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Geo-Biological Coupling of Authigenic Carbonate Formation and Autotrophic Faunal Colonization at Deep-Sea Methane Seeps I: Geo-Biological Settings

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Additional information is available at the end of the chapter

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Abstract

Methane (CH₄) in sub-seafloor sediment is generated both biologically and non-biologically from organic and inorganic sources. A major part of the sub-seafloor methane is oxidized before leakage via “anaerobic oxidation of methane” (AOM) in the subsurface. The AOM-survivor methane, which is relatively minor part of the subsurface methane, leaches to the overlying water column and is eventually subject to thorough anaerobic and aerobic oxidation in the water column. The AOM with sulfate results in the generation of carbon dioxide and sulfide; the former (CO₂) is incorporated into authigenic carbonate and autotrophic biomass, and the autotrophy is energetically driven by oxidation of the latter (H₂S). These processes are typically observed at focused sites that are generally known as “methane seeps” or hydrocarbon seeps, or occasionally called as cold seeps in comparison with hydrothermal vents. Methane seeps are typically formed in passive and active continental margins, occasionally with unique features such as exposed methane hydrates, mud volcanoes, asphalt volcanoes, salt diapirs, and brine pools. Accordingly, authigenic carbonates and unique biological communities are shaped at respective methane seeps. This chapter overviews geological and biological setting for the formation of methane seeps associated with unique landscapes of carbonates and biomes.

Keywords: hydrocarbon seep, cold seep, gas hydrate, methanogenesis, chemoautotrophy, thiotrophy, methanotrophy, anaerobic oxidation of methane (AOM), sulfate–methane transition zone (SMTZ)

1. Introduction

In the view of planetary carbon cycling, the carbon-based terrestrial “life” can be seen as an intermediate between the oxidized end (carbon dioxide, CO₂) and the reduced end (methane,

CH_4), as depicted as “organics” (simplistically expressed as CH_2O) in **Figure 1**. The Earth’s carbon cycling is largely driven by about 120,000 terawatts (TW) of the Solar radiation reaching the Earth’s surface,¹ and about 47 TW [1] from the Earth’s internal heat, which is due equally to the decay of radioactive isotopes such as uranium-238 (^{238}U), thorium-232 (^{232}Th), and potassium-40 (^{40}K) in crust and mantle [2] and to the residual heat from planetary accretion during proto-Earth formation [3].

The life is not only intermediate but also transient, and the life is otherwise dissipated, maintained by continuous supplies of oxidizing and reducing powers, simplistically represented by oxygen O and hydrogen H, respectively, after “split of water” [4]. The surface of the red planet, or red rust planet, Mars, is oxidized by Solar ultraviolet (UV) radiation due to lack of the UV-absorbing ozone layer in its thin atmosphere, resulting in the predominance (>95% v/v) of CO_2 in the Martian atmosphere [5]. The gas giant Jupiter’s

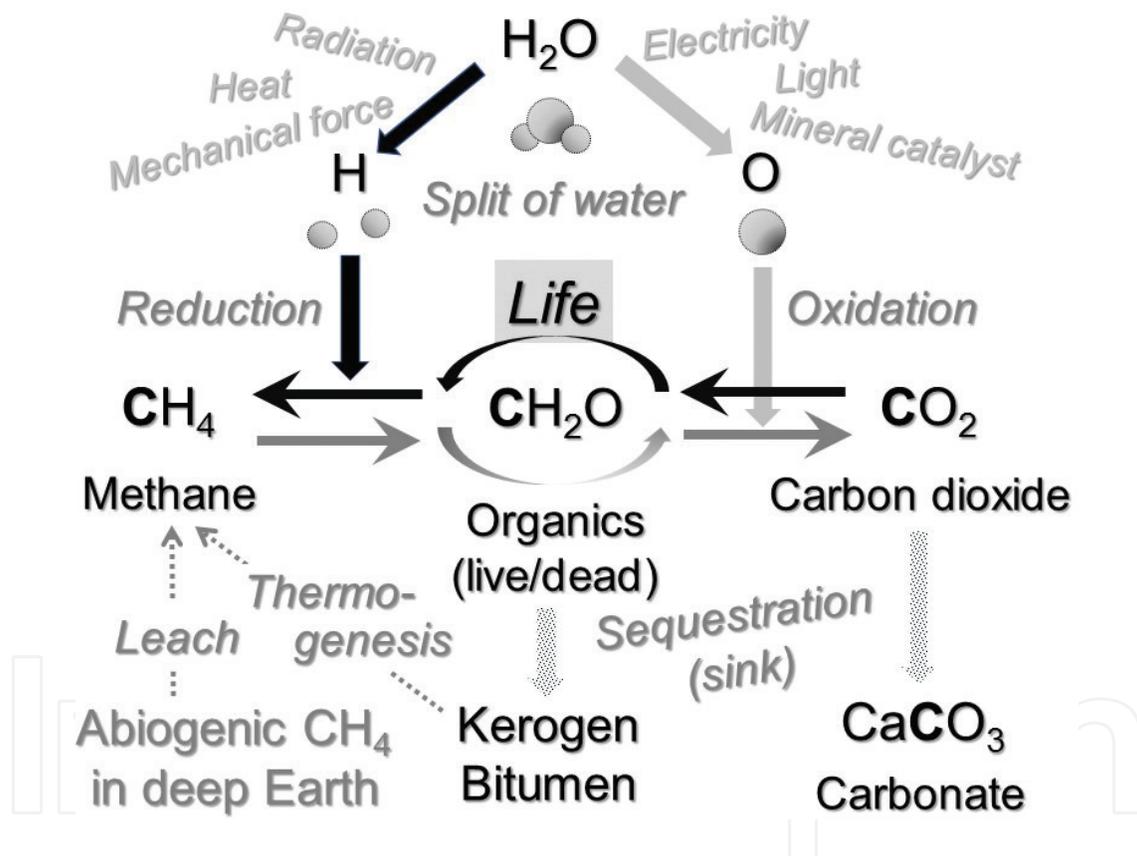


Figure 1. Schematized general view of carbon dynamics with reference to “life” and life-supporting “split of water” as the source of redox potential. Life is interpreted as the intermediate carbon compounds between the reduced end (CH_4) and oxidized end (CO_2) of the carbon cycle, and the cycle is driven by the supply of redox power from the split of water in a variety of manners.

¹The canonical Solar constant ($1365.4 \pm 1.3 \text{ W m}^{-2}$) established in the 1990s or the recent Solar minimum value ($1360.8 \pm 0.5 \text{ W m}^{-2}$) [85], multiplied by the Earth’s cross-sectional area ($1.274 \times 10^{14} \text{ m}^2$) and the Earth’s albedo (0.297 ± 0.005) [86], yields about $1.2 \times 10^{17} \text{ W}$ (120,000 TW) of the Solar energy (light and heat) reaching the Earth’s surface.

atmosphere consists of 89.8% H₂, 10.2% He, 0.3% CH₄, and others (CO₂ not detected) with some uncertainties [6]. By contrast, the Earth's atmosphere contains CO₂ (400 ppm) and CH₄ (1.7 ppm) simultaneously [7], which is regarded as a biomarker combination of a habitable planet [8]. In this context, the detection of CH₄ (mean 0.69 ppb) in the Martian atmosphere and its variability (up to 7.2 ppb) [9] was exciting enough to ignite a search-for-life on Mars. Then, the emerging problem is where and how methane is supplied on the fully oxidized Mars [10] as well as on the Earth whose surface is also oxidized by photosynthetically generated O₂. Deep-sea methane seepage is one of the methane sources to the Earth's surface, although its significance on a long time scale is yet to be fully understood.

While methane cycling occurs within the range of the global carbon cycling in atmosphere, hydrosphere (manly ocean), lithosphere (defined as crust and mantle in this chapter), and biosphere, it is also indirectly connected to the carbon sequestration or sink into lithosphere (**Figure 1**). That is, part of methane is to be sequestered for long term, probably more than millennium long, separation from biogeochemical cycling, and such indirect sequestration occurs via the formation of authigenic carbonate at methane seeps commonly, typically, and unequivocally.

Carbonate in lithosphere represents a vast majority of the Earth's carbon pool (**Figure 2**). Most of the carbonate was precipitated in "early ocean," resulting in sequestration or removal of abundant CO₂ from "early atmosphere" that was likely similar to the modern Venus atmosphere consisting of about 8.9 MPa, or 89 bar, CO₂ (96.5% of total 9.2 MPa) [11], compared

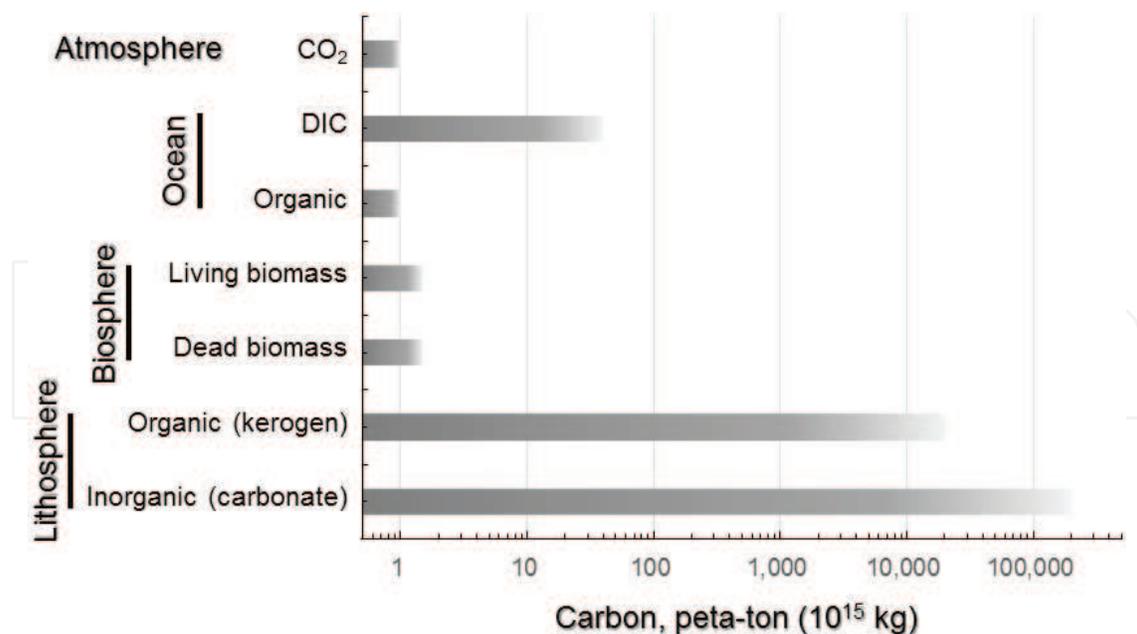


Figure 2. Global carbon pools in various forms. Most of global carbon has already been sequestered in the lithospheric kerogen (organic) and carbonate (inorganic). Methane seeps still contribute to the sequestration via authigenic carbonate formation. Abbreviation: dissolved inorganic carbon (DIC).

with the modern Earth atmosphere of about 40 Pa CO_2 (0.04% of total 0.1 MPa) [12]. The mass sequestration of CO_2 during “early Earth” era is currently recognized as the vast estimate of sedimentary carbonate in the lithosphere. Modern carbonate formation at methane seeps corresponds only to a tiny fraction of the already-sequestered carbonate in the past; however, it is an ongoing process, and there should be much more seeps yet to be found. That is, the more seeps are found, the more importance will be taken into account.

This chapter provides an overview of methane seeps in the deep sea that harbor and sustain unique biological communities depending not only on small amounts of photosynthetic primary production (photoautotrophy) transported from the shallow euphotic zone to the deep aphotic zone but mainly on *in situ* chemosynthetic primary production (chemoautotrophy). The latter production utilizes methane directly or exploits methane-derived biogeochemical products such as sulfide (H_2S , HS^-) via “anaerobic oxidation of methane” (AOM). As AOM produces CO_2 and bicarbonate (HCO_3^-), it facilitates the formation of authigenic carbonate, which should be connected to the colonization of chemoautotrophic organisms. The carbonate formation and faunal colonization are so connected that they often form “conglomerates” during their concomitant growths [13]. Geological and biological settings for the geo-bio connection are exemplified.

2. Geo-biological backgrounds of methane seeps

Methane seeps are also referred as cold seeps and hydrocarbon seeps. Seeping fluids are not literally cold; the fluids are geothermally warmed and often slightly warmer than ambient waters. They are called “cold” only to indicate that the seep fluids are relatively colder than the hydrothermal vent fluids that may reach $>300^\circ\text{C}$. Seeping fluids sometimes contain hydrocarbons other than methane, for example, ethane, propane, and even petroleum. However, methane occupies a vast majority of the leaked hydrocarbon components, provides a material source for authigenic carbonate formation, and sustains exotic biological communities like oases in the deep sea that depend on methane and methane-derived productions. For these reasons, this chapter uses the term “methane seep” prior to others.

2.1. Origin and generation of methane

In relation to human life, methane is a colorless and odorless gas and is lighter than air. It is nontoxic but may be suffocative in confined rooms. Methane is also an important greenhouse gas but is naturally generated and emitted; its emission is not intentionally controllable by human efforts, which is different from the case of CO_2 .

From a cosmological viewpoint, methane is regarded as a primordial molecule, as it occurs in the interstellar medium despite its low abundance, that is, 1–4% of carbon monoxide (CO) abundance [14]. Viewed from astrochemistry, methane was generated primordially and is still being generated foremost in interstellar molecular clouds. This astrochemical methane, in turn, can be seen as a part of original matter for the formation of proto-Solar system disk and thus of proto-Earth. Earth was formed through accretion of planetesimals [3], a large amount of methane would have been brought into the Earth during the accretion (and is still being

exogenously delivered by meteorites and possibly by comets) and may still remain in Earth's interior as primordial methane and other hydrocarbons [15].

Besides the residual of primordial methane, methane is newly generated and regenerated by various processes through the carbon cycling of the Earth. Both biological (biotic, biogenic) and non-biological (abiotic, abiogenic) processes are involved in the generation of methane, also known as methanogenesis. In addition, both organic and inorganic matters serve as the starting materials for methanogenesis.

Therefore, methanogenesis pathways are roughly sorted into four categories: biotic of organic origin (fermentation), biotic of inorganic origin (CO_2 respiration), abiotic of organic origin (thermogenesis), and abiotic of inorganic origin (geothermal version of the Fischer-Tropsch process or Sabatier reaction) due to geothermalism and magmatism in crystalline rocks, as schematically outlined in **Figure 3** that employs the stable isotope signatures known as $\delta^{13}\text{C}$ and $\delta^2\text{H}$ (δD) of CH_4 as described later (adapted from [16] with δ values for atmospheric CH_4 from [17]). Generally, δ values are indicative of origins or sources, while the differences in the δ values, also known as " Δ " values, may reflect pathways/processes of methane generation/consumption or oxidation [18, 19].

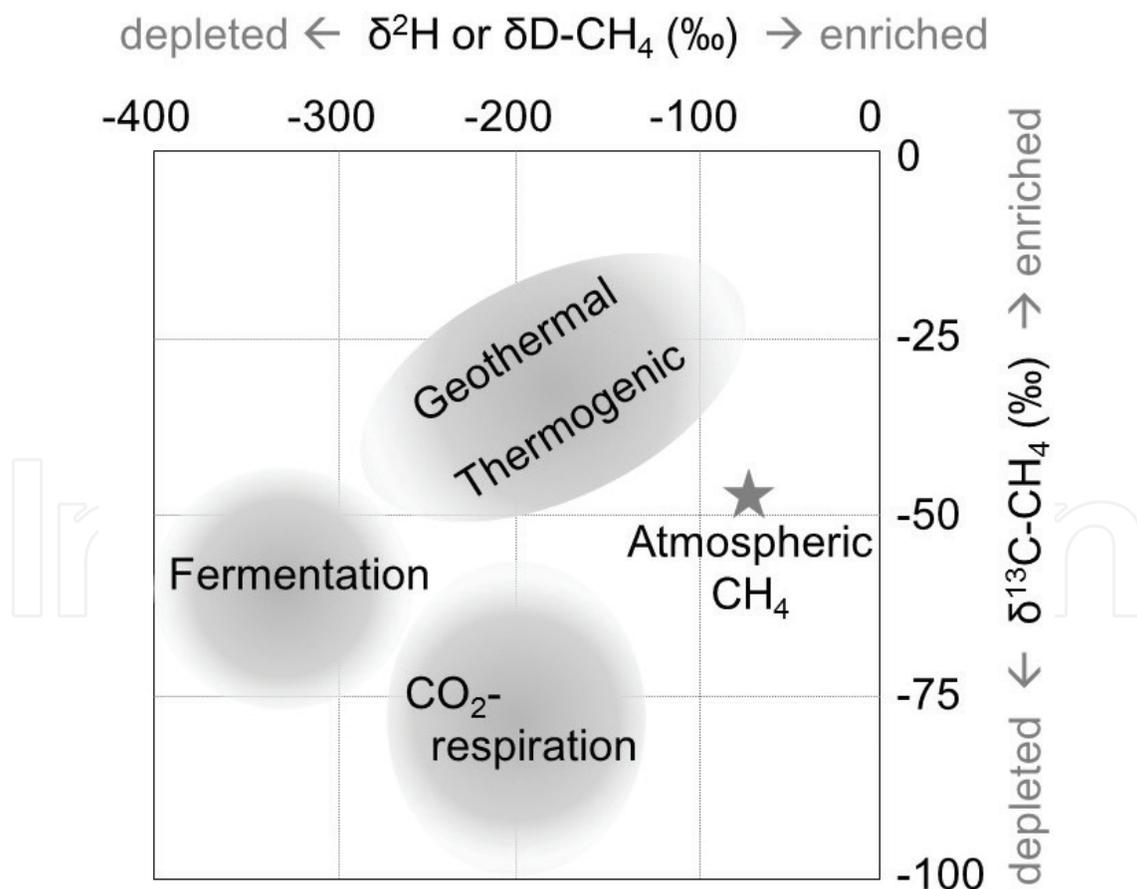


Figure 3. $\delta^2\text{H}$ (δD)- $\delta^{13}\text{C}$ diagram of methane of different origins. Biogenic methane from organic matter (by fermentation) and from inorganic CO_2 (by CO_2 -respiration) is distinguishable from abiogenic methane from organic matter (by thermogenesis) and from CO_2 (by geothermal Sabatier reaction).

The origins and generation pathways, as well as consumption (oxidation) and conversion pathways, of methane stated earlier are summarized in **Figure 4**. In addition, the sources of H_2 for both biogenic and abiogenic CO_2 reduction (methanogenesis of inorganic origin) can be both organic and inorganic; the former (organic-derived H_2) can be from fermentative and/or thermogenic degradation of organic matter, while the latter could be of magmatic origin as well as “split of water.” Those H_2 sources and generation mechanisms are listed in **Table 1**, including “mechanical” split-of-water along geological (lithological) faults [20], as well as briefly referred in **Figure 1**.

2.1.1. Biogenic methane of organic origin: fermentation

Methane in common originates biologically, especially microbiologically, from anaerobic degradation, or fermentation, of organic matter, during which oxygen (O) is removed

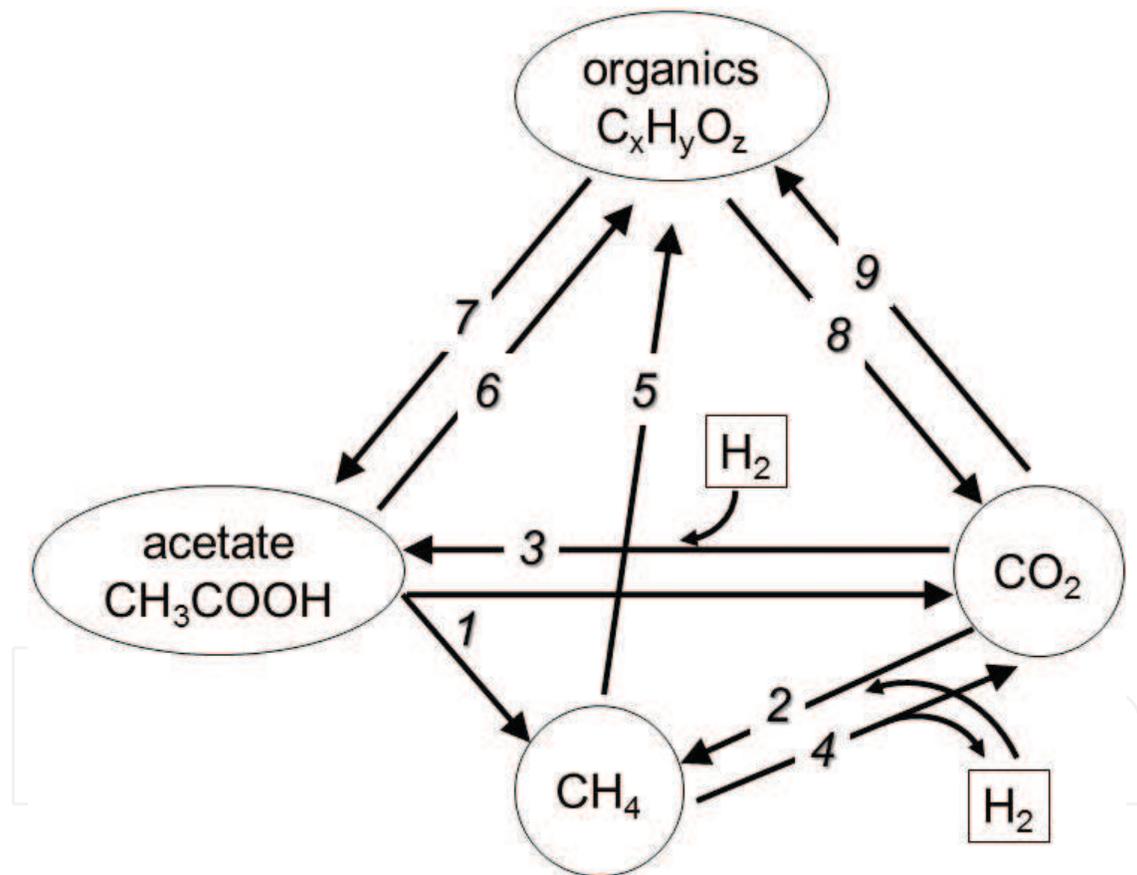


Figure 4. Schematized geochemical dynamics of methane. Origins and fates of methane are depicted with reference to key compounds (acetate and other organic matters as well as CO_2) and key paths including addition and removal of H_2 . Aerobic oxidations and inputs/outputs of water are not shown. Acetate is a source of methane via syntrophic acetoclastic methanogenesis (path 1) and serves as a reductant for anaerobic sulfate reduction (as part of path 8). H_2 used for Sabatier-type methanogenesis (path 2) and autotrophic acetogenesis (path 3) is of both biotic and abiogenic origins. Anaerobic oxidation of methane, or AOM, occurs via reverse methanogenesis (path 4) and with nitrate (as part of path 8). Methane and acetate are used for biosynthesis of organics (paths 5 and 6), and organics are degraded via acetate-fermentation (path 7) and anaerobic oxidations with sulfate, nitrate, Fe^{3+} , etc. (path 8). Organics may be produced via chemoautotrophy (path 9).

Biogenic	Split-of-water by light (via light reaction of photosynthesis)
	Fermentation (including syntrophic H ₂ generation)
	Reverse methanogenesis (CH ₄ + H ₂ O → CO ₂ + H ₂)
Abiogenic	Thermogenic supply (via diagenesis of sedimentary organic matter)
	Magmatic supply (from crystalline rocks of crust and mantle)
	Lithologic split-of-water (e.g., serpentinization)
	Split-of-water by radiation
	Split-of-water by light (ultraviolet)
	Mechanical split-of-water (e.g., fault-activated H ₂ generation [20])

Split-of-water (H₂O → H₂ + O₂) serves as the major source of H₂ in the Earth's biosphere. Split-of-water by electricity is not included, as it mostly occurs artificially. H₂ generation via reverse methanogenesis during anaerobic oxidation of methane (AOM) is involved. Abiogenic magmatic H₂ may include primordial H₂ and H₂ from split-of-water by heat, as well as thermogenic H₂ migrated from sedimentary organic matter in diagenesis.

Table 1. Biogenic and abiogenic sources of H₂.

from organic matter (simplistically CH₂O). Fermentation is a common process and occurs in various environs. An example is enteric fermentation in gastrointestinal tracts of cellulose-digesting termites and ruminants such as cattle and sheep. It is often said that flatus of termites and ructus (belching) of cows contain methane and thus contribute to global warming, as methane is a 28–36 times more powerful greenhouse gas than CO₂ [21], and flatus of non-cellulose-digesting animals such as dog and man would contain small amounts (usually <1%) of methane, too.

Anaerobic digestion of food wastes generates methane as “biogas” [22], and anaerobic degradation of organic burials in landfills, paddy fields, and swamps also release methane as expressed in Japanese as “*sho-ki*” meaning “marsh gas.” These processes and environs are mostly biological rather than geological and based on anaerobic breakdown of preexisting organic matter. In this context, methane is regarded as a by-product, an end product or an “exhaust,” in contrast to our customary concept of methane as a “fuel,” in such a name as biogas, from the viewpoint of human interest. In any connotation, biogenic methane produced in the past is an important component of natural gas as part of fossil fuels.

2.1.2. Biogenic methane of inorganic origin: CO₂ respiration

Biogenic methane is also produced from the inorganic carbon dioxide, CO₂, through the process that is regarded as essentially the reduction of CO₂ with H₂, that is, CO₂ + 2H₂ → CH₄ + H₂O. This process can be seen as a biological version of the Fischer-Tropsch process or Sabatier reaction and is based on the biological process known as Wood-Ljungdahl pathway or reductive acetyl CoA pathway (discussed later). The “reduction of CO₂ with H₂” is also viewed as the “oxidation of H₂ with CO₂,” which is biologically translated as a type of anaerobic respiration (oxidation) using CO₂ as an oxidant instead of O₂ in aerobic H₂ oxidation [23].

This view of CO₂ respiration recalls the microbiological processes of “sulfate reduction,” as portrayed simplistically $\text{SO}_4^{2-} + \text{H}_2 \rightarrow \text{HS}^- + \text{H}_2\text{O}$, in the other name of “sulfate respiration”; and “nitrate reduction,” $\text{NO}_3^- + \text{H}_2 \rightarrow \rightarrow \rightarrow \rightarrow \text{N}_2 + \text{H}_2\text{O}$ (again simplistic but consisting of four reductions), in the other name of “nitrate respiration” (as well as denitrification).

In both reduction and respiration views, CH₄ can be regarded as a by-product or an “exhaust,” in contrast to our usual notion of methane as a “fuel,” as described earlier. More important (than the reduction and respiration views) is the source of H₂ that is noted as molecular hydrogen (H₂) or a reductant (electron donor, H⁺ + e⁻). Although degrading organic matter may serve as a source of H₂ or “H⁺ + e⁻,” this type of methanogenesis should be regarded as “of inorganic origin,” because “inorganic origin” only points the source of carbon (CO₂), not the source of H₂ that can be organic or inorganic (**Table 1** and discussed later). For example, methane is produced by a consortium of propionate-degrading and acetogenic bacteria and methanogenic archaea. Although details are yet to be fully elucidated, propionic acid (CH₃CH₂COOH) is degraded by syntrophic propionate-degrading and acetogenic bacteria (simplistically $\text{CH}_3\text{CH}_2\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2$), and methane is produced via both “acetoclastic” ($\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$) and “hydrogenotrophic” methanogenesis ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) [24]. The former (acetoclastic methanogenesis) is taken as “of organic origin” and the latter (hydrogenotrophic methanogenesis, i.e., CO₂ respiration) is regarded as “of inorganic origin,” although they comprise a one amalgamated process. Certainly, fractions of CO₂ and H₂ may truly be inorganic of primordially magmatic origin; however, not a small part of H and C atoms would have experienced “organic” phases through biogeochemical cycling, and distinction between organic and inorganic origins may only be a matter of immediate origins.

In addition, a recent experiment showed that CO (not CO₂) and H₂ are used for an energetic metabolism by symbionts of the gutless marine oligochaete worm *Olavius algarvensis* Giere, Erséus & Stuhlmacher, 1998, that inhabit non-vent, non-seep but anaerobic seagrass-degrading sediment rich in CO and H₂ [25]. This process may lead to a realistic biological version of the Fischer-Tropsch synthesis where CO rather than CO₂ plays the major role.

2.1.3. Abiogenic methane of organic origin: Thermogenesis

Methanogenesis based on anaerobic organic breakdown also occurs in abiogenic (non-biological) pathways. This process is geological rather than biological and occurs by elevated heat and pressure against the organic matter buried in deep subsurface strata. The thermal breakdown of organic burials is known as “thermogenesis,” as part of geological “diagenesis,” in contrast to “biogenesis” that occurs in the so-called physiological temperatures, except activities of hyperthermophilic methanogenic microorganisms (not many known species of archaea [26]) at focused geothermal sites. Formation temperatures for biogenic and thermogenic methane are generally estimated to be <50°C and 157–221°C, respectively [27], which roughly reflects formation depths, that is, shallower and deeper zones of methane generation, respectively.

During diagenetic thermogenesis of methane, carbon and hydrogen isotopes are subject to discrimination or fractionation, as occurring in biological methanogenesis, too; however, the tendency and degree of isotope fractionations are distinguishable between geological and

biological methanogenesis, as described in detail in Section 3.1. Generally, thermogenic methane has more ^{13}C and ^2H (deuterium, D), that is, higher (enriched) $\delta^{13}\text{C}$ and δD , respectively, than biogenic methane does [28].

2.1.4. Abiogenic methane of inorganic origin: Fischer-Tropsch process or Sabatier reaction

Regardless of bio-/thermogenesis, generated methane is of organic origin. Adding to the organic origin, methanogenesis of inorganic origin occurs, too, via both biological and geological pathways to reduce carbon dioxide CO_2 with molecular hydrogen H_2 to yield methane (CH_4) and water (H_2O). The bulk reaction is essentially the same as the oxidation of H_2 with CO_2 , which corresponds to anaerobic respiration using CO_2 as the oxidant (instead of aerobic respiration using O_2 as the oxidant) in a biological context. Translated into a geological context, the biological CO_2 respiration corresponds to the geothermally activated Fischer-Tropsch synthesis and Sabatier reaction [29] that are well-known processes in chemical engineering.

A similar but different pathway in terms of carbon origin (CaCO_3 instead of CO_2) has been assumed for abiotic methanogenesis in deeper subsurface, that is, mantle of the Earth [30, 31], though the size of methane pool in mantle has not been well estimated. In a Fischer-Tropsch or a Sabatier manner, CaCO_3 as well as CO_2 is reduced with H_2 to generate geothermal CH_4 . In addition, serpentinization, a water-rock interaction, has been regarded as the major H_2 -supplying and thus CH_4 -supplying process [32]. However, as the reaction rate of serpentinization was recently revised to be slower than previously expected [33], its significance in abiotic methanogenesis has been subject to reevaluation [29, 34].

2.2. Migration and seepage of methane

A certain part of methane that originates in the subsurface will immediately migrate upward and reach the surfaces of land and seafloor by diffusion, buoyancy, compression (due to geo-pressure and subduction-driven tectonic squeeze), or geo-/hydrothermal circulations. Methane may also migrate and will be pooled for some while (in a geological sense) in the subsurface reservoirs and then eventually migrates upward and reaches the surfaces by pressurization as well as diffusion and buoyancy. Leakage of subsurface methane takes the forms of seepage, venting, eruption, and so on [35]. These forms represent processes and pathways, and this section focuses more on the latter (pathways), employing the ideas and terminologies presumed for possible methane seepage on Mars [10], despite some differences.

Subsurface methane may reach surface via “macro-seepage,” “mini-seepage,” and “micro-seepage.” The “macro” implies seeps that are visible by naked eyes, and the “mini” and “micro” are invisible by naked eyes and visible with the help of specified instruments. The distinction is just like the one between macroorganisms and microorganisms; the latter can only be seen under microscopes. Regarding their activities and fluxes, compared with hydrothermal vents that vigorously eject high flux of “focused flow,” macro-seeps are less active but efflux similarly focused flow of seep fluids via subsurface channels. Bubbles of methane gas are occasionally visible in water columns, for example, in the Eel River Basin, off northern

California [36] and Northern Gulf of Mexico [37]. By contrast, mini- and micro-seeps slowly exhale “diffuse flow” through sediment matrix pores, and the slow flows are virtually invisible and not readily detectable.

Macro-seepage is formed by subsurface channels often connected with faults. Macro-seepage is also associated with the decomposition of subsurface methane hydrates, or gas hydrates, triggered by shifts in subsurface temperature and pressure due to high-rate sedimentation, subsurface movement such as salt diapirs and mud volcanoes (described later), and so on [38]. The number of seafloor macro-seeps is unknown but may exceed the number of terrestrial macro-seeps, that is, >10,000 [39].

Mini-seepage occurs around macro-seeps, in the transition zone from focused flow centers to zero seepage surroundings. By contrast, micro-seepage is independent of macro-seepage and probably caused mainly by ongoing microbial methanogenesis in sediments. It is the least intensive, compared with the most intensive hydrothermal venting and less intensive macro-seepage. However, micro-seeps likely occur the most extensively on land and seafloor, as implied by the power law probability distributions or “size frequency distributions” [40]. The total flux of mini-seepage is unknown; however, due to their globally widespread occurrence, it is estimated that micro-seeps exhale up to 25 million tons year⁻¹ of methane, which is a little more than the estimate from macro-seeps [39].

Despite the importance of invisible seeps in global methane flux, this chapter focuses on visible seeps to comprehend geo-biological landscape of methane seepage more easily. The landscape is characterized by both biological communities and authigenic carbonate rock and will lead to a concept of methane seeps not only as oases for biological communities but also as immediate sinks of leaking methane.

2.3. Anaerobic oxidation of methane (AOM)

Methane is flammable, in a day-to-day sense, in air with oxygen, and the combustion is, in a chemical sense, termed oxidation (of methane with oxygen, and reduction of oxygen with methane). Likewise, methane is oxidizable in water without oxygen but with, for example, sulfate and nitrate. This non-aerobic (non-O₂-involved) process is viewed as “anaerobic oxidation of methane” in a chemical sense, which has been often abbreviated as “AOM” in a geochemical tradition, because AOM has tremendous importance in geochemistry and also in geo-biology, as well as in resource geology and global climate change issues.

AOM was first reported in 1976 from the unusually anoxic water columns and sediments of the Cariaco Trench [41]. Methane should have been leaked from the anoxic “trench” to the overlying oxic water column and oxidized aerobically; however, it seemed that methane is already oxidized in the anoxic trench. There was a clear negative correlation between the concentrations of methane and sulfate (as well as a positive correlation between the concentrations of methane and sulfide).

Then, AOM with sulfate was postulated and formulated as thermodynamically possible as $\text{CH}_4 + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{CO}_2 + 2\text{H}_2\text{O}$, $\Delta G^0 = -22.8 \text{ kcal mole}^{-1}$. Geologically, the “site” or “zone” where this reaction occurs was questioned, and it is now recognized as the “sulfate-methane

transition zone" (SMTZ) at relatively shallow depths in sediments (not in water column). That is, SMTZ is the zone of AOM. On the other hand, microorganisms that perform AOM, that is, co-metabolism of methane oxidation and sulfate reduction, were prefigured, but no such microbes were known at that time.

Once prefigured, microbiologists started isolating and obtaining pure cultures of the corresponding microorganisms; however, it has not yet been successful until today. In 1999, the involvement of archaea in AOM was demonstrated by $\delta^{13}\text{C}$ -depletion in archaeal lipid biomarkers (due probably to $\delta^{13}\text{C}$ -depletion in the source CH_4), and, using non-culture-dependent technique (16S rRNA gene sequencing), predominance of methanogenic archaea in the Eel River Basin sediment (including the SMTZ layer) was revealed [42].

This finding led to the idea of "reverse methanogenesis" [43, 44] that convert CH_4 to CO_2 to provide reducing power [$\text{H}^+ + e^-$] to sulfate reduction. The hypothetical reverse-methanogenic archaeal phylotypes (based on 16S rRNA genes) were named "anaerobic methanotrophs" (ANME) [43]. Then, the next question was who scavenges the by-product hydrogen ($\text{H}^+ + e^-$), ANME or a partner sulfate-reducer.

Eventually in 2000, also using non-culture-dependent techniques, a microbial consortium of archaeal-bacterial symbiosis was demonstrated by microscopy coupled with microbial group-specific staining from the Hydrate Ridge sediment at a 780-m depth [45]. The AOM players were reverse-methanogenic ANME archaea and sulfate-reducing bacteria, and the consortium, or a clump of cells, is composed of archaeal cells inside and bacterial cells outside.

Other than reverse-methanogenic ANME, acetogenic and methylogenic ANMEs are also involved in the AOM processes [46]. In any case, hydrogen ($\text{H}^+ + e^-$) is released from CH_4 by ANMEs and scavenged by sulfate-reducing bacteria. In addition, other hydrogen scavengers are also involved in AOM. That is, microorganisms that utilize nitrate, nitrite, and Fe^{3+} as oxidants (electron acceptors), which are nitrate- /nitrite- /iron-reducing bacteria, are known and more will be known [47, 48].

Detailed mechanism of AOM has slowly been understood in particular reference to electron transfer [49, 50]; however, metabolic interplays between ANME and anaerobic respirers have not fully elucidated yet. For example, it is generally recognized that, in SO_4 -rich marine and NO_3 -rich freshwater habitats, sulfate- and nitrate-respirers play roles in AOM, respectively; however, some examples are not readily explained by the general recognition: in a freshwater wetland, AOM is associated with sulfate reduction, not nitrate reduction [51], and, also in a freshwater wetland, active AOM occurs below the nitrate-rich zone, that is, in a sulfate-poor Fe-rich zone [52].

Most of the seep methane is oxidized to CO_2 , and only little reaches the sea surface to enter atmosphere. Oxidation of methane occurs aerobically in water column and anaerobically in sediments. It is estimated that anaerobic oxidation of methane (AOM) accounts for >50% reduction in the methane emission from freshwater wetland [51] and ~100% "sink" at seafloor methane seeps [53] as discussed later. Based on the stoichiometry of methane and oxygen consumptions, the advocator of the AOM hypothesis and her colleague stated that "a substantial fraction of the methane that fuels seep ecosystems is sourced from deep carbon buried kilometers under the sea floor" [54].

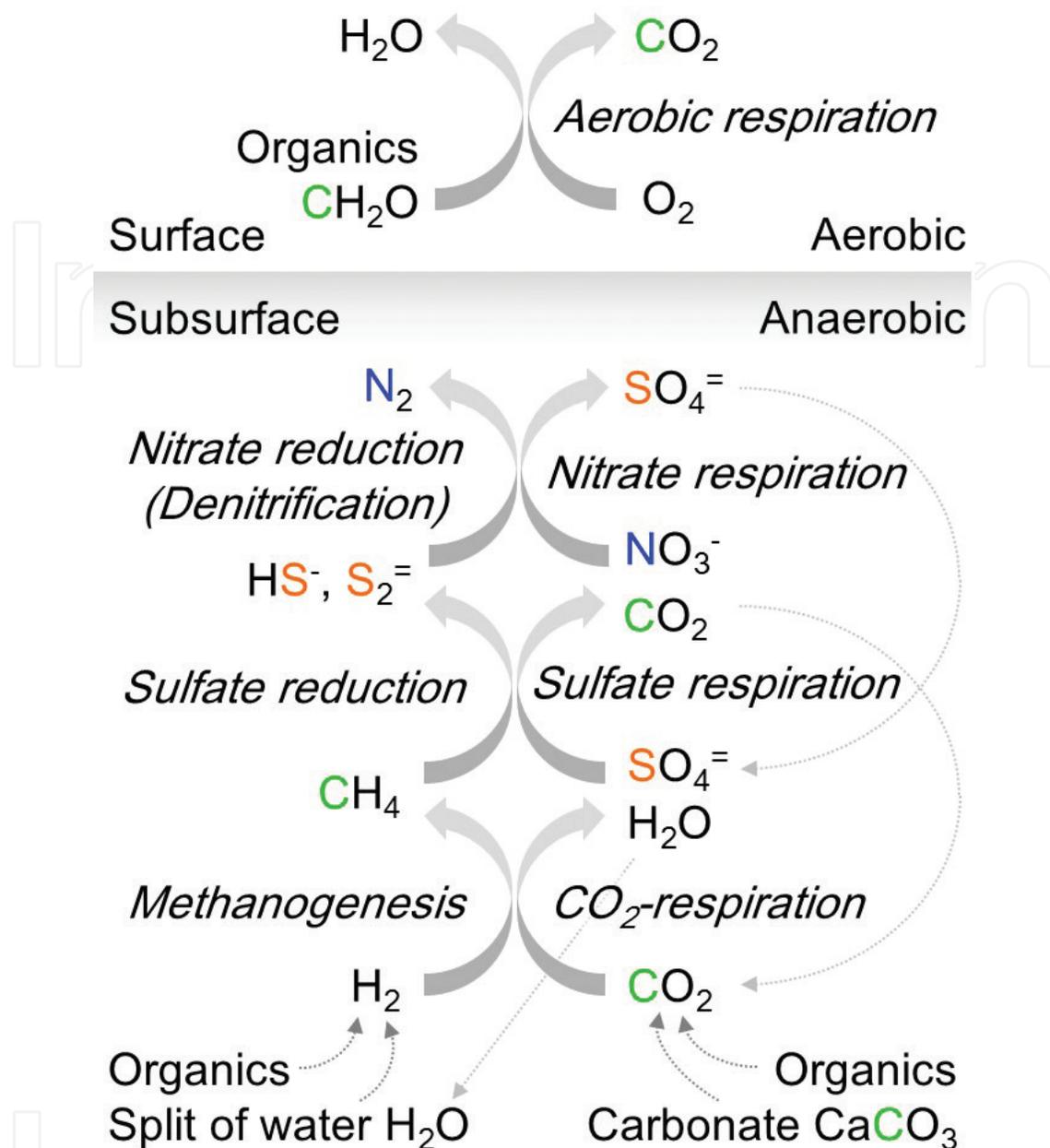


Figure 5. Chain of anaerobic respirations. Although there a battery of anaerobic respirations, only CO_2 -respiration (methanogenesis), sulfate respiration (sulfate reduction), and nitrate respiration (nitrate reduction or denitrification) are shown. These respirations are connected by taking "exhaust" of a process (respiration) as "fuel" for the subsequent process.

In summary, during AOM with sulfate, carbon dioxide and sulfide are produced; the former (CO_2) is incorporated into authigenic carbonate and autotrophic biomass, and the autotrophy is energetically driven by oxidation of the latter (H_2S). By these processes, that is, AOM, carbonate authigenesis, and chemo-autotrophy, methane seepage functions as "sink" as well as "source" of methane that was once sequestered in sub-seafloor.

2.4. Chain of anaerobic respirations

Three major biological processes at methane seeps, that is, hydrogenophilic methanogenesis (reduction of CO_2 with H_2), AOM, and chemoautotrophy, are unified together from a

viewpoint of “respiration.” This section explicates inter-connectivity and inter-dependency of respirations, particularly anaerobic respirations, which is hypothesized for the anoxic sub-seafloor of methane seeps.

Anaerobic respirations that provide energetic bases for chemoautotrophy and methanotrophy are not inter-dependent per se; however, they may virtually be inter-connected in anaerobic environments such as the methane seep sediments. Such inter-connections are schematically depicted as “chain” as only briefly shown in **Figure 5**, where CO₂ respiration (autotrophic hydrogenophilic methanogenesis) initiates the chain, followed by anaerobic methanotrophy (AOM) via sulfate respiration (sulfate reduction), by anaerobic thiotrophy via nitrate respiration (nitrate reduction, denitrification).² Chain elements are connected through the exhaust-fuel relationships, in which the exhaust from a process (respiration) is used as the fuel for the next one. Methane as the exhaust of CO₂ respiration (methanogenesis) becomes the fuel for AOM exhaling sulfide, which in turn becomes the fuel for nitrate respiration.

The chain of anaerobic respirations is still only conceptual; however, it should be useful and expandable to overview wide-ranged inter-relationships of geo-biological processes occurring in methane seeps.

3. Geo-biological settings of methane seeps

Locations of seafloor methane seeps, or sometimes methane vents, are closely tied with origins, generation processes, and migration pathways of methane, which are possible under specific conditions, set by certain geo-biological settings. If the conditions are right, the occurrence of methane seeps is expected even on extra-terrestrial planets and moons such as the red planet Mars and the Saturn’s satellite Titan [10]. Conditions being right, “early Earth” and even “early Mars” would have borne methane seeps/vents that would lead to emergence of life, with dual roles of methane as “fuel and exhaust” in a recent hypothesis [55]. Then, how and where methane seeps emerge is outlined in this section.

3.1. Methane seeps in continental margins: active and passive

Not a small part of methane generated in the sub-seafloor is derived from organic degradation, in biogenic or abiogenic pathways. Therefore, continental margins that receive a large amount of organic matter from land and/or from coastal upwelling are thought to be the primary geographical setting for the formation of methane seeps. Sedimentary organic matter is subject to speedy burial due to high sedimentation rate, subject to anaerobic degradation by microorganisms to produce acetate and H₂ as well as methane, and subject to geopressure and geotherm to form diagenetic methane.

Continental margins as recipients of terrestrial source materials (organic matter) give an impression of being “passive.” In fact, continental margins are largely categorized into “passive”

²Oxidation of sulfide with nitrate, which is thiotrophic (thioautotrophic) biomass production based on nitrate-respiration, is seen in bacterial species belonging to the genus *Beggiatoa* Trevisan, 1842 [87]. This process was once expected for the symbiont of the hydrothermal vent tubeworm (*Riftia pachyptila* Jones, 1981) [88], but the possibility was denied later [89].

margins and “active” margins from a geological, particularly geophysical point of view. Passive margins in this context mean tectonically non-active or inactive margins, while active margins refer to the continental margins under influence of plate tectonic activities. Hence, active and passive margins denote tectonically active and inactive margins, respectively. Both margins receive inputs of terrigenous organic matter in a similar manner by river flows and erosions but to different degrees, that is, to relatively smaller and greater degrees, respectively, due to the reasons described in the following subsections.

3.1.1. Active margins

Active margins are facing plate boundaries between continental plates and oceanic plates, most of which are convergent margins (subduction zones); transform faults may also face but not so often. The rest of the plate boundaries are divergent zones (spreading axes or rifts). Rare examples of continental margin rifts are known in the Gulf of California and the Red Sea; they are only rarely seen and thus not dealt with in this chapter.

The plate-plate convergence results in subducting depressions of seafloor on the ocean side and uplift of mountain ranges on the land side, both of which run in parallel to and not too far from the coastlines. Examples are taken from the west coasts of the North and South America continents, that is, the Rocky and Andean Mountains, respectively. Rivers that flow westward (seaward) are relatively short and hosted by narrow watersheds, and therefore they transport relatively small amounts of terrigenous (allochthonous) organic matter contained in sediments to the continental margins.

In addition to the transport of allochthonous organic matter, autochthonous production (photosynthetic primary production) of organic matter occurs in light-penetrated surface waters, and certain part of the primary production is exported to underlying water column and to bottom. According to a detailed estimation, of the global primary production of 54×10^{12} kg C year⁻¹, about 4% (2.3×10^{12} kg C year⁻¹) is exported to bottom, and about 0.5 and 0.02% are buried in the margins (50–2000 m) and deep seafloor (>2000 m deep) [56], respectively, where “kilogram carbon” (kg C) equals “giga ton carbon” (Gt C) as well as “pentagram carbon” (Pg C), all indicating 10^{15} g C. Of global ocean area (about 3.5×10^{14} m²), margins occupy only about 9%, that is, 3% by shelves (50–200 m deep) and 6% by slopes (200–2000 m deep); however, organic burial in margins (2.9×10^{11} kg C year⁻¹) is about 2.4 times greater than that in deep seafloor.

Compared with passive margins, active margins take relatively small part of the whole margin areas. However, active margins off west coasts of the North and South Americas, as well as passive margins off west coasts of Africa [57], receive the benefit of “coastal upwelling” driven by eastern boundary currents: Canary, Benguela, California, and Humboldt Currents. Coastal upwelling brings nutrients to surface water to enhance primary production, resulting in a facilitated organic transport and burial in sediments of the margins.

By contrast, active margins off eastern coasts of Eurasia continent and adjacent island arcs (archipelagos) receive less benefits from the coastal upwelling weakened by the intensified western boundary current, Kuroshio. Although they are part of the same “ring of fire” or circum-Pacific plate boundaries together with the western margins of the Americas, they are not equal counterparts in terms of upwelling benefits. Nevertheless, tectonic “squeeze”

driven by subduction may equally benefit the formation of methane seeps in the active margins. An example may be the methane seep that was recently discovered in the forearc basin off Sumatra of the Sunda Arc [58].

Besides sedimentation, active margins have features of methane seepage associated with plate subduction. For example, “out-of-sequence thrusts” potentially serve as channel-forming faults for deep methane to migrate and seep more smoothly [59]. Tectonic “squeeze” (due to subduction compression) of methane-bearing strata may also facilitate the migration and seepage of methane [60, 61]. The deepest seeps of this type were found in the hadal zone of the Japan Trench at 7326-m depth in 1998 [62] and at 7336-m depth in 1999 [63], which is also the globally deepest biological community based on chemoautotrophy or methanotrophy. Topographic features include ridges, escarpments, valleys, canyons, seamounts, and so on.

3.1.2. *Passive margins*

Passive margins occupy greater widths and areas compared with the areas occupied by active margins. They also receive larger amounts of sediments containing terrigenous organic matter transported by the inflowing rivers from the greater watershed areas. The organic burials are eventually degraded to generate methane that will migrate by diffusion, buoyancy, or gravity depression, will be trapped by sealing strata, or will reach seafloor surface to seep. The seeps are often found at bases of escarpments and outcrops as well as in valleys and canyons.

Historically, methane seepage was first discovered in the passive margins of the Gulf of Mexico (GoM). In 1983, brine seepage associated with gutless tubeworms and mussels that resemble hydrothermal vent fauna was discovered at a 3200-m-deep base on the GoM side of the Florida Escarpment [64]. In 1984, oil seepage associated with gutless tubeworms and clams was discovered in the off-Louisiana coast of GoM [65], which was associated with subsurface methane hydrate (gas hydrate) [66]. The off-Louisiana sites have been a focus of petroleum industry and thus have been studied intensively. The “Bush Hill” (27°47.5' N, 91°15' W, mound crest about 540-m deep) in the Green Canyon of industrial interest is the methane seep version of the hydrothermal pilgrim sites of “Garden of Eden” and “Rose Garden” of the Galápagos Rift [67]. After the “Deepwater Horizon” drilling rig explosion near Bush Hill, ecology of the shore, water column, and benthic ecosystems have been studied extensively [16].

A unique example in the passive margin is the Cariaco Trench, or Cariaco Basin, located in the passive margin off Venezuela, which is a Dead Sea-type pull-apart basin. Because its sharply depressed topography blocks exchange with the overlying oxic water, the basin is totally anoxic in the water column from the depth of 200–300 m down to the maximum depth of about 1400 m as well as in sediments [68]. Due to the unique anoxia, a wave of studies on “anaerobic oxidation of methane” (AOM) originated from here in 1976 [41], and the Ocean Time Series Program called CARIACO (Carbon Retention in a Colored Ocean) was started in 1995 and is still ongoing.

Other examples of passive margins are found in the eastern margin of the North and South Americas, whose western margins provide examples of the active margins as stated earlier. In contrast to active margins, most of which are limitedly located along the circum-Pacific “ring of fire,” passive margins occupy a vast majority of continental margins. Other than off

Americas, a number of methane seeps will be discovered in the passive margins that have been less surveyed. The passive margins off the land masses of Africa, Greenland, Svalbard, Siberia, India, Australia, China, Antarctica, and so on are under recent surveys or targeted for future surveys and exploitations [69–71].

3.2. Methane hydrates (gas hydrates)

Gas hydrates are a two-phase ice-like structure composed of crystalline water lattice (as the host molecule) and caged gas (as the guest molecule). When natural gas is trapped, they are often called “methane hydrate,” focusing on the major component of natural gas and on industrial exploitability. As water ice is stable under specific temperature and pressure conditions, methane hydrates are stable only in the “gas hydrate stability zone” (GHSZ) of suitable geotherms and geopressures. The GHSZ depths in subterranean and sub-seafloor vary according to gradients of geotherms and pressures (geopressures and hydrostatic pressures). Once gradients are subject to a shift due to, for example, global warming and isostatic rebound, methane hydrates will dissociate to release methane (and other gases), possibly resulting in the formation of methane seeps [71].

Carbon storage in sub-seafloor methane hydrates is estimated to be around 500 Gt C (0.5×10^{15} kg C) at maximum [72], almost half of total atmospheric CO₂ carbon. The estimates vary by two orders of magnitude, depending on rates of sedimentation, compaction, and seepage. Seepage, however, serves as a “sink” that convert methane via oxidation to CO₂ and further to CaCO₃ precipitates (authigenic carbonate rocks, as described later) that sequester carbon back into lithosphere [73]. Therefore, microbial activities involved in methane oxidation and carbonate precipitation should be evaluated to acknowledge the roles of methane seeps as “source” and “sink” for leaching methane.

A different but similar process of methane supply from sub-seafloor is thawing of submarine permafrost, and up to 100% of thaw-released methane is subject to anaerobic oxidation in the permafrost sediments [53]. Because submarine permafrost is protected from intense cold by unfrozen bottom waters (minimum about -2°C) and subject to geotherm since the Holocene inundation, they are more susceptible to thaw and release methane than terrestrial permafrost. Therefore, the evaluation of anaerobic oxidation of methane (AOM) in submarine permafrost and associate methane seepage is an urgent matter of concern.

3.3. Mud volcanoes

Volcanoes in a general sense expel high-temperature lavas, ashes, rocks, vapor, and gases by explosively, not continuously but occasionally. While volcanoes which show that such magmatic eruptions are igneous volcanoes, mud volcanoes may be regarded as sedimentary volcanoes. Mud volcanoes exhale gas (in an eruptive manner), mud, and slurry, which are not driven by a magmatic activity and not necessarily geo-hydrothermally structured, while “asphalt volcanoes” [74] may be generated by geothermally heated supercritical water [75]. More than 600 mud volcanoes have been known on land, and several thousands are assumed on seabed although the entire picture is unclear. On land or in the sea, mud volcanoes are

located in the active margins, and they are primarily driven by over-pressurization of gas-bearing fluids. The hydrocarbon components of the gas are generally of thermogenic origin, rarely of microbial origin [76], and mud volcanoes may be regarded as geothermally driven in the sense of gas formation.

Seabed mud volcanoes are often associated with a topographic feature of “pockmarks,” that is, seafloor depressions as traces of eruptions or mud volcanic craters [77] as well as methane seepage (occasionally with gas bubbles) and carbonates. Microbial mats are also often observed around the pockmark seeps, and some microbiological studies have been conducted, for example, at the 1-km-wide Haakon Mosby mud volcano in the Barents Sea, Arctic Ocean, where gutless tubeworms (*Oligobrachia haakonmosbiensis* Smirnov, 2000 and *Sclerolinum conortum* Smirnov, 2000) colonize in dependence most likely on endosymbiotic sulfur-oxidizing bacterial chemoautotrophy, that is, thiotrophy or thioautotrophy [78, 79].

3.4. Salt diapirs and brine pools

Buried salt deposits in ex-marine basins are compressed to form evaporites, particularly halite, that is, rock salt. The density of pure halite is about 2.16 g cm^{-3} and may not increase by further burial compression, while overlying sediments will increase in density (from initially about 2 g cm^{-3}) by continued sedimentation atop. When the density of overlying sediment reaches eventually about 2.5 g cm^{-3} , rock salt starts to rise due to gravitational instability, or Rayleigh–Taylor instability, and the salt movement is also called “salt tectonics.” Rock salt is not only “light” but also “soft” enough to deform for rising, bending, and intruding fissures and faults, where movements are called salt tectonics or salt diapirism and form salt diapirs or salt domes [80].

Salt diapirs are generally impermeable and serve as “cap” and “seal” against the underlying gas/oil reservoirs and gas hydrates that may be dissociated to release free gas. Over-pressurized gas/oil may crack salt diapirs, and the cracked fractures serve as conduits for gas and oil to seep. In reverse, salt diapir may penetrate gas hydrates. For example, chemical and geological structures of water columns, seabed, and sub-seafloor of the Blake Ridge and Cape Fear diapir seeps, southeastern US Atlantic margin, have been well characterized [81]. It may also be remembered that the first discovered methane seep was one of such salt diapir seeps [64].

Salt diapirs may also fall to form pockmarks [82]. Such pockmarks are filled with brine waters to form “brine pools.” It should be noted that the brine pools seen in Antarctic waters are different from the salt diapir brine pools; the Antarctic ones are formed by the sinking of brine water expelled from freezing seawater. Salt diapir brine pools are also associated with methane seepage and host chemosynthesis-based fauna [83, 84].

4. Conclusive remarks

Methane plays important roles as the most reduced C1 compound in the global carbon cycling and as the readily oxidizable intermediate in the oxic surface environment, besides its roles as

a powerful greenhouse gas to global warming and a fuel to human civilization. Therefore, the processes involving generation and degradation (oxidation) of methane, whether biological or not, encompass momentous biogeochemical significance.

Methane seeps are the point sources of methane emission from subsurface to surface environments. In addition, moreover, deep-sea methane seeps serve as important “sinks” that trap the major greenhouse gases of CH₄ and CO₂ to be sequestered in carbonate rocks. The carbonate formation in methane seeps is thus relevant to global climate issues. The geological process, that is, authigenesis of carbonates, is probably maintained or even accelerated by the actions of micro- and macroorganisms inhabiting the methane seeps and is therefore said to be “boon” of geo-biological couplings.

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Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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