ANNUAL REVIEWS

Annual Review of Earth and Planetary Sciences

The Geology and Biogeochemistry of Hydrocarbon Seeps

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Annu. Rev. Earth Planet. Sci. 2020. 48:205–31

First published as a Review in Advance on January 6, 2020

The *Annual Review of Earth and Planetary Sciences* is online at earth.annualreviews.org

https://doi.org/10.1146/annurev-earth-063016-020052

Keywords

hydrocarbon seep, carbon cycle, biogeochemical cycling, geobiology, gas hydrate, carbonate

Abstract

Hydrocarbon seeps, deep sea extreme environments where deeply sourced fluids discharge at the seabed, occur along continental margins across the globe. Energy-rich reduced substrates, namely hydrocarbons, support accelerated biogeochemical dynamics, creating unique geobiological habitats. Subseafloor geology dictates the surficial expression of seeps, generating hydrocarbon (gas and/or oil) seeps, brine seeps, and mud volcanoes. Biogeochemical processes across the redox spectrum are amplified at hydrocarbon seeps due to the abundance and diversity of reductant; anaerobic metabolism dominates within the sediment column since oxygen is consumed rapidly near the sediment surface. Microbial activity is constrained by electron acceptor availability, with rapid recycling required to support observed rates of hydrocarbon consumption. Geobiologic structures, from gas hydrate to solid asphalt to authigenic minerals, form as a result of hydrocarbon and associated fluid discharge. Animal-microbial associations and symbioses thrive at hydrocarbon seeps, generating diverse and dense deep sea oases that provide nutrition to mobile predators.

- Hydrocarbon seeps are abundant deep sea oases that support immense biodiversity and where specialization and adaptation create extraordinary lifestyles.
- Subseafloor geology shapes and defines the geochemical nature of fluid seepage and regulates the flux regime, which dictate the surface expression.

- High rates of anaerobic oxidation of methane require coupling to multiple processes and promote diversity in the anaerobic methanotroph microbial community.
- The recent discovery of novel phyla possessing hydrocarbon oxidation potential signals that aspects of seep biogeochemistry and geobiology remain to be discovered.

1. INTRODUCTION

Hydrocarbons range in complexity from the simplest form, methane, to the many and varying constituents of petroleum. Sedimentation of organic-rich materials along continental margins creates conditions ripe for subsequent hydrocarbon production through biological and thermogenic processes over tens to hundreds of millions of year timescales. In shallow anoxic sediments, biogenic methane and potentially ethane through butane are produced through microbially mediated methanogenesis and alkanogenesis (Claypool & Kaplan 1974, Hinrichs et al. 2006, Oremland et al. 1988). With increasing depth in the sediment column, the geothermal gradient (20–50° per km of depth) creates optimal conditions ($T > 150$°C at depths of 2,500–5,000 m) for catagenesis and metagenesis of organic matter, generating thermogenic alkanes as well as C_5 and heavier compounds—for example, n-alkanes, cylcoalkanes, aromatics, and ultimately oil—after long chain components are consumed (Abrams 2005, Horsfield & Rullkötter 1994).

Hydrocarbons represent a substantial pool of carbon—4,220–5,680 Pg C—that cycles slowly over geologic timescales (Sundquist & Visser 2003). Within sediments, hydrocarbons accumulate in porous formations (reservoirs), and the concentration gradient from within to outside a reservoir drives a flux of hydrocarbons at a rate that is dictated by reservoir porosity (Abrams 2005). Recycling occurs on a timescale of $\sim 10^7$ years as hydrocarbons move through sediments via networks of faults that connect deep reservoirs to the seabed; oxidation and mineralization occur throughout this journey.

Natural hydrocarbon discharge from deep reservoirs may be pulsed or steady and may persist for short or long time periods. Seepage is driven by the modest overpressure that exists within reservoirs and occurs at the seabed, effectively reintroducing oil and gas into the carbon cycle. Some components of the methane system (e.g., shallow near seabed gas and/or gas hydrate) can recycle more rapidly, being reintroduced into the active carbon cycle on timescales of 10^2–10^6 years (Jahren et al. 2005, Sundquist & Visser 2003). Along continental margins across the globe, the flux of hydrocarbons sculpts the biology, chemistry, and geology of affected habitats (Joye & Kleindienst 2017).

Hydrocarbon seep: a location along the seabed where oil and/or gas move through and are discharged naturally into the adjacent compartment (i.e., the water column); the sediments at hydrocarbon seeps are oil stained and often oil and gas saturated

The presence of natural gas seeps in the Gulf of Mexico (hereafter Gulf) in 1976 predated the discovery of hydrothermal vents (Bernard et al. 1976). But reports of seafloor hydrocarbon seeps occurred in the 1980s—first reported in the Gulf and then off the coast of Oregon (Anderson et al. 1983, Paull et al. 1984, Suess et al. 1985)—a few years after the discovery of hydrothermal vents in the Pacific (Ballard 1977). These so-called cold seeps share many similarities with their hydrothermal cousins. Hydrocarbon seeps are sites where deeply sourced geofluids discharge from the seabed; however, the discharging fluids are cold/cool (at or slightly above ambient, rarely more than tens of degrees Celsius), not boiling (>350°C) and tend toward circumneutral (pH $\sim$ 7) instead of being acidic (pH $<$ 4) like vent fluids. The chemistry of the discharging fluids is also different—hydrothermal vents discharge fluids enriched in geogenic methane, hydrogen sulfide, hydrogen, and reduced metals, whereas hydrocarbon seeps discharge fluids enriched in biogenic and thermogenic gases, oil, and brine of differing composition. Finally, fluid discharge rates at seeps are, in general, lower than fluid discharge rates at vents (Suess 2014). Both hydrocarbon seeps and hydrothermal vents lead to unique geobiological signatures of the local environment (Callender et al. 1990, Cordes et al. 2009, Joye & Kleindienst 2017).

Estimates of the oil and gas reserves that underlie cold seeps are fairly well constrained (see above), but the rate of hydrocarbon seepage into the environment is poorly constrained in most ecosystems. While the stock of natural gas in the Gulf system is estimated to be 607 × 10^{12} m^3 (Boswell et al. 2012), the magnitude of methane fluxes from deep reservoirs is poorly known (Solomon et al. 2009). Extensive work in the Gulf after the *Deepwater Horizon* oil spill in 2010 generated robust estimates of oil seepage (MacDonald et al. 2015). The roughly 914 natural seeps in the Gulf discharge between 2.53 and 9.48 × 10^4 m^3 oil $year^{-1}$ across the system, with the majority discharged in the western portion of the basin (MacDonald et al. 2015). This systemwide natural input contrasts starkly with the input from the *Deepwater Horizon* oil well blowout (78 × 10^5 m^3 oil at a daily rate of 10^5 m^3 day^{-1}) that was released from the damaged well. Relative to large accidents such as the *Deepwater Horizon* oil spill, about 1.1 × 10^5 m^3 oil $year^{-1}$ is released into North American waters by other anthropogenic activities (boats, runoff, etc.).

2. SIGNATURES OF HYDROCARBON SEEPAGE

2.1. Geological Underpinning

Basins along passive margins are widely recognized as important sites of oil and gas generation and accumulation; these basins account for ∼60% of the total expanse of marginal environments globally (Judd et al. 2002, Xie et al. 2019). Many of the passive margin petroleum-rich basins also contain evaporites (89%) (Hudec & Jackson 2006), and these salt deposits contribute to hydrocarbon formation through their thermal properties and migration through salt tectonics (Xie et al. 2019). Examples of petroleum-rich, salt-influenced marginal systems include the Campos Basin, Gabon Basin, Gulf, Lower Congo Basin, North Sea, Persian Gulf, and Santos Basin (Xie et al. 2019). Hydrocarbon accumulation along active margins, mainly as methane, is more localized and restricted to areas of tectonic compression (i.e., accretionary prisms), which focuses organic matter and stimulates biological methanogenesis (Claypool et al. 2006, Heeschen et al. 2005, Ijiri et al. 2018). Examples of methane seeps associated with accretionary prisms include the Cascadia Margin (Heeschen et al. 2005), the Nankai Trough (Ijiri et al. 2018), the Costa Rica Margin (Kahn et al. 1996), and the Hikurangi Margin (Ruff et al. 2013).

Hydrocarbons accumulate in sediments, in localized pockets (i.e., gas-rich lenses in shallow, organic-rich sediments), and/or in large, porous reservoirs laden with oil and gas within sedimentary rocks. In sedimentary basins, hydrocarbon migration through the system is influenced by the distribution of salt bodies (Kramer & Shedd 2017). Salt is ductile, and its movement generates basin and range topography along the seabed and fault networks that serve as thoroughfares that guide hydrocarbon flow through the system (Brun & Fort 2018, Kramer & Shedd 2017). As deeply sourced fluids migrate through faults and interact with salt bodies, fluid chemistry is altered, generating distinct geochemical signatures (Brooks et al. 1990) (**Figures 1** and **2**).

One of the most well-studied hydrocarbon basins is the Gulf (Joye et al. 2016). The Gulf is home to a broad variety of surface expressions of hydrocarbon discharge, including mud volcanoes, brine seeps, pools, and basins; oil and gas seeps; gas hydrates; asphalt volcanoes; and carbonate pavements (MacDonald et al. 2000). Geochemical and microbial alteration of oil and gas during migration through the sediment column generates terminal metabolic end products (CO_2, CH_4) and organic intermediates (**Figure 1**). Interaction with salt bodies further alters the fluid, generating brines infused with oil and gas; brine-sediment interaction enriches discharging fluids with ammonium, phosphate, silicate, and dissolved organic matter (DOM) (Bowles et al. 2016,

Salt tectonics: the processes associated with the movement of evaporite salt deposits within a sedimentary sequence

Mud volcano: location where fluids and/or fluidized mud, often saturated with gas and/or oil, are erupted from the seabed; discharged fluids are often warmer by tens of degrees Celsius above bottom water

Brine seep: site of brine expulsion resulting in brine-influenced sediments and flows, pools filled with brine, and—in some cases—brine basins

Gas (methane) hydrate: crystalline solid comprising water and gas, predominately methane but also ethane, propane, and butane, found under appropriate temperature-pressure-salinity conditions

Asphalt volcano: seafloor discharge areas where asphalt along with oil and gas are discharged, generating asphalt/tar flows and structures

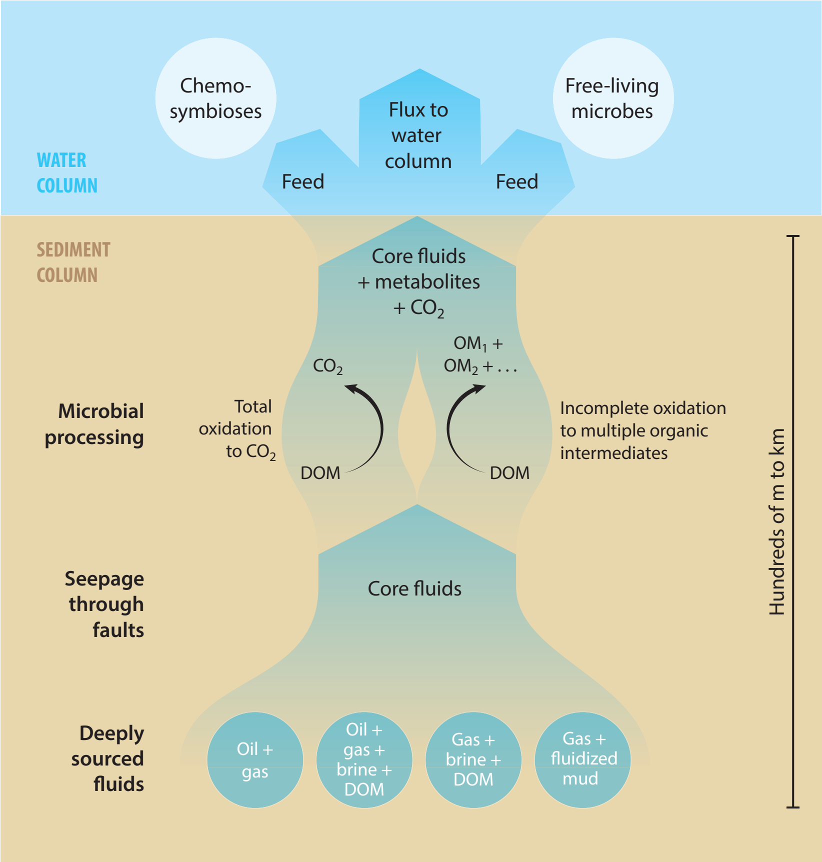


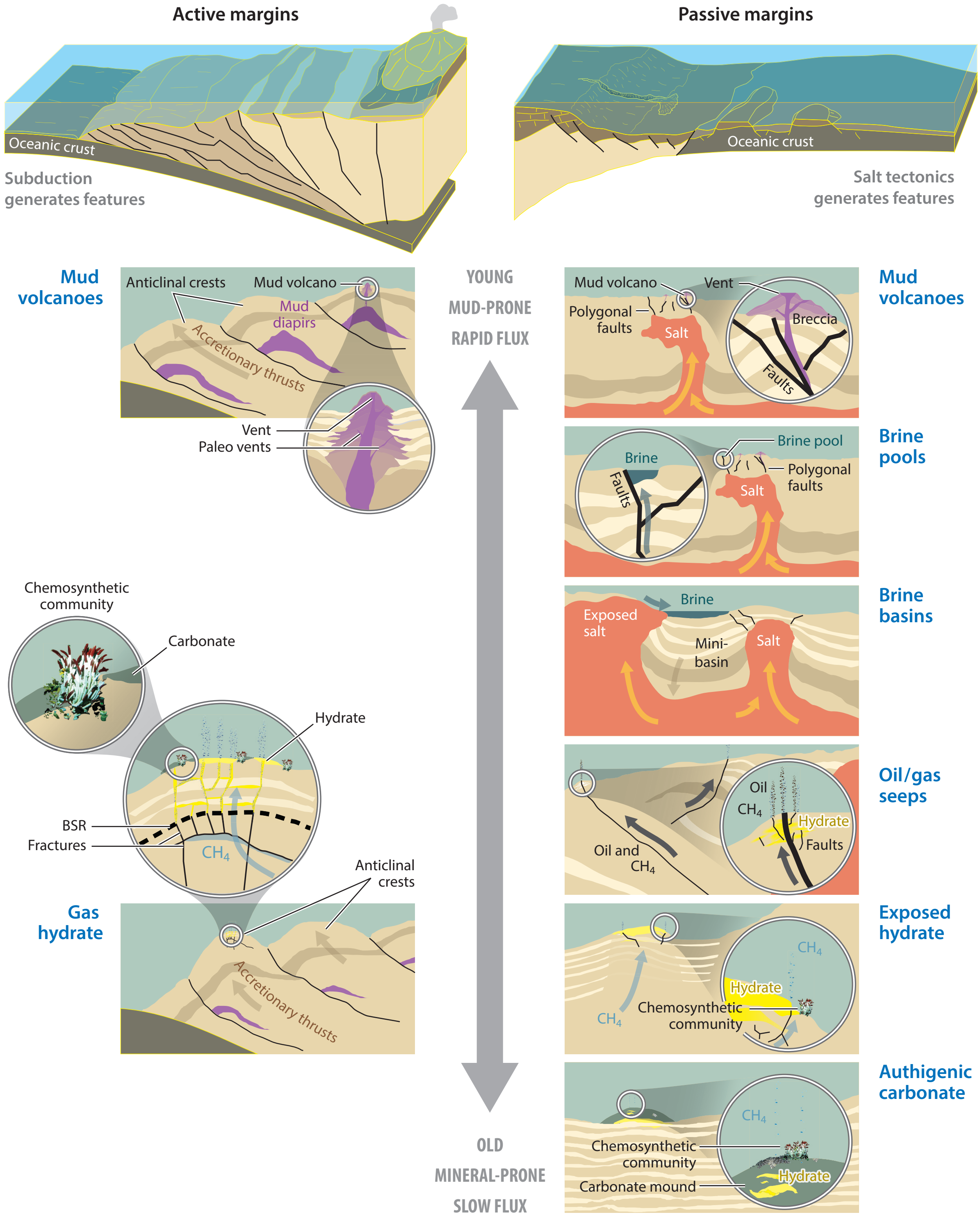
Figure 1

Deeply sourced fluxes and their biogeochemical impact. The deep fluids that fuel hydrocarbon seeps fall into four categories: oil + gas, oil + gas + brine + dissolved organic matter (DOM), gas + brine + DOM, and gas + fluidized mud. During upward transit through fault networks, source fluids are altered through microbial processing, which generated intermediates and terminal metabolites. At the sediment-water interface, source fluids, metabolites, and reaction products (e.g., dissolved inorganic carbon) are further transformed by biological processes mediated by free-living and chemosymbiotic associations. Some fraction of the deeply sourced materials may be discharged to the water column, impacting water column processes.

Joye et al. 2005, Joye et al. 2010, Kennicutt 2017) (**Figure 1**). At the seabed, discharging fluids provide metabolic fuel to support free-living microorganisms and chemosynthetic-symbiotic animal associations (**Figure 1**). Some fraction of the energy transported from the deep subsurface bypasses the biological filter along the seabed and is transferred from the sediment system to the overlying water column, where the discharged materials influence pelagic habitats and microbial communities.

2.2. Surface Expressions of Hydrocarbon Seepage

Hydrocarbon seepage creates distinct surficial expressions and habitats, each representing a unique habitat fingerprint (**Figure 2**). Hydrocarbon seeps are often classified according to the fluid flow regime: high discharge, mud-prone systems (e.g., mud volcanoes) versus low-discharge,



(Caption appears on following page)

Figure 2 (*Figure appears on preceding page*)

The geological underpinning of hydrocarbon seeps. Along active margins, hydrocarbon seeps are associated with accretionary processes, generating mud volcanoes and in some cases gas hydrate. Along passive margins, a range of seep environments exist, from high-flux, mud-prone systems—mud volcanoes, brine pools, and brine basins—to moderate-flux oil and gas seeps with gas hydrate to slow-flow mineral-prone systems characterized by authigenic carbonates. Abbreviation: BSR, bottom-simulating reflector.

Authigenic carbonates: calcium (magnesium) carbonate minerals that form spontaneously, forming nodules, casts, and pavements that serve as carbon sinks and biological habitat

mineral-prone systems (e.g., authigenic carbonates) (Roberts & Carney 1997, Roberts et al. 2006). Mud volcanoes discharge water (or brine), gas—mainly methane but also CO_2 and in some cases other low–molecular weight alkanes—and fine-grained sediment in a semiliquid state; some systems co-discharge oil and gas (**Figure 3*a***).

Mud volcanoes form in areas where clay dewatering occurs and fluid expulsion is driven by compression; these features occur in areas of high sediment deposition rate (passive margins) or tectonic activity (compression, active margins) (Dimitrov 2002, Dimitrov 2003). When the fluids beneath a mud volcano are heated through interaction with buried salt, a warm, buoyant fluid

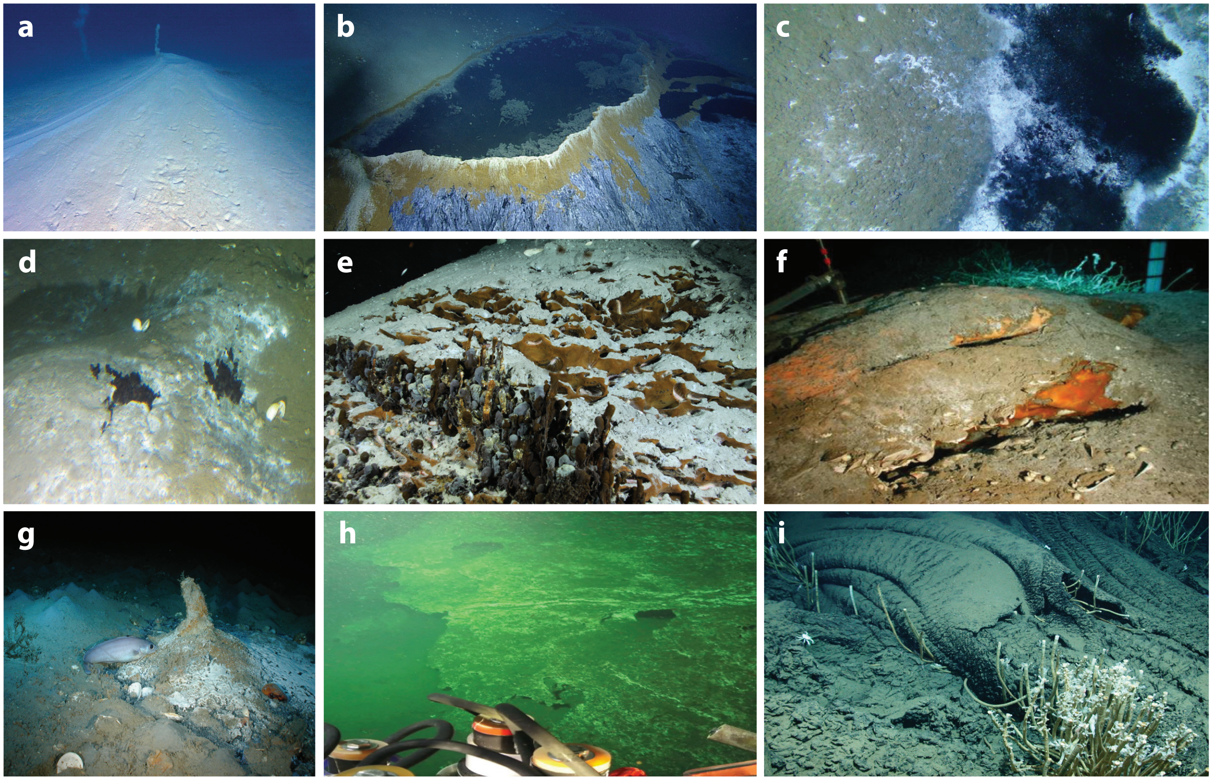


Figure 3

Geological habitats. (*a*) Flower Garden Banks, Gulf of Mexico, mud volcano. (*b*) Mineral terraces filled with hypersaline brine. (*c*) Black, highly reduced brine flowing along the sediment surface at Green Canyon block 600. (*d*) Oil and tar discharging from oil-saturated sediments at a hydrocarbon seep in the Gulf of Mexico. (*e*) Oil-saturated deep slope (ca. 1,200 m) gas hydrate mound with tar chimneys. (*f*) Oil-saturated upper slope (ca. 500 m) gas hydrate mound. (*g*) Authigenic barite chimney near a mud volcano in the Gulf of Mexico. (*h*) Carbonate pavement at a hydrocarbon seep along the Sonora Margin, Sea of Cortez. (*i*) Asphalt flow near the Chapopote asphalt volcano, Gulf of Mexico, colonized by tubeworms, mussels, and crabs (2016). Photos courtesy of (*a*) NOAA Flower Garden National Marine Sanctuary, (*b*) Ocean Exploration Trust (OET) and Nautilus Live, (*c,d,f,g*) S.B. Joye (University of Georgia), (*e*) Dr. Ian MacDonald (Florida State University), (*h*) S.B. Joye (University of Georgia) and the Schmidt Ocean Institute, and (*i*) Dr. Gerhard Bohrmann (MARUM, University of Bremen).

that rises toward the surface is generated (Kopf 2002, Milkov 2000). Mud volcano habitats are dynamic, often displaying violent eruptions at seemingly random periodicity (MacDonald et al. 2000). Mud volcanoes range in size from meters to kilometers in diameter and are easily discovered and mapped using remotely operated vehicle or ship-based multibeam echosounder mapping (Ruppel et al. 2005). Discharge of fine particles often limits development of animal communities, compared to gas and oil seeps, but animal communities can develop along the edges of the eruptive zone.

At slower brine seepage rates, hypersaline pools form in localized depressions along the seafloor (Joye et al. 2009; MacDonald et al. 2000, 2004) (**Figures 2** and **3*b*,*c***). Brine flows can also accumulate in deep basins, forming chemically challenging and unique pelagic habitats—for example, the Orca Basin in the Gulf (Pilcher & Blumstein 2007, Shokes et al. 1977) or the Bannock and Urania Basins in the Mediterranean (Borin et al. 2009, Hallsworth et al. 2007). Deep sea brine habitats represent some of the most extreme habitats on Earth, given the combination of high ionic strength, unique chemistry (e.g., high magnesium or metal concentration), and high pressure (Hallsworth et al. 2007).

Subtle differences in the environmental geochemistry across a habitat type—for example, the distribution of major ions in brine pool fluids—arise from variations in local geology (i.e., salt composition, depth from the seabed to underlying salt) (Joye et al. 2010). The discharge of brine fluids provides a significant source of nutrients—ammonium, phosphate, and silicate—as well as nonhydrocarbon DOM to the deep sea (Bowles et al. 2016, Joye et al. 2010). Gas hydrate habitats also discharge DOM (Pohlman et al. 2011), but the concentrations in brines dwarf those documented from hydrate environments and brine fluxes are more pronounced, suggesting that brines are more important dissolved organic carbon (DOC) sources to the deep ocean. These habitats support unique microbial communities, and at the edge of brine pools, dense accumulations of chemosynthetic fauna occur (MacDonald et al. 1990).

Comigration and discharge of oil and gas in the absence of brine generate seeps characterized by discrete bubble discharge from the seafloor (Johansen et al. 2017, Levin et al. 2016) or slow percolation through sediments, which generates oil-stained and, in some cases, oil-saturated locales (Abrams & Dahdah 2011, Kennicutt 2017) (**Figure 3*d***). When hydrocarbon discharge occurs within the gas hydrate stability zone, gas hydrate may form at the sediment-water interface, in addition to within the sediment column (Boswell et al. 2012; Brooks et al. 1987, 1990, 1994) (**Figure 3*e*,*f***). Many hydrocarbon seeps are characterized by widespread occurrence of gas hydrate (Boswell et al. 2012). Gas hydrate (or clathrate) is a frozen crystalline solid that concentrates low–molecular weight alkanes, mainly methane, within the interstitial cavities; gas hydrate focuses methane by 160 times relative to concentrations found typically in seawater.

Gas hydrate forms within a well-defined temperature-pressure window under conditions of sufficient water availability, where high pore fluid gas concentration exists and where gas supplies are steady (Collett et al. 2008). Gas hydrates represent the largest reservoir of methane on Earth and occur in marine sediments across the globe, in the polar regions, on land (tundra), and in subseafloor permafrost (Joye & Kleindienst 2017, Kennicutt 2017). Salinity can also influence hydrate stability. In situations where hydrocarbons comigrate with brine, the salt and heat provided by the brine can impede gas hydrate formation (Ruppel et al. 2005). Gas hydrate forms spontaneously under appropriate conditions, but if conditions change—for example, bottom waters warm—hydrate can sublime, releasing the materials trapped in clathrate cages. During formation, sediment and in some cases oil are incorporated into the hydrate lattice; microbial activity within these sediment inclusions, and to some degree in the solid hydrate itself, occurs, making hydrate a unique geobiological habitat (Orcutt et al. 2004).

Barite chimney: barium sulfate (barite) mineral structures form where reduced, barium-rich fluids encounter sulfate-rich fluids, driving the spontaneous precipitation of barite chimneys

Salt diapir: a vertical intrusion of evaporite mineral (halite, anhydrite, or gypsum) sourced well beneath the seabed into the surrounding strata

Two types of authigenic minerals form at hydrocarbon seeps: barite chimneys and carbonates. Barite chimneys are most often associated with higher flow environments, such as mud volcanoes (**Figure 3*g***). When reducing, barium-rich fluids mix with sulfate-rich seawater, barium sulfate, barite, spontaneously precipitates (Aharon 1996). Barite chimneys often mark the location of fluid discharge points and are often associated with microbial mats as well as endolithic microbial communities (Stevens et al. 2015).

Persistent discharge of hydrocarbons, and subsequent oxidation of labile components by microbial communities, leads to accumulation of bicarbonate, which drives the precipitation of authigenic carbonate (Meister et al. 2018, Roberts & Aharon 1994, Smith & Coffin 2014) (**Figure 3*h***). Carbonate nodules, blocks, and pavements are hallmarks of hydrocarbon seepage (Roberts et al. 2009). The mineralogy of carbonates records the chemical conditions in the depositional environment. While aragonite is usually the dominant form of carbonate present (Feng et al. 2014, Zwicker et al. 2018), at brine seeps where calcium concentrations may be depleted, calcium-magnesium carbonates can be abundant, underscoring the role carbonates play in recording the chemistry of the seeping fluid (Joye & Kleindienst 2017).

Carbonate formation plays an important role in hydrocarbon seep dynamics, as carbonates can influence fluid flow by obstructing flow paths, thus generating new areas of seepage (Suess 2014). Accumulation of carbonate at seeps is most pronounced at intermediate discharge rates (3–40 cm year^{-1}), with precipitation rates decreasing at lower and higher rates of discharge (Karaca et al. 2010). Many hydrocarbon seep ecosystems are characterized by widespread authigenic carbonate pavements (**Figure 3*h***). These mineral formations can be extensive, and their carbon isotopic composition shows an inextricable linkage to hydrocarbon, especially methane, oxidation, and hence hydrocarbon seepage (Suess 2014). Carbonate minerals represent a porous stable habitat for colonization and proliferation of both microbial (Marlow et al. 2014) and animal communities (e.g., corals) (Cordes et al. 2009).

Asphalt volcanoes are an unusual type of hydrocarbon seep expression (**Figure 3*i***). First discovered in 2004 in a field of salt diapirs known as the Campeche Knolls, the Chapopote asphalt volcano was discovered at a depth of 3,000 m (MacDonald et al. 2004). As the name suggests, these features are characterized by accumulations of asphalt and tar typically saturated with oil and gas. Asphalt volcanoes have been reported across a range of water depths (Alcazar et al. 1989, MacDonald et al. 2004, Valentine et al. 2010), appear to result from discharge of heavy petroleum (Bruning et al. 2010), and are driven, potentially, by interaction with supercritical water (Hovland et al. 2005). Asphalt volcanism is very different from more typical modes of oil and gas discharge. The residual asphalt and tar structures result from periodic incursions of quasi-molten hydrocarbons that move laterally over the seep site, producing extravagant three-dimensional structures that can have a pronounced vertical component (Bruning et al. 2010). However, like other oil- and gas-influenced habitats, asphalt volcanoes are generated through salt tectonics.

2.3. Relevance of Hydrocarbon Seeps

Hydrocarbon seeps are diverse and heterogeneous environments. Significant spatial and temporal variability is the norm (Garcia-Pineda et al. 2015), and over time, seep systems evolve from high-flow to low-flow regimes as salt tectonics shifts fault networks and authigenic carbonate formation forces new plumbing (Clark et al. 2010, Leifer et al. 2004). Hydrocarbon seepage supports a broad array of biological processes and accumulation of immense diversity and biomass (Levin et al. 2016). Even after hydrocarbon seepage abates, the authigenic fingerprint of seepage—carbonate mineral nodules, rocks, and pavements—serves as hard ground for settlement and proliferation of deepwater corals, expanding the impact of seepage (Cordes et al. 2008).

For years, hydrocarbon seeps and hydrothermal vents were considered isolated oases in the deep sea (Åström et al. 2017, Levin et al. 2016). At seeps, deeply sourced energy inputs fuel primary production, and this production fuels development of a complex, biomass-rich chemosynthetic ecosystem of seep endemics and mobile predators that is substantially more rich than no-seep areas (Åström et al. 2017, Levin et al. 2016). A diverse array of biogeochemical processes accelerates at and around seeps, creating critical geobiological engines that contribute significantly to local and global biogeochemical cycles (see Section 3.1). Substantial evolutionary and ecological connectivity exists between seep habitats (Levin et al. 2016). And seep systems are much more connected to the surrounding environment and the upper water column than initially thought.

Seepage affects local physical, chemical, and biological regimes in the water column and influences the coupled benthic-pelagic system. Seeping fluids can generate biological signatures, such as increases in chlorophyll (D'souza et al. 2019) or primary production (Ardyna et al. 2019) in surface waters, as well as chemical signatures, such as stimulating hypoxia by hydrogen sulfide intrusions (Emeis et al. 2004, Weeks et al. 2002), that strongly impact the water column all the way to the surface. Hence, seafloor seepage can promote mixing between the deep ocean and surface ocean, influencing physical mixing in profound ways that make seeps an unrecognized contributor to oceanic connectivity.

Chemosynthetic ecosystem: complex biological ecosystem including microorganisms, meiofauna, and megafauna that is fueled by the activity of free-living and symbiotic microbial communities

Redox zonation: series of electron acceptors—oxygen → nitrate ~ manganese oxide → iron oxide → sulfate → carbon dioxide—over depth in the sediment column

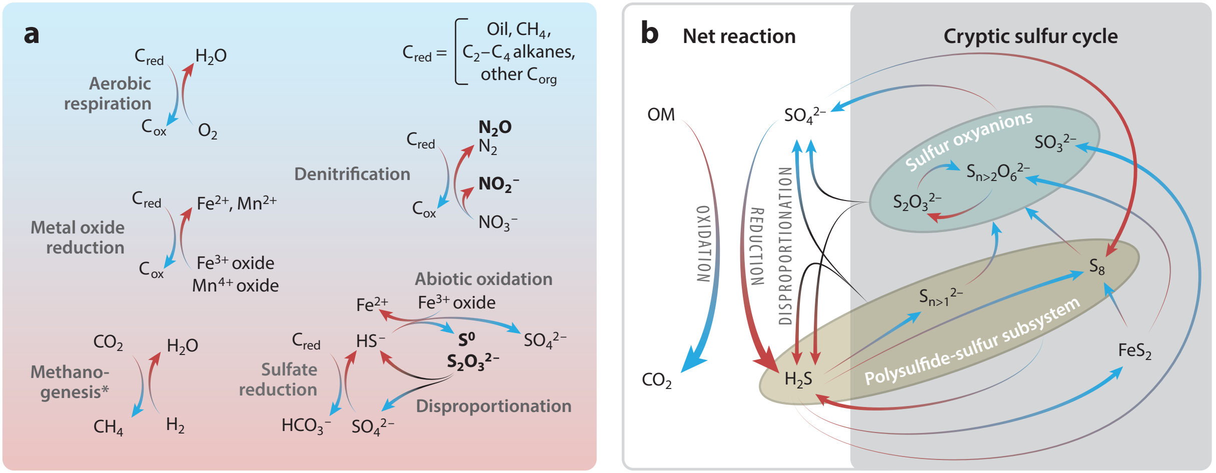
3. BIOGEOCHEMISTRY OF HYDROCARBON SEEPS

3.1. Setting and Framework

Hydrocarbon seep systems act as rich microbial reactors that support a plethora of biogeochemical processes and interactions. Processes that occur slowly in other environments are often accelerated at energy-rich seeps, making these hot spots ideal natural laboratories for exploring biogeochemical dynamics. Studies of seep ecosystems have enabled fundamental advancements in understanding globally important processes, such as the anaerobic oxidation of methane (AOM) (Boetius et al. 2000), and are ideal environments for studying microbial interactions and symbiosis (Dubilier et al. 2008, Fisher 1990).

Microorganisms extract metabolic energy from the coupled reduction-oxidation reactions they mediate. Redox zonation is a term used to describe vertical stratification of the biogeochemical processes that cycle organic matter over depth. Such zonation reflects an emergent property arising from differences in the thermodynamic energy yield of reactions, as well as reaction kinetics (Vallino & Algar 2016). Together these factors dictate the successive consumption of available electron acceptors and steady accumulation of reaction products in a depth horizon and over depth profiles (Jørgensen & Kasten 2006). Redox zonation occurs across systems—in sediments, soils, and water bodies—at different scales, depending on the supply of electron donors and acceptors and the physical mixing regime.

At hydrocarbon seeps, oil and gas are the dominant oxidants, especially in offshore habitats where terrestrial and marine organic matter inputs are limited (Joye et al. 2004). Along the redox spectrum, organic matter oxidation coupled to oxygen reduction yields the most energy, followed by nitrate and manganese oxide reduction, then iron oxide reduction, then sulfate reduction (SR), and finally methanogenesis (**Figure 4**). A number of factors complicate this idealized scenario, including the mineralogy and availability of metal oxides (Riedinger et al. 2017), which dictate their rate of reaction, the presence of burrowing animals (Jørgensen & Kasten 2006), and bubble discharge (Foucher et al. 2015). Improved descriptions of the thermodynamics and energetics of biogeochemical cycles (Vallino & Algar 2016) are needed to provide a more consistent and fruitful framework for assessing differences between ecosystems and to identify the factors driving emergent patterns across systems. Also, understanding interactions and couplings requires focused experimental efforts carried out under environmentally relevant conditions.



*Methane is also produced via acetate fermentation and reduction of methylated substrates

Figure 4

(*a*) Major biogeochemical processes at cold seeps. Coupling between the oxidation of reduced carbon (C_{red}) and various electron-accepting processes along an idealized depth zonation is shown here. At hydrocarbon seeps, the reduced carbon fueling metabolism includes methane and oil, alkanes, and other particulate and dissolved organic carbon (other C_{org}). Aerobic respiration generates the most energy, but oxygen is consumed quickly. Nitrate reduction proceeds via reduction of nitrate to nitrate and then to nitrous oxide or dinitrogen. Metal oxide reduction—iron or manganese oxide—follows next. Sulfur cycling is well described at seeps. Sulfate reduction is tightly coupled to sulfur oxidation via abiotic and biological processes that regenerate sulfate, thereby fueling high rates of gross sulfate reduction. Intermediates that accumulate to environmentally significant concentrations are shown in bold type. Finally methanogenesis occurs through a variety of mechanisms; methlytrophic methanogenesis is likely the most important pathway of methanogenesis at seeps. (*b*) Net and cryptic sulfur cycling. Cryptic cycling enables rapid and efficient regeneration of sulfate through abiotic and biotic processes. Sulfur oxyanions and reduced sulfur species exhibit dynamic subcycles in the sediment sulfur system.

The sequence of biogeochemical processes described above is often intimately connected (Kappler & Bryce 2017), and the redox signature of the bulk environment can mask the complexity of processes occurring behind the scenes. So-called cryptic elemental cycles (Hansel et al. 2015) (**Figure 4*b***) are driven by the presence of highly reactive, often short-lived reaction intermediates that are present at low concentration. Cryptic cycles play important roles in elemental cycles and may serves to bridge elemental cycles (**Figure 4*b***). In particular, cryptic sulfur cycling at cold seeps may play a critical role in facilitating processes near redox interfaces (Beulig et al. 2019).

3.2. Biogeochemical Redox Zonation

Biogeochemical redox zonation at hydrocarbon seeps depends on the nature and concentration of reduced substrates in the fluid (e.g., oil and gas, DOC, ammonium, sulfide) and the magnitude and variability of discharge rate. Metabolism of deeply sourced hydrocarbons or other energy-rich substrates in shallow sediments and near the sediment-water interface generates a complex geochemical milieu that drives downstream metabolisms (Joye & Kleindienst 2017). For example, high rates of SR generate sulfide, which stimulates sulfide oxidation by free-living and symbiotic microorganisms (Bailey et al. 2009, Dombrowski et al. 2018). Biogeochemical cycling at seeps is highly coupled and interactive, and seep systems support some of the highest rates of metabolism documented in natural environments (Bowles et al. 2010).

The extremely high rates of metabolism occur because of an abundance of energy-rich substrates (Joye et al. 2004), but how these high rates of metabolism are maintained is unclear (see

Section 3.3.3). Even modest rates of hydrocarbon seepage lead to rapid oxygen consumption rates, compressing and steepening redox profiles (Boetius & Wenzhöfer 2013). Metabolic activity and geochemical signatures at seeps tend to be very patchy because fluids migrate through localized conduits and are discharged periodically through vents and along surface-breaching faults (Joye & Kleindienst 2017, Suess 2014). Dense microbial communities, such as microbial mats and biofilms (Joye et al. 2004), and diverse animal assemblages (Cordes et al. 2009) mark locations of diffuse hydrocarbon seepage and advective fluid discharge.

The chemical cocktail and flux regimes of a seep create a unique biogeochemical fingerprint and generally distinguish seeps from background shelf or slope environments. In environments lacking hydrocarbon discharge, the sedimentary organic matter fueling microbial processes is derived from terrestrial and marine sources. Organic matter is attenuated slowly over depth through remineralization, which produces metabolic end products—for example, dissolved inorganic carbon (DIC), nitrogen (DIN) mainly as ammonium (NH_4^+), and phosphorus (DIP)—in proportion to local Redfield ratio, the ratio of C-N-P in freshly deposited organic matter. At offshore sites, this organic matter is largely derived from phytoplankton, but near shore, this material is derived from autochthonous (plankton) and allocthonous (terrigenous) sources. Because hydrocarbons contain little N and P, their oxidation results in accumulation of DIC but not DIN or DIP. Strong deviations in regenerated C-N-P from the local (plankton/terrigenous) Redfield ratio of organic matter can infer hydrocarbon oxidation. Chloride concentrations are constant over depth, and sulfate may be depleted, albeit at depths of tens to hundreds of centimeters, depending on the organic matter content and lability. Below the depth of sulfate depletion, methane can accumulate, sometimes to millimolar concentrations, again, depending on organic matter availability.

The sediment profiles observed at hydrocarbon seeps are very different (Joye et al. 2010). Seep sediments are more organic carbon rich, sometimes containing up to 10% organic carbon by weight, and oil staining of sediments is apparent. DIC and hydrogen sulfide reach concentrations up to or exceeding 15 m*M*. Sulfate depletion is common within the upper 20 cm, and pore fluid methane concentrations often approach saturation, close to 100 m*M* (Lapham et al. 2013). The accumulation of DIC is not matched by accumulation of DIN or DIP, however, as would be observed in normal marine sediments (Joye et al. 2004).

Unlike terrestrial or marine-derived organic matter that contains a consistent proportion of N and P, hydrocarbons introduce little N and no P into a system. Most often oils contain <0.1 wt% N, although heavy oils and bitumen contain more (up to 1 wt% N). Thus, hydrocarbon oxidation generates DIC and organic intermediates, but no other nutrients are recycled. As a result, most hydrocarbon seeps are inherently nutrient limited, with an abundance of organic matter but a limited supply of nitrogen and phosphorus to support biological biomass production (Joye et al. 2004). Brine seeps are an exception to this statement, since brines are rich in DIN, DIP, and dissolved silicate (Bowles et al. 2016).

At brine seeps, pore fluids have chloride concentrations that are 2–4 times seawater concentrations (up to molar levels). Sulfate is often completely depleted near the surface due to active upward advection of brine, and sulfide does not accumulate because of sulfate limitation (Bowles et al. 2016, Joye et al. 2010). In contrast to oil and gas seeps, hydrocarbon-influenced brine seeps also discharge deeply sourced ammonium, phosphate, and silicate to surface environments, making these sites important nutrient sources to the deep sea (Bowles et al. 2016). The global significance of brine-derived nutrients to the deep sea is unclear, but given the widespread nature of mud volcanoes and brine seeps along continental margins and the often vigorous nature of the discharge, the source magnitude may be significant and better constraints on nutrient input from these habitats to the deep sea are needed (Joye et al. 2010).

3.3. Microbially Mediated Processes

Hydrocarbon seeps support diverse and abundant microbial communities that foster active and dynamic biogeochemical cycling of materials. Seep habitats represent globally relevant habitats that serve as effective gatekeepers, regulating exchange between the ancient—i.e., old carbon from deep hydrocarbon reservoirs—and the active—i.e., present day—carbon cycle. Microbial processes mediate and moderate these exchanges. High rates of energy input make seeps perfect habitats for examining patterns and regulation of microbial dynamics, for studying microbial processes and interactions and biogeochemical cycles, and for discovering new microorganisms and metabolic innovations.

3.3.1. Tracing the sources and fate of oil and gas. Biogenic methane is generated in three ways—hydrogenotrophic (bicarbonate reduction to methane using hydrogen as reductant), acetoclastic (acetate fermentation yields CH_4 and CO_2), and methylotrophic (methanol, methane thiol, dimethylsulfide, or other simple substrates) methanogenesis. Thermogenic and biogenic methane sources can be distinguished through measurement of the stable isotopic composition of carbon ($\delta^{13}C$) and deuterium (δD) (Whiticar 1999). Biological processes select against the heavy isotope in preference for the light isotope. The $\delta^{13}C$ for biogenic methane is more ^{13}C depleted, ranging between −60 to −110‰, compared to −30 to −40‰ for thermogenic CH_4, which is more ^{13}C enriched. The δD values of biogenic and thermogenic gas overlap to some degree but can be used to separate different biogenic sources.

The biogenic sources have distinct signatures. Methylotrophic methanogenesis generates ^{13}C-enriched methane (−60‰); methane from hydrogenotrophic processes is more ^{13}C depleted (−110‰). Acetoclastic methanogenesis expresses less fractionation due to acetate limitation (usually −50 to −65‰). Radiocarbon ($\Delta^{14}C$) provides an additional measure to distinguish thermogenic and biogenic methane sources (Pohlman et al. 2011). Measurement of clumped isotopes—occurring when a molecule contains two or more rare isotopes—in methane offers a way to further refine source-sink dynamics (Eiler 2007). Knowing the isotopic value for methane versus oil (which is typically more ^{13}C enriched, around −27 to −29‰) and tracking the carbon into products (e.g., DIC, biomarkers, or intermediates) can disentangle metabolic coupling in hydrocarbon seep environments (Jaekel et al. 2013, Joye et al. 2010).

3.3.2. Aerobic versus anaerobic metabolism. At cold seeps, hydrocarbon oxidation is the dominant metabolism and is often coupled to SR (Joye et al. 2010). Mineralization of seep-derived or brine-derived DOM can contribute to carbon cycling, but the sheer abundance of hydrocarbons makes them the dominant reductant. Oxygen is rapidly consumed by microorganisms dwelling in the upper few millimeters of sediments or living symbiotically with animals at the sediment-water interface (Boetius & Wenzhöfer 2013). Oxygen is also consumed by abiotic reactions that recycle reduced substrates (e.g., hydrogen sulfide). A great deal of oxygen consumption is due to the activity of thiotrophic and methanotrophic microorganisms, both free-living organisms and those living in symbiosis (Boetius & Wenzhöfer 2013, Dubilier et al. 2008). Since oxygen is rapidly consumed, the majority of the sediment column is anoxic (Grünke et al. 2012) and anaerobic metabolisms dominate.

The high sulfate concentration in seawater—28 mM—makes it the most abundant and, often, important electron acceptor at cold seeps. SR coupled to oil oxidation (Arvidson et al. 2004, Bowles et al. 2010, Joye et al. 2004, Orcutt et al. 2005), methane oxidation (Boetius et al. 2000), and alkane oxidation (Bose et al. 2013; Jaekel et al. 2013, 2015; Singh et al. 2017) occurs at cold seeps, although activity is rarely partitioned between these different metabolisms. The electron donor for SR can be assessed by tracking the isotopic composition of the DIC pool ($\delta^{13}C$-DIC) (Siegert et al. 2011).

The $\delta^{13}C$ of methane is typically more depleted in ^{13}C (−40 to −90‰, depending on whether the gas is biogenic or thermogenic) than oil (−29 to −33‰) (Joye et al. 2010), so DIC generated via AOM is more depleted in ^{13}C than DIC generated via oil oxidation. Authigenic carbonates record the source of DIC and allow tracking of microbial metabolisms over longer timescales, as well as hints of processes occurring over geologic timescales.

Reduced sulfur is reoxidized by a variety of sulfur-oxidizing bacteria, including conspicuous giant vacuolate sulfur bacteria that form mats and patches in areas of elevated microbial activity. Sulfur is also recycled through disproportionation, an inorganic fermentation-like reaction. Disproportionation occurs when compounds of intermediate redox state—elemental sulfur, thiosulfate, or sulfite—serve as both electron donor and acceptor, generating hydrogen sulfide and regenerating sulfate at cold seeps.

Nitrate, iron, and manganese oxides can be abundant in seep sediments, and iron dynamics is closely coupled to sulfur dynamics (Arvidson et al. 2004, Joye et al. 2004). Reports of denitrification (Bowles & Joye 2011) and metal oxide reduction (Beal et al. 2009) at cold seeps are scarce, largely because these processes lack a straightforward rate assay that can be easily employed to track rates. Measured rates of denitrification in the upper ~10 cm of seep sediments were high, requiring a rapid turnover of the nitrate pool (approximately a day) (Bowles & Joye 2011). Methanogenesis occurs at cold seeps through all known mechanisms (Orcutt et al. 2005), although methylotrophic processes are the most significant, accounting for more than 80% of methane production (Vigneron et al. 2015, Zhuang et al. 2018). Methane production rates are low—pmol cm^{-3} day^{-1}—compared to rates of AOM and SR (e.g., hundreds of nmol cm^{-3} day^{-1} to μmol cm^{-3} day^{-1}), but methanogenic activity is significant enough to drive the isotopic composition of methane into the biogenic range in some cases (Joye et al. 2010, Vigneron et al. 2015). A more focused effort describing the importance and dynamic of sulfate-independent metabolism at seeps and of methane production at seeps is warranted.

Different seep habitats support different modes of metabolisms. The vast majority of microbial activity assessments at hydrocarbon seeps have focused on oil- and gas-rich environments (Joye et al. 2004, 2010; Treude et al. 2003), with fewer measurements focusing on mud volcano/brine environments (Joye et al. 2009; Niemann et al. 2006a,b). Rates of metabolism at different types of cold seeps—oil and gas seeps versus brines—are similarly elevated, but rates at mud volcanoes and in brine habitats tend to be limited by sulfate availability due to rapid rates of fluid advection of sulfate-free brine (Bowles et al. 2016, Joye et al. 2010). Hydrocarbon seeps of all types exhibit extreme degrees of spatial variability in the patterns of activity, making it difficult to extrapolate localized measurements to a habitat or system (Bowles et al. 2016, Joye et al. 2010). Fermentation and high rates of unexpected processes such as acetogenesis occur in brine habitats (Joye et al. 2009), distinguishing them significantly from oil and gas seeps.

3.3.3. Anaerobic oxidation of methane.

The process that has received the most attention by far at hydrocarbon seeps is AOM (Knittel & Boetius 2009). Methane is a climate-active greenhouse gas, and marine sediments hold vast stores of methane as dissolved gas and as gas hydrate. Geochemical profiles and mass balances provided the first hint of the AOM process (Barnes & Goldberg 1976, Martens & Berner 1974). About a decade later, contemporaneous SR and AOM were detected in marine sediments using radiotracer assays (Iversen & Jørgensen 1985). Twenty years after the first suggestions of AOM, laboratory experiments with methane-rich sediments revealed syntrophic coupling between SR and AOM, providing a metabolic explanation for the CH_4 and SO_4^{2-} profiles observed in sediments (Equation 1) (Hoehler et al. 1994).

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^{\ -} + HS^- + H_2O - 17\ \text{kJ}\ (\text{mol}\ SO_4^{-2})^{-1} \qquad 1.$$

A significant breakthrough came in 1999 when Hinrichs et al. (1999) discovered extremely ^{13}C-depleted archaeal lipids in methane seep sediments and suggested these lipids were from anaerobic methanotrophs (ANMEs). This finding stimulated a focused research effort that revolutionized the understanding of AOM (Knittel & Boetius 2009). The next year, Boetius et al. (2000) provided visual evidence of consortia of ANME archaea and sulfate-reducing bacteria using fluorescence in situ hybridization. And then Orphan et al. (2001) used nanoscale secondary ion mass spectrometry to show that the aggregates of ANME and sulfate-reducing bacteria were extremely depleted in ^{13}C, documenting their incorporation of CH_4 into biomass. The process driving the geochemical profiles of sulfate and methane was confirmed, but still, no pure cultures of any ANME archaea, or other ANMEs, are available at present (although enrichment cultures are).

Today, we know that the AOM dynamic goes far beyond syntrophic coupling to SR and that its understanding is not yet complete. Evidence exists for AOM coupling to sulfate, nitrite, nitrate, and Fe(III) and Mn(IV) oxide reduction (see, e.g., Equations 2–5) (Beal et al. 2009; Boetius et al. 2000; Ettwig et al. 2010, 2016; Haroon et al. 2013). Recently, nanowire-dependent direct interspecies electron transfer between methane-oxidizing and sulfate-reducing microorganisms was documented (McGlynn et al. 2015, Wegener et al. 2015). Conductive minerals, such as magnetite and pyrite, could also facilitate interspecies electron transfer in sediments (Kato et al. 2012).

$$8NO_2^- + 3CH_4 + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O - 928\ \mathrm{kJ}\ (\mathrm{mol}\ NO_2^-)^{-1} \qquad 2.$$

$$8NO_3^- + 5CH_4 + 8H^+ \rightarrow 5CO_2 + 4N_2 + 14H_2O - 765\ \mathrm{kJ}\ (\mathrm{mol}\ NO_3^-)^{-1} \qquad 3.$$

$$4MnO_2 + CH_4 + 7H^+ \rightarrow HCO_3^- + 4Mn^{2+} + 5H_2O - 550\ \mathrm{kJ}\ (\mathrm{mol}\ MnO_2)^{-1} \qquad 4.$$

$$8Fe(OH)_3 + CH_4 + 15H^+ \rightarrow HCO_3^- + 8Fe^{2+} + 21H_2O - 270\ \mathrm{kJ}\ (\mathrm{mol}\ Fe(OH)_3)^{-1} \qquad 5.$$

Elucidating the factors that shape hydrocarbon seep microbial communities and regulate the rates of their metabolism is the next challenge. Seep microbial communities experience fluctuating and unpredictable methane concentration fields; exposure to extremely high ($>$50 mM) concentrations occurs periodically (Lapham et al. 2013), as does exposure to very low CH_4 concentration. During periods of high methane exposure, AOM rates can reach extremely high levels, and under such circumstances, AOM appears to be coupled to electron acceptors other than sulfate and is likely coupled to multiple processes simultaneously (Bowles et al. 2010, 2019).

Most studies of AOM evaluated rates at ambient pressure (not in situ) and assessed only one potential electron acceptor (e.g., SR). At the pressure typical of the deep sea, methane concentration is far greater than that possible in incubations at 1 atmosphere. Even at 1 atmosphere and 1 mM CH_4, the reaction stoichiometry of AOM and SR does not always support 1:1 coupling (Alperin & Hoehler 2009, Orcutt et al. 2005). Furthermore, AOM rates determined at methane concentrations more representative of in situ conditions ($>$15 mM CH_4) suggest that multiple contemporaneous pathways of AOM exist at seeps and that this may be the norm in fluctuating flux seep habitats (Bowles et al. 2019).

Placing seep biogeochemical processes in the context of fluctuating methane concentration fields generates a new perspective of seep dynamics. Previous studies have underscored the necessity of rapid sulfur recycling to maintain the high SR rates observed at seeps, SR that is purportedly linked to AOM (Bowles et al. 2010, Joye et al. 2004, Litchschlag et al. 2010). Similarly high rates of N and reduced metal (Fe, Mn) recycling would be required to support high rates of AOM coupled to N, Mn, and/or Fe reduction (Bowles et al. 2019). Metabolic phasing, where AOM is coupled to different electron acceptors at different times, pending electron donor and acceptor availability, could make AOM an efficient and effective sink for methane at hydrocarbon seeps across a range of environmentally relevant conditions.

Multiple modes of AOM and metabolic phasing involving a range of potential electron acceptors are more likely because any one process could become substrate limited eventually and most significantly at times of high methane flux (Bowles et al. 2019). Comprehensive assessment of AOM under realistic—for example, at high methane concentration—conditions, and considering multiple electron acceptors, is essential for understanding its environmental dynamic. To this end, in situ observatories capable of tracking both methane and oil concentration dynamics, documenting the physical environment, collecting biological samples, and performing rate assays under in situ conditions (e.g., Orcutt et al. 2017) offer a ripe opportunity for advancing the field of hydrocarbon seep biogeochemistry.

3.3.4. Nutrient limitation. Hydrocarbons are energy-rich substrates, but their chemical composition means that their metabolism is constrained by the availability of external nutrients, namely N and P. The stoichiometry of DIC, DIN, and DIP is skewed heavily toward DIC, suggesting severe N limitation, P limitation, or colimitation of N-P (Joye et al. 2004). The capacity for biological nitrogen fixation exists at cold seeps (Dekas et al. 2009, 2014; Miyazaki et al. 2009), and the process is clearly important but not well constrained. It is likely that multiple physiological groups mediate N_2 fixation at seeps, including potentially methanogenic archaea, methanotrophic archaea, and sulfate-reducing bacteria (Bertics et al. 2013, Dekas et al. 2009).

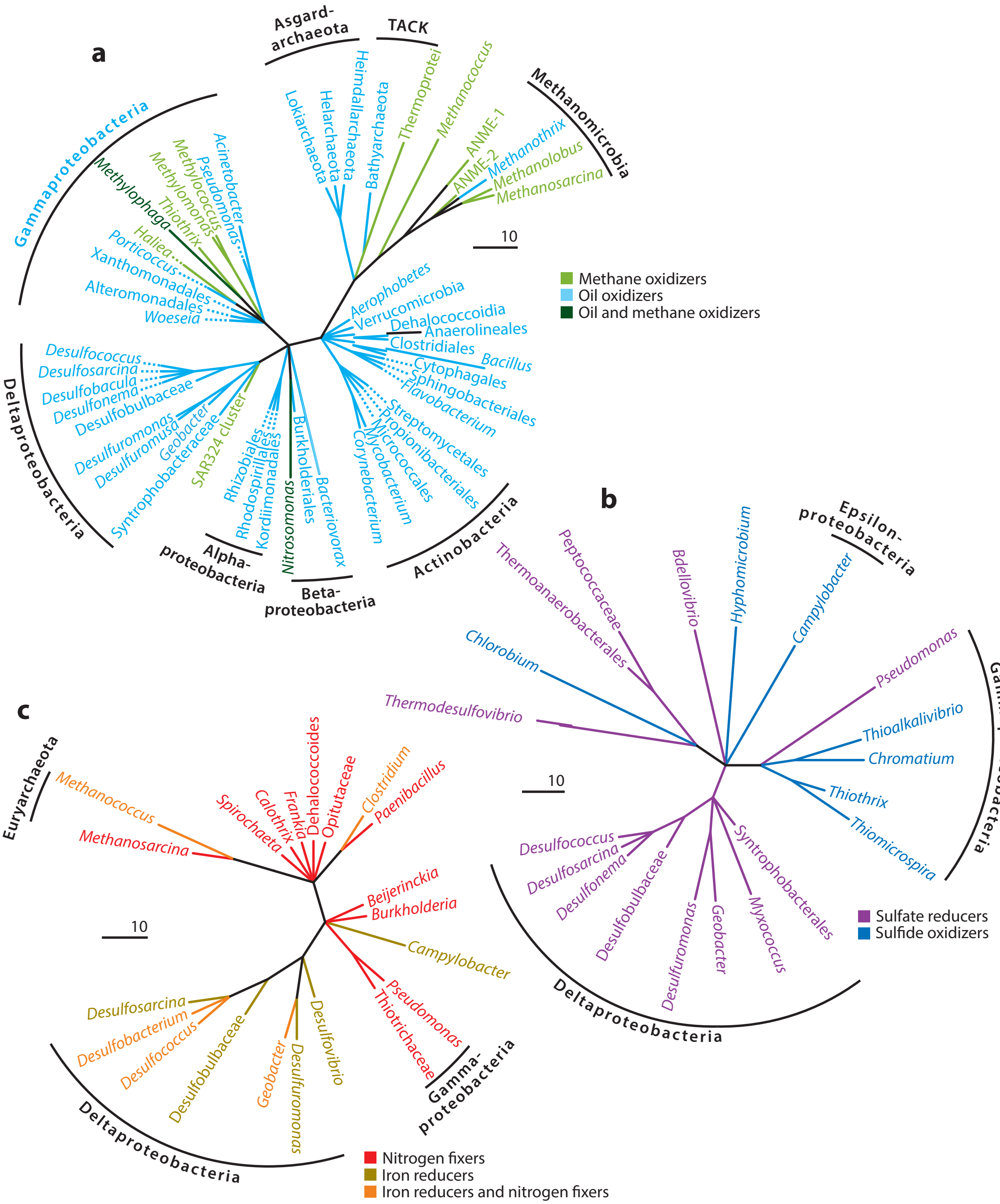
The source of phosphorus supporting accumulation of biomass at cold seeps is more difficult to explain. Phosphorus reaches the deep sea via sedimentation from the surface as organic or inorganic phosphorus, or via discharge of deeply sourced brine fluids. Discharging brines are known to be an important source of N and P to the deep sea, although the regional and global magnitude of this input is not constrained. In areas such as the Gulf, where brine seeps are common, brine-derived P inputs could be significant. Once phosphorus has been introduced into the system, sulfur-oxidizing microorganisms, especially giant sulfur-oxidizing bacteria such as *Beggiatoa* and *Thiomargarita*, may serve to concentrate it (as polyphosphate) and recycle it. Metabolism of such polyphosphates likely plays an important role in seep P cycling (Jones et al. 2015).

4. GEOBIOLOGY

4.1. Microbiology

Hydrocarbon seepage drives diverse microbial communities that mediate hydrocarbon oxidation and a plethora of other interconnected processes (**Figure 5**). Microbial processes create and support biological diversity across trophic levels at cold seeps. Chemoautotrophic and heterotrophic processes intermingle to oxidize and transform hydrocarbons, coupling hydrocarbon metabolism to other microbially mediated processes (**Figure 5*b*,*c***) and fueling highly productive and diverse ecosystems. A number of recent papers described the microbiome of oil seeps, methane seeps, and oil-gas seeps (Hawley et al. 2014, Ruff et al. 2015, Vigneron et al. 2017), their metabolic potential (Dong et al. 2019) and spatial heterogeneity (Ristova et al. 2014), and how the microbiome develops when fluid seepage changes (Ruff et al. 2018). The present understanding of the microbiology of cold seeps is presented here in a summary fashion.

Hydrocarbon seepage appears to select for a fairly specialized microbial community, and this community has been revealed effectively using metagenomics, enabling a remarkable phase of discovery. Seeps select for organisms on global and local scales; the long-lived nature of hydrocarbon



(Caption appears on following page)

Figure 5 (*Figure appears on preceding page*)

Key microbial groups and their diversity at hydrocarbon seeps. (*a*) Phylogenetic distribution of major groups of oil oxidizers, methane oxidizers, and organisms that may mediate both oil and methane oxidation. Significant, previously unrecognized hydrocarbon oxidizing diversity is present in the TACK (Thaumarchaeota, Aigarchaeota, Crenarchaeota, and Korarchaeota) and Asgardarchaeota superphyla, and more likely remains to be discovered. (*b*) Phylogenetic diversity in sulfate-reducing bacteria and sulfide-oxidizing bacteria lies mainly in the Epsilonproteobacteria, Gammaproteobacteria, and Deltaproteobacteria, but members of the Clostridiales are also capable of sulfate reduction. (*c*) The capability to fix nitrogen and reduce iron oxides is widely distributed at hydrocarbon seeps, underscoring the potential importance of these processes in deep sea hydrocarbon seep habitats.

seeps also fuels diversification at local levels that helps define the seep microbiome (Ruff et al. 2015). Spatial heterogeneity is high at seeps (Ristova et al. 2014), but seeps are distinct from non-seep environments. Oil and methane and alkane metabolism is widely distributed across the tree of life (**Figure 5*a***), and these organisms are well represented at seeps. For example, oil-oxidizing, sulfate-reducing bacteria are well known, but oil oxidizers are also members of the Actinobacteria and Gammaproteobacteria (**Figure 5*a***). Oil and methane metabolism has recently been reported in unexpected places, for example, the Asgardarchaeota and Bathyarchaeota (Dombrowski et al. 2018, Evans et al. 2015). Recent metagenomics surveys suggest that anaerobic methane and alkane oxidizers are much more widespread than previously recognized (Borrel et al. 2019, Dombrowski et al. 2018, Wang et al. 2019).

Much remains to be discovered regarding the partitioning of oil and gas metabolism between the diverse organisms now suspected to participate in the process(es). For example, Dombrowski et al. (2018) explored diversity of hydrothermally heated sediments, but the results warrant similar investigations of the role of Asgardarchaeota in hydrocarbon seep sediments. The model they propose for hydrothermal sediments—flexible and highly plastic microbial communities that respond efficiently to fluctuating environmental conditions—is similarly applicable to hydrocarbon seeps.

Sulfur, nitrogen, and iron cycling metabolism is less phylogenetically widespread (**Figure 5*b*,*c***). SR is focused in the Deltaproteobacteria, while sulfur oxidation is found mainly in the Gammaproteobacteria and Epsilonproteobacteria. The most common sulfide oxidizers at seeps fall within the Thiotrichaceae and include *Beggiatoales*, *Thioploca*, and *Thiothrix*, among others. As noted earlier, the potential for nitrogen fixation exists across a number of metabolic groups, underscoring its importance at cold seeps and calling for more detailed studies of the process. Interestingly, iron-reducing microorganisms are also quite abundant at seeps, suggesting that iron reduction could play an important role in these habitats, as suggested by recent metabolic studies that suggest a more important role for AOM coupling to iron reduction than is recognized at present.

4.2. Chemosymbiosis and Animals

The macrobiological communities at cold seeps depend on seep-derived energy sources, namely hydrogen sulfide, methane, and perhaps alkanes. Symbiotic associations are widespread at hydrocarbon seeps (Dubilier et al. 2008) (**Figure 6**). Thick and often colorful microbial mats mark locations of fluid discharge along the seabed like bull's-eyes (**Figure 6*c*,*g***). Chemosymbiotic animals are endemic to seeps, and the most abundant megafauna at hydrocarbon seeps are supported by such symbiotic partnerships. Chemosynthetic bivalves in the families Solemyidae, Lucinidae, Vesicomyidae, Thyasiridae, and Mytilidae are also common at hydrocarbon seeps (**Figure 6*a*,*b*,*e***). Most bivalves harbor sulfide-oxidizing symbionts, but *Bathymodiolus* mussels oxidize methane (e.g., *B. childressi*), with some species (*B. brooksi* and *B. heckeri*) hosting dual methane- and sulfide-oxidizing symbionts (Duperron et al. 2005). Mussels take up methane and oxygen passively by diffusion from the surrounding fluid. Mussels inhabit oil-gas seeps and brine seeps, often forming dense accumulations along the edges of brine flows and near mud volcanoes (MacDonald et al. 1990) (**Figure 6*b*,*e***).

Chemosymbiotic: refers to symbiosis between a microorganism and a higher organism where the microorganism provides chemically derived energy to the higher organism

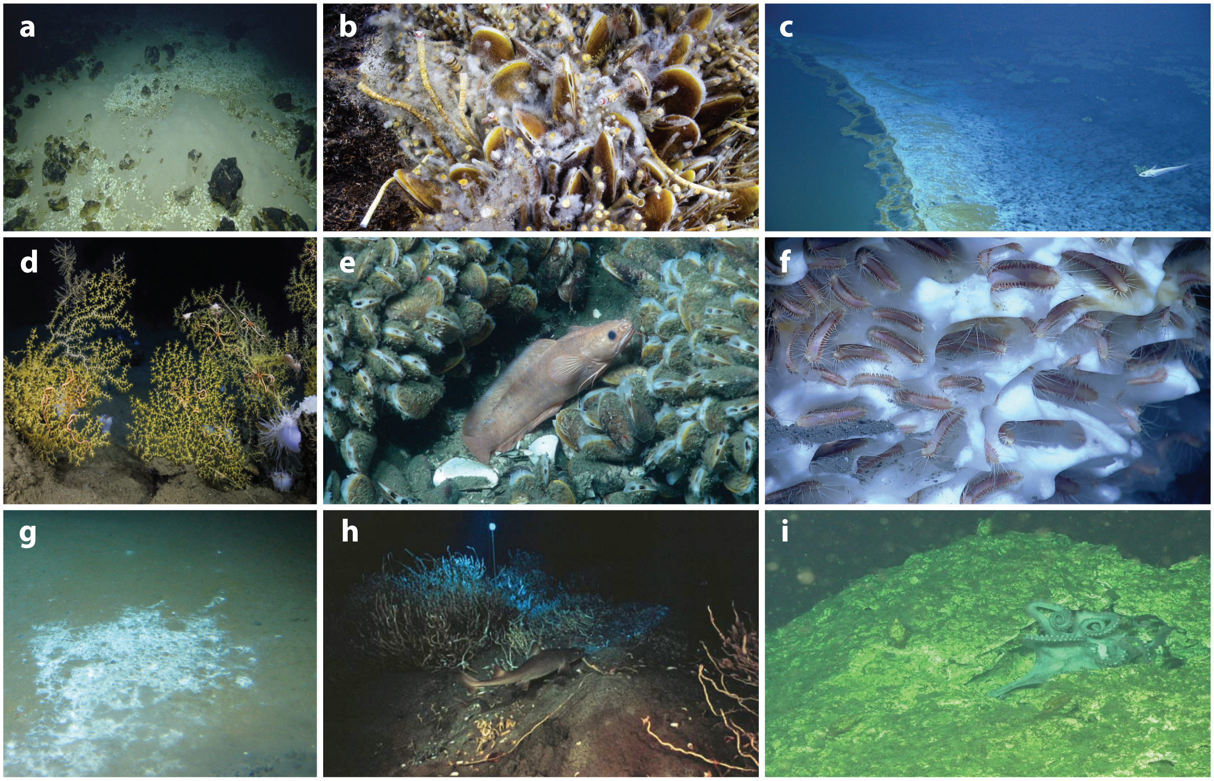


Figure 6

Animals inhabiting seep ecosystems. (*a*) Mussel aggregations (*light colors*) along sediments along fluid discharge faults. Mussel beds track discharge points of enriched fluids. (*b*) Chemosynthetic *Bathymodiolus* mussel community at the edge of a brine pool in the Gulf of Mexico. (*c*) Sulfur-oxidizing microbial mats (*white*) along the edge of a brine pool. (*d*) Paramuricea sea fans with brittle stars, anemone, and squat lobsters. (*e*) A species of rockling (family Lotidae), among chemosymbiotic mussels. (*f*) Ice worms (*Hesiocaeca methanicola*) burrowing in methane hydrate. (*g*) White microbial mat occupying an ~50-cm area of diffuse seepage. (*h*) Small (~1.5 m long) shark near a *Lamellibranchia* tubeworm bush. (*i*) Deep sea octopus seeking refuge inside a carbonate structure along the Sonora Margin, Sea of Cortez. Photos courtesy of (*a*,*g*) S.B. Joye (University of Georgia); (*b*,*c*,*d*) ECOGIG/Ocean Exploration Trust; (*e*) Deepwater Canyons 2013—Pathways to the Abyss expedition, NOAA-OER/BOEM/USGS; (*f*) NOAA Okeanos Explorer Program; (*h*) Gulf of Mexico 2002, NOAA/OER; and (*i*) S.B. Joye (University of Georgia) and the Schmidt Ocean Institute.

Siboglinid tubeworms—namely *Escarpia*, *Lamellibranchia*, and *Seepiophila*—harbor sulfide-oxidizing symbionts (Levin et al. 2016) (**Figure 6*b***). These animals harvest sulfide from their roots, which penetrate into the sediment, and oxygen and bicarbonate from their plumes to provide nutrition to their gammaproteobacterial symbionts. Individual *Lamellibranchia* can reach 2 m in length and are some of the oldest living invertebrates, living for centuries (Bergquist et al. 2000). Tubeworms have specialized hemoglobins that bind and transport oxygen and sulfide to their symbionts. Some seep animals lack symbionts but are seep specialists nonetheless. In 1998, Fisher et al. (2000) discovered specialized polychaetes—so-called ice worms, *Hesiocaeca methanicola*—inhabiting the surface of exposed gas hydrate (**Figure 6*f***). Subsequent work illustrated that ice worms are widespread throughout the Gulf. Other animals, such as mobile crabs, fish, and octopus (**Figure 6*h*,*i***), take advantage of the nutrition available at seeps and move in and out of these habitats, obtaining some of their diet at these locales (Fisher et al. 2007).

Cold-water corals often settle and grow upon authigenic carbonates derived from seepage, but corals are not explicitly seep associated (**Figure 6*d***) and are not known to derive nutrition from seep sources (Cordes et al. 2008). Still, corals contribute spectacularly to the biodiversity of cold seeps in their terminal phase. Lace corals (stylasterids), stony corals (scleractinians), black corals (antipatharians), soft corals (alycyonaceas), and sea fans (gorgonians) exist in the deep sea, often thriving in areas where authigenic carbonates were deposited. Cold-water corals do not depend on sunlight to fuel symbiosis and prefer cold water. These organisms obtain the entirety of their nutrition by filter feeding. One of the most common reef-building deepwater corals is *Lophelia pertusa*, an organism with a cosmopolitan distribution in cold waters. Encrusting sponges are also abundant at seeps, inhabiting any available surface and being quite common on tubeworm tubes and carbonates (Bowden et al. 2013).

5. CONCLUSIONS AND FUTURE OUTLOOK

Hydrocarbon seepage is a persistent feature of slope and shelf environments across the globe that impart unique geological, biogeochemical, and geobiological signatures on the seabed (Roberts et al. 2006). Underlying geology exerts a strong control on the surface expression of hydrocarbon seepage. The comingling of oil and gas with brine discharge creates a unique nexus where hydrocarbon seepage enters a nutrient-rich environment, but at brine seeps, animal utilization of the habitat may be limited by the presence of fluidized mud and/or toxic brine. At gas-oil seeps, nutrient limitation may ultimately restrain biomass accumulation.

Microbial processes proliferate at hydrocarbon seeps through development of specialized communities that are well tuned to local biogeochemical regimes. Anaerobic metabolisms dominate at hydrocarbon seeps because oxygen is rapidly consumed at or near the sediment-water interface by free-living and symbiotic microbial communities, as well as by animal respiration. SR and AOM are the two microbial processes that have received the most attention at hydrocarbon seeps, but other processes are also important.

Available evidence suggests that coupling of AOM to other processes—for example, nitrite, nitrate, iron-oxide, or manganese-oxide reduction—is not only likely but also necessary. High rates of AOM fueled by near-saturated methane concentrations (e.g., $CH_4 > 50$ mM) would rapidly consume sediment pools of any individual electron acceptor. Periods of high methane flux could lead to sequential depletion of oxidant pools through metabolic phasing. The intermittent nature of hydrocarbon seepage at cold seeps provides a natural reset for biogeochemical regimes, as reduced metabolite pools could be reoxidized, resetting the system in preparation for subsequent periods of high methane flux. Developing a full understanding of the dynamic linkages between the array of biogeochemical processes known to occur at cold seeps will require experiments conducted under controlled conditions in the laboratory as well as experiments conducted in situ using landers and other deployable instrumentation that is able to fully capture the range of relevant environmental conditions typical of the deep sea.

SUMMARY POINTS

1. Hydrocarbon seeps are important seafloor habitats that occur across the globe and support accelerated rates of biogeochemical cycling and diverse microbial and animal communities.
2. The extreme nature of hydrocarbon seeps selects for uniquely adapted microbial and animal communities.

3. Hydrocarbon seepage affects local sediment biogeochemistry and sediment-water interface dynamics and is also inherently connected with processes in the water column.
4. Fluxes of hydrocarbons through sediments and into the water column are moderated by microbial activity through a suite of interconnected metabolisms.
5. Metabolic phasing may be a characteristic of high-flux, high-activity hydrocarbon seep ecosystems that promotes efficient consumption of oil and gas and microbial diversity.

FUTURE ISSUES

1. How are hydrocarbon seeps connected with the surrounding benthic and pelagic environments? Is this connectivity changing?
2. More sophisticated biogeochemical and analytical chemical approaches are needed to track and partition microbial metabolism at seeps under quasi in situ conditions.
3. Development of in situ instrumentation and measurement tools to document the rates and capacity of biogeochemical processing at hydrocarbon seeps (see the sidebar titled Outlook).
4. How will ocean acidification and warming deep waters influence the biogeochemistry of hydrocarbon seeps?
5. What factors limit the ability of seep microbial communities to respond to changing hydrocarbon flux regimes?

OUTLOOK

The impact of cold seeps is not limited to the seabed, as evidenced by recent reports linking seafloor seepage and surficial processes at water depths of >1,000 m, underscoring the role that cold seeps play in modulating benthic-pelagic coupling. Connectivity is not a new concept, but such benthic-driven dynamics require that we fundamentally revise the scales upon which we consider seep impact(s) and the way we incorporate these impacts into models. Quantifying seep fluxes requires development of improved chemical (methane, oxygen, and sulfide) sensors integrated in platforms with acoustic Doppler current profilers. The importance of metabolic phasing is a step forward, but much remains to be discovered regarding how anaerobic oxidation of methane is coupled to different electron-accepting processes over space and time. To understand the regulation and dynamics of microbial processes at seeps requires in situ assessment of activity and experiments conducted under realistic conditions [i.e., quasi in situ T, (substrate), pressure].

Cold seeps are uniquely prone to perturbation resulting from global change. Ocean acidification, warming waters, and the spread of hypoxic/anoxic conditions may fundamentally alter seep ecosystems. Warming waters may destabilize surficial methane hydrate deposits and increase fluxes of both methane and oil to the oceanic water column. Surface-breaching gas hydrates not only stymie methane flux but also slow oil discharge. Destabilization of these hydrates could increase the flux of hydrocarbons through the sediments, reducing the efficiency of consumption and promoting exchange between benthic and pelagic compartments. It is critical to identify the factors that regulate the ability of seep microbial communities to respond to increased hydrocarbon fluxes. Since cold seeps are often nutrient limited, increased hydrocarbon fluxes could exacerbate nutrient limitation and reduce the efficiency of the benthic hydrocarbon biofilter.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

Preparation of this review was supported by grants from the US National Science Foundation's Biological Oceanography Program (OCE-1357360) and the Gulf of Mexico Research Initiative's Ecosystem Impacts of Oil and Gas in the Gulf (ECOGIG-2) research consortium. Several photographs were obtained through support of the Schmidt Ocean Institute. I thank Dr. Erik Marty, Rachael Karns, and Zachary Marinelli for assistance with preparation of graphics and/or materials used to develop this review.

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