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

Takeshi Naganuma

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.76976

Abstract

Methane (CH$_4$) 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 (CO$_2$) is incorporated into authigenic carbonate and autotrophic biomass, and the autotrophy is energetically driven by oxidation of the latter (H$_2$S). 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, CO$_2$) and the reduced end (methane, CH$_4$).
CH₄), as depicted as “organics” (simplistically expressed as CH₂O) 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 (²³⁸U), thorium-232 (²³²Th), and potassium-40 (⁴⁰K) 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 CO₂ in the Martian atmosphere [5]. The gas giant Jupiter’s

---

¹The canonical Solar constant (1365.4 ± 1.3 W m⁻²) established in the 1990s or the recent Solar minimum value (1360.8 ± 0.5 W m⁻²) [85], multiplied by the Earth’s cross-sectional area (1.274 × 10¹⁴ m²) and the Earth’s albedo (0.297 ± 0.005) [86], yields about 1.2 × 10¹⁷ 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 (mainly 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 sequestrated in the lithospheric kerogen (organic) and carbonate (inorganic). Methane seeps still contribute to the sequestration via authigenic carbonate formation. Abbreviation: dissolved inorganic carbon (DIC).](http://dx.doi.org/10.5772/intechopen.76976)
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-sequestrated 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 \textit{in situ} chemosynthetic primary production (chemoautotrophy). The latter production utilizes methane directly or exploits methane-derived biogeochemical products such as sulfide (H$_2$S, 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 $>300^\circ$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 δ$^{13}$C and δ$^2$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. δ$^2$H (δD)-δ$^{13}$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).](http://dx.doi.org/10.5772/intechopen.76976)
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 H₂ for both biogenic and abiogenic CO₂ reduction (methanogenesis of inorganic origin) can be both organic and inorganic; the former (organic-derived H₂) 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 H₂ 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.
from organic matter (simplistically CH$_2$O). 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 CO$_2$ [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: CO$_2$ respiration

Biogenic methane is also produced from the inorganic carbon dioxide, CO$_2$, through the process that is regarded as essentially the reduction of CO$_2$ with H$_2$, that is, CO$_2$ + 2H$_2$ $\rightarrow$ CH$_4$ + H$_2$O. 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 CO$_2$ with H$_2$” is also viewed as the “oxidation of H$_2$ with CO$_2$,” which is biologically translated as a type of anaerobic respiration (oxidation) using CO$_2$ as an oxidant instead of O$_2$ in aerobic H$_2$ oxidation [23].
This view of CO\(_2\) respiration recalls the microbiological processes of “sulfate reduction,” as portrayed simplistically SO\(_4^{2-}\) + H\(_2\) → HS\(^-\) + H\(_2\)O, in the other name of “sulfate respiration”; and “nitrate reduction,” NO\(_3^-\) + H\(_2\) → N\(_2\) + H\(_2\)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, CH\(_4\) 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 H\(_2\) that is noted as molecular hydrogen (H\(_2\)) or a reductant (electron donor, H\(^+\) + e\(^-\)). Although degrading organic matter may serve as a source of H\(_2\) or “H\(^+\) + e\(^-\),” this type of methanogenesis should be regarded as “of inorganic origin,” because “inorganic origin” only points the source of carbon (CO\(_2\)), not the source of H\(_2\) 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 (CH\(_3\)CH\(_2\)COOH) is degraded by syntrophic propionate-degrading and acetogenic bacteria (simplistically CH\(_3\)CH\(_2\)COOH + H\(_2\)O → CH\(_4\)COOH + CO\(_2\) + H\(_2\)), and methane is produced via both “acetoclastic” (CH\(_2\)COOH → CH\(_4\) + CO\(_2\)) and “hydrogenotrophic” methanogenesis (CO\(_2\) + H\(_2\) → CH\(_4\) + H\(_2\)O) [24]. The former (acetoclastic methanogenesis) is taken as “of organic origin” and the latter (hydrogenotrophic methanogenesis, i.e., CO\(_2\) respiration) is regarded as “of inorganic origin,” although they comprise a one amalgamated process. Certainly, fractions of CO\(_2\) and H\(_2\) 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 CO\(_2\)) and H\(_2\) 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 H\(_2\) [25]. This process may lead to a realistic biological version of the Fischer-Tropsch synthesis where CO rather than CO\(_2\) 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 hyper-thermophilic 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 $^2$H (deuterium, D), that is, higher (enriched) $\delta^{13}$C and $\delta$D, 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 $\text{CO}_2$ with molecular hydrogen $\text{H}_2$ to yield methane ($\text{CH}_4$) and water ($\text{H}_2\text{O}$). The bulk reaction is essentially the same as the oxidation of $\text{H}_2$ with $\text{CO}_2$ which corresponds to anaerobic respiration using $\text{CO}_2$ as the oxidant (instead of aerobic respiration using $\text{O}_2$ as the oxidant) in a biological context. Translated into a geological context, the biological $\text{CO}_2$ 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 ($\text{CaCO}_3$ instead of $\text{CO}_2$) 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, $\text{CaCO}_3$ as well as $\text{CO}_2$ is reduced with $\text{H}_2$ to generate geothermal $\text{CH}_4$. In addition, serpentinization, a water-rock interaction, has been regarded as the major $\text{H}_2$-supplying and thus $\text{CH}_4$-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-O\(_2\)-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 δ^{13}C-depletion in archaeal lipid biomarkers (due probably to δ^{13}C-depletion in the source CH₄), 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 CH₄ to CO₂ to provide reducing power [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 (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 (H⁺ + e⁻) is released from CH₄ 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 SO₄²⁻-rich marine and NO₃⁻-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 CO₂ 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].
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$_2$S). 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 sequestrated 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 chemosynthesis 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 CO$_2$ 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). The 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 CO$_2$ 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 H$_2$ 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”

---

*Oxidation 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 $54 \times 10^{12}$ kg C year$^{-1}$, about 4% ($2.3 \times 10^{12}$ 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 $3.5 \times 10^{14}$ m$^2$), 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 ($2.9 \times 10^{11}$ 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 geopressesures. The GHSZ depths in subterranean and sub-seafloor vary according to gradients of geotherms and pressures (geopressesures 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 \((0.5 \times 10^{15} \text{ kg C})\) at maximum [72], almost half of total atmospheric CO\(_2\) 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 CO\(_2\) and further to CaCO\(_3\) precipitates (authigenic carbonate rocks, as described later) that sequestrate 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 sub-marine 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 babbles) 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 contortum* Smirnov, 2000) colonize in dependence most likely on endosymbiotic sulfur-oxidizing bacterial chemosynthesis, 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 CH$_4$ and CO$_2$ to be sequestrated 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.

Acknowledgements

The author is obliged to the crew and operation teams of manned and unmanned deep-sea vehicles and support ships of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) for deep-sea expeditions.

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.

Author details

Takeshi Naganuma

Address all correspondence to: takn@hiroshima-u.ac.jp

Graduate School of Biosphere Science, Hiroshima University, Higashi-Hiroshima, Japan

References

[1] Davies JH, Davies DR. Earth’s surface heat flux. Solid Earth. 2010;1:5-24. DOI: 10.5194/se-1-5-2010

[2] Gando A, Gando Y, Ichimura K, Ikeda H, Inoue K, Kibe Y, et al. Partial radiogenic heat model for Earth revealed by geoneutrino measurements. Nature Geoscience. 2011;4:647-651. DOI: 10.1038/ngeo1205

[3] Goldreich P, Ward WR. The formation of Planetesimals. The Astrophysical Journal. 1973;183:1051-1062. DOI: 10.1086/152291
[4] Naganuma T. An astrobiological view on sustainable life. Sustainability. 2009;1:827-837. DOI: 10.3390/su1040827

[5] NASA Goddard Space Flight Center. Mars Fact Sheet [Internet]. 2016. Available from: https://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html [Accessed: Apr 4, 2017]

[6] NASA Goddard Space Flight Center. Jupiter Fact Sheet [Internet]. 2017. Available from: https://nssdc.gsfc.nasa.gov/planetary/factsheet/jupiterfact.html [Accessed: Apr 4, 2017]

[7] NASA Goddard Space Flight Center. Earth Fact Sheet [Internet]. 2017. Available from: https://nssdc.gsfc.nasa.gov/planetary/factsheet/earthfact.html [Accessed: Apr 4, 2017]

[8] Seager S, Bains W. The search for signs of life on exoplanets at the interface of chemistry and planetary science. Science Advances. 2015;1:e1500047. DOI: 10.1126/sciadv.1500047

[9] Webster CR, Mahaffy PR, Atreya SK, Flesch GJ, Mischna MA, Meslin PY, Farley KA, Conrad PG, Christensen LE, Pavlov AA, Martin-Torres J, Zorzano MP, McConnochie TH, Owen T, Eigenbrode JL, Glavin DP, Steele A, Malespin CA, Archer Jr PD, Sutter B, Coll P, Freissinet C, McKay CP, Moores JE, Schwenzer SP, Bridges JC, Navarro-Gonzalez R, Gellert R, Lemmon MT. MSL science team. Mars atmosphere. Mars methane detection and variability at Gale crater. Science. 2015;347:415-417. DOI: 10.1126/science.1261713

[10] Oehler DZ, Etiope G. Methane seepage on Mars: Where to look and why. Astrobiology. 2017;17:1233-1264. DOI: 10.1089/ast.2017.1657

[11] NASA Goddard Space Flight Center. Venus Fact Sheet [Internet]. 2016. Available from: https://nssdc.gsfc.nasa.gov/planetary/factsheet/venusfact.html [Accessed: Apr 4, 2017]

[12] Shaw GH. Earth’s Early Atmosphere and Oceans, and the Origin of Life. New York: Springer; 2015. 113 p. ISBN: 978-3319219714

[13] Naganuma T, Okayama Y, Hattori M, Kanie Y. Fossil worm tubes from the presumed cold-seep carbonates of the Miocene Hayama Group, central Miura Peninsula, Japan. Island Arc. 1995;4:199-208. DOI: 10.1111/j.1440-1738.1995.tb00143.x

[14] Lacy JH, Carr JS, Evans NJ II, Baas F, Achtermann JM, Arens JF. Discovery of interstellar methane-Observations of gaseous and solid CH\textsubscript{4} absorption toward young stars in molecular clouds. The Astrophysical Journal. 1991;376:556-560. DOI: 10.1086/170304

[15] Gold T. Terrestrial sources of carbon and earthquake outgassing. Journal of Petroleum Geology. 1979;1:3-19. DOI: 10.1111/j.1747-5457.1979.tb00616.x

[16] Kennicutt MC. Oil and gas seeps in the Gulf of Mexico. In: Ward CH, editor. Habitats and Biota of the Gulf of Mexico: Before the Deepwater Horizon Oil Spill. New York: Springer; 2017. pp. 275-358. DOI: 10.1007/978-1-4939-3447-8_5

[17] Umezawa T, Brenninkmeijer CAM, Röckmann T, van der Veen C, Tyler SC, Fujita R, Morimoto S, Aoki S, Sowers T, Schmitt J, Bock M, Beck J, Fischer H, Michel SE, Vaughn BH, Miller JB, White JWC, Brailsford G, Schaefer H, Sperlich P, Brand WA, Rothe M, Blunier T, Lowry D, Fisher RE, Nisbet EG, Rice AL, Bergamaschi P, Veidt C, Levin I. Intercomparisons of δ\textsuperscript{13}C and δD measurements of atmospheric CH\textsubscript{4} for combined use...
of datasets from different laboratories. Atmospheric Measurement Techniques Discussions. 2017;2017:1-44. DOI: 10.5194/amt-2017-281

[18] Bergamaschi P, Lubina C, KöNigstedt R, Fischer H, Veltkamp AC, Zwaagstra O. Stable isotopic signatures ($\delta^{13}C$, $\deltaD$) of methane from European landfill sites. Journal of Geophysical Research. 1998;103:8251-8265. DOI: 10.1029/98JD00105

[19] Loyd SJ, Sample J, Tripati RE, Defliese WF, Brooks K, Hovland M, Torres M, Marlow J, Hancock LG, Martin R, Lyons T, Tripati AE. Methane seep carbonates yield clumped isotope signatures out of equilibrium with formation temperatures. Nature Communications. 2016;7:12274. DOI: 10.1038/ncomms12274

[20] Hirose T, Kawagucci S, Suzuki K. Mechanoradical $H_2$ generation during simulated faulting: Implications for an earthquake-driven subsurface biosphere. Geophysical Research Letters. 2011;38:L17303. DOI: 10.1029/2011GL048850

[21] United States Environmental Protection Agency. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2015. EPA-401-P-17-001. 2017. 633 p. Available from: https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2015

[22] Paritosh K, Kushwaha SK, Monika Yadav M, Pareek N, Chawade A, Vivekanand V. Food waste to energy: An overview of sustainable approaches for food waste management and nutrient recycling. BioMed Research International. 2017;2017:2370927. DOI: 10.1155/2017/2370927

[23] Aragno M, Schlegel HG. The hydrogen-oxidizing bacteria. In: Starr MP, Stolp H, Trüper HG, Balows A, Schlegel HG, editors. The Prokaryotes. Berlin: Springer; 1981. pp. 865-889. DOI: 10.1007/978-3-662-13187-9_70

[24] Mucha H, Lingens F, Trösch W. Conversion of propionate to acetate and methane by syntrophic consortia. Applied Microbiology and Biotechnology. 1988;27:581-586. DOI: 10.1007/BF00451636

[25] Kleiner M, Wentrup C, Holler T, Lavik G, Harder J, Lott C, Littmann S, Kuypers MM, Dubilier N. Use of carbon monoxide and hydrogen by a bacteria-animal symbiosis from seagrass sediments. Environmental Microbiology. 2015;17:5023-5035. DOI: 10.1111/1462-2920.12912

[26] Jabłoński S, Rodowicz P, Łukaszewicz M. Methanogenic archaea database containing physiological and biochemical characteristics. International Journal of Systematic and Evolutionary Microbiology. 2015;65:1360-1368. DOI: 10.1099/ijs.0.000065

[27] Stolper DA, Lawson M, Davis CL, Ferreira AA, Santos Neto EV, Santos Neto EV, Lewan MD, Martini AM, Tang Y, Schoell M, Sessions AL, Eiler JM. Gas formation. Formation temperatures of thermogenic and biogenic methane. Science. 2014;344:1500-1503. DOI: 10.1126/science.1254509

[28] Piceno YM, Reid FC, Tom LM, Conrad ME, Bill M, Hubbard CG, Fouke BW, Graff CJ, Han J, Stringfellow WT, Hanlon JS, Hu P, Hazen TC, Andersen GL. Temperature and injection water source influence microbial community structure in four Alaskan North
Slope hydrocarbon reservoirs. Frontiers in Microbiology. 2014;5:409. DOI: 10.3389/fmicb.2014.00409. eCollection 2014

[29] Etiope G. Abiotic CH$_4$ in ultramafic rocks: Follow the Sabatier reaction rules. In: Goldschmidt 2017 Abstracts; 13-18 August 2017; Paris: Goldschmidt Conference; Abstract 1081. 2017. Available from: https://goldschmidtabstracts.info/abstracts/abstractView?id=2017001182

[30] Scott HP, Hemley RJ, Mao H, Herschbach DR, Fried LE, Howard WM, Bastea S. Generation of methane in the Earth's mantle: In situ high pressure–temperature measurements of carbonate reduction. Proceedings of the National Academy of Sciences of the United States of America. 2004;101:14023-14026. DOI: 10.1073/pnas.0405930101

[31] Etiope G, Lollar BS. Abiotic methane on Earth. Reviews of Geophysics 2013;51:276-299. DOI: 10.1002/rog.20011

[32] Konn C, Charlou JL, Holm NG, Mousis O. The production of methane, hydrogen, and organic compounds in ultramafic-hosted hydrothermal vents of the mid-Atlantic ridge. Astrobiology. 2015;15:381-399. DOI: 10.1089/ast.2014.1198

[33] McCollom TM. Abiotic methane formation during experimental serpentinization of olivine. Proceedings of the National Academy of Sciences of the United States of America. 2016;113:13965-13970. DOI: 10.1073/pnas.1611843113

[34] Bradley AS. The sluggish speed of making abiotic methane. Proceedings of the National Academy of Sciences of the United States of America. 2016;113:13944-13946. DOI: 10.1073/pnas.1611843113

[35] Talukder AR. Review of submarine cold seep plumbing systems: Leakage to seepage and venting. Terra Nova. 2012;24:255-272. DOI: 10.1111/j.1365-3121.2012.01066.x

[36] Valentine DL, Blanton DC, Reeburgh WS, Kastner M. Water column methane oxidation adjacent to an area of active hydrate dissociation, Eel River Basin. Geochimica et Cosmochimica Acta. 2001;65:2633-2640. DOI: 10.1016/S0016-7037(01)00625-1

[37] Johansen C, Todd AC, Macdonald IR. Time series video analysis of bubble release processes at natural hydrocarbon seeps in the northern Gulf of Mexico. Marine and Petroleum Geology. 2017;82:21-34. DOI: 10.1016/j.marpetgeo.2017.01.014

[38] Bishnoi PR, Natarajan V. Formation and decomposition of gas hydrates. Fluid Phase Equilibria. 1996;117:168-177. DOI: 10.1016/0378-3812(95)02950-8

[39] Etiope G. Natural Gas Seepage. The Earth’s Hydrocarbon Degassing. Cham, Switzerland: Springer; 2015. 199 p. ISBN: 978-3319146003

[40] Krumbein WC. Size frequency distributions of sediments. Journal of Sediment Research. 1934;4:65-77. DOI: 10.1306/D4268EB9-2B26-11D7-8648000102C1865D

[41] Reeburgh WS. Methane consumption in Cariaco Trench waters and sediments. Earth and Planetary Science Letters. 1976;28:337-344. DOI: 10.1016/0012-821X(76)90195-3
[42] Hinrichs KU, Hayes JM, Sylva SP, Brewer PG, DeLong EF. Methane-consuming archaeobacteria in marine sediments. Nature. 1999;398:802-805. DOI: 10.1038/19751

[43] Hallam SJ, Putnam N, Preston CM, Detter JC, Rokhsar D, Richardson PM, DeLong EF. Reverse methanogenesis: Testing the hypothesis with environmental genomics. Science. 2004;305:1457-1462. DOI: 10.1126/science.1100025

[44] Scheller S, Goenrich M, Boecher R, Thauer RK, Jaun B. The key nickel enzyme of methanogenesis catalyses the anaerobic oxidation of methane. Nature. 2010;465:606-608. DOI: 10.1038/nature09015

[45] Boetius A, Ravenschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A, Amann R, Jørgensen BB, Witte U, Pfannkuche O. A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature. 2000;407:623-626. DOI: 10.1038/35036572

[46] McGlynn SE. Energy metabolism during anaerobic methane oxidation in ANME archaea. Microbes and Environments. 2017;32:5-13. DOI: 10.1264/jsme2.ME16166

[47] Caldwell SL, Laidler JR, Brewer EA, Eberly JO, Sandborgh SC, Colwell FS. Anaerobic oxidation of methane: Mechanisms, bioenergetics, and the ecology of associated microorganisms. Environmental Science & Technology. 2008;42:6791-6799. DOI: 10.1021/es80120b

[48] Cui M, Ma A, Qi H, Zhuang X, Zhuang G. Anaerobic oxidation of methane: An “active” microbial process. MicrobiologyOpen. 2015;4:1-11. DOI: 10.1002/mbo3.232

[49] Gao Y, Lee J, Neufeld JD, Park J, Rittmann BE, Lee H-S. Anaerobic oxidation of methane coupled with extracellular electron transfer to electrodes. Scientific Reports. 2017;7:5099. DOI: 10.1038/s41598-017-05180-9

[50] Wegener G, Krukenberg V, Riedel D, Tegetmeyer HE, Boetius A. Intercellular wiring enables electron transfer between methanotrophic archaea and bacteria. Nature. 2015;526:587-590. DOI: 10.1038/nature15733

[51] Segarra KEA, Schubotz F, Samarkin V, Yoshinaga MY, Hinrichs K-U, Joye SB. High rates of anaerobic methane oxidation in freshwater wetlands reduce potential atmospheric methane emissions. Nature Communications. 2015;6:7477. DOI: 10.1038/ncomms8477

[52] Weber HS, Habicht KS, Thamdrup B. Anaerobic methanotrophic archaea of the ANME-2d cluster are active in a low-sulfate, iron-rich freshwater sediment. Frontiers in Microbiology. 2017;8:619. DOI: 10.3389/fmicb.2017.00619

[53] Winkel M, Mitzscherling J, Overduin PP, Horn F, Winterfeld M, Rijkers R, Grigoriev MN, Knoblauch C, Mangelsdorf K, Wagner D, Liebner S. Anaerobic methanotrophic communities thrive in deep submarine permafrost. Scientific Reports. 2018;8:1291. DOI: 10.1038/s41598-018-19505-9

[54] Boetius A, Wenzhöfer F. Seafloor oxygen consumption fuelled by methane from cold seeps. Nature Geoscience. 2013;6:725-734. DOI: 10.1038/ngeo1926

[55] Russell MJ, Nitschke W. Methane: Fuel or exhaust at the emergence of life? Astrobiology. 2017;17:1053-1066. DOI: 10.1089/ast.2016.1599
[56] Dunne JP, Sarmiento JL, Gnanadesikan A. A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor. Global Biogeochemical Cycles. 2007;21:GB4006. DOI: 10.1029/2006GB002907

[57] McGregor HV, Dima M, Fischer HW, Mulitza S. Rapid 20th-century increase in coastal upwelling off Northwest Africa. Science. 2007;315:637-639. DOI: 10.1126/science.1134839

[58] Siegert M, Krüger M, Teichert B, Wiedicke M, Schippers A. Anaerobic oxidation of methane at a marine methane seep in a forearc sediment basin off Sumatra, Indian Ocean. Frontiers in Microbiology. 2011;2:249. DOI: 10.3389/fmicb.2011.00249

[59] Carson B, Kastner M, Bartlett D, Jaeger J, Jannasch H, Weinstein Y. Implications of carbon flux from the Cascadia accretionary prism: Results from long-term, in situ measurements at ODP Site 892B. Marine Geology. 2003;198:159-180. DOI: 10.1016/S0025-3227(03)00099-9

[60] Sibuet M, Olu K. Biogeography, biodiversity and fluid dependence of deep-sea cold-seep communities at active and passive margins. Deep-Sea Research Part II. 1998;45:517-567. DOI: 10.1016/S0967-0645(97)00074-X

[61] Leifer I, Kamerling MJ, Luyendyk BP, Wilson DS. Geologic control of natural marine hydrocarbon seep emissions, coal oil point seep field, California. Geo-Marine Letters. 2010;30:331-338. DOI: 10.1007/s00367-010-0188-9

[62] Fujikura K, Kojima S, Tamaki K, Maki Y, Hunt J, Okutani T. The deepest chemosynthesis-based community yet discovered from the hadal zone, 7326 m deep, in the Japan Trench. Marine Ecology Progress Series. 1999;190:17-26. DOI: 10.3354/meps190017

[63] Fujiwara Y, Kato C, Masui N, Fujikuran K, Kojima S. Dual symbiosis in the cold-seep thyasirid clam Maorithyas hadalis from the hadal zone in the Japan Trench, western Pacific. Marine Ecology Progress Series. 2001;214:151-159. DOI: 10.3354/meps214151

[64] Paull CK, Hecker B, Commeau R, Freeman-Lynde RP, Neumann C, Corso WP, Golubic S, Hook JE, Sikes E, Curray J. Biological communities at the Florida Escarpment resemble hydrothermal vent taxa. Science. 1984;226:965-967. DOI: 10.1126/science.226.4677.965

[65] Kennicutt MC II, Brooks JM, Bidigare RR, Fay RR, Wade TL, McDonald TJ. Vent-type taxa in a hydrocarbon seep region on the Louisiana slope. Nature. 1985;317:351-353. DOI: 10.1038/317351a0

[66] Brooks M, Benjamin H, William C, Bryant R, Kennicutt MC II, Mann RG, McDonald TJ. Association of gas hydrates and oil seepage in the Gulf of Mexico. Organic Geochemistry. 1986;10:221-234. DOI: 10.1016/0146-6380(86)90025-2

[67] NOAA Ocean Explorer. Galápagos Rift [Internet]. Revised 2017. Available from: http://oceanexplorer.noaa.gov/explorations/02galapagos/galapagos.html [Accessed: Apr 4, 2017]

[68] Richards FA, Vaccaro RF. The Cariaco Trench, an anaerobic basin in the Caribbean Sea. Deep Sea Research. 1953;3(56):90005-90003. DOI: 214-228. DOI: 10.1016/0146-6313
[69] Haas A. Carbonate authigenesis and worm tube mineralization – Biogeochemical and geobiological processes at methane seeps on the Congo deep-sea fan [thesis]. Bremen: Universität Bremen; 2008

[70] Feng D, Chen D. Authigenic carbonates from an active cold seep of the northern South China Sea: New insights into fluid sources and past seepage activity. Deep-Sea Research Part II. 2015;122:74-83. DOI: 10.1016/j.dsr2.2015.02.003

[71] Wallmann K, Riedel M, Hong WL, Patton H, Hubbard A, Pape T, Hsu CW, Schmidt C, Johnson JE, Torres ME, Andreassen K, Berndt C, Bohrmann G. Gas hydrate dissociation off Svalbard induced by isostatic rebound rather than global warming. Nature Communications. 2018;9:83. DOI: 10.1038/s41467-017-02550-9

[72] Piñero E, Marquardt M, Hensen C, Haeckel M, Wallmann K. Estimation of the global inventory of methane hydrates in marine sediments using transfer functions. Biogeosciences. 2013;10:959-975. DOI: 10.5194/bg-10-959-2013

[73] Marlow JJ, Steele JA, Ziebis W, Thurber AR, Levin LA, Orphan VJ. Carbonate-hosted methanotrophy represents an unrecognized methane sink in the deep sea. Nature Communications. 2014;5:5094. DOI: 10.1038/ncomms6094

[74] MacDonald IR, Bohrmann G, Escobar E, Abegg F, Blanchon P, Blinova V, Brückmann W, Drews M, Eisenhauer A, Han X, Heeschen K, Meier F, Mortera C, Naehr T, Orcutt B, Bernard B, Brooks J, de Faragó M. Asphalt volcanism and chemosynthetic life in the Campeche Knolls, Gulf of Mexico. Science 2004;304:999-1002. DOI: 10.1126/science.1097154

[75] Hovland M, MacDonald IR, Rueslåtten H, Johnsen HK, Naehr T, Bohrmann G. Chapopote Asphalt Volcano may have been generated by supercritical water. EOS Transactions American Geophysical Union. 2005;86:397-402. DOI: 10.1029/2005EO420002

[76] Mazzini A, Etiope G. Mud volcanism: An updated review. Earth Science Reviews. 2017;168:81-112. DOI: 10.1016/j.earscirev.2017.03.001

[77] Loncke L, Mascle J, Fanil Scientific Parties. Mud volcanoes, gas chimneys, pockmarks and mounds in the Nile deep-sea fan (Eastern Mediterranean): Geophysical evidences. Marine and Petroleum Geology. 2004;21:669-689. DOI: 10.1016/j.marpetgeo.2004.02.004

[78] Niemann H, Lösekann T, de Beer D, Elvert M, Nadalig T, Knittel K, Amann R, Sauter EJ, Schlüter M, Klages M, Foucher JP, Boetius A. Novel microbial communities of the Haakon Mosby mud volcano and their role as a methane sink. Nature. 2006;443:854-858. DOI: 10.1038/nature05227

[79] Lösekann T, Robador A, Niemann H, Knittel K, Boetius A, Dubilier N. Endosymbioses between bacteria and deep-sea siboglinid tubeworms from an Arctic cold seep (Haakon Mosby mud volcano, Barents Sea). Environmental Microbiology. 2008;10:3237-3254. DOI: 10.1111/j.1462-2920.2008.01712.x
[80] Vendeville BC, Jackson MPA. The rise of diapirs during thin-skinned extension. Marine and Petroleum Geology. 1992a;9:331-354. DOI: 10.1016/0264-8172(92)90047-I

[81] Brothers LL, Van Dover CL, German CR, Kaiser CL, Yoerger DR, Ruppel CD, Lobecker E, Skarke AD, Wagner JKS. Evidence for extensive methane venting on the southeastern U.S. Atlantic margin. Geology. 2013;41:807-810. DOI: 10.1130/G34217.1

[82] Vendeville BC, Jackson MPA. The fall of diapirs during thin-skinned extension. Marine and Petroleum Geology. 1992b;9:354-371. DOI: 10.1016/0264-8172(92)90048-J

[83] Woodside JM, Volgin AV. Brine pools associated with Mediterranean ridge mud diapirs: An interpretation of echo-free patches in deep tow sidescan sonar data. Marine Geology. 1996;132:55-61. DOI: 10.1016/0025-3227(95)00153-0

[84] Smith EB, Scott KM, Nix ER, Korte C, Fisher CR. Growth and condition of seep mussels (Bathymodiolus childressi) at a Gulf of Mexico brine pool. Ecology. 2000;81:2392-2403. DOI: 10.2307/177462

[85] Kopp G, Lean JL. A new, lower value of total solar irradiance: Evidence and climate significance. Geophysical Research Letters. 2011;38. DOI: L01706. DOI: 10.1029/2010GL045777

[86] Goode PR, Qiu J, Yurchyshyn V, Hickey J, Chu M-C, Kolbe E, Brown CT, Koonin SE. Earthshine observations of the Earth's reflectance. Geophysical Research Letters. 2001;28:1671-1674. DOI: 10.1029/2000GL012580

[87] Kamp A, Stief P, Schulz-Vogt HN. Anaerobic sulfide oxidation with nitrate by a freshwater Beggiatoa enrichment culture. Applied and Environmental Microbiology. 2006;72:4755-4760. DOI: 10.1128/AEM.00163-06

[88] Hentschel U, Felbeck H. Nitrate respiration in the hydrothermal vent tubeworm Riftia pachyptila. Nature. 1993;366:338-340. DOI: 10.1038/366338a0

[89] Girguis PR, Lee RW, Desaulniers N, Childress JJ, Pospesel M, Felbeck H, Zal F. Fate of nitrate acquired by the tubeworm Riftia pachyptila. Applied and Environmental Microbiology. 2000;66:2783-2790. PMCID: PMC92073
