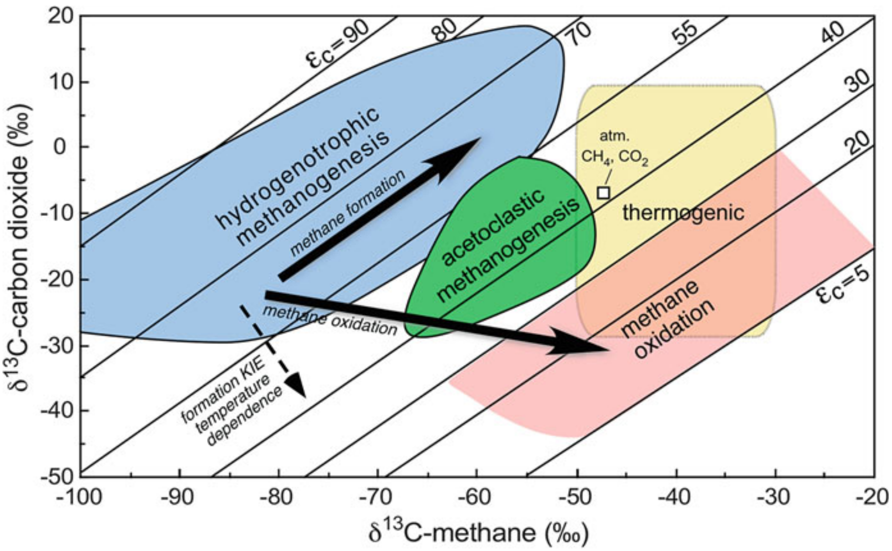


Fig. 14 Empirical differentiation of hydrogenotrophic (HM) and acetoclastic (AM) methanogenic pathways based on $\delta^{13}C\text{-}CO_2$ and $\delta^{13}C\text{-}CH_4$ of coexisting CO_2 or CH_4. The isotope separation lines shown are given as $\varepsilon_{C(CO2\text{-}CH4)}$ (Eq. A). For reference, the $\delta^{13}C\text{-}CO_2$–$\delta^{13}C\text{-}CH_4$ regions of atmospheric, thermogenic, and methane oxidation are shown, along the generalized methanogenic and methanotrophic trajectories (after Whiticar 1999). The thin dashed line shows the direction for a possible temperature dependence of the KIE during methanogenesis

from HM is the combination of $\varepsilon_{D\ (H2O\text{-}CH4)}$ and $\varepsilon_{C(CO2\text{-}CH4)}$ as shown in Fig. 13. An important feature of this plot is that the absolute isotope ratios for the gas and water are not important, rather just the magnitudes of the separation between $\delta^2H\text{-}H_2O$–$\delta^2H\text{-}CH_4$ and $\delta^{13}CO_2$–$\delta^{13}CH_4$.

Molecular ratios, such as CH_4/C_2H_6 or $CH_4/(C_2H_6 + C_3H_6)$ (aka Bernard parameter or $C_1/(C_2+ C_3)$, Bernard et al. 1976), are frequently used to distinguish microbial gas from thermogenic sources. The concept is based on the low amounts of microbiologically formed ethane and propane compared to methane, i.e., $C_1/(C_2+ C_3) > 100$ or even much higher ($\sim10^5$). Thermogenic "wet" gases often have $C_1/(C_2+ C_3) < 50$, but high maturity or humic thermogenic gases, e.g., shale gases, coal gases, etc., can be "dry" gases with $C_1/(C_2+ C_3) \sim10^2$–10^3. Typically to distinguish microbial from thermogenic gas, $C_1/(C_2+ C_3)$ is combined with $\delta^{13}CH_4$ to generate the Bernard diagram (Bernard et al. 1976).

Figure 15 is a rendition of this Bernard diagram that illustrates the regions occupied by the different gas types (Whiticar 1994). In addition, the trajectories of the secondary effects of mixing, migration, maturation (vitrinite reflectance or VR), and methane oxidation are shown. The magnitudes of microbial formation of ethane and propane have been long-standing issues, particularly as they can confound the signature of thermogenic gases used in petroleum exploration (Claypool 1999). In recent sediments and soils, usually there are at least trace levels of higher light

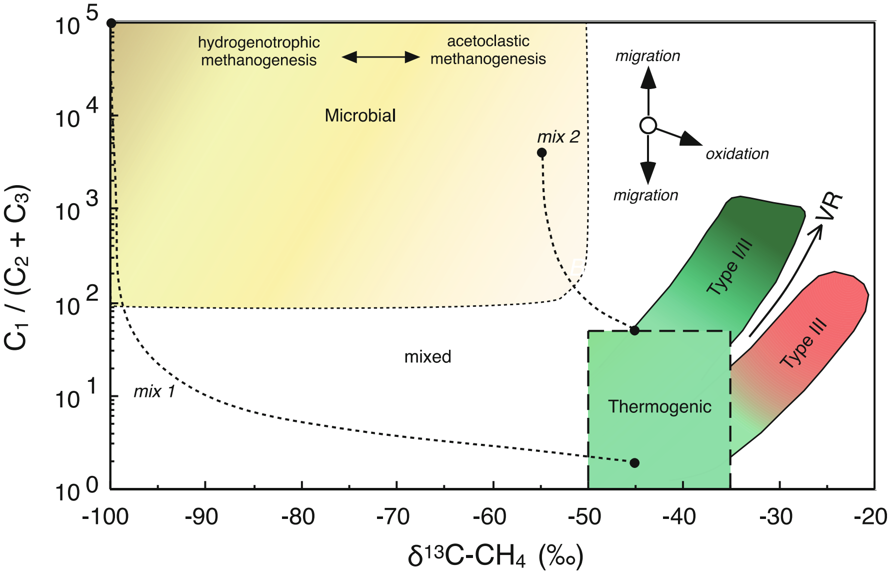


Fig. 15 Bernard diagram that combines the hydrocarbon gas molecular ratio ($C_1/[C_2 + C_3]$) and $\delta^{13}C\text{-}CH_4$ (after Bernard 1976; Whiticar 1994). The different methanogenic pathways and thermogenic types and maturities (VR), as well as the trajectories for mixing, migration, and oxidation, are shown

hydrocarbons (ethane-propane) present. Determination of the origin of these low amounts of light hydrocarbons is often challenging and potentially from a variety of microbial, thermogenic, abiotic, etc. sources and histories (Whelan et al. 1980; Vogel et al. 1982). Oremland et al. (1988) demonstrated microbial ethane formation from reduced, ethylated sulfur compounds, namely, ethanethiol (ESH) and diethylsulfide (DES), in gas samples and cultures from anoxic sediments from multiple locations. They also reported minor propanogenesis from propanethiol. The incubations required higher H_2 levels and 2-bromoethanesulfonic acid (BES), a (imperfect) methanogenesis inhibitor. Subsequently, others have reported microbial ethane in cultures (Koene-Cottaar and Schraa 1998) and surface casing vent flow from well bores (Taylor et al. 2000). Ethanogenesis and propanogenesis have also been shown by Hinrichs et al. (2006) and Xie et al. (2013) from incubation of tidal flat muds with ethanethiol, propanethiol, and BES, albeit with low H_2 levels. This suggests that the product ethylene was more important than H_2 for the ethanogenesis. Their archaeal 16S rRNA analyses also suggest that the order Methanomicrobiales (*Methanocalculus* spp.) were potentially responsible for the C_2 and C_3 formation.

Although methanogens are referred to as obligate anaerobes (Wolfe 1971), there are studies showing that they function or exist for periods of time in oxic settings as methanogenic endosymbionts in anaerobic ciliates (Schwarz and Frenzel 2005) or oxygen-limited settings (Kiener and Leisinger 1983; Kirby et al. 1981; Huser et al. 1982; Peters and Conrad 1996; Zitomer 1998) and in microniches (Field et al. 1995).

It has long been recognized due to the presence of methane oversaturation in the ocean upper water column that microbial methane formation can occur in these oxygenated surface waters (Lamontagne et al. 1973; Scranton and Brewer 1977; Burke Jr et al. 1983). This "oceanic methane paradox" (Kiene 1991) has been explained by several sources, including enteric methane production, i.e., in zooplankton and fecal pellets (e.g., Traganza et al. 1979; Sieburth 1987; Bianchi et al. 1992; Marty 1993; Karl and Tilbrook 1994), microbial methane formation in anaerobic microzones (Rusanov et al. 2004), leaching of nearshore groundwaters (Brooks 1979), or advection from shelf sources (Ward 1992).

More recently, alternative non-methanogenic explanations have been proposed, such as methane formation as a by-product of the bacterial degradation of dimethylsulfoniopropionate precursors from phytoplankton metabolism (e.g., Karl et al. 2008; Damm et al. 2010), aerobic microorganisms utilizing phosphonate esters (Kamat et al. 2013; Repeta et al. 2016), or marine algae (Lenhart et al. 2016). These non-archaeal sources are analogous to the aerobic, abiotic methane formation in plants and soils reported by, e.g., Keppler et al. (2006) and Jugold et al. (2012).

The diversity of methanogens and methanogenic pathways is controlled at a larger scale by growth environments. However, as is well illustrated by the above "oceanic methane paradox," such traditional classifications, e.g., marine or terrestrial, provide some guidance but are generally too simplistic. Factors, including diagenetic position, availability of "competitive" versus "noncompetitive" substrates for methanogens, microbial oxidation, etc., can dramatically influence the occurrence and distribution of methane.

3 Microbial Methane in Marine Environments

The estimate for the amount of microbial methane generated in marine sediments is largely uncertain, but it comprises roughly 1/3 of the naturally generated, microbial methane (estimated range is 10–40%). This estimate is confounded by a suite of factors, including the production and consumption rates and the transport mode (e.g., diffusion, advection, seepages) in the sediments. In addition, thermogenic and abiotic sources can both contribute to the marine sediment methane budget, particularly by submarine seepages (Etiope and Klusman 2002). For marine sediment microbial methane generation, Reeburgh et al. (1993) reported ~80 Tg CH_4 year^{-1}, Hovland et al. 1993 suggested 8–65 Tg CH_4 year^{-1}, whereas Hinrichs and Boetius (2002) cited ~300 Tg CH_4 year^{-1}. Modelling by Wallmann et al. (2006) reduced these estimates to a range of 5–33 Tg CH_4 year^{-1}, with a preferred value of ~13 Tg CH_4 year^{-1}, similar to 26 Tg CH_4 year^{-1} given by Boetius and Wenzhöfer (2013). Methane emissions from the marine environment (sediments and water column sources) to the atmosphere are also not well constrained and have been estimated to be 10–30 Tg CH_4 year^{-1} (Watson et al. 1990; Kvenvolden and Rogers 2005; Boetius and Wenzhöfer 2013).

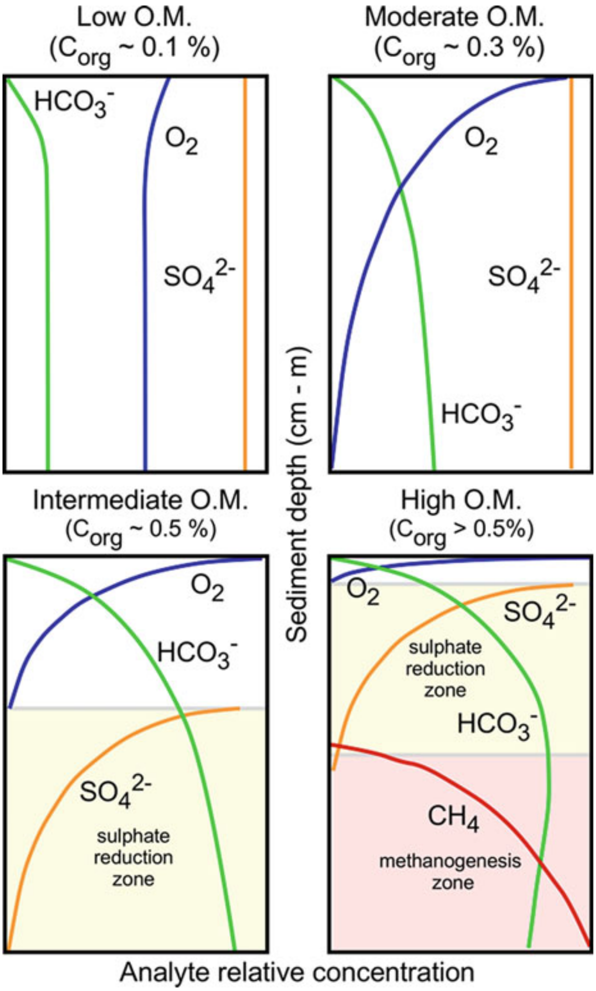
Since the 1970s (e.g., Froelich et al. 1979; Berner 1980), a diagenetic sequence for the remineralization of organic matter has been recognized for marine sediments based on redox and free energy associated with the reactions (Table 2).

Stumm and Morgan (1981) and Stigliani (1988) clearly illustrated the cascading series of oxidation-reductions or "redox ladder" associated with organic matter remineralization. As a consequence, there is a diagenetic succession with marine sediment depth for the remineralization of organic matter, as represented schematically in Fig. 6. As remarked by Jørgensen (1977), different physiological groups show a zonation similar to the chemical ones. For example, in marine sediments, the activity of SRBs typically removes acetate before it can become available for methanogens. In such cases, methanogenesis by the hydrogenotrophic pathway (Eq. 1) dominates over the acetoclastic pathway (Eq. 2).

Table 2 Energetics of selected diagenetic reactions for organic matter remineralization and methane oxidation in marine sediments. (From Zinder 1993; Schink 1997; Thauer 1998; Amend and Shock 2001; Deutzmann and Schink 2011; Ferry 2011; Whitman et al. 2006). Note: Free energies are at standard state and will vary in nature with actual temperature, pressure, and the choice and actual activities of the reactants

Diagenetic stage	Representative formula	ΔG° (kJ mol^{-1}, 25 °C)
Propionate metabolism/acetogenesis	$C_2H_5COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3H_2$	+76
Butyrate metabolism/acetogenesis	$C_3H_7COO^- + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2$	+49
Oxic respiration	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	−883
Aerobic methane oxidation	$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$	−818
Nitrate reduction	$CH_3COOH + 8/5NO_3^- + 8/5H^+ \rightarrow 4/5\,N_2 + 2CO_2 + 14/5H_2O$	−848
Iron reduction	$CH_3COOH + 8Fe^{3+} + 2H_2O \rightarrow 8Fe^{2+} + 2CO_2 + 8H^+$	−495
Sulfate reduction	$CH_3COOH + 2H^+ + SO_4^{2-} \rightarrow 2CO_2 + 2H_2S + 2H_2O$	−133
Anaerobic oxidation of methane denitrification	$CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4\,N_2 + 10H_2O$	−928
Anaerobic oxidation of methane-sulfate reduction	$CH_4 + SO_4^{2-} + H^+ \rightarrow CO_2 + HS^- + 2H_2O$	−21
Acetoclastic methanogenesis	$CH_3COO^- + H^+ - > CO_2 + CH_4$	−36
Methanol methanogenesis	$CH_3OH + H_2 - > CH_4 + H_2O$	−113
Ethanol syntrophic co-culture acetogenesis-methanogenesis	$2CH_3CH_2OH + CO_2 - > 2CH_3COO^- + 2H^+ + CH_4$	−112
Hydrogenotrophic methanogenesis	$CO_2 + 4H_2 - > CH_4 + 2H_2O$	−131
Formate methanogenesis	$4CHOO^- + 4H^+ - > 3CO_2 + CH_4 + 2H_2O$	−130

Fig. 16 Variations in the distribution of terminal electron acceptors (TEAs) and oxidation reactions in marine environments as a function of depth and depending on organic matter contents (0.1 to >0.5% C_{org} by wt.)



The surface-most sediments are typically the most oxidized with increasing degrees of reducing conditions at greater depth (age). Bioturbation mixes and oxygenates the surface sediments, which can deepen O_2 penetration and thus depress the diagenetic zonation. Bioturbation by macrofauna can in instances of near-surface methane also promote the flux of methane to the water column (e.g., Bonaglia et al. 2014) or conversely can enhance methane consumption (e.g., Childress et al. 1986). In sediments with lower levels of labile organic matter (C_{org} <0.2 wt.%), such as the mid-North Pacific, dissolved O_2 around 250 μM can be found in the surficial interstitial fluids (Fig. 16, panel 1). These sediments with mostly recalcitrant organic matter can remain aerobic for 10s of meters depth (e.g., D'Hondt et al. 2015). In such oxic settings, there may be insufficient organic matter to exhaust the dissolved O_2 or other oxidants that are co-buried or diffusing in the sediments (Table 2).

Sulfate reduction (SR) and methanogenesis are not encountered in such environments unless there are substantial amounts of organic compounds advecting up from greater depth, e.g., from petroleum or gas hydrate-related seeps. Oxygen concentrations of ~10 ppm are known to inhibit methanogenesis due to the O_2 sensitivity of enzymes and cofactors in methanogens (e.g., Schonheit et al. 1981; Ragsdale and Kumar 1996), thus restricting the methanogenic zone.

Marine sediments with higher amounts of labile organic matter (e.g., C_{org} ~0.3 wt.%, Fig. 16, panel 2), such as many shelf deposits, have rates of oxidant utilization during organic decomposition that exceed the influx of O_2 from the overlying water column (e.g., Rittenberg et al. 1955). The presence of O_2 is often restricted to the uppermost millimeter or centimeter of sediment due to the low solubility of O_2 and it being the favorite electron acceptor (e.g., Wallmann et al. 1997; Hensen and Zabel 2000).

Once O_2 is exhausted, then the microbial community switches to less energetic, suboxic oxidants, such as nitrate, nitrite and manganese (Mn(IV)), and iron (Fe(III) oxides. The lack of free oxygen restricts the types of infauna and hence inhibits the degree and decreases the depth of bioturbation. Typically, if there is sufficient labile organic matter present to consume the interstitial O_2, e.g., C_{org} ~0.3–0.5 wt.%, then these suboxic species will also be quantitatively consumed. At that point, dissolved sulfate becomes the next oxidant utilized (Fig. 16, panel 3). Dissimilatory sulfate reduction by sulfate-reducing bacteria (SRBs) acts as the next, albeit poorer, TEA for the anaerobic respiration of organic matter (e.g., Starkey 1948, Table 2). Hydrogen sulfide is one of the reaction products that is toxic and can inhibit bioturbation at the sediment surface (e.g., Atkinson and Richards 1967). In some cases, the sulfate reduction zone (SRZ) even extends into the water column, e.g., the Black Sea (Luther III et al. 1991) or Saanich Inlet (Capelle et al. 2018). In most sediments, the H_2S is rapidly complexed and removed from the interstitial water as metallic monosulfides and eventually as pyrite. The biology of SRBs have been researched for over a century (e.g., Beijerinck 1895; Van Delden 1903), but in recent sediments, detailed distributions of SRBs were reported later by Jørgensen (1977) and others. It is interesting to note that at the base of the SRZ, sulfate concentrations are not always fully depleted, and sulfate can persist at ~100 s μM levels into the methane accumulation zone (MAZ) (e.g., Neretin et al. 2004). The explanation for this is unclear, but it may be that low sulfate concentrations fall below the threshold for use by SRBs (Leloup et al. 2007) or potentially that there is a sulfur cycle below the sulfate-methane transition zone (SMTZ, e.g., Mitterer 2010) that involves sulfide reoxidation (Knab et al. 2008; 2009).

The final diagenetic link in the remineralization chain of organic matter is thought to be methanogenesis, whereby methanogens use carbon rather than oxygen as the final TEA (Table 2). Generally, organic-rich sediments (e.g., Corg ~0.3–0.5 wt.%, Fig. 16, panel 3) consume the oxygenated oxidants (O_2 – SO_4^{2-}), enabling the formation and accumulation of higher quantities of methane. In some marine environments with high organic loading, the anaerobic diagenetic zone can extend up into the water column resulting in the presence of high methane contents

(~10 µM), e.g., Saanich Inlet (Lilley et al. 1982) or Black Sea (Reeburgh et al. 1991; Schubert et al. 2006).

There are interesting suggestions that methanogenesis may not always be the “final diagenetic link” mentioned above. Instead, under certain conditions during late-stage diagenesis, methanogenesis could transition to iron reduction, utilizing iron oxides (Crowe et al. 2011; Sivan et al. 2011). This has been shown to be biologically feasible (e.g., Lovley and Phillips 1986; Lovley 2006; Weber et al. 2006). It also appears to be more easily recognized in freshwater settings (e.g., Roden and Wetzel 1996). As discussed later, iron-coupled reactions may also play an important role in the anaerobic oxidation of methane (AOM) (e.g., Ettwig et al. 2016). However, the importance of such iron-related processes is currently uncertain, but potentially relevant, particularly in earlier Earth history.

Not shown in Fig. 5 are the noncompetitive substrates that can also be utilized by methanogens. In sulfate-bearing environments, such as marine sediments or hypersaline settings, e.g., Mono Lake (Oremland et al. 1993), methanogens are generally outcompeted by SRBs for fermentation products such as hydrogen and acetate (competitive substrates) (e.g., Lovley et al. 1982), or based on energetics (Oremland and Taylor 1978; Schönheit et al. 1982; Lovley and Klug 1983). In the SRZ, methanogens can function using the non-competitive substrates, such as methanol, dimethylsulfide, and methylated amines, that are not utilized by SRBs (e.g., Winfrey and Ward 1983; Oremland et al. 1982; Oremland and Polcin 1982; Kiene et al. 1986; Maltby et al. 2018) (Table 1). In settings with higher H_2 production, it seems that methanogens can also successfully compete with SRBs (Hoehler et al. 2001; Buckley et al. 2008). There have been some more recent suggestions that SRBs and methanogens, using substrates competitively, can coexist in the SRZ (Sela-Adler et al. 2017; Dale et al. 2008; Ozuolmez et al. 2015; Zhuang et al. 2016, 2018). Although further validation is sought, the existing studies strongly suggest that methanogenesis and sulfate reduction (SR) may coexist under particular conditions. As will be discussed, methane that is formed from non-competitive substrates or other processes in the SRZ generally does not accumulate there because of extensive AOM in the SRZ that consumes any methane produced or migrating there (e.g, Xiao et al. 2017, 2018).

Normally, in marine sediments there is a clear demarcation between the SRZ and the methane accumulation zone (MAZ), with only a short overlap between them, i.e., the SMTZ, as illustrated in Fig. 6. In settings where the methanogenesis is more intense, the accumulation of dissolved methane can reach and exceed the saturation concentration. This leads to bubble formation at depth (Fig. 17). Such free gas accumulations have long been remotely recognized in recent sediment packages as “acoustically turbid zones” or “Becken Effekt” (e.g., Schüler 1952; Busby and Richardson 1957; Edgerton et al. 1966; Werner 1968; Hinz et al. 1969; Anderson et al. 1971; Schubel 1974; Van Weering 1975; Judd and Hovland 1992). Initially, H_2S and N_2 were among the gases suggested to cause acoustic turbidity. However, the works of Claypool and Kaplan (1974), Martens and Berner (1974), and Whiticar (1978) demonstrated that the presence of methane bubbles is responsible (Fig. 17).

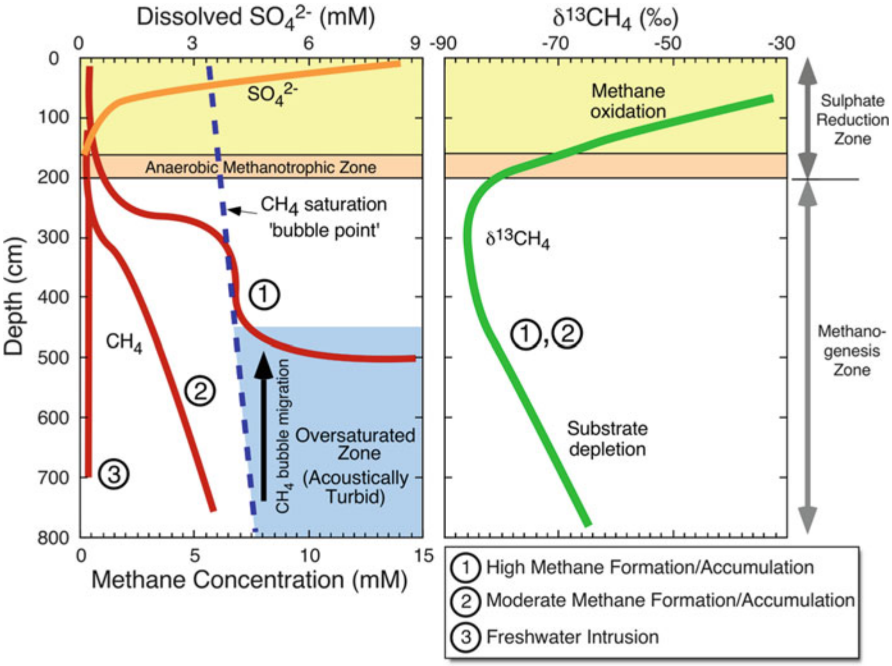


Fig. 17 Schematic sulfate, methane, and δ^{13}C-CH$_4$ distributions in organic rich, anaerobic marine sediments. Example is from Eckernförde Bay, Germany (Whiticar 2002)

In some cases, the upward migration of, for example, thermogenic methane from greater depth can also create such acoustic turbidity (e.g., Judd and Hovland 2009).

As depicted in Figs. 6 and 16, substantial concentrations of methane are first measured once sulfate has been drawn down to less than ~0.5 mM. The interesting spatial interplay observed between the sulfate and methane distributions and the SMTZ in marine sediments was the subject of intense work in the 1970s (e.g., Claypool and Kaplan 1974; Martens and Berner 1974; Barnes and Goldberg 1976; Whiticar 1978). In simple terms, the concave downward shape of the depth profile of dissolved sulfate concentration in Figs. 6 and 16 is the result of the balance between the downward diffusion of sulfate, microbial uptake by SRBs, and the upward pore fluid advection. Some sulfate is consumed by the oxidation of organic matter (Table 2), but AOM is also an important, if not the dominant, sink for dissolved sulfate (e.g., Boetius et al. 2000). Although today AOM is an accepted process, this was not always the case. In fact, before the 1980s the process was highly controversial. Early geochemical studies concluded that AOM was necessary to maintain the concave upward profiles of methane observed in interstitial fluids below the SRZ (Figs. 6 and 16) (e.g., Claypool and Kaplan 1974; Martens and Berner 1974; Barnes and Goldberg 1976; Whiticar 1978). These authors surmised that diffusion and advection of methane alone could not establish the methane gradients observed.

The net equation for the generalized process of AOM was initially suggested (e.g., Reeburgh 1976) to be

$$CH_4 + SO_4{}^{2-} \rightarrow HS^- + HCO_3{}^- + H_2O \left(\Delta G^\circ = -16.6\ \mathrm{kJ\ mol^{-1}}\right). \tag{12}$$

Some of the more common complaints by microbial ecologists against AOM by SRBs at that time were that (a) this process could not be replicated in pure cultures (e.g., Zehnder and Brock 1979) and (b) the ~16–18 kJ mol^{-1} free energy yield of this exergonic reaction (Eq. 12) was below the biological energy quantum (e.g., Schink 1997; Sørensen et al. 2001). Although "obligate methane oxidizers" were discussed in freshwaters (e.g., Naguib and Overbeck 1970; Whittenbury et al. 1970) and that "…an association between the methane oxidizers and the sulfate reducers can be deduced" (Cappenberg 1972), the exact process remained uncertain. This was further complicated by the stark difference in sulfate concentrations between marine and freshwater systems and the possible lack of a SMTZ in the latter.

4 Microbial Methane in Freshwater and Terrestrial Environments

Low salinity and low dissolved sulfate environments, such as most terrestrial/lacustrine water columns and sediments, wetlands, soils, etc., have diagenetic remineralization stages analogous to those of marine and hypersaline settings (e.g., Capone and Kiene 1988; Roden and Wetzel 1996) (Fig. 6). Despite the obvious differences in concentrations of oxidizing agents and organic matter types between salt and freshwaters, those replete in organic carbon follow the sequential reduction of O_2, $NO_3{}^-$, Mn(IV), Fe(III), $SO_4{}^{2-}$, and finally methanogenesis (e.g., Ponnamperuma 1972; Patrick and Reddy 1978; Zehnder and Stumm 1988; Achtnich et al. 1995). The dissolved O_2 concentration thresholds are approximately 6–10 μM O_2 for denitrification, ~1.5 μM O_2 for Mn(IV) reduction, and 1.5 μM O_2 for Fe(III) reduction (Tiedje 1988; Seitzinger et al. 2006; McMahon and Chapelle 2008). It was recognized in a series of papers that the presence of these oxidants leads to bacteria outcompeting the methanogens (Lovley and Phillips 1987; Lovley and Goodwin 1988; Lovley 1991).

Sulfate concentrations in freshwater environments are low compared to marine (~50–500 μM vs. ~25–30 mM) and can be rapidly consumed, i.e., SRZ in freshwater environments is much less significant. As a consequence, the remineralization of organic matter by methanogenesis in freshwater settings is suggested to be 2–5 times greater than by SR. This remains controversial because of the potential for rapid recycling of sulfate in freshwaters (Ingvorsen and Jørgensen 1984), thereby increasing its reuse and hence proportion utilized. For comparison, methanogens in marine sediments may only remineralize 5–10% as much carbon compared to SRBs (Canfield 1993).

Due to the likely diminished role of SRBs competing for substrates and consuming methane, methanogenesis can occur much closer to the sediment surface than in saline environments, i.e., in some cases at levels <30 μM sulfate and within cms of the interface (e.g., Kuivila et al. 1989; Koizumi et al. 2003). At levels >60 μM sulfate, the SRBs still outcompete the methanogens in freshwaters (Winfrey and Zeikus 1977; Ingvorsen and Brock 1982; Lovley and Klug 1986). This difference in sulfate between marine and freshwater can lead for the latter to a spatial compression of the oxic, suboxic, and methane formation zones shown in Fig. 6. The low levels of sulfate and SRBs competing for acetate in anaerobic freshwater conditions mean that acetoclastic methanogenesis (Eq. 2, Fig. 5) can be a major methanogenic pathway. Non-competitive substrates can also be utilized, but the amounts are low compared with acetoclastic and hydrogenotrophic methanogenesis (Winfrey and Zeikus 1977).

In several anoxic lakes and wetland sites, a transition with sediment depth is observed from predominantly acetoclastic methanogenesis (Eq. 2) higher in the diagenetic profile to a regime at greater depth/age increasingly dominated by hydrogenotrophic methanogenesis (Eq. 1). This methanogenic pathway transition feature has been supported by a range of methods, including stable isotope measurements, incubation and inhibitor culture experiments, 16S rRNA, and mcrA genes (e.g., Martens et al. 1992; Avery et al. 1999; Chan et al. 2005; Lu et al. 2005; Alstad and Whiticar 2011; Hershey et al. 2014; Lofton et al. 2015; Cadieux et al. 2016; Yang et al. 2017). This transition appears to largely reflect the exhaustion of organic substrates available for acetoclastic methanogenesis, leaving hydrogenotrophic methanogenesis to continue at depth with continued remineralization.

Common for anaerobic freshwater systems (sediments and sometimes stratified water columns) is that the concentration of dissolved methane can quickly rise above the methane saturation point, leading to bubble formation and thus ebullition of gas from the sediments and soils due to buoyancy. The importance of the spatial compression of the hypoxic and methane accumulation zones in freshwaters is that methane can more easily evade the microbial oxidation biofilter that consumes methane *in situ*. This means that a greater proportion of methane can escape by ebullition and diffusion into the troposphere from freshwater environments than from marine sources (Strayer and Tiedje 1978; Reeburgh et al. 1993; Bastviken et al. 2008). Global methane emissions from freshwaters are estimated to be ~100 Tg CH_4 year^{-1} (Bastviken et al. 2011), which is substantially higher than oceanic source estimates (10–30 Tg CH_4 year^{-1}) and high-latitude emissions from tundra (~35 Tg CH_4 year^{-1}, e.g., Fung et al. 1991).

The pool of nitrate (100–200 μM) in freshwaters can exceed sulfate (e.g., Mulholland et al. 2008) and thus compared with marine environments NO_3^- may be more important as a methane oxidizer (Fig. 5). Due to the short and rapid gas migration paths in soils and in freshwater columns, *in situ* methane consumption is reduced. The result is that ebullition, diffusion, and advection are major processes for the release of microbial methane from permafrost thawing, natural wetlands, and freshwaters into the atmosphere (e.g., Klapstein et al. 2014). These releases account for ~20% of the total tropospheric methane emissions budget compared with ~5% from the oceans.

Soils offer diverse environments for methanogens. These can be roughly divided into the vadose and water-saturated zones. The latter can have rapid invasion of O_2, which maintains aerobic conditions and limits methanogenesis. In some cases, anoxic microsites can serve as a refugia for methanogenic archaea (e.g., Watanabe et al. 2007). Some studies even report CH_4 production in dry, oxic environments (e.g., Andersen et al. 1998; von Fischer 2002; Teh et al. 2005; von Fischer and Hedin 2007).

In the water-saturated zone, the 0.3 mM O_2 in fully oxygenated waters is rapidly consumed leading to anaerobic conditions and methanogenesis. This has been studied extensively for flooded soils, rice paddies, wetlands, lakes, and tundras (e.g., Holzapfel-Pschorn et al. 1985; Achtnich et al. 1995; Chanton 2005; Dalal et al. 2008; Oertel et al. 2016). In addition to soil moisture, temperature, pH, and vegetation types and gas transport mechanisms, including diffusion and plant ventilation, all play critical roles in governing the production, consumption, and emissions of methane from these settings (Zeikus and Winfrey 1976; de Bont et al. 1978; Dacey 1981; Conrad et al. 1987; Whiting and Chanton 1992; Westermann 1993; Dunfield et al. 1993). Figure 18 outlines the major processes involved with the production, consumption, and transport of methane in inundated freshwater

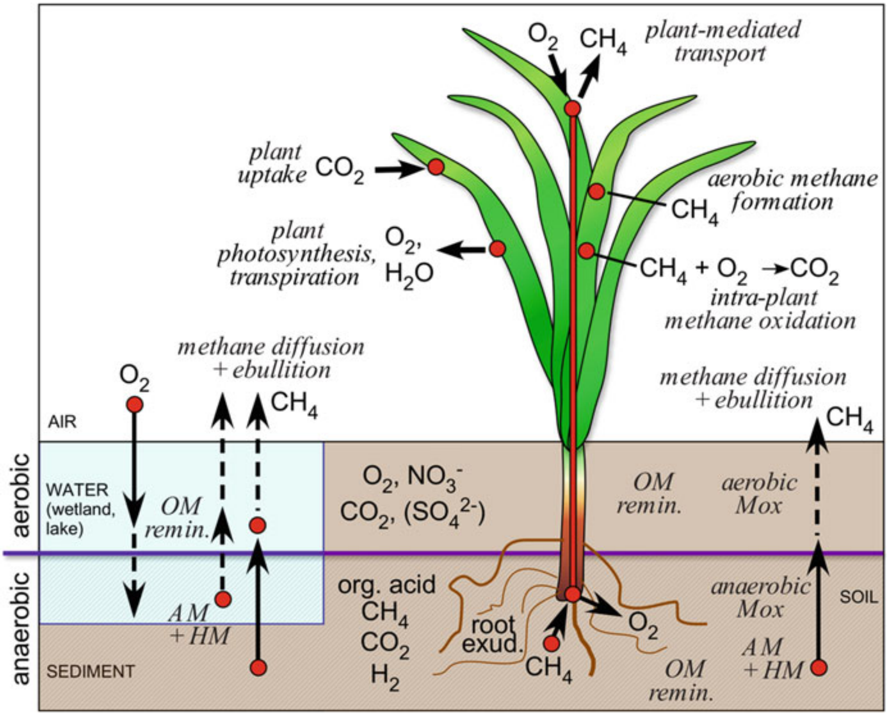


Fig. 18 Schematic of processes related to methanogenic and methanotrophic mechanisms in plants, soils, and inundated freshwater environments (wetlands, lakes, rice paddies, etc.). (Modified from Xu et al. 2016)

environments. This includes acetoclastic and hydrogenotrophic methanogenesis and methanotrophy.

The transport mechanisms include ebullition and molecular diffusion out of the soils and sediments but also plant-based aerenchyma transport in macrophytes (Colmer 2003; Chanton 2005) or in vascular plants (Shannon et al. 1996; Ström et al. 2012). Molecular diffusion in air is about 10^4 times faster than in the dissolved phase (methane diffusion coefficients at 25 °C in air ~2.0×10^{-1} cm^2 s^{-1}, Winn 1950, and in water ~2×10^{-5} cm^2 s^{-1}, Witherspoon and Saraf 1965). Therefore, enhanced emission from the gas phase in plants versus waterlogged soils or waters is expected. For example, Tyler et al. (1997) estimated that plants account for 98% of the CH_4 emissions from a Texas paddy field. Watanabe et al. (1999) reported that up to 60% of the methane emitted from rice fields originated from root exudates in the rice rhizosphere. Root exudates are also known to modulate methane production in peatlands and Arctic wetlands (Shannon et al. 1996; Ström et al. 2012). Similarly, Knoblauch et al. (2015) reported that plant-mediated transport accounted for 70–90% of total CH_4 fluxes from their polygonal tundra study site in Siberia. In the absence of the vascular plants, the majority of the methane was oxidized and not emitted due to the increased methane residence time.

Plants themselves are also a potential source of methane formation. Zeikus and Ward (1974) and Schink et al. (1981) reported methanogenesis related to the anaerobic degradation of wetwood and pectin in living trees. Trees have also been shown to transport methane (Rusch and Rennenberg 1998; Terazawa et al. 2007). The methanogenic potential of anaerobic mosses is not well constrained (Knoblauch et al. 2015), and mosses, especially the aerobic layers, are more likely a source of CH_4 consumption and reduced atmospheric CH_4 flux (Basiliko et al. 2004; Liebner et al. 2011; Parmentier et al. 2011). Methane consumption in emergent fen mosses in an Arctic lake during the Holocene Thermal Maximum was reported by Elvert et al. (2016) based on the presence of ^{13}C-depleted bacterial hopanoids, e.g., hop-17(21)-ene, with $\delta^{13}C$ as low as -55.9 ‰.

In addition to production and active CH_4 transport, plants can be the site of substantial CH_4 consumption (Fig. 18). For example, Schütz et al. (1989), Frenzel (2000), Groot et al. (2003), and Zhang et al. (2014) described methane uptake by aerobic methanotrophs in rice plant rhizospheres.

Finally, there is the controversial aerobic (abiotic) formation of methane in plants, first suggested by Keppler et al. (2006) and Crutzen et al. (2006). This mechanism was disputed by Dueck et al. (2007), Beerling et al. (2008), and Kirschbaum and Walcroft (2008) but subsequently defended by processes involving ultraviolet radiation, temperature, water, cutting injuries, and reactive oxygen species by Keppler et al. (2008), Wang et al. (2008), Vigano et al. (2008, 2009), Brüggemann et al. (2009), Qaderi and Reid (2009), Bloom et al. (2010), and Bruhn et al. (2012). Interestingly, this aerobic methane production process is also suspected in ocean settings (Karl et al. 2008; del Valle and Karl 2014).

5 Microbial Methane in Special Environments

Methanogens, known as “a community of survivors” (Friedmann 1994), can exist in a wider range of environments than just the common natural and anthropogenic sources of methane, e.g., wetlands, sediments, ruminants, landfills, etc. (Fig. 3). Chaban et al. (2006) provide a comprehensive table of the various environments and genera. The diversity of environments includes high pressures, extreme temperatures, salinities, and pH range settings. These prokaryotic organisms, termed extremophiles or polyextremophiles, are typically, but not exclusively, from the domain Archaea and include some methanogens, extreme halophiles, thermophiles, hyperthermophiles, and thermoacidophiles. A detailed microbiological description of the diversity of environments can be found in several excellent review papers that cover this material (e.g., Ferry 1993; Dworkin et al. 2006; Rosenberg et al. 2014).

However, it is important here to at least briefly review the range in habitats. For example, the hyperthermophilic methanogen *Methanopyrus kandleri* strain 116 has been grown in cultures at temperatures of ~122 °C (Takai et al. 2008). This pushed the boundaries of Kashefi and Lovley (2003) who isolated the Archaea Strain 121 from the Mothra hydrothermal vent field, which grew at 85–121 °C. These are considerably higher temperatures than reported for *Pyrolobus fumarii* up to 113 °C (Blöchl et al. 1997) or the methanogens *Methanopyrus* at 110 °C (Huber et al. 1989), *Methanocaldococcus jannaschii* up to 90 °C (Miller et al. 1988), *Methanocaldococcus indicus* up to 86 °C (L’Haridon et al. 2003), and *Methanotorris formicicus* up to 95 °C (Takai et al. 2004). Methanogenesis has also been observed in natural settings, for example, at the hydrothermal fields at the Endeavour Segment of the Juan de Fuca Ridge (Lilley et al. 1993). Although even higher growth temperatures, up to 150 °C, had been postulated (e.g., Stetter et al. 1990; Daniel 1992; Segerer et al. 1993), the deep subsurface biosphere has a general upper limit of 80–90 °C (Parkes et al. 1994; Wilhelms et al. 2001), which corresponds to subsurface depths of 1.5–3 km, depending on the geothermal gradient.

Piezophilic or barophilic hyperthermophiles have been grown under conditions up to 40 MPa (~4,100 m water depth) for the methanogen *Methanopyrus kandleri* (Takai et al. 2008) or up to 120 MPa for *Pyrococcus* CH1 (Zeng et al. 2009).

Psychrophilic or cryophilic methanogens have also been studied extensively in cold and deep lakes and in high-latitude locations (permafrost, sediments, and lakes). Nozhevnikova et al. (2003) incubated methanogens down to 1 °C, including *Methanosarcina lacustris*, from Lakes Baldegg and Soppen. Similarly, psychrophilic methanogens have been studied in the Antarctic, namely, *Methanogenium frigidum* and *Methanococcoides burtonii* by Franzmann et al. (1997) and Saunders et al. (2003). Empirical evidence, i.e., direct measurement of microbial methane, also indicates the presence of psychrophilic methanogens, e.g., in Antarctic marine sediments at -1.3 °C (Whiticar et al. 1986) and Swedish lake sediments at 4 °C (Due et al. 2010). Rivkina et al. (2002, 2004), using $NaH^{14}CO_3$, demonstrated that methanogens could be successfully incubated down to -16.6 °C, albeit with extremely low growth rates, in loamy peat permafrost soils drilled at the Kolyma Lowland (ca. 1 m, 2920 ± 40 ybp). Experiments with methanogens have also been demonstrated methanogenesis to be viable in frozen ice cores, such as the GISP2 at 3,044 m and -9 °C (Price and Sowers 2004) and the Bolivian Sajama glacier ice at 15,400 ybp, -10 °C (Campen et al. 2003). The latter observed CH_4 levels in the ice up to eight times the expected atmospheric levels, which could be best explained by *in situ* methanogenic activity of archaea living on nutrients concentrated in liquid veins at the triple junctions of ice grains (Tung et al. 2006). In contrast to permafrost with more abundant radioactive K, Th, and U in their soils, ice may provide unique, critical longer-term refugia ($>10^6$ year) for methanogen survival against DNA radiation damage from ionizing radiation (e.g., cosmic rays and α particles) (Price 2009). The disadvantage to permafrost is that nutrient abundance is lower in ice veins, which can limit methanogens.

Salinity and pH also create environmental constraints for methanogens. Haloalkaliphilic methanogens have been active and isolated from the hypersaline soda lakes, e.g., in USA (Mono and Big Soda Lakes, S = 40–95 g/l, pH =10, Oremland and Miller 1993), Egypt (Wadi al Natrun, pH = 8.1–9.1, Boone et al. 1986), Kenya (Lake Magadi, S up to 300 g/l, pH = 7-8, Kevbrin et al. 1997) India (Lonar Lake, S = 5.6-7.6 g/l, pH = 9.0-10.5, Antony et al. 2013) and Asia (Siberian soda lakes and Kulunda Lake, S up to 100 g/l, pH = 9.5–11, Nolla-Ardèvol et al. 2012; Sorokin et al. 2014; Sorokin et al. 2015). In concert, dessication tolerance studies have also been conducted on a suite of methanogens, including *Methanocaldococcus jannaschii*, *Methanothermobacter thermautotrophicus*, *Methanosarcina barkeri*, and *Methanopyrus kandleri* (Martins et al. 1997; Beblo et al. 2009).

Methanogens also occupy subsurface locations, such as aquifers (Gieg et al. 2014) in oil and gas fields (Gray et al. 2009), deep geothermal aquifers, e.g., *Methanosaeta* and *Methanothermobacter* in the Pannonian aquifer, Romania (Chiriac et al. 2018), *Methanospirillum* in the Great Artesian Basin of Australia (Kimura et al. 2005), and deep sedimentary rocks of Piceance Basin, USA (Colwell et al. 1997). The degradation of oil and gas to methane by syntrophic, acetoclastic, and hydrogenotrophic methanogenesis is a common occurrence (Dolfing et al. 2008; Rowan et al. 2008; Jones et al. 2008). Deposits of coal also offer substrates for methanogenesis, albeit via complex pathways (Penner et al. 2010; Guo et al. 2014; Baublys et al. 2015; Iram et al. 2017).

Methanogenesis also operates in subsurface rocks. Pedersen (1997) and Kotelnikova and Pederson (1998) reported acetoclastic and hydrogenotrophic methanogens from boreholes into granite-granodiorites at Äspö HRL, Sweden. Methanogenesis has been reported at similar settings, e.g., Lidy Hot Springs, USA (Chapelle et al. 2002), Columbia River Basalt Group, USA (Stevens and McKinley 1995), Witwatersrand Basin mines, South Africa (Ward et al. 2004; Slater et al. 2006; Simkus et al. 2016), Snake River Plain Aquifer, USA (Newby et al. 2004), Kidd Creek and Copper Cliff South, Canada (Doig 1994), Con and Giant mines, Canada, and Enonkoski mine, Finland (Sherwood Lollar et al. 1993, 2006). Thus, it is possible for methanogens to be viable at considerable depth (pressure and both high and low temperatures) in the subsurface in rocks, soils, sediments, and ice, provided certain living conditions are met, including liquid water, nutrients, and pore space (> few μm).

Although outside this review, it should be noted that there are also abiotic methane occurrences, including pyrogenic sources (Bousquet et al. 2006) and deep oceanic and subsurface environments, that can in some cases confound the source interpretations of methane (Etiope and Sherwood Lollar 2013). Certainly, these processes are important to characterize the occurrences of methane on Earth but also other planets and moons. The interplay between biotic and abiotic processes of methane formation and oxidation in deep earth settings, such as in the Fennoscandian Shield (Kietäväinen and Purkamo 2015), are schematically shown in Fig. 22. Abiotic methane is typically formed by gas-water-rock reactions and magmatic processes. These include carbonate methanation (Giardini et al. 1968; Yoshida et al. 1999), abiotic CO_2 reduction (Kelley and Früh-Green 1999; Seewald et al. 2006), and Fischer-Tropsch type reactions, i.e., serpentinization of ultramafic rocks/Sabatier reactions (e.g., Szatmari 1989; McCollom and Seewald 2001; Potter and Konnerup-Madsen 2003; Etiope and Ionescu 2015). Equations 13 and 14 give examples of abiotic methanation by the incongruent Fischer-Tropsch serpentinization of olivine, followed by the reduction of CO_2 with H_2 to CH_4:

$$6[(\mathrm{Mg}_{1.5}\mathrm{Mg}_{0.5})]\mathrm{SiO}_4 + 7\mathrm{H}_2\mathrm{O} \rightarrow 3[\mathrm{Mg}_3\mathrm{Si}_2\mathrm{O}_5(\mathrm{OH}_4)] + \mathrm{Fe}_3\mathrm{O}_4 + \mathrm{H}_2, \tag{13}$$

$$\mathrm{CO}_2 + 4\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O}. \tag{14}$$

6 Methane Oxidation

The biotic and abiotic oxidations of methane are critical mechanisms that effectively remove methane from sediments, soils, waters, and the atmosphere. In the atmosphere abiotic methane oxidation occurs via a complex chain of photochemical reactions initiated by the hydroxyl radical abstraction reaction with methyl and methylperoxy radicals, methanol, formaldehyde, and carbon monoxide as intermediate products (Levy 1972; Levine et al. 1985; Cicerone and Oremland 1988; Hein et al. 1997):

$$\mathrm{CH}_4 + \mathrm{OH}\bullet \rightarrow \mathrm{CH}_3\bullet + \mathrm{H}_2\mathrm{O} \overset{+\mathrm{O}_2}{\rightarrow} \mathrm{CH}_3\mathrm{O}_2\bullet + \mathrm{H}_2\mathrm{O}. \tag{15}$$

This OH radical abstraction reaction is the most important sink of tropospheric methane at ~420 Tg CH_4 year^{-1} (Khalil and Rasmussen 1983; Crutzen 1991; Whiticar and Schaefer 2007). The other atmospheric methane sinks are (1) microbial soil uptake, ca. 25–40 Tg CH_4 year^{-1} (Seller and Conrad 1987; Conrad 1996; Topp and Pattey 1997), (2) stratospheric removal, ~40 Tg CH_4 year^{-1} (Boucher et al. 2009), and (3) chlorine sink, particularly in the Marine Boundary Layer, ~30 Tg CH_4 year^{-1} (Wang et al. 2002; Allan et al. 2005, 2007).

The abiotic oxidation of hydrocarbons, including methane, has also been reported in geologic formations up to 100–180 °C by the reduction of anhydride via thermochemical sulfate reduction (TSR) (e.g., Orr 1974; Krouse et al. 1988; Kiyosu and Krouse 1989; Machel 2001; Pan et al. 2006), according to general Equation 16:

$$\mathrm{CaSO_4 + hydrocarbons \rightarrow CaCO_3 + H_2S + H_2O \pm S \pm CO_2}. \tag{16}$$

6.1 Biological Methane Oxidation

Biological oxidation or consumption of methane occurs by both aerobic and anaerobic processes. The microbiology has been treated by numerous reviews, including Hanson and Hanson (1996), Conrad (1996), Lidstrom (2007), Bowman (2011), and Zhu et al. (2016). Methanotrophy constitutes the biofilter that removes methane that could ultimately emit from sediments, soils, and waters to the troposphere (e.g., King 1992; Reeburgh 1996). Approximately 40% or 582 Tg CH_4 year^{-1} of the methane generated annually in the biosphere reaches the atmosphere. This aerobic and anaerobic removal of methane has important global climate consequences on geologic and anthropogenic time scales, including before and after the Great Oxidation Event (2.32–2.45 Ga, e.g., Kerr and Vogel 1999; Goldblatt et al. 2006; Catling et al. 2007; Daines and Lenton 2016) and for today's changing atmospheric radiative forcing.

6.2 Aerobic Methane Oxidation

Aerobic methane oxidation with O_2 (MOx, aka AMO or AeOM) is a well-studied bacterial process (Fig. 5) (e.g., King 1992; Hanson and Hanson 1996; Lidstrom 2006; Serrano-Silva et al. 2014), including phylogenetics and ecophysiology (e.g., Knief 2015). Methanotrophic bacteria utilize CH_4 and some other C_1 compounds as their carbon source(s), ultimately converting them by transduction with dehydrogenases to CO_2 via intermediates, such as methanol, formaldehyde, and formate (Roslev and King 1995; Dedysh and Dunfield 2011; McDonald et al. 2008). Originally, the organisms were understood to be obligate methylotrophs, i.e., unable to grow on C–C compounds. However, there is evidence that some are indeed facultative methanotrophs (e.g., Im et al. 2011). The basic equation (Eq. 17) for aerobic methane consumption (e.g., Dalal and Allen 2008, Table 2) is

$$\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}\ \left(\Delta G^{\circ} = -818\ \mathrm{kJ\ mol^{-1}}\right). \tag{17}$$

Aerobic methanotrophs have been known since at least the early work of Söhngen (1906), who isolated aerobic methane-oxidizing bacteria (MOB). They are a particular subgroup of methylotrophic bacteria capable of producing methane monooxygenases (MMO) enzymes (e.g., Bowman 2006; Blumenberg et al. 2007; Bürgmann 2011; Ménard et al. 2012). The two forms of these enzymes are a membrane-bound, particulate form with a copper active center (pMMO) and the soluble form with non-heme iron (sMMO) (Knief 2015; Ghashghavi et al. 2017; Kallistova et al. 2017). Generally, the methanotrophic genera have the genus prefix "Methylo," excepting *Crenothrix polyspora*. They are divided using multiple characteristics into three assemblages, namely, type I methanotrophs (RuMP pathway, e.g., *Methylobacter* and *Methylomonas*), type II methanotrophs (serine pathway, e.g., *Methylosinus*, *Methylocella*, and *Methylocystis*), and type X methanotrophs (both RuMP and serine pathways, e.g., *Methylococcus capsulatus*) (e.g., Hanson and Hanson 1996; Conrad 1996). The MMO requires O_2 and is present in (1) a soluble form (types II and X methanotrophs) and (2) membrane-bound enzyme form (type I) related to the ammonium monooxygenase (AMO) of nitrifying bacteria (Holmes et al. 1995).

Although AeOM was thought to be indirectly coupled with denitrification (Rhee and Fuhs 1978; Modin et al. 2007), aerobic methane oxidation can also be directly coupled to denitrification (AME-D) depending on the O_2 concentration (Costa et al. 2000; Kits et al. 2015). Due to the similarity of MMO with ammonia monooxygenase, many MOB may be able to perform ammonia oxidation as well. In addition, some MOB can fix N_2 at low O_2 concentrations. Zhu et al. (2016) proposed the overall stoichiometric equation for the aerobic methane oxidation with denitrification and oxygen (Eq. 18) as

$$CH_4 + 1.1O_2 + 0.72NO_3^- + 0.72H^+ \rightarrow 0.36N_2 + CO_2 + 2.36H_2O. \qquad (18)$$

In some cases, methanotrophs are extremophiles and thus inhabit a wide range of environments (Trotsenko and Khmelenina 2002; Islam et al. 2008; Pol et al. 2007), e.g., thermophiles (up to 62 °C, Bodrossy et al. 1995), psychrophiles (4 °C, Omelchenko et al. 1996; Wartiainen et al. 2006), acidophiles (pH 5.0, Dedysh et al. 2000), alkaliphiles (pH 10.0, Sorokin et al. 2000), and halophiles (5.6% NaCl, Fuse et al. 1998; Kalyuzhnaya et al. 2008). Some methanotrophs appear to be light sensitive, with inhibition by light in lakes (Oswald et al. 2015).

Depending on methane concentrations, soil methanotrophy can be differentiated into high and low affinity (e.g., Nayak et al. 2007; Conrad 2009). Low-affinity methanotrophs are typically associated with high methane concentration environments and Michaelis-Menten kinetics with high K_m, V_{max}, and Th_a parameters (Bender and Conrad 1992). High-affinity methanotrophs have low K_m, V_{max}, and Th_a Michaelis-Menten kinetic parameters and are associated with low methane concentrations, such as atmospheric methane (1.8 ppm) diffusing into typically dry soils (<60% water-filled pore space) (Bender and Conrad 1992; Dunfield et al. 1999; Dunfield and Conrad 2000). Type II methanotrophs, e.g., *Methylocystis*, appear to dominate in such low CH_4 concentration environments. These methanotrophs are important in soils and lakes for the uptake of tropospheric methane, representing about 5–8% of the 480 Tg CH_4 year^{-1} total tropospheric sink. This includes the methane sinks in forest and upland soils (Benstead and King 1997; Henckel et al. 2000). The uptake is strongly dependent on several factors, including CH_4 and O_2 contents, temperature, soil moisture content, and pH (e.g., Dunfield et al. 1993; Oertel et al. 2016). In freshwater lakes, AeOM is important for regulating CH_4

emissions, as aerobic methanotrophs consume 30–99% of the CH_4 produced (Bastviken et al. 2008). Global methane emissions from freshwaters are estimated to be ~100 Tg CH_4 year^{-1} (Bastviken et al. (2011), which is substantially higher than oceanic source estimates (10–30 Tg CH_4 year^{-1}) and high-latitude emissions from tundra (~35 Tg CH_4 year^{-1}, e.g., Fung et al. 1991).

Studies have shown that temperate forest soils may consume more methane than tropical soils and that deciduous forest soils have higher rates than coniferous forest soils (e.g., Meyer et al. 1997). The degree of soil disruption can also influence the rates of consumption, with evidence of more methane consumption in pristine soils than disturbed or regrowth forest soils. Soil moisture, texture, compaction, and fertilization can also affect the rate of methane diffusion in soils and thus influence the uptake rate (Boeckx et al. 1997; Del Grosso et al. 2000; Templeton et al. 2006).

Aerobic methane oxidation also occurs in both marine and freshwater columns (e.g., Scranton and Brewer 1977; Whiticar and Faber 1986; De Angelis et al. 1993; Valentine et al. 2001). This process, albeit with generally slow rates, i.e., 10–200 pM year^{-1} (Scranton and Brewer 1977; Rehder et al. 1999; Grant and Whiticar 2002), is also effective at reducing methane emissions from the water column to the atmosphere.

Methanotrophs can occupy and function in a variety of symbiotic situations, such as planktonic aerobic methanotrophs (Tavormina et al. 2010), marine invertebrates, such as tubeworms, provannid snails, cladorhizid sponges, and deep-sea bathymodiolin mussels (e.g., Childress et al. 1986; DeChaine and Cavanaugh 2006; Petersen and Dubilier 2009). The presence of aerobic methanotrophs in sediments and soils can sometimes be detected with specific biomarker molecules, such as specific sterols (4,4-dimethyl and 4α-methyl sterols) and hopanoids (diploptene, diplopterol, 3β-methyl diplopterol) (e.g., Bird et al. 1971; Bouvier et al. 1976; Zundel and Rohmer 1985; Hinrichs et al. 2000; Elvert and Niemann 2008; Berndmeyer et al. 2013; Rush et al. 2016; Spencer-Jones et al. 2015). More recently, gene sequencing, for example, using 16S rRNA, is a valuable tool to identify methanotrophs (e.g., DeChaine and Cavanaugh 2006; Duperron et al. 2006; Wendeberg et al. 2012).

6.3 Anaerobic Oxidation of Methane (AOM)

Anaerobic oxidation of methane (AOM) is operative mostly in anoxic marine sediments, equivalent to the sulfate-methane transition zone (SMTZ). However, the actual process still remains a puzzle, with various options for pathways. AOM is important as it has been estimated to consume >70 to 300 Tg CH_4 year^{-1} methane (Reeburgh 1996; Hinrichs and Boetius 2002; Boetius and Wenzhöfer 2013). This range in consumption is comparable to the 582 Tg CH_4 year^{-1}released to the troposphere from all sources. AOM may consume 75–95% of the methane produced in marine sediments (Valentine 2002) and exceed some estimates of current microbial methane generated in them, e.g., 5–33 Tg CH_4 year^{-1} (Wallmann et al. 2002). This discrepancy, i.e., the excess AOM, may partly be due to the additional oxidation of methane from geologic seeps and gas hydrates. It is estimated that 5–25% of the methane in sediments flux into the water column, where it is mostly consumed by aerobic methanotrophs. The rates of AOM are highly variable, depending on environment, ranging at various sites from ~1 to 3,000 nM year^{-1} (up to 11 mol CH_4 m^{-2} year^{-1}, e.g., Hinrichs and Boetius 2002; Luff et al. 2005; Regnier et al. 2011). Torres et al. (2002) and Joye et al. (2004) noted for the cold seeps at Hydrate Ridge and the Gulf of Mexico that the high rates of AOM and SR in active seeps appear to depend on the flux of methane and fluid advection. This is analogous to the increase in culture AOM activity with higher methane partial pressures (Nauhaus et al. 2002).

The oxidation capacity of dissolved sulfate (seawater ~29 mM) plays a central role in the consumption of methane as it is typically 50–100 times that of the other electron acceptors combined (O_2, NO_3^-, Mn(IV), Fe(III)). Following on the early culture work of Davis and Yarbrough (1966), the process of AOM was proposed by geochemists based on interstitial fluid data (e.g., Reeburgh 1976; Claypool and Kaplan 1974; Martens and Berner 1974; Barnes and Goldberg 1976). The primary geochemical evidence for AOM was the juxtaposition of dissolved sulfate and methane in anoxic marine sediments as shown in Figs. 5 and 16, panel 4. Reeburgh (2007, Table 2) compiled an exhaustive list of similar examples.

In organic replete sediments, the dissolved sulfate in the sulfate-reduction zone (SRZ) is rapidly consumed, at a rate faster than diffusive replenishment from the overlying sediments and water column. In the SRZ, methane concentrations are low, but not necessarily zero. Beneath the SRZ, methane starts to accumulate, sometimes to levels greater than the bubble point. The depth (diagenetic) separation between the presence of dissolved sulfate and methane could potentially be explained by substrate competition between the sulfate-reducing bacteria (SRBs) and the methanogens, i.e., the latter were outcompeted and restricted in activity until the available dissolved sulfate was largely depleted. In contrast, there can be minor amounts of methanogenesis in the SRZ, e.g., by noncompetitive substrates; however, larger accumulations are generally not observed due to largely quantitative methanotrophy in the SRZ. Furthermore, Cappenberg (1975) proposed that sulfide inhibition of methanogenesis in the SRZ could prevent the production and thus buildup of methane there.

However, such interpretations are all confounded by the typical concave upward distribution of the methane concentration profile, particularly as it approaches the sulfate-methane interface (SMTZ). Simple methanogenesis with upward diffusive and advective fluxes of methane is unable to create such a profile, and there must be net consumption to maintain the observed methane gradient in Figs. 5 and 16, panel 4 (Whiticar 1978). The issue was that an organism responsible for AOM could not be found or isolated. Thorough discussions of the various microbial options and lines of evidence for AOM have been well reviewed by, e.g., Valentine and Reeburgh (2000), Hinrichs and Boetius (2002), and Valentine (2002).

The classical view of anaerobic consumption of methane coupled to sulfate reduction (AOM-SR) involves a syntrophic relationship between methane-consuming archaea and sulfate-reducing bacteria (SRB) (Alperin and Reeburgh 1985;

Hoehler and Alperin 1996; Boetius et al. 2000; Orphan et al. 2001a; Valentine 2002; Orcutt et al. 2008) according to Eq. 19 (Table B):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \left(\Delta G^\circ \simeq 16 \text{ to} - 40 \text{ kJ/mol}\right) \tag{19}$$

We now know that anaerobic consumption of methane is not uniquely tied to sulfate reduction (AOM-SR). Despite the varieties and uncertainties of material and energy pathways (Regnier et al. 2011; Wang et al. 2017) and the direct or indirect coupling of AOM with sulfate reduction or other terminal electron acceptors (TEAs) (Sørensen et al. 2001; Orcutt et al. 2005), AOM remains an important global CH_4 sink. This is most clearly observed in high methane flux environments, such as anaerobic sediments or waste treatment facilities.

Initially, the concept of AOM by "reverse methanogenesis" was put forward by Zehnder and Brock (1979, 1980) using sulfate as the TEA. This was based on incubation experiments suggesting that methanogens are able to "…Oxidize a small amount of methane anaerobically." This process helped explain the low rates of AOM demonstrated by AOM-SR inhibition studies. Reverse methanogenesis also likely involves the formation of acetate, although methanol and H_2 were also postulated as products. They showed with ^{14}C-labelled CH_4 that the oxidation was consistently less than the concurrent methanogenesis (<1% AOM vs. methanogenesis), so net CH_4 oxidation was uncertain. This led more recently to the term "trace methane oxidation" (TMO) by Moran et al. (2005). The proposed acetate formation pathway by Zehnder and Brock (1979, 1980) (Eq. 20) is

$$CH_4 + HCO_3^- \rightarrow CH_3COO^- + H_2O, \tag{20}$$

but the authors expressed concerns about the energetics, and they included the possibility of a consortium, e.g., with sulfate reducers. Pure methanogen cultures in low H_2 and high CH_4 concentrations by Valentine et al. (2000) could not sustain H_2 production, and methane oxidation was not seen. Valentine and Reeburgh (2000) and Caldwell et al. (2008) also remarked that the many methanogens, who use acetate and methylated compounds rather than H_2 for methanogenesis, would not be good candidates for reverse methanogenesis, thus limiting the range of potential archaea. Partial support for reverse methanogenesis among other options was raised by Hoehler et al. (1994) and Harder (1997). They described a variation, also put forth by Zehnder and Brock (1979, 1980), that utilized a methanogen-sulfate reducer consortium, whereby methanogens oxidize methane with water (Eq. 21).

$$\text{Methane oxidation}: CH_4 + 3H_2O \rightarrow HCO_3^- + 4H_2 + H^+ \tag{21}$$

However, the buildup of molecular hydrogen from such a reaction would energetically inhibit the methanogens (Valentine et al. 2000). Sulfate reduction is evoked whereby SRBs scavenge the hydrogen syntrophically to allow methane oxidation to proceed exergonically, thereby maintaining the necessary lower H_2 partial pressure (P_{H2} ~1.1 μatm or 0.3 nM) (Eq. 22).

$$\text{Sulfate reduction} : SO_4^{2-} + 4H_2 + H^+ \rightarrow HS^- + 4H_2O \qquad (22)$$

This gives rise to the frequently reported overall reaction in Eq. 16 with potentially enough energy to support ATP synthesis (e.g., Harder 1997; Valentine and Reeburgh 2000; Widdel and Rabus 2001).

Although it does address the association of SRBs with AOM, concerns were raised as to whether the sulfate reducers could account for the amount of methane oxidation required, i.e., 15–100% of the total sulfate reduced (Iversen 1984), and the energy requirements (Orcutt and Meile 2008; Regnier et al. 2011).

Hallam et al. (2004) and Timmers et al. (2017) revived this "reverse methanogenesis" hypothesis using genomic information in methane-oxidizing Archaea, whose cells contain most, but not all, of the genes typically associated with CH_4 production. The papers also suggested that a pathway of methane oxidation whereby hydrogenotrophic methanogenesis (Eq. 1) essentially runs in reverse with archaea but with assistance from bacteria, i.e., a consortium of methane-oxidizing archaea and SRBs. Associated with this is the possibility of interspecies electron carriers, for example, proposed by Hoehler et al. (1994), DeLong (2000), and Wegener et al. (2015) such that methane oxidizers directly shuttle energy to the SRBs, i.e., direct interspecies electron transfer ("DIET," Lovley 2017). In contrast, Gao et al. (2017) pointed out that AOM is also associated with extracellular electron transfer ("EET"), especially for the reduction of solid electron acceptors.

To date, other than aerobic methane oxidation with O_2, there still has been no single microorganism identified that can oxidize methane. The suggestion that there may be a consortium of organisms that perform methane oxidation and SR was supported by phylogenetic studies but also geochemical evidence including stable isotope ratios, radiocarbon tracer experiments, and biomarker molecules. The problem of the missing isolated organisms for AOM is further complicated by the variety of possible syntrophic partners and TEAs now believed to be involved, including sulfate, iron and manganese oxides, nitrate, nitrite, and humic acids. Also uncertain is the question of the *EET*ing and *DIET*ing options for direct versus indirect interspecies electron transfer.

The consumption of methane by organisms is associated with predictable carbon and hydrogen kinetic isotope effects. As a consequence, AeOM and AOM consume $^{12}C^{1}H_4$ faster than the heavier isotopologues $^{13}CH_4$, $^{12}C^{1}H_3{}^{2}H$, etc. This isotope enrichment trend due to microbial methane oxidation is shown in Fig. 9 (Whiticar 1999). The $\delta^{13}C\text{-}CH_4$–$\delta^{2}H\text{-}CH_4$ slope for microbial oxidation generally varies from 1:5 to 1:10 and tends to be larger for AeOM than AOM (Whiticar 1999; Kinnaman et al. 2007). The range of carbon and hydrogen enrichment for methane oxidation based on empirical measurements and incubations is 5–31 for $\varepsilon_{C(CH4)}$ and 37.5–320 for $\varepsilon_{D(CH4)}$ (Whiticar and Faber 1986; Alperin et al. 1988; Whiticar 1999; Kinnaman et al. 2007; Feisthauer et al. 2011; Wang et al. 2016; Penger et al. 2012; Rasigraf et al. 2012).

Microbial methane oxidation leads to diagnostic isotope separations between the oxidized methane and the resultant products, e.g., CO_2. Figure 13 shows the general region for $\delta^{13}CO_2$–$\delta^{13}CH_4$ pairs determined by AeOM or AOM and the approximate trajectory of the isotope shift (after Whiticar 1999). The main difficulty in using $\delta^{13}CO_2$–$\delta^{13}CH_4$ pairs to track methanotrophy is that there are multiple other sources of CO_2 that potentially can admix and thus confound the $\delta^{13}CO_2$ values and interpretation. Often, it is the shift in $\delta^{13}CH_4$ that is more diagnostic. The methane oxidation trend shown in Fig. 12 reflects the, perhaps obvious, fact that the trace amounts of oxidation water added by methanotrophy and thus H-isotope contribution to the formation water (e.g., Eqs. 13 and 16) essentially will not appreciably affect the isotope ratio of the formation water. Similarly, the methane oxidation trend in Fig. 13 is driven mostly by changes in $\delta^{13}CH_4$ and $\delta^{2}H\text{-}CH_4$, rather than by $\delta^{13}CO_2$ or $\delta^{2}H\text{-}H_2O$. However, in extremely dry systems, perhaps deep rock environments, the amount of water is so restricted that any H_2O involved with methanogenesis (e.g., Eqs. 1, 3, and 4), AeOM (e.g., Eqs. 18 and 19), or AOM (e.g., Eqs. 21 and 22) could conceivably have a measurable influence on the $\delta^{2}H\text{-}H_2O$ of the formation water.

Biomarker molecules, in combination with isotopes, are also effective tools to track AOM. Microbial and thermogenic methane is both ^{12}C-enriched (“isotopically light”) relative to normal organic matter, so when methane is consumed, the carbon in the organisms involved will grow with a distinctively ^{12}C-enriched signal. This is incorporated into their biomarker molecules, such as the putative archaeal compounds archaeol, biphytanediol, crocetane, hydroxyarchaeols, 2,6,10,15,19-pentamethylicosane (PMI), glyceryl dialkyl glyceryl tetraethers (GDGTs), and acyclic and cyclic biphytanes, as well as, in the bacterial biomarkers, such as diplopterol, fatty acids, and alkyl ethers (e.g., Elvert et al. 1999, 2000; Hinrichs et al. 1999, 2000; Pancost et al. 2000; 2001; Bian et al. 2001; Orphan et al. 2001b; Schouten et al. 2001; Thiel et al. 1999, 2001; Wakeham et al. 2003; Summons 2013). In fact, the most ^{12}C-enriched naturally occurring organic compound known, the isoprenoid crocetane, has a $\delta^{13}C$ of −130 ‰ (Elvert et al. 2000). These ^{12}C-enriched compounds are strong evidence for the archaea-bacterial collaboration for AOM. In contrast, Biddle et al. (2006), based on $\delta^{13}C$ of archaeal cells and intact polar lipids from OPD cores off Peru, concluded that only a small fraction, if any, of the archaeal populations relied on methane as a carbon source. So there seems to be additional processes that perhaps can mask the ^{12}C-enriched compounds from oxidized methane. Part of the answer may lie in the rate of AOM, for example, methane seeps at the sediment-water interface surface have high rates compared with deep sediments with low rates.

Radioactive, ^{14}C-labelled substrates (e.g., $^{14}CH_4$ and $^{14}CO_2$) have been used successfully to elucidate the pathways of anaerobic methanotrophy (e.g., Kosiur and Warford 1979; Iversen and Jørgensen 1985, and more recently by Treude et al. 2003). It is interesting to note that although these labelled experiments showed that methanotrophs could oxidize CH_4, the SRBs could not be shown to produce $^{14}CO_2$ from pure $^{14}CH_4$. Stable, ^{13}C-labelled methane has also been used to track the transfer of $^{13}CH_4$ to $^{13}CO_2$ and ^{13}C-DIC (e.g., Beal et al. 2009; Meulepas et al. 2010). The ^{13}C-DIC formed from $^{13}CH_4$ is a robust measure of AOM because ^{13}C-DIC from other natural, non-^{13}C-enriched sources is only ~1%.

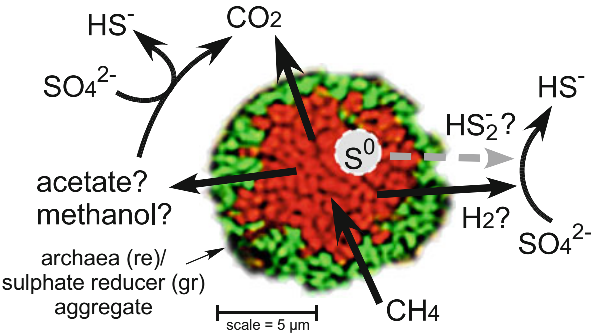
Some of the strongest evidence for the AOM pathways has come from physiologic information using molecular gene sequencing. The archaeal methanotrophs clusters, based on the archaeal 16S rRNA genes, are termed anaerobic methane-oxidizing archaea (ANaerobic MEthanotrophic archaea or ANME, e.g., Hinrichs et al. 1999; Boetius et al. 2000). In every case ANME is found to be highly intolerant of O_2, e.g., restricted to anaerobic sediments. However, ANME are cosmopolitan and found over a range of temperatures, with thermophiles operating up to 95 °C (Schouten et al. 2003; Teske et al. 2002; Wegener et al. 2015) and at pHs ranging from 4 to 11 (Inagaki et al. 2006; Brazelton et al. 2006). Drake et al. (2015) identified AOM in granites from the Laxemar area, Sweden, with extremely ^{13}C-depleted, methane-derived secondary carbonates ($\delta^{13}C_{carb}$ of −125 ‰ VPDB) at ~750 m depth. Carbon-13 depleted carbonates filling fractures in the granitic rocks of the Swedish Stripa pluton were also reported by Clauer et al. (1989) to potentially have an AOM signal, further showing the ubiquitous nature of AOM in the anoxic subsurface.

Currently, three distinct, euryarchaeal, methanotrophic groups or clades, with sub-clusters, have been identified, namely, ANME-1 (subclusters a and b), ANME-2c (subclusters c and d), ANME-2a (subcluster e), and ANME-3 (subcluster f) (Niemann et al. 2006; Knittel and Boetius 2009; Bhattarai et al. 2017). ANME-1 is associated with *Methanomicrobiales* and *Methanosarcinales*, whereas ANME-2 relates to *Methanosarcinales* and ANME-3 to *Methanococcoides* spp. (Timmers et al. 2017). ANME-1 and ANME-2 are both found in the SMTZ, pointing to some association with SRBs. It appears though that ANME-2 support higher AOM rates than ANME-1 (Nauhaus et al. 2005; Michaelis et al. 2002). They also distinguish themselves in that ANME-2 is associated with the diagnostic *sn*-2-hydroxyarchaeol and lipid biomarker crocetane, whereas ANME-1 is dominated by intact tetraethers (GDGT) (Blumenberg et al. 2004; Elvert et al. 2005; Niemann and Elvert 2008).

Visualization of the putative AOM aggregates of some ANME with SRBs has been made on fluorescent-labelled oligonucleotide probes with the fluorescent in situ hybridization (FISH) technique (Fig. 19). These show the syntrophic nature of the organisms (e.g., Boetius et al. 2000; Michaelis et al. 2002; Orphan et al. 2002).

On the other hand, it seems that select ANME archaea, especially certain ANME-1, appear to perform AOM alone, i.e., do not seem need a bacterial partner and thus

Fig. 19 Potential AOM pathways with ANME and SRBs. (Modified from Boetius et al. 2000)



may be further examples of reverse methanogenesis (Knittel et al. 2005; Orphan et al. 2002). Milucka et al. (2012) reported that ANME-2 organisms were able to reduce sulfate during AOM without SRBs (Fig. 19). Their suggestion involves the reduction of sulfate to elemental sulfur and then disulfide by ANME-2 during AOM (Eq. 23). The bisulfide is then disproportionated to sulfide and sulfate by SRBs (Eq. 24). The overall reaction is equivalent to Eq. 19:

$$7CH_4 + 8SO_4^{2-} + 5H^+ \rightarrow 4HS_2^- + 7HCO_3^- + 11H_2O \left(\Delta G^\circ = -26.5\ \text{kJ/mol}\right) \tag{23}$$

$$4HS_2^- + 4H_2O \rightarrow SO_4^{2-} + 7HS^- + 5H^+ \left(\Delta G^\circ = -12.7\ \text{kJ/mol}\right). \tag{24}$$

This AOM process with the intermediate to elemental sulfur could explain SR without or limited SRBs in systems such as the deep subsurface (e.g., Lollar et al. 1993; Kotelnikova 2002). Alternatively, the elemental sulfur in the AOM path could be oxidized by Mn(IV) or Fe(III) to sulfate, as put forth by Lovley and Phillips (1994), e.g., Eq. 25:

$$S^0 + 6Fe^{3+} + 4H_2O \rightarrow SO_4^{2-} + 6Fe^{2+} + 8H^+ \left(\Delta G^\circ - 71\ \text{kJ/mol}\right). \tag{25}$$

Adding to the AOM options, are the possibilities that nitrate, nitrite, iron, and manganese oxides can also act as electron accepters instead of, or in addition to, sulfate during methane oxidation. These are interesting examples of AOM, as their involvement in AOM instead of sulfate appears to violate the basic terminal electron acceptor sequence (Table 2). However, the amounts of these oxidizers in sediments are substantially less than dissolved sulfate, so unless there is recycling of N-, Mn-, and Fe oxides, they can only account for minor amounts of the total methane consumption in sediments. Sulfate is still thought to be the most significant oxidant in AOM.

Beal et al. (2009) proposed AOM with MnO_2 and $Fe(OH)_3$ reduction as shown in Eqs. 26 and 27:

$$CH_4 + 4MnO_2 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O\left(\Delta G^\circ = -556\ \text{kJ/mol}\right). \tag{26}$$

$$CH_4 + 8Fe(OH)_3 + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 21H_2O\left(\Delta G^\circ = -270\ \text{kJ/mol}\right). \tag{27}$$

By adding the manganese and iron minerals birnessite and ferrihydrite, as TEAs, to cultures with ^{13}C-labelled methane, the authors observed enhanced AOM. The archaeal groups believed responsible belong to the Marine Benthic Group D (MBGD), as identified by 16S rRNA and methyl coenzyme M reductase (mcrA) gene diversity.

Beal et al. (2009), Oni and Friedrich (2017), and others make the argument that ANME-1 and ANME-2d can perform AOM independent of SRBs and that the mere proximity to SRBs does not necessarily indicate any direct electron transfer linkages between AOM and SR. Studies by Treude et al. (2014) in the Beaufort Sea sediment showed a coupling of Mn(IV) or Fe(III) reduction to AOM beneath the SMTZ, i.e., also without SR. Similar results were reported by several workers, including Biddle et al. (2006), Crowe et al. (2011), Sivan et al. (2011), Amos et al. (2012), Jorgensen et al. (2012), Wankel et al. (2012), Segarra et al. (2013), Riedinger et al. (2014, 2015), and Egger et al. (2014). Some of these studies are in marine, brackish, and transitional environments, illustrating that the amounts or fluxes of sulfate or SRBs may not always be key components in AOM. Gao et al. (2017) reported that AOM with MnO_2 as TEA ($\Delta G^\circ = -63.8$ kJ/mol e^-) is ~15 times higher than sulfate-driven AOM ($\Delta G^\circ = -4.1$ kJ/mol e^-). For comparison, AOM with $Fe(OH)_3$ ($\Delta G^\circ = -11.1$ kJ/mol e^-) is 2.7 times higher than SR while for nitrite ($\Delta G^\circ = -116.1$ kJ/mol e^-) is 28 times that of SR.

In addition to metals oxides, both nitrate and nitrite have also been implicated as electron acceptors for AOM, in lieu of sulfate. The bacterial denitrifying anaerobic oxidation of methane (DAMO) process is suggested by Raghoebarsing et al. (2006) to proceed according to Eqs. 28 and 29:

$$5CH_4 + 8NO_3^- + 8H^+ \rightarrow 5CO_2 + 4N_2 + 14H_2O \left(\Delta G^\circ = -765\,\text{kJ/mol}\right), \quad (28)$$

$$3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O \left(\Delta G^\circ = -928\,\text{kJ/mol}\right), \quad (29)$$

and by Islas-Lima et al. (2004) as Eq. 30:

$$5CH_4 + 8NO_3^- \rightarrow 5CO_2 + 4N_2 + 8OH^- + 6H_2O \left(\Delta G^\circ = -960\,\text{kJ mol}^{-1}\right) \quad (30)$$

Raghoebarsing et al. (2006), using 16S rRNA gene sequence analyses, ^{13}C-labelled methane, and ^{15}N-labelled nitrate, documented that AOM was coupled to nitrite and/or nitrate reduction via an intra-aerobic methane oxidation pathway similar to the AOM-SR consortium. Their freshwater experiments ensured that oxygen was not involved, and hence AOM was performed only with denitrification. They found that the ANME-2 methanotrophic archaea was the dominant cluster in concert with the denitrifying bacteria "*Candidatus* Methylomirabilis oxyfera" (*M. oxyfera*). Similar AOM denitrification results with "*Candidatus* Methanoperedens nitroreducens" (ANME-2d) were found by Haroon et al. (2013). To complicate matters, Ettwig et al. (2008) concluded from their culture experiments with denitrifying bacteria that archaea are not required for AOM with nitrite as electron acceptor. Further, Ettwig et al. (2010) also used ^{15}N-labelled nitrite and genomics with ^{18}O-labelled water to show that *M. oxyfera* could reduce nitrite to nitric oxide and then using the *in situ* produced oxygen from the disproportionation of nitric oxide for methane oxidation.

Hu et al. (2015) described an analogous 3-reaction AOM process that involved the combination of anaerobic ammonium oxidation (anammox) with denitrifying

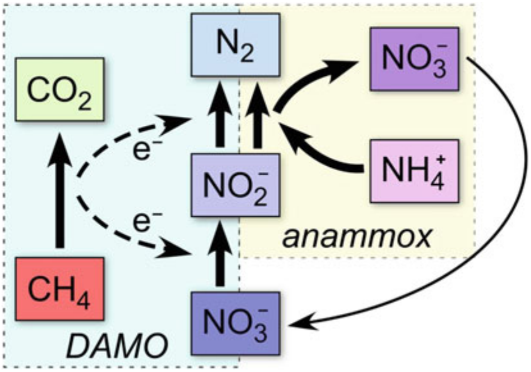


Fig. 20 Potential AOM pathways with DAMO and anammox. (After Hu et al. 2015)

anaerobic methane oxidation DAMO (Fig. 20). Ironically, until the work on anammox by Van de Graaf et al. (1990) and Mulder et al. (1995), anaerobic ammonium oxidation, like AOM, was thought not to occur in nature. Now, it is considered to contribute critically to the ~50% of the marine N_2 production (Strous and Jetten 2004). Nitrite is reduced by anammox and then AOM with nitrite and nitrate reduction by DAMO (Eqs. 31, 32, and 33, respectively):

$$NO_2^- + 0.76NH_4^+ \rightarrow 0.77N_2 + 0.2NO_3^-, \tag{31}$$

$$0.38CH_4 + NO_2^- + H^+ \rightarrow 0.38CO_2 \rightarrow 0.5N_2 + 1.25H_2O\,, \tag{32}$$

$$0.25CH_4 + NO_3^- \rightarrow 0.25CO_2 + NO_2^- + 0.5H_2O\,. \tag{33}$$

Initially it seemed that DAMO bacteria preferred nitrite and could utilize nitrite alone in AOM, whereas AOM decreased with nitrate (Ettwig et al. 2008). Ding et al. (2017) showed the possible decoupling of DAMO archaea from DAMO bacteria. Ultimately, DAMO culture growth depends on the mix of nitrogen utilized. He et al. (2015) required 600 days to enrich DAMO bacteria when only using nitrite, whereas a mixture of nitrite and nitrate was somewhat faster (≥480 days, Raghoebarsing et al. 2006). In comparison, the combination of nitrate and ammonium by Haroon et al. (2013) shortened the culturing time to 350 days. Subsequently, Fu et al. (2017) found that using nitrate, nitrite, and ammonium together could shorten growth times to ~80 days, approximately the same as AOM with SRBs (e.g., Knittel and Boetius 2009). Thus even though DAMO proceeds with the different N sources individually, it appears that combinations enhance growth and AOM.

ANME-2 archaea were shown by Scheller et al. (2016) to use external electron acceptors, such as humic acids and humic acid analogues, e.g., anthraquinone-2,6-disulfonic acid (AQDS) for AOM. These archaea are proposed to conduct AOM without syntrophic interactions, i.e., could directly transfer electrons to extracellular Fe(III) or Mn(IV) minerals without the need for SRBs. These AOM reactions with quinone-containing humic acids could be represented by Eq. 34 (Wang et al. 2017):

$$CH_4 + 4AQDS + 3H_2O \rightarrow HCO_3^- + H^+ + A4H_2QDS. \qquad (34)$$

Wang et al. (2017) calculated that AQDS reduction coupled to ammonia oxidation was energetically viable, but not necessarily a good reaction “surrogate” for humic substances coupled with AOM. Therefore, the AOM pathway with AQDS at this point is uncertain.

The above discussion mostly pertains to marine systems replete, at least initially, in dissolved sulfate (~29 mM), supporting AOM-SR. In freshwater environments, such as oligotrophic lakes, dissolved sulfate is typically 10 to ~400 μM (Holmer and Storkholm 2001), which is thought to be too low for SR processes to be thermodynamically favorable (Smemo and Yavitt 2011). As a result of the low sulfate, it was traditionally thought that AOM, i.e., AOM-SR, was limited. There are lakes with higher sulfate, e.g., meso- and eutrophic lakes, that can have >500 μM $SO_4{}^{2-}$. Lake Cadagno, for example, has 2 mM $SO_4{}^{2-}$, and AOM-SR is suspected, although AOM-Mn/Fe could not be excluded (Schubert et al. 2011). Sulfate can be elevated in some lakes due to intense evaporation, saltwater incursions, wastewater, or drainage from mining operations, supporting AOM-SR (Martinez-Cruz et al. 2017).

Under low sulfate conditions in freshwaters, methanotrophy generally proceeds using O_2 and sometimes using $NO_2{}^-$, $NO_3{}^-$, Mn^{4+}, and Fe^{3+} as TEAs. In lakes with low $[SO_4{}^{2-}]$, Mn(IV), and Fe(III), reductions coupled to AOM are favorable reactions and are known to occur (Nordi et al. 2013; Sivan et al. 2011) and where aerobic methanotrophs are likely involved (Bar-Or et al. 2017; Martinez-Cruz et al. 2017). There are also observations that organic acid-mediated AOM can be an important pathway in lakes (Reed et al. 2017).

Clearly, there are multiple, possible pathways for AOM that appear to function with and without the need for sulfate or SRBs and with and without the need for direct electron transfer and utilizing various redox couples. This leads to AOM processes and sequences far more complicated than the early juxtaposition of sulfate depletion and methane accumulation zones in sediment profiles observed by geochemists in the 1970s.

7 Atmospheric Methane

Much of the current research on methane pertains to its effects in the atmosphere and on climate as, after carbon dioxide, methane is the second most important anthropogenic greenhouse gas (GHG).

The methane residence time of ~9–11 years, a perturbation lifetime of ~12.4 year, and radiative efficiency of ~3.63×10^{-4} Wm^{-2} ppb^{-1} (i.e., radiative forcing per molecule, Myhre et al. 2013) together with the increase in atmospheric methane since the preindustrial era (1750) of ~1,200 ppb contribute an additional 0.48 Wm^{-2} of direct radiative forcing (CH_4, 0.33 Wm^{-2} + OH feedback, 0.11 Wm^{-2}, Schimel et al. 1996). Furthermore, the additional amount of oxidized atmospheric methane leads to an increase in tropospheric O_3 and stratospheric H_2O that contribute an additional 0.11 Wm^{-2} and 0.02 Wm^{-2}, respectively (Prather et al. 1995; Hansen and

Sato 2001; Ramaswamy et al. 2001), for a total radiative forcing of 0.57 Wm^{-2} (Ramaswamy et al. 2019). The total methane radiative forcing is ~21% of the long-lived GHG budget of 2.77 Wm^{-2}. This does not account for the radiative forcing of CO_2 derived from CH_4 oxidation.

The magnitudes of the various sources and sink controlling the atmospheric methane burden remain incompletely constrained. In addition to individual flux estimates, the combination of methane stable carbon and hydrogen isotope ratios of the individual major sources can help produce a bottom-up budget for the measured atmospheric values, as shown in Figs. 3 and 4 (Whiticar and Schaefer 2007). These two plots also show the respective offsets between the $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ weighted inputs and the actual atmospheric isotope values. The isotope offsets are the result of the isotope effects associated with the various removal processes of methane from the troposphere. By weighting the magnitude of the different sink fluxes and their respective isotope fractionations, we can estimate the overall enrichment factors for carbon, ε_C ~7.4 ‰, and hydrogen, ε_D ~200 ‰ (Whiticar and Schaefer 2007). The averaged values of individual methane carbon and hydrogen signatures ($\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$) of the major emission sources with their respective flux strengths (tg/year) can be illustrated (Fig. 22). It must be noted that the columns in Fig. 22 only illustrate the average values for the different sources and do not show the range, which is sometimes large, in methane C- and H-isotope values for any particular source. Also the groupings of source types in the budgets differ between authors and papers. The weighted input average of the sources in Fig. 22 for $\delta^{13}C\text{-}CH_4$ is −54.2 ‰ and for $\delta^{2}H\text{-}CH_4$ is −295 ‰, compared with the present-day tropospheric value of $\delta^{13}C\text{-}CH_4$ of −47 ‰ and − 86 ‰, shifted due to the isotope effects of the sinks. Refinements of the methane flux source and sink terms and their representative $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ values continue to be made (e.g, Sherwood et al. 2017), which will improve our bottom-up flux source estimations and signatures. It should also be noted that there are latitudinal changes in tropospheric methane mixing ratio, $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$. For example, Umezawa et al. (2012) reported North-South Pacific Ocean methane transects for the time period of 2007–2009 from 33°N to 39°S. They found for the upper troposphere a continual shift in methane mixing ratio, $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ from ~1810 ppb, −47 ‰, and − 87 ‰ in the north to ~1770 ppb, −46.9 ‰, and − 85 ‰ in the south. Similarly, in the lower troposphere, they found a continual shift in methane mixing ratio, $\delta^{13}C\text{-}CH_4$ and $\delta^{2}H\text{-}CH_4$ from ~1840 ppb, −47 ‰, and − 93 ‰ in the north to ~1750, −46.8 ‰, and − 82 ‰ in the south. Considering the relatively rapid tropospheric mixing time of ~1 year, these interhemispheric gradients can help localize changes in fluxes.

In addition to stable isotopes, carbon-14 measurements on methane (Eisma et al. 1994; Quay et al. 1999; Petrenko et al. 2016) and ethane measurements (Helmig et al. 2016; Dalsoren et al. 2018) can also be particularly useful to indicate the inputs of fossil carbon methane (thermogenic and most abiotic methane) to the atmosphere (Wahlen et al. 1989). Based on the accepted 5,730 year half-life of ^{14}C, methane from sources > ~10^5 year, e.g., geologic sources, have diminishingly small amounts of ^{14}C and can be considered to have only “dead” carbon. In contrast, most biologic methane is derived from recent carbon sources. Thus the abundance of $^{14}CH_4$ in the atmosphere further constrains the input flux of older sources. Owing to the recent increase in unconventional natural gas production, e.g., shale gas, there are concerns about fugitive methane emissions from wells and gas processing/transmission infrastructures to the atmosphere. The amounts and isotope signatures of these gas emissions is contraversial and emphasizes the further need to refine methane sources and sinks on the underconstrained atmospheric methane budgets (Whiticar and Schaefer 2007; Schaefer et al. 2016; Schwietzke et al. 2016; Howarth 2019; Milkov et al. 2020).

As of January 2020, the mean monthly global tropospheric methane reached a high of 1873.5 ± 2 ppb (esrl.noaa.gov/gmd/ccgg/trends_ch4/), which is a ~260% increase over the preindustrial Holocene mixing ratio of ~722 ppb (WMO 2018). Since 1983, tropospheric methane has increased from 1625 ppb at rates of 2–14 ppb/year (annually 0.1–0.9%), except for a short "stabilization period" or hiatus in the rise of tropospheric methane from years 2000 to 2007 (Fig. 21, Dlugokencky et al. 1994; Dlugokencky 2019). Initially, Dlugokencky et al. (2003) offered that instead of a pause, the hiatus was simply a new steady-state condition, whereas others mentioned the curtailment of emissions from other sourses, including coal, oil, and gas operations, anaerobic waste treatment plants, landfills, agricultural practices, etc. However, as tropospheric methane has been increasing again since 2007, Nisbet et al. 2014, Turner et al. (2019) and ohers have countered that the hiatus was only an anomalous period. This appears to be true, now 13 years post-2007, there is an

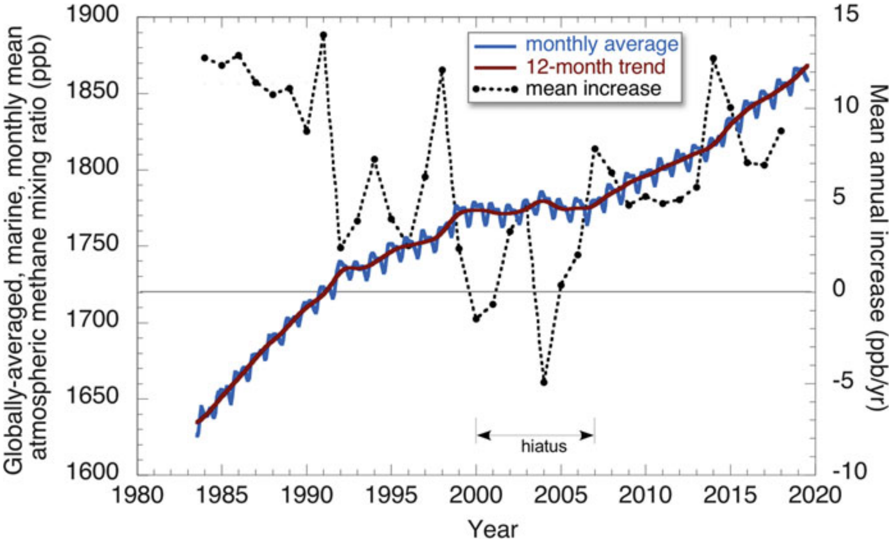


Fig. 21 Time series of NOAA/ESRL global, marine, atmospheric methane data for (1) monthly averaged mixing ratios (ppb or nmolmol^{-1}, dry air mole fraction), (2) 12-month running mean of monthly averaged mixing ratios, and (3) mean annual increase (ppb/year). The hiatus is the methane stabilization period of 2000 to 2007 (Dlugokencky et al. 1994; Dlugokencky 2019)

continual increase in methane at a growth rate of ~ 9 ppb/year, similar to pre-2000 trend.

Despite the brief pause, the NOAA/ESRL database shows a long-term increase in tropospheric methane from 1625 ppb since 1983, at an overall average annual rate of 6.4 ppb/year. It is interesting to note that the rate of increase in tropospheric methane before the hiatus (1983–2000) and after the hiatus (2007–2019) is similar (average is 8.4 ppb/year vs. 7.1 ppb/year), including maximum growth rates of 14.02 (1991) and 12.74 (2014) (Fig. 21, Dlugokencky 2019). During the hiatus the increase in tropospheric methane was only 0.48 ppb/year.

Several theories are proposed to explain the hiatus from 2000 to 2007 (e.g., Pison et al. 2013; Turner et al. 2019; Saunois et al. 2019), but there is no consensus yet. Bousquet et al. (2006) suggested that a decrease in anthropogenic emissions, such as fossil emissions in the Northern Hemisphere, caused the hiatus and that interannual variability is due to wetland and fire emissions emissions. In contrast, Kai et al. (2011) with the combination of atmospheric CH_4 mixing ratios and $\delta^{13}C$-CH_4 state that the hiatus is consistent with long-term reductions in agricultural emissions or other microbial source(s) within the Northern Hemisphere, such as rice agriculture. They claim that the $\delta^{13}C$-CH_4 values preclude reduced fossil fuel emissions as the primary cause of the slow-down. This is juxtaposed with claims of a drop in fossil fuel emissions during that period by Schaefer et al. (2016) using $\delta^{13}C$-CH_4; by Aydin et al. (2011) and Simpson et al. (2012) using the decrease atmospheric ethane concentrations; and by Chen and Prinn (2006) using models. A decrease in biomass burning based on carbon monoxide data has also been suggested as the cause of the hiatus (Worden et al. 2017).

Kai et al. (2011) commented that the relatively constant atmospheric δ^2H-CH_4 eliminates a change in the hydroxyl radical (OH•), the largest methane sink, as the cause for the hiatus. This position contrasts with that of Rigby et al. (2008) who postulated that decreases in OH• concentrations were responsible. Rice et al. (2016), Turner et al. (2017), and McNorton et al. (2018) also supported changes to the hydroxyl sink.

The cause of the subsequent rise in atmospheric methane mixing ratio since 2007 (Fig. 21, Saunois et al. 2019) remains uncertain, with mismatches between top-down approaches based on atmospheric inversion models compared with bottom-up models parameterized with individual source and sink types. Increasing fossil fuel emissions and lower latitude wetlands (e.g., Northern Eurasia) and agriculture are postulated sources (Kirschke et al. 2013; Pison et al. 2013; McNorton et al. 2018). Increasing emissions of atmospheric ethane and propane support renewed emissions from oil and natural gas production (Franco et al. 2016; Hausmann et al. 2016; Helmig et al. 2016). Poulter et al. (2017) staddle this by downplaying global wetlands and suggesting a combination of fossil fuels and agriculture increases and a decrease in the photochemical sink as the cause. Nisbet et al. (2019) also suggest a possible decrease in the atmospheric sink but also noted the poorly constrained options of changes in the contributions of microbial, thermogenic, and pyrogenic methane.

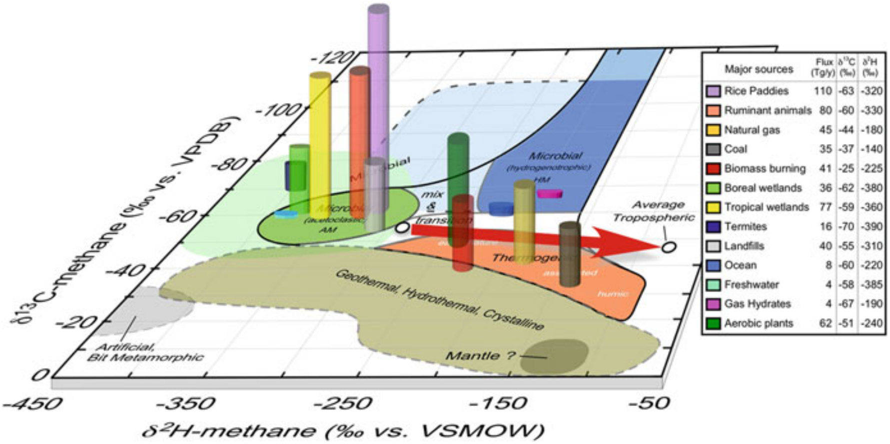


Fig. 22 3D combination CD plot of δ^{13}C-CH$_4$ vs. δ^2H-CH$_4$ showing the averaged values for the major methane emission source types and the magnitude (bar height) of their respective atmospheric fluxes (Tg/year). Note that the true range in isotope values for the individual sources is not depicted. The integrated input δ^{13}C-CH$_4$ and δ^2H-CH$_4$ signal to the troposphere from the sources and the respective C- and H-isotope fractionationations by the sinks are also indicated. (Based on Whiticar and Schaefer 2007)

However, there is increasing evidence, including methane carbon isotopes and interhemispheric gradients, that high-latitude sources, such as permafrost, thermokarst lakes, wetlands, and potentially shallow gas hydrates, could be responsible (e.g., Walter et al. 2006; Dlugokencky et al. 2011; Tan and Zhuang 2015; Dimdore-Miles et al. 2018). Possible reductions in the global methane sinks, not only increases in source emissions, must also be considered in the overall budget, i.e., decreases in (1) tropospheric/stratospheric hydroxyl radical abstraction reactions (Saueressig et al. 2001; Rice et al. 2003), (2) reactions of methane with chlorine in the marine boundary layer (Allan et al. 2005), and (3) methanotrophic uptake in soils (Ridgwell et al. 1999).

The lack of concensous explaining the renewed increase in atmospheric methane is unfortunate. It is important to identify the relevant shifts in sources and sinks to determine if and how we can effect changes to reduce emmisions from a climate change perspective (Fig. 22).

8 Summary

Methane is ubiquitous on Earth and contributes importantly to our energy economies, climate forcing, and carbon budgets. Under the present oxidizing atmosphere, methane cycles with carbon dioxide through a suite of biologic and abiotic pathways. Figure 23 shows a larger-scale, summary view of the methane cycle. Contributions to the methane pool come from the variety of methanogenic pathways, i.e., hydrogenotrophic (HM), acetoclastic (AM), and methylotrophic methanogenesis.

The catagenic formation of thermogenic methane from mature kerogens is also a major component. Abiotic sources, including methanation, radiolysis, and magmatic and mantle origins, also contribute unknown amounts to the methane budget, albeit substantially less than the biologic sources. Microbially mediated aerobic (AeOM) and anaerobic (AOM) methane oxidation (Fig. 23) are important biofilters that consume the majority of methane produced in sediments, soils, and lakes. Photochemical and abiotic oxidation of methane, e.g., fires, also reduce methane in the atmosphere. We are slowly establishing more reliable estimates of methane formation and oxidation rates, sizes of major methane pools (hydrates, hydrocarbon reservoirs, sediments/soils), and the magnitude of methane fluxes. Although the

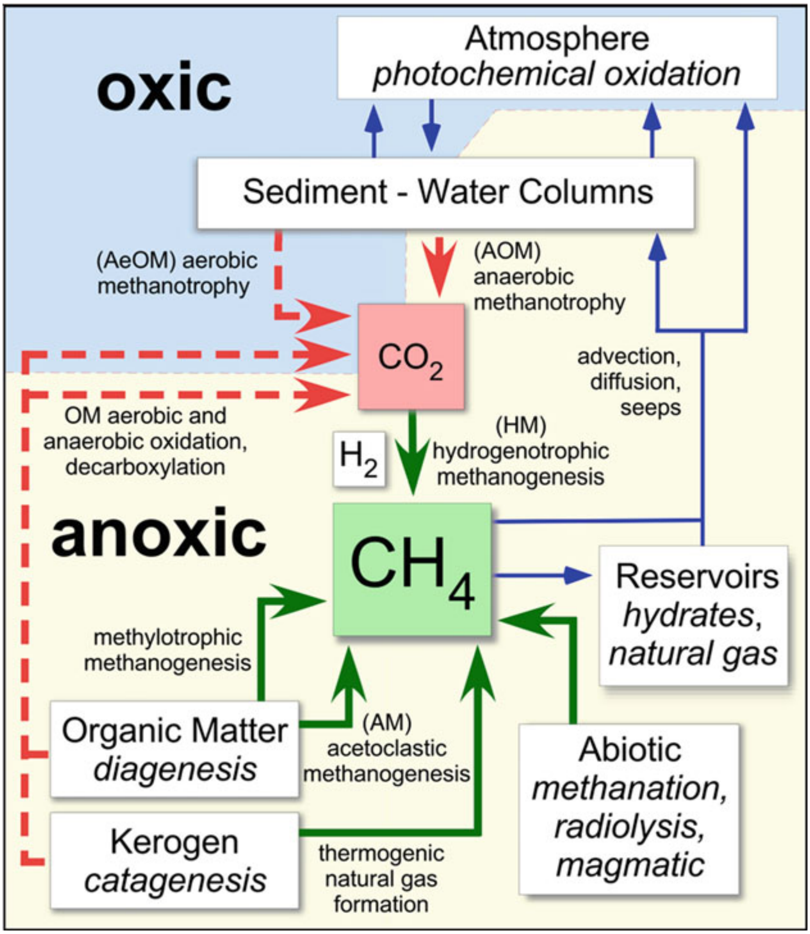


Fig. 23 Summary schematic of biotic and abiotic processes of methane formation and oxidation. The blue-shaded section is oxic, and the yellow shaded is anoxic. Methane formation processes are shown as thicker, solid, green arrow lines, while oxidation processes are dashed, red arrow lines. Transport mechanisms are shown as thin, blue arrow lines

constraints on these estimates are improving, experience demonstrates that our knowledge on this topic remains incomplete and that surprises are still possible.

Looking forward, one of the most critical aspects regarding methane biogeochemistry that needs more and immediate attention is the ongoing risk that methane poses with respect to climate change. The potential for large changes in the existing methane budget, e.g., due to shelf hydrate destabilization or permafrost sources, land-use changes, and natural gas production, requires careful attention to understanding of the mechanisms and magnitudes of the processes controlling the methane sources and sinks.

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