

CHAPTER 5

OIL AND GAS SEEPS IN THE GULF OF MEXICO

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5.1 INTRODUCTION

A seep is a natural phenomenon where gaseous or liquid hydrocarbons, or both, leak from the ground (Figure 5.1). Seeps can occur on land and beneath the ocean above subsurface petroleum sources and accumulations. Seeps can have biogenic or thermogenic origins. Biogenic hydrocarbons are mostly methane and result from bacterial metabolism. Thermogenic hydrocarbons result from organic matter exposure to high temperatures in the deep subsurface. These two distinct origins of hydrocarbons impart unique chemical and isotopic compositions. Deep-seated buoyant thermogenic hydrocarbons can migrate along geological layers, across strata via faults and fractures in rocks and sediments, or they can be exposed as outcrops of oil-bearing rocks. Most seeps are generally under low pressures that produce slow rates of release. Oil and gas seeps are common globally and have been exploited by humans since Paleolithic times (Chisholm 1911; Etiope 2015). Seeps are highly variable in composition and include gases, crude oil, liquid bitumen, asphalt, and tar. Thermogenic seeps are often accompanied by water and brine (salt) containing inorganic solutes dissolved from source formations and the strata they migrate through. Seeps were targets for early exploration and exploitation of petroleum and ultimately led to the modern oil and gas industry. It has long been recognized that surface seeps indicate the existence of petroleum beneath them and are the basis for widely used fossil fuel exploration techniques known collectively as *surface prospecting*. Seeps can be ephemeral or may persist for many years. Worldwide, natural seeps release vast amounts of oil and gas to the environment every year and have for millions of years (NASA 2000; Hunt 1996). Often, while the collective volumes are large, seeps generally release petroleum slowly enough to allow surrounding organisms to avoid, adapt to, and, in some instances, even thrive in their presence (Coleman et al. 2003).

Understanding the location, type, and volume of petroleum seepage is important as indicators of deeper petroleum reservoirs, the presence of faults, and geohazards. Seeps release oil to the sea and greenhouse gases to the atmosphere (Etiope 2009, 2012, 2015; Coleman et al. 2003; Ciais et al. 2013). Conversely, the geographic distributions of oil and gas production and reserves, subsurface geology and sedimentary basins, salt structures, sea-surface slicks, seep-related water column and seafloor features, gas hydrate, and cold-seep communities can be used to infer the presence of seeps.

5.2 HISTORY

5.2.1 History of Oil and Gas Seeps Worldwide

Over millions of years, the preserved remains of dead plants and animals have been buried deep in the Earth by overlying sediments. This burial results in rising temperatures and

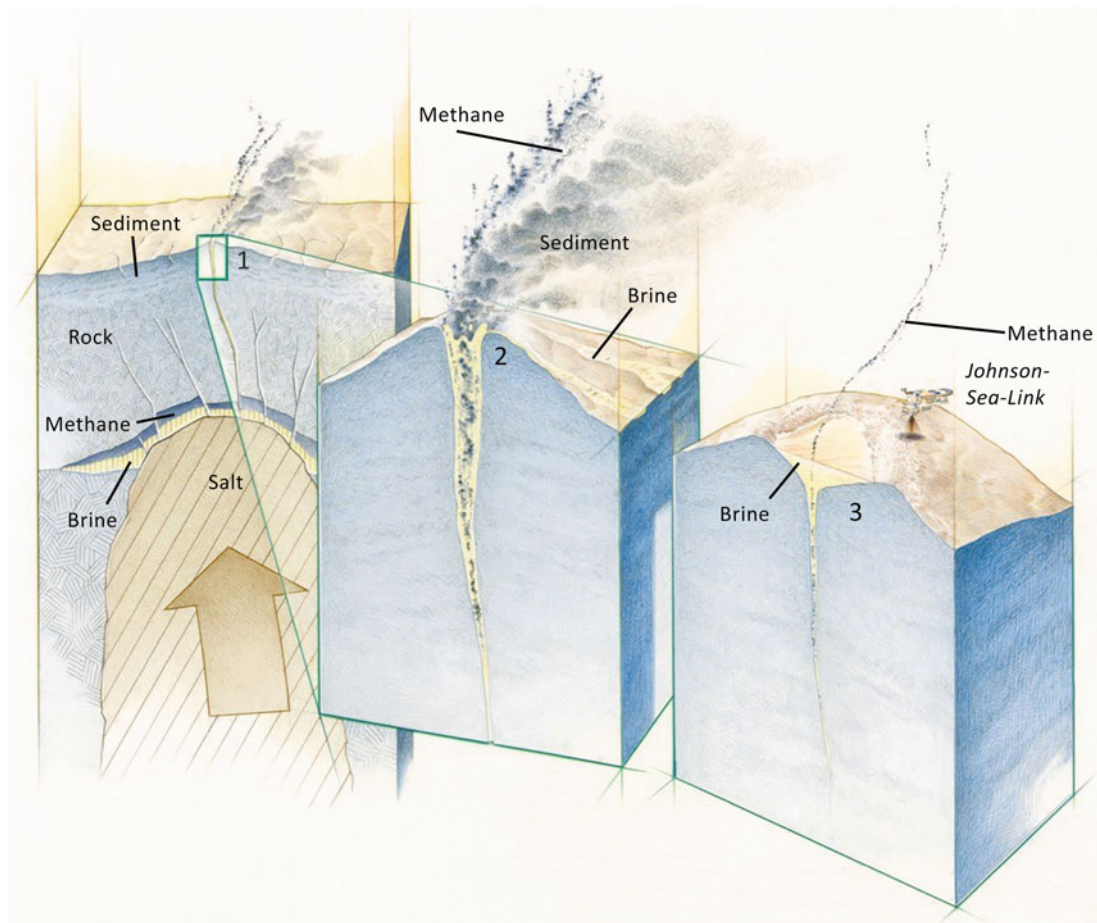


Figure 5.1. Schematic diagram of a typical marine seep location and associated features: (1) rising pillars of salt (diapirs) fracture the overlying strata creating migration pathways from deep-seated reservoirs to the near-surface; (2) the efflux of gases and fluids can disrupt and mix with overlying sediments creating seabed mounds and/or craters that are often associated with gas and/or liquid plumes in the overlying water column; and (3) seeping brines that are denser than sea water can accumulate in the depression forming a sea-bottom lake of high salinity water (MacDonald and Fisher 1996; Bruce Morser/National Geographic Creative, used with permission). *Johnson-Sea-Link* refers to a scientific research submersible (<http://oceanexplorer.noaa.gov/technology/subs/sealink/sealink.html>).

pressures due to Earth's internal residual heat from planetary accretion, radioactive decay, and increasing overburden. These conditions lead to the breakdown or cracking of complex biochemicals into lower-molecular-weight compounds including hydrocarbons. Once formed, liquids and gases are less dense than water or brine in the surrounding strata and tend to move upward under the force of buoyancy. If the petroleum fluids survive upward migration and avoid being trapped in the subsurface, they reach the surface forming petroleum seeps (Figure 5.2). Chisholm (1911) noted that "...bitumen, in its various forms, [is] one of the most widely-distributed of substances occurring in strata of every geological age from the lowest Archean rocks to those now in process of deposition..." Surface petroleum seeps have been part of the landscape throughout human history (Hunt 1996; Kvenvolden and Cooper 2003; Etiope 2015).

The first evidence of humans using petroleum from seeps dates to more than 40,000 years ago, associated with stone tools used by Neanderthals at sites in Syria (Hirst 2009; Etiope 2015).

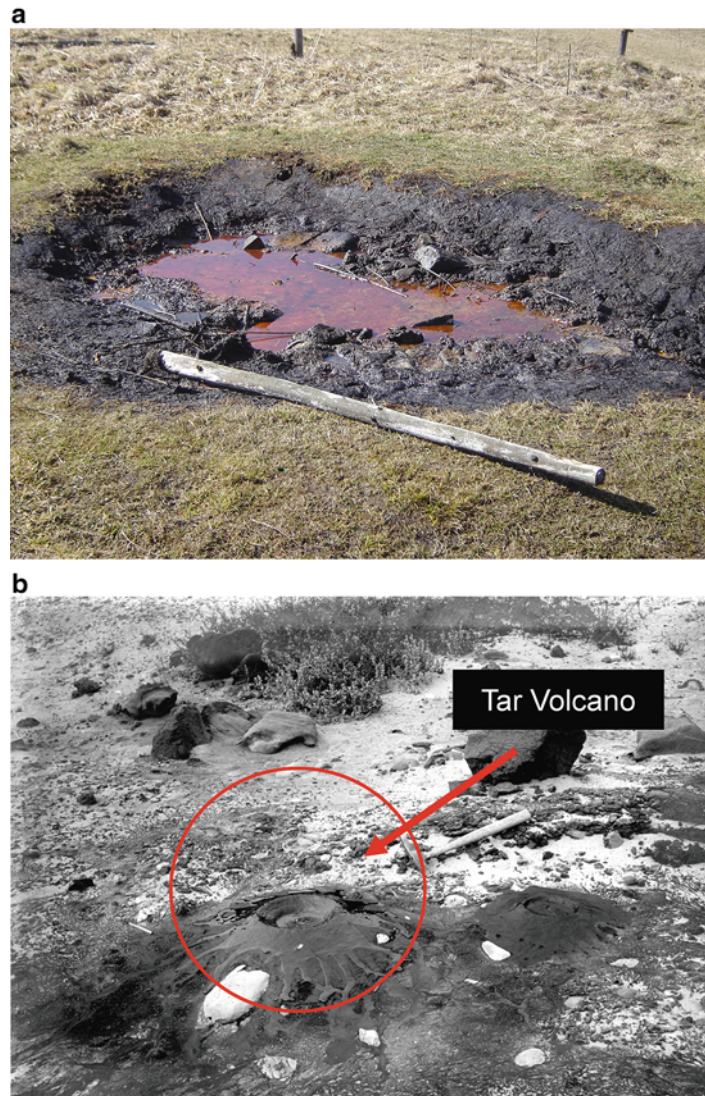


Figure 5.2. Photographs of typical petroleum seeps on land: (a) natural oil (petroleum) seep near Korňa, Kysucké Beskydy, Western Carpathians, Slovakia. Flysch belt (photo from http://en.wikipedia.org/wiki/Petroleum_seep; attributed to Branork [own work: 2008], CC BY 3.0) and (b) tar volcano in the Carpinteria Asphalt mine (R. Arnold, USGS, https://commons.wikimedia.org/wiki/File:Tar_volcano_in_the_Carpinteria_Asphalt_mine.jpg).

The use of seeping petroleum as a sealant, adhesive, building mortar, incense, and decorative application on pots, buildings, or human skin has been documented worldwide (Krishnan and Rajagopal 2003). More than 5,000 years ago, ancient Sumerians, Assyrians, and Babylonians used asphalt from seeps along the Euphrates for waterproofing (PBS 2004). Ancient Egyptians used liquid oil for medicinal purposes and embalming (Harwell and Lewan 2002; Barakat et al. 2005; Rullkötter and Nissenbaum 1988). In North America, prehistoric Native Americans used tar as a glue to bind stone tools to wooden handles and as a waterproof caulking for baskets and canoes (Harris and Jefferson 1985). In 480 BC, Persian military forces used oil-soaked flaming arrows during the siege of Athens (PBS 2004). The first oil well is believed to have been drilled in 347 AD when the Chinese used bamboo poles to bore as deep as

244 meters (m) (800 feet [ft]) into the subsurface (Kuhn 2004). In the sixteenth century, oil imported from Venezuela was used to treat Holy Roman Emperor Charles V for gout. The word *petroleum*, Latin for rock oil, was first used by German mineralogist Georg Bauer in 1556 (PBS 2004). In the eighteenth century, Lewis Evans's "Map of the Middle British Colonies in America" noted the presence of petroleum seeps in Pennsylvania (PBS 2004). During the Revolutionary War, Native Americans taught George Washington's troops how to treat frost-bite using seep oil, and Seneca Oil was advertised as a cure-all tonic. As early as 1815, some streets in Prague were lit with petroleum-fueled lamps (PBS 2004).

The modern history of petroleum exploitation is closely linked to petroleum seeps. Kerosene was produced from seepage oil in 1823. The process of refining kerosene from coal was developed in 1846 (PBS 2004; Kindersley 2007). This process was improved to refine kerosene from seeps in 1852. The first rock oil mine was dug in central Europe in 1853. In 1854, Benjamin Silliman was the first American to fractionate petroleum by distillation. These advances were rapidly adopted around the world (PBS 2004). The first commercial oil well was drilled in Poland in 1853 and the second in nearby Romania in 1857 at seep sites. This was followed by the opening of the world's first oil refineries (Stoicescu and Ionescu 2014). By the end of the nineteenth century, the Russian Empire led the world in petroleum production. In North America, the first oil well was dug in Oil Springs (named for a nearby seep) in Ontario, Canada, in 1858 (Kolbert 2007). The U.S. petroleum industry began in 1859 on Oil Creek (named for a nearby seep) near Titusville, Pennsylvania (PBS 2004). In the 1860s to the 1900s, sources of oil were discovered in association with petroleum seeps in Peru (1863), the Dutch East Indies (1885), and Persia (1908), as well as in the Americas in Venezuela, Mexico, and the Canadian province of Alberta. By 1910, some of these sites were being developed at an industrial level. In the late nineteenth century and early twentieth century, the demand for petroleum, created by improvements in the internal combustion engine and replacement of horse-drawn carriages, quickly outstripped the supply from seep-related sources. Surface seeps remained a primary indicator of deeper reservoirs of petroleum for many years until the advent of seismic technologies that could visualize the deep subsurface. The first commercial discoveries of oil using seismic methods were in 1924 in Mexico and Texas (Sheriff and Geldart 1995).

During World War I, oil was increasingly viewed as a strategic asset due to the use of oil-powered naval ships, new horseless army vehicles (such as trucks and tanks), and military airplanes (PBS 2004). Oil use during the war increased so rapidly that a severe shortage developed in 1917–1918. By the middle third of the twentieth century, transformative changes occurred in the oil industry. Beginning with Standard Oil's activities in Saudi Arabia, oil prospecting began a global expansion. The internationalization of oil exploration, production, and distribution played an important role in World War II. Superior access to oil aided the Allied effort. Scientific discoveries and inventions also created a vast market for petroleum products in plastics, synthetic chemicals, and other industries.

5.2.2 History of Oil and Gas Seeps in the Gulf of Mexico

Petroleum has seeped to the surface in the Gulf of Mexico region for many millions of years (Geyer 1980; Geyer and Giammona 1980—the source of the following summary; NASA 2000). The Karankawa Indians living on Padre Island in pre-Columbian times decorated pottery and waterproofed boats with seeping oil. In the sixteenth and seventeenth century, Spanish explorers caulked their ships with tar from the beaches of south Texas and Louisiana. Oviedo y Valdés referred to asphalt in the New World in 1533, and Sebastian Ocampo recorded the presence of liquid hydrocarbons in the Bay of Havana, Cuba, in 1508. In the late nineteenth and

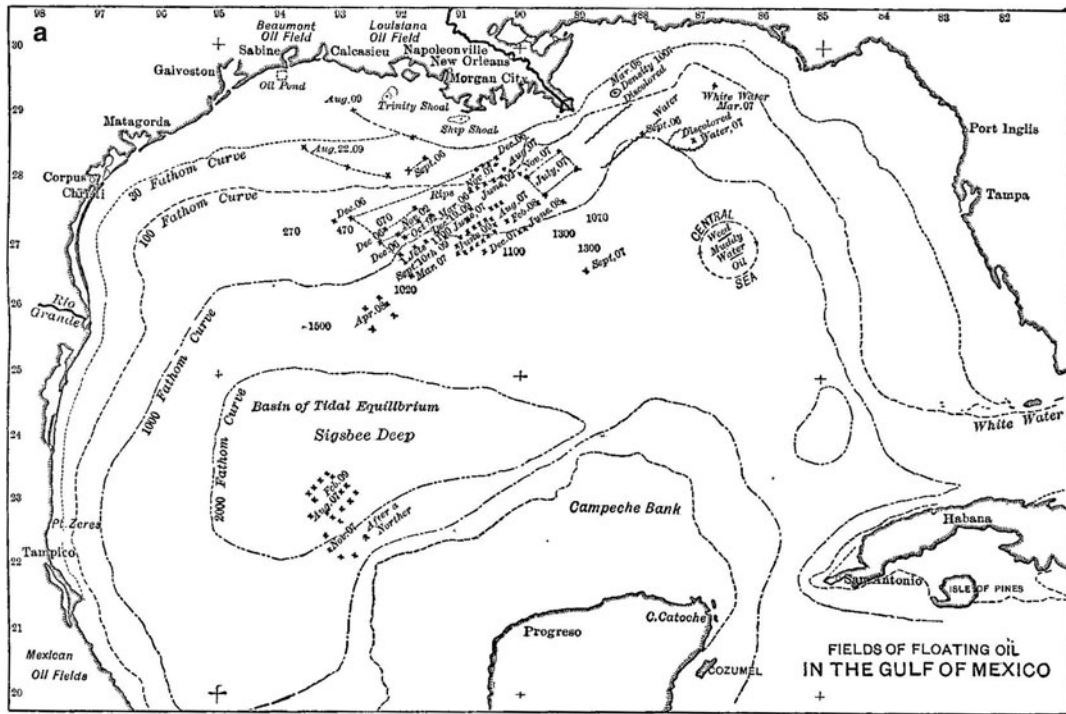
early twentieth century, large cakes of petroleum or asphalt were frequently found on the beaches between Sabine Pass and Matagorda, Texas. There have been numerous reports of sea-surface oil slicks in the Gulf of Mexico (Figure 5.3). In the early 1900s, there were regular reports of enormous patches of oil by ships navigating Gulf of Mexico waters, including oil bubbling to the surface. In 1933, there were 30 instances of oil seeps reported in the Gulf of Mexico. Prior to commercial offshore production of oil, a beach survey in 1955 reported tar with a presumed seep source on all beaches in the northern Gulf of Mexico from Mexico to central Florida.

In the Gulf of Mexico region, petroleum seeps on land are numerous and historically important. On January 10, 1901, a drill pipe spurting mud, gas, and oil blew out at Spindletop near Beaumont, Texas, (drilled on a seep) transforming Texas into a major petroleum producer (Figure 5.4). This was preceded by oil discoveries at seeps in East Texas in the late 1800s. Spindletop was the first salt-dome oil well and led to the first oil boom and numerous other onshore discoveries associated with petroleum seeps (Petty 2010). The companies established to develop Gulf of Mexico oil fields, including Gulf Oil, Sun Oil, Magnolia Petroleum, the Texas Company, and Humble Oil, are now major energy companies (Texas Almanac 2014). Between 1902 and 1912, wells were drilled in north-central Texas with discoveries in Brownwood, Petrolia, Wichita Falls, and west of Burkburnett. During the 1920s, numerous discoveries were made in east, west central, and the panhandle of Texas. During the following years, onshore oil discoveries were found across Texas and in other coastal states to the east, mostly confined to the northwestern region of the Gulf of Mexico. From the 1910s to 1930s, the use of piers, pilings, concrete platforms, barges, and artificial islands extended oil and gas exploration into coastal bays, lagoons, and offshore. By the 1940s, the first fixed platforms were being used, and the first oil discovery, drilled out of sight of land, was in 1947 off the Texas shore. In many instances, the origins of onshore oil and gas seeps were traced into the offshore region.

5.3 PREVALENCE

As the history above demonstrates, petroleum seeps have been reported worldwide and in the Gulf of Mexico for thousands of years. Vestiges of ancient seeps in the geological record at numerous locations worldwide demonstrate the common occurrence of seeps over geological time and that seeps persist for finite periods of time (Callender et al. 1990; Callender and Powell 1992; Campbell et al. 2002). Inventories likely underreport the prevalence of seeps for several reasons. Large areas of the Earth's surface—including remote and difficult-to-access areas such as Antarctica, the Arctic Ocean, the interiors of Africa and South America, and the deep sea—remain unexplored for seeps (Figure 5.5). Once released to the surface, seeping petroleum is subject to a range of processes that alter its composition, and some processes mask the presence of seeps. In addition, energy companies consider the location of seeps a competitive advantage, so many seeps go unreported in the open literature.

Based on surveys in 2009 and 2015, reported petroleum seeps were mostly located in the northern hemisphere as are a majority of the world's oil and gas reserves (Figures 5.5 and 5.6) (Etiope 2009, 2015). In these surveys, seeps were most often reported on land, which is likely due to the long history and relative ease of visual observations. Seeps in the ocean often require detection by satellite, airborne sensors, and/or direct sampling; although visual reports of surface oil slicks are numerous (Figure 5.3). Global inventories are few, mostly rely on visual detection, and often do not include seeps detected by a wide range of other indicators that signify their presence now or in the past. Areas where petroleum seeps occur may have multiple seeps. Estimating the volume of leakage is often difficult; thus, inventories mostly count the



FIELDS OF FLOATING OIL IN THE GULF OF MEXICO.

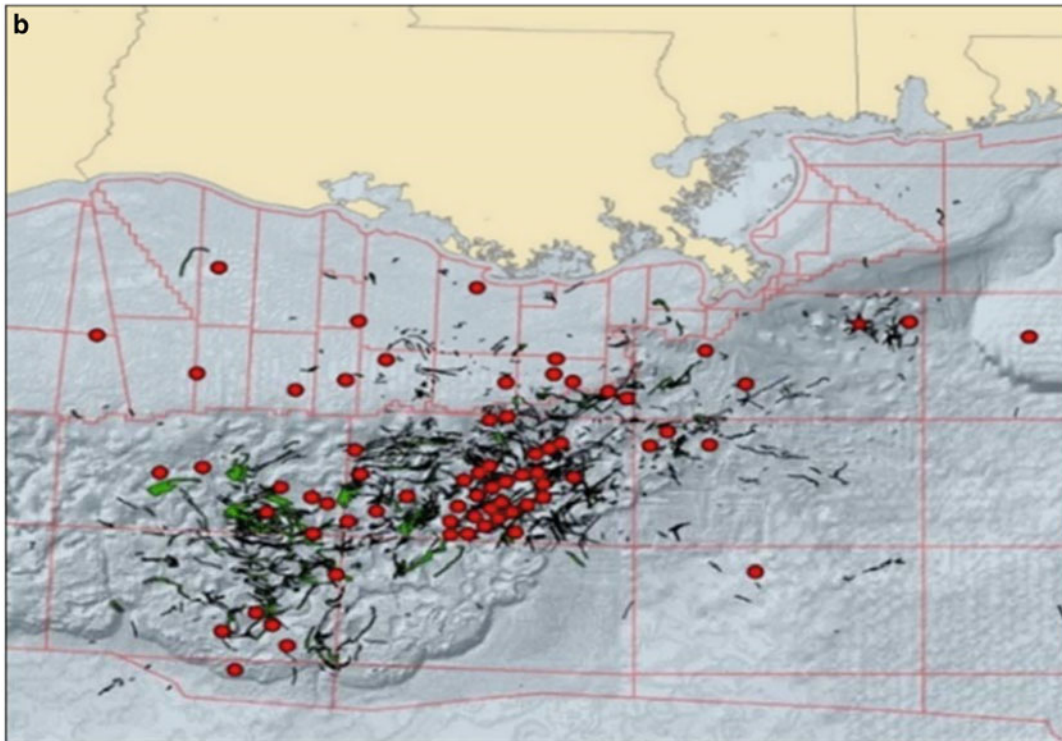


Figure 5.3. Maps of (a) historical reports of floating oil [red dots in (b)]; Soley (1910) and (b) oil slicks (black lines) in the northern Gulf of Mexico 1991–2009 (determined from analysis of synthetic aperture radar, graphic provided by CCG’s NPA Satellite Mapping, used with permission).



Figure 5.4. Spindletop blows (photo from http://commons.wikimedia.org/wiki/File:Lucas_gusher.jpg).

number of seeps and do not attempt to estimate volumes. In contrast, marine seep volumes (as loadings) have received attention due to their important contribution to oil in the sea, and the volume of global gas seeps have been estimated as contributors to greenhouse gases (Coleman et al. 2003; Etiope 2015).

To assess the association of seepage and subsurface accumulations of petroleum, Schumacher (2012) compiled seepage survey results for more than 2,700 exploration wells and compared the results with subsequent drilling outcomes. Locations were in frontier and mature basins, onshore and offshore, and in a wide variety of geologic settings. Subsurface drilling targets were from 300 m (984 ft) to more than 4,900 m (16,076 ft), and there was a full spectrum of trap styles. The presence of seepage was inferred from soil gas, microbial, iodine, radiometric, and/or magnetic surface surveys. Eighty-two percent of wells associated with surface seepage anomalies were considered commercial discoveries, and 11 % of wells drilled without a documented surface seepage anomaly resulted in discoveries. The measure of association was economic viability determined by external factors, and not the presence or absence of petroleum in the subsurface. The sites chosen for analysis in this study were not random; they were based on conventional prospect evaluation methods. This study illustrates

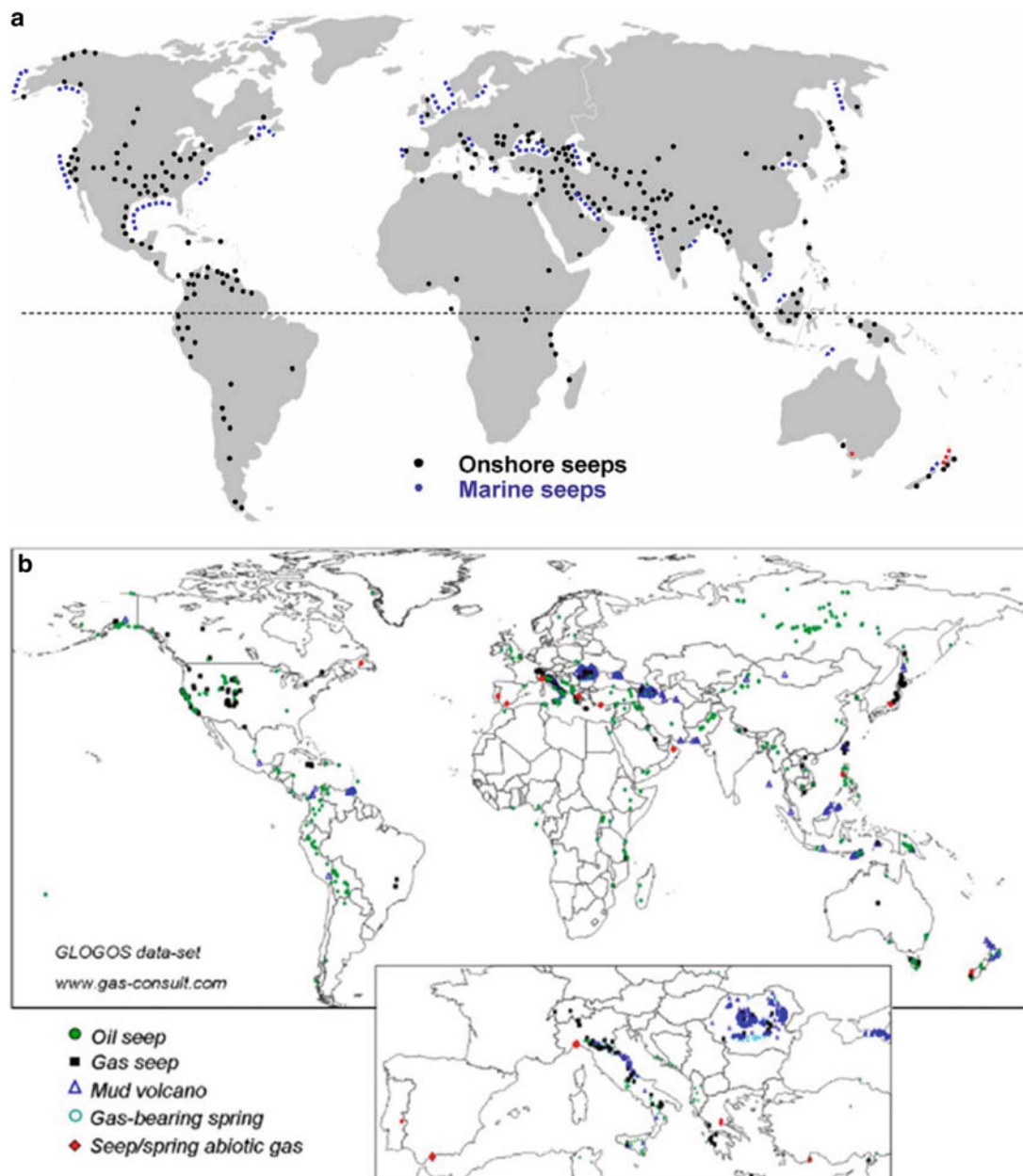


Figure 5.5. Global prevalence of petroleum seeps: (a) more than 1,150 seeps in 84 countries (Etiopie 2009; examples in Russia, the Arctic Ocean, and Antarctica were not included in the survey) and (b) distribution of onshore seeps including about 2,100 seeps in 86 countries (from the global data set of onshore gas and oil seeps [GLOGOS]; Etiopie, 2015; reprinted with permission of Springer).

that seeps are often only surveyed for in areas suspected of being oil and gas prospects, thus limiting geographic coverage.

Estimates of the volume of gases seeping on land are numerous (Etiopie 2015). These estimates take into account spatial and temporal variability, susceptibility to rapid alteration once exposed at the surface, and release of gases and volatiles directly into the

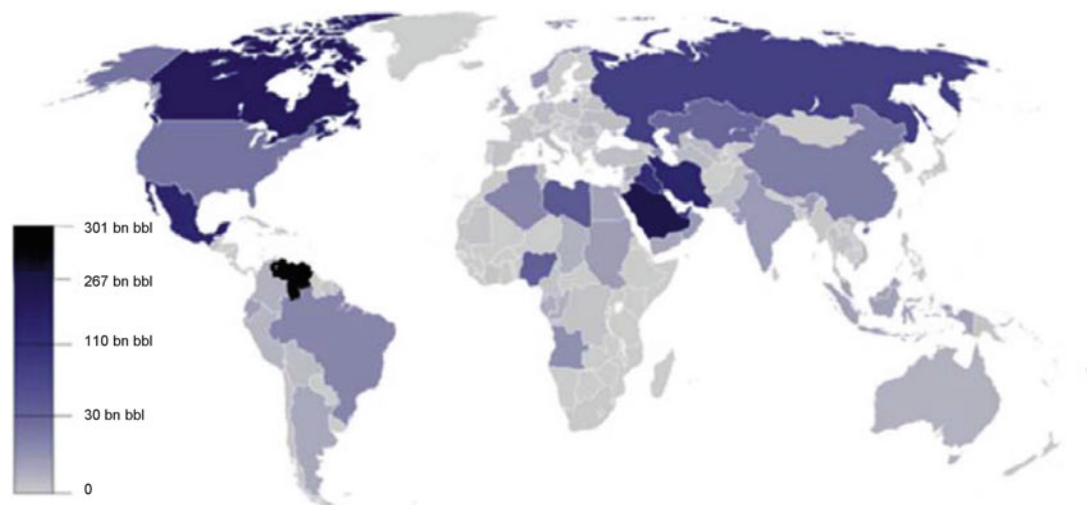
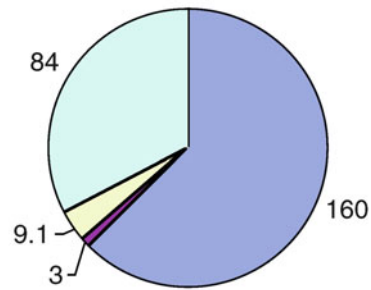
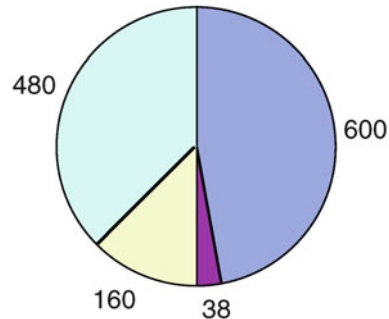


Figure 5.6. A map of world oil reserves (2013; graphic from http://en.wikipedia.org/wiki/List_of_countries_by_proven_oil_reserves).

overlying atmosphere. Marine oil seeps have been extensively studied and quantified as well (Figure 5.7) (Coleman et al. 2003). Compared to the long history of land-based observations of seepage, offshore seepage detection is a relatively recent development—one exception being historical reports of sea-surface slicks (Figure 5.3). Advances in techniques to detect seeps in the ocean and the expansion of oil and gas exploration into the offshore regions in the last 50–60 years greatly increased geographic coverage and the number of reported marine seeps. Annual oil seepage to the marine environment was estimated to be 600,000 tonnes (i.e., metric tons) (180 million gallons [gal]) globally and 160,000 tonnes (47 million gal) in North America from 1990 to 1999 (Kvenvolden and Cooper 2003; Coleman et al. 2003; Table 5.1). While variable, natural seeps are estimated to contribute about 45 % of the oil entering the marine environment worldwide and about 60 % in North American waters, with the remainder due to the extraction, transportation, and consumption of petroleum (Figure 5.7 and Table 5.1) (Coleman et al. 2003). In North American waters, the largest natural seeps are located in the Gulf of Mexico and offshore of southern California.

The immensity of the volume of oil released by seeps in the Gulf of Mexico is indicated by the larger relative contribution of petroleum seepage to oil in North American waters as compared to worldwide estimates (Coleman et al. 2003). The alteration of petroleum, once released to the environment, introduces considerable uncertainty in estimating the volume of petroleum seepage. Gaseous hydrocarbons are particularly susceptible to alteration after seepage and are rarely considered in global seep inventories since little is known about the rates and volumes of seepage, though gas seeps are known to be common (Kvenvolden and Cooper 2003). Most gas seepage is either dissolved in seawater or quickly metabolized by microbes, leaving scant evidence of its presence. Because methane is a greenhouse gas, the contribution of atmospheric methane from natural seepage (mostly biogenic in origin) has been estimated (Etiope 2015). While petroleum seeps have been reported extensively worldwide, global inventories remain incomplete and uncertainties in volume estimates are large.

Oil seeps account for approximately 95 % of the total oil input to northern Gulf of Mexico waters (Figure 5.8) (Coleman et al. 2003). As with global estimates, the full extent of oil and gas

a North American Marine Waters**b** Worldwide Marine Waters

■ Natural Seeps
■ Extraction of Petroleum
■ Transportation of Petroleum
■ Consumption of Petroleum

Figure 5.7. Relative contribution of average, annual releases (1990–1999) of petroleum hydrocarbons (in kilotonnes) from natural seeps to the marine environment in (a) North American waters and (b) worldwide compared with other sources (republished with permission of Emerald Group Publishing Limited from Coleman et al. 2003; permission conveyed through Copyright Clearance Center, Inc.)

Table 5.1. Average, Annual Releases (1990–1999) of Petroleum (oil) to the Marine Environment by Source (in thousands of tonnes, Coleman et al. 2003) (a tonne equals about 300 gal of oil, Kvenvolden and Cooper 2003)

Region	North America			Worldwide		
	Best Est.	Min.	Max.	Best Est.	Min.	Max.
Natural seeps	160	80	240	600	200	2,000
Extraction of petroleum	3.0	2.3	4.3	38	20	62
Transportation of petroleum	9.1	7.4	11	150	120	260
Consumption of petroleum	84	19	2,000	480	130	6,000
Total	260	110	2,300	1,300	470	8,300

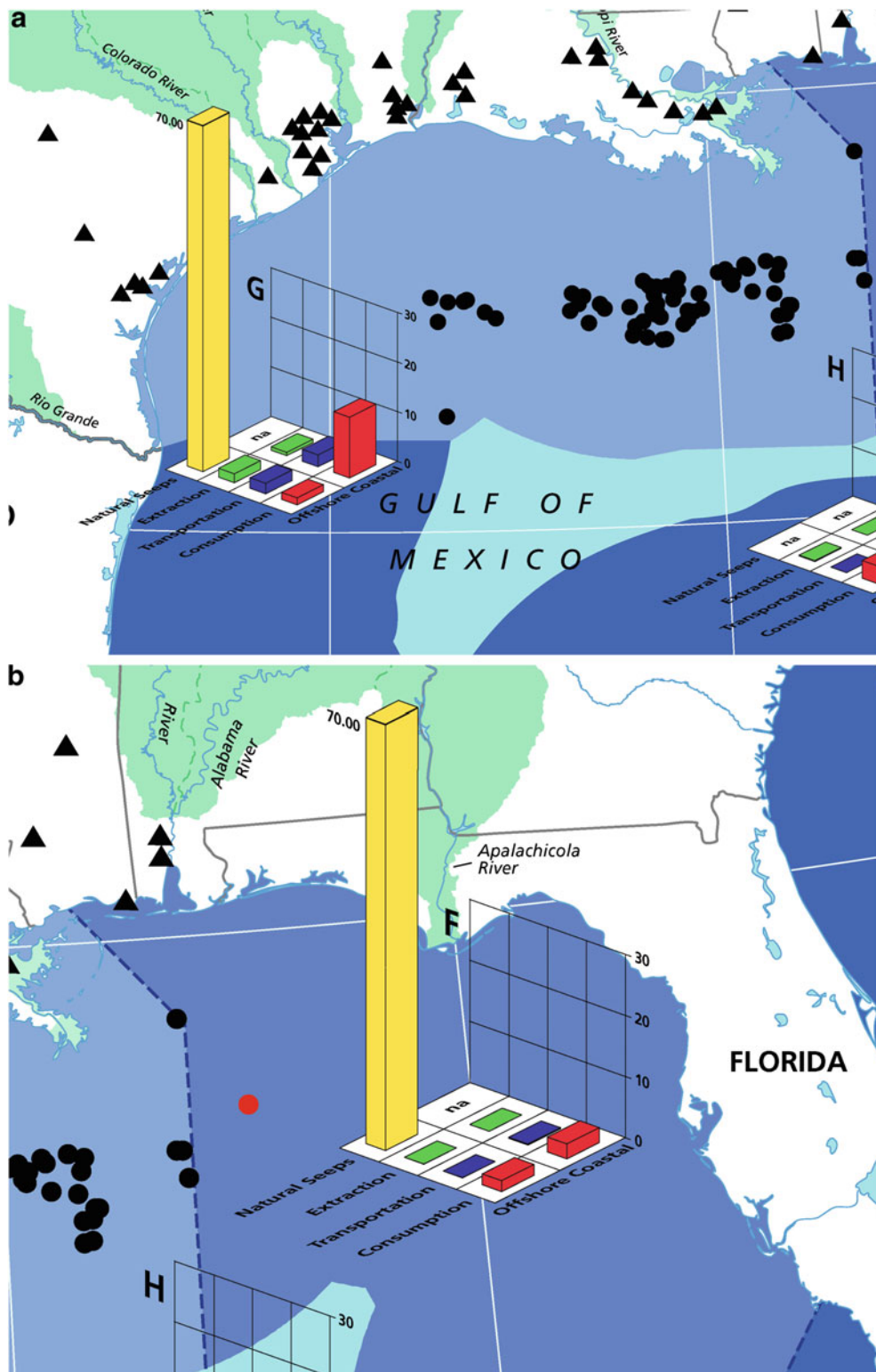


Figure 5.8. Average annual input of petroleum hydrocarbons in thousands of tonnes to the coastal Gulf of Mexico for 1990–1999 (yellow = natural seeps, green = extraction, purple = transportation, and red = consumption) (modified from Coleman et al. 2003).

seepage in the Gulf of Mexico is difficult to quantify due to challenges in detection (e.g., occurs subsea), differences in quantification methods (e.g., satellite observations and sampling by corer), dispersion by ocean currents, gaps in geographic coverage, and variable and uncertain seep volumes and rates (Coleman et al. 2003; Wilson et al. 1974; De Beukelaer 2003; De Beukelaer et al. 2003). Within these uncertainties, natural seepage of oil has been estimated to exceed 140,000 tonnes (42 million gal) annually in northern Gulf of Mexico waters (Coleman et al. 2003). Comparing overall petroleum input to the Gulf of Mexico in the 1990s, annual oil seepage inputs were estimated to be as follows:

- 140,000 tonnes (42 million gal) total natural annual loadings: 70,000 (21 million gal) tonnes in the northeastern Gulf of Mexico and 70,000 tonnes (21 million gal) in the northwestern Gulf of Mexico.
- 25,400 tonnes (7.62 million gal) total anthropogenic annual loadings: 4,400 tonnes (1.32 million gal) in the northeastern Gulf of Mexico and 21,000 tonnes (6.3 million gal) in the northwestern Gulf of Mexico.

The inputs to the northern Gulf of Mexico coastal waters were estimated to be as follows:

- Negligible total natural annual loadings (few known seeps)
- 17,740 tonnes (5.322 million gal) total anthropogenic annual loadings: 2,660 tonnes (798,000 gal) in the northeastern Gulf of Mexico and 15,080 tonnes (4.524 million gal) in the northwestern Gulf of Mexico.

A tonne equals about 300 gal of oil (Kvenvolden and Cooper 2003). Kvenvolden and Cooper (2003) provide a detailed review of estimates of oil seepage rates as of 1975, 1985, and 2000. In the latest estimates (Coleman et al. 2003), the authors note that the number of regions known to have significant seeps increased mainly due to detection by satellite remote-sensing techniques. The authors note further that seepage rates in the Gulf of Mexico are much higher than first estimated in 1975 and 1985 as the number of known seeps has significantly increased. Based on satellite remote sensing, MacDonald (1998) and MacDonald et al. (1993, 1996) estimated total seepage to be from 4,000 to 73,000 tonnes (1.2–21.9 million gal) per year in the northern Gulf of Mexico (Kvenvolden and Cooper 2003). Assuming a seep rate for the entire Gulf of Mexico is about double the northern Gulf of Mexico estimate, the total Gulf of Mexico seep rate is estimated to be about 140,000 tonnes per year (42 million gal).

Based on these estimates, most petroleum seepage occurs in the northwestern and north-central deepwater region of the Gulf of Mexico coincident with oil and gas production and is negligible in coastal waters. The high estimate for the offshore northeastern Gulf of Mexico region is due to one seep site reported in the far western part of the northeastern sector, but oil seeps are generally absent in the region. Similar estimates are less certain for the southern Gulf of Mexico, but many seeps are known in this region both onshore and offshore.

5.4 PETROLEUM GEOLOGY

The well-established principles of the geology of petroleum systems set the stage and the conditions for why and where petroleum seeps occur (Figures 5.9 and 5.10). Petroleum seeps result from direct migration from the source to the surface or as a result of a breach in the seal of a reservoir. The force of buoyancy and differentials in pressure drives migration of hydrocarbons toward the surface. It often has been observed that nearly all subsurface occurrences and accumulations of petroleum leak to some degree at some point in time. Oil and gas often migrate directly from subsurface sources without pooling, and some seeps are

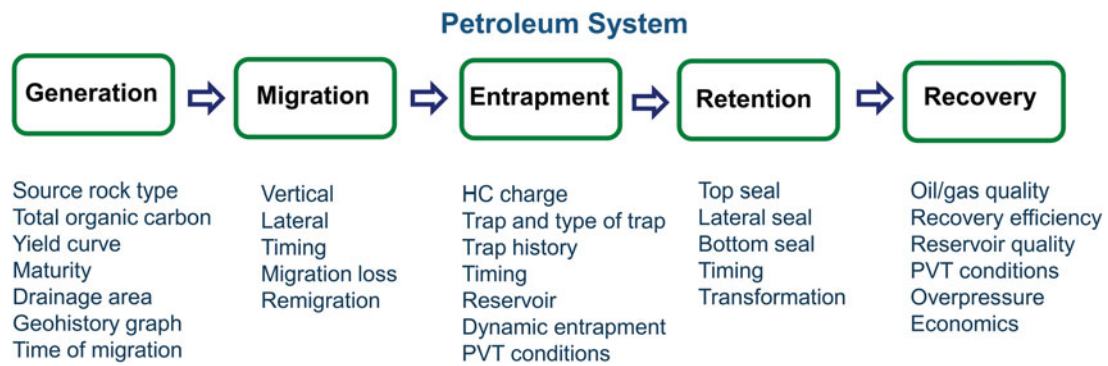


Figure 5.9. Elements of a petroleum system (M.H. Nederlof, reproduced with permission; <http://www.mhnederlof.nl/petroleumsystem.html>).

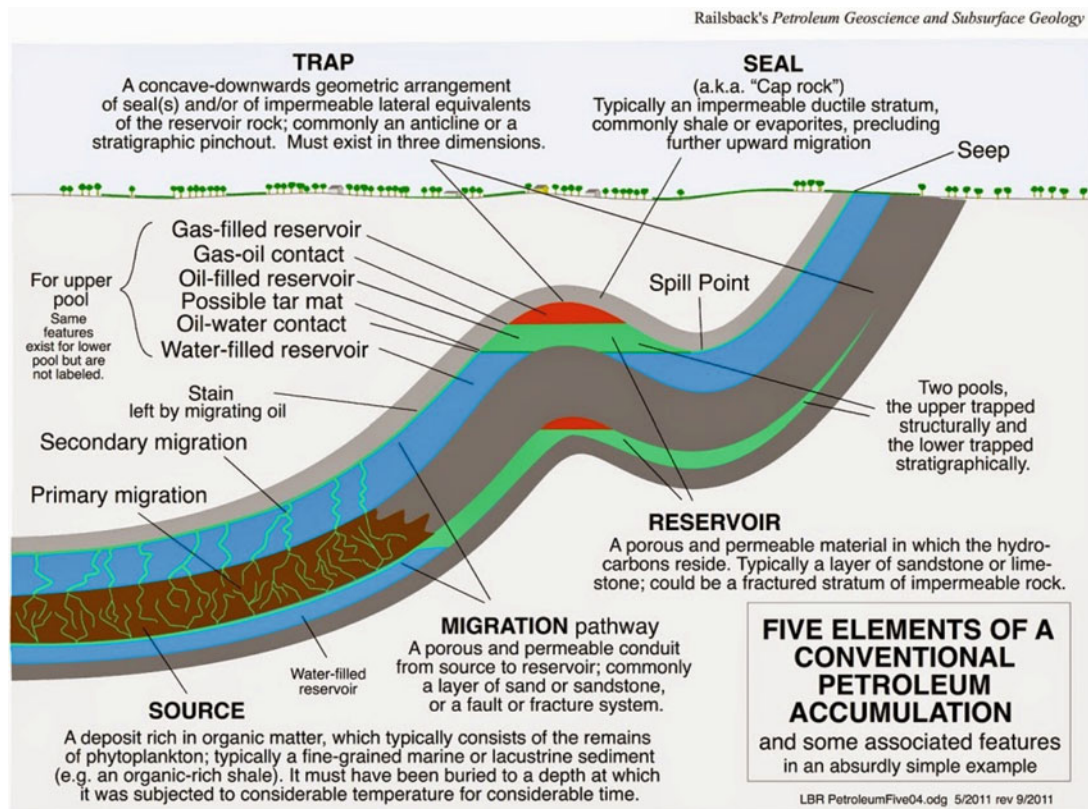


Figure 5.10. A petroleum system includes a mature source rock, migration pathway, reservoir rock, trap, and seal. The relative timing of formation of these elements and the processes of generation, migration, and accumulation are critical for hydrocarbon accumulation and preservation (from Railsback 2011; reprinted with permission).

outcrops of oil-bearing rocks (e.g., tar sands and exposed source rocks). In instances of seepage from underlying reservoirs, seals are breached due to overpressure and/or mechanical disruption (i.e., faults) by upward intrusions of less dense materials, such as salt diapirs and tectonic forces.

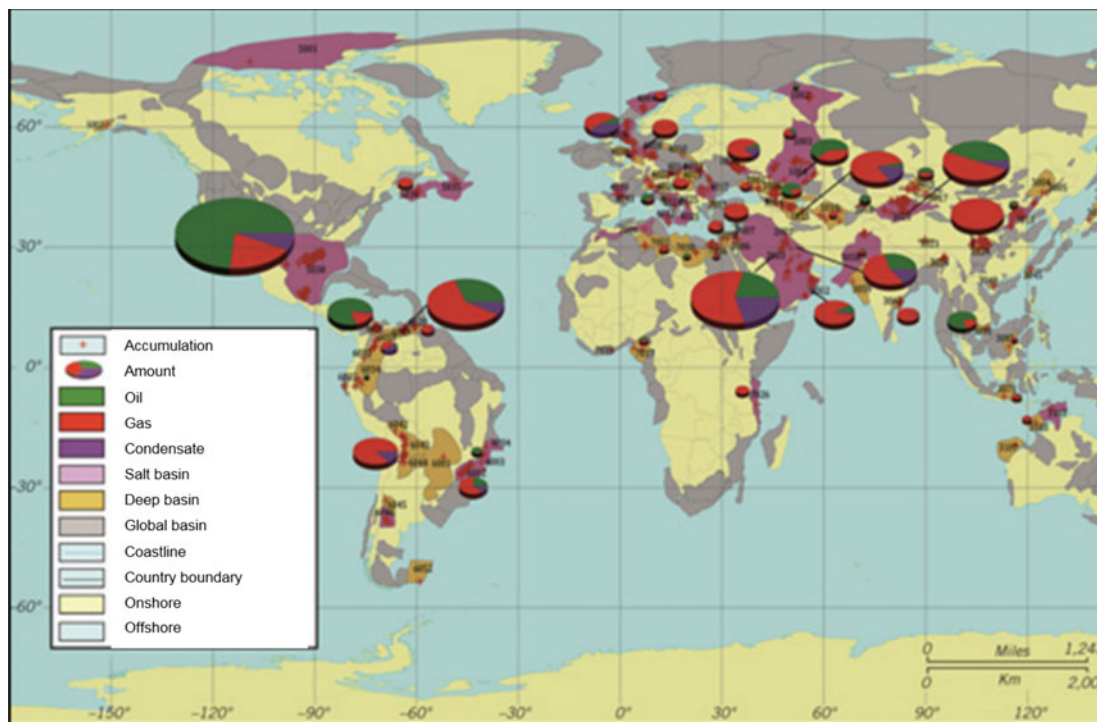


Figure 5.11. Worldwide distribution of deep oil and gas basins defined as occurring in reservoirs at burial depths deeper than ~4,572 m (~15,000 ft) (Cao et al. 2013).

Overpressure is caused by the rapid loading of fine-grained sediments, which prevents expulsion of water and equalization of the pressures created by the overburden. Intermittent resealing of breaches can occur and slowing or cessation of burial allows time for excess pressures to dissipate. Fluid expansion, which is a change in volume, is a second cause of overpressure. Overpressure is caused by the thermal expansion of water, clay dehydration, and the thermal cracking of source-rock organic matter to form oil and gas. Depending on the degree of overpressure and the mechanical strength of the encasing rocks, seepage can be widespread and diffuse. A slow seepage rate is commonly referred to as *microseepage*. In instances when the rocks fracture, focused high-volume seepage is commonly referred to as *macroseepage*.

The Gulf of Mexico is a prolific petroleum basin containing vast volumes of subsurface oil and gas (Figure 5.11) (Cao et al. 2013). The region is an archetype for petroleum seepage since the geologic history and setting are ideally suited for seepage. In fact, there may be no leakier basin of its size on the Earth's continental margins. The Gulf of Mexico has been a long-term depocenter that has received enormous sediment discharges from major river systems creating source and reservoir rocks (Figure 5.12). The Gulf of Mexico contains multiple, deeply buried source rocks that are thermally mature (Figure 5.13). Salt tectonics driven by the underlying Middle Jurassic Louann Salt created migration pathways from the source rock to reservoirs and to the surface (Figure 5.14).

5.4.1 Source Rocks and Petroleum Generation

A *source rock* is the rock from which hydrocarbons have been, or are capable of being, generated and is a necessary element of a viable petroleum system (Figure 5.15) (Hunt 1996).

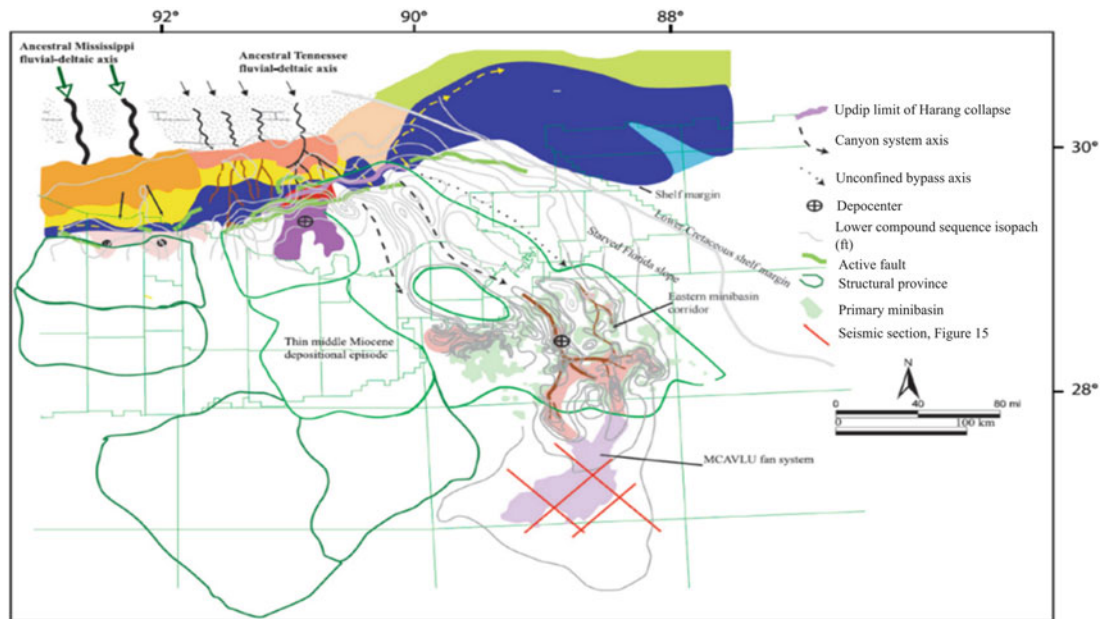


Figure 5.12. Map of Middle Miocene depocenters (Combells-Bigott and Galloway 2006; AAPG © 2006, reprinted by permission of the AAPG whose permission is required for further use).

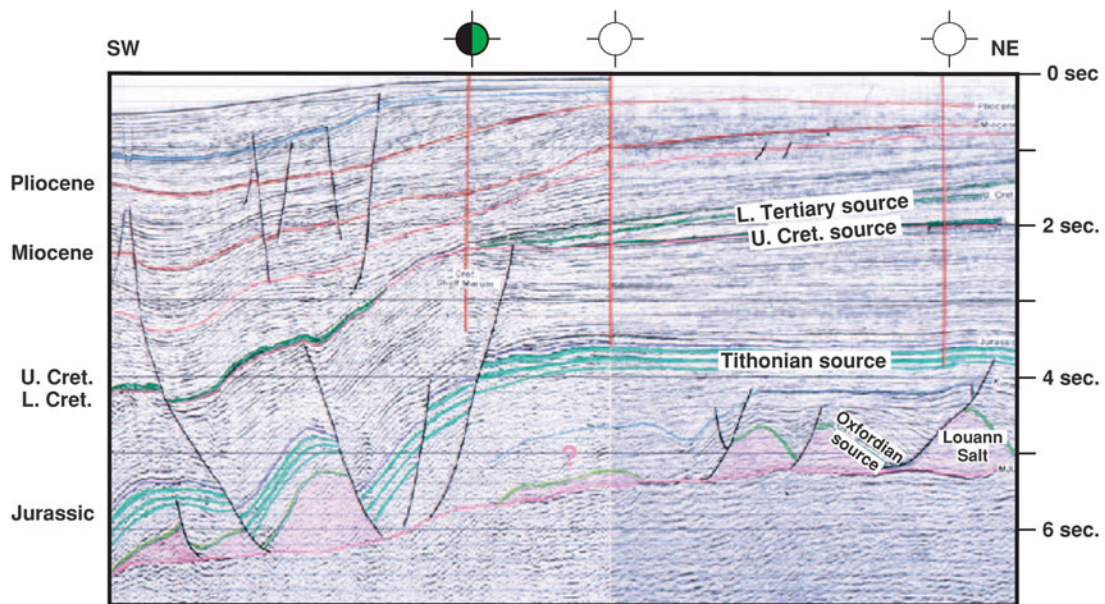


Figure 5.13. One of many wells that have penetrated multiple potential source rocks in the Gulf of Mexico (Hood et al. 2002; AAPG © 2002, reprinted by permission of the AAPG whose permission is required for further use) [L. Tertiary Lower Tertiary, U./L. Cret. Upper/Lower Cretaceous, sec. seconds].

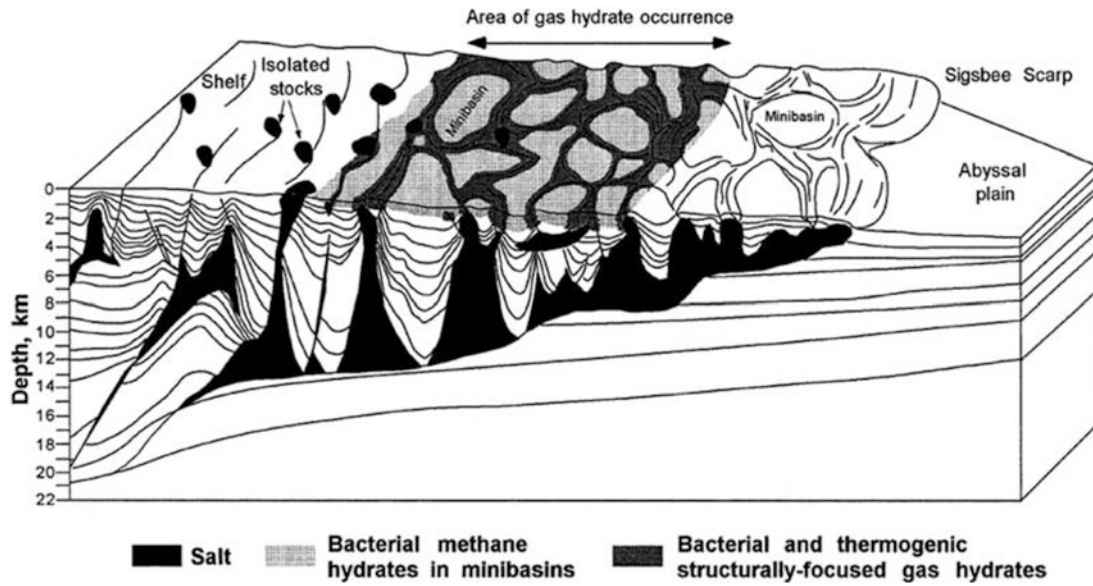


Figure 5.14. The subsurface structure of the northwestern Gulf of Mexico continental slope (Milkov and Sassen 2001; reprinted with permission from Elsevier).

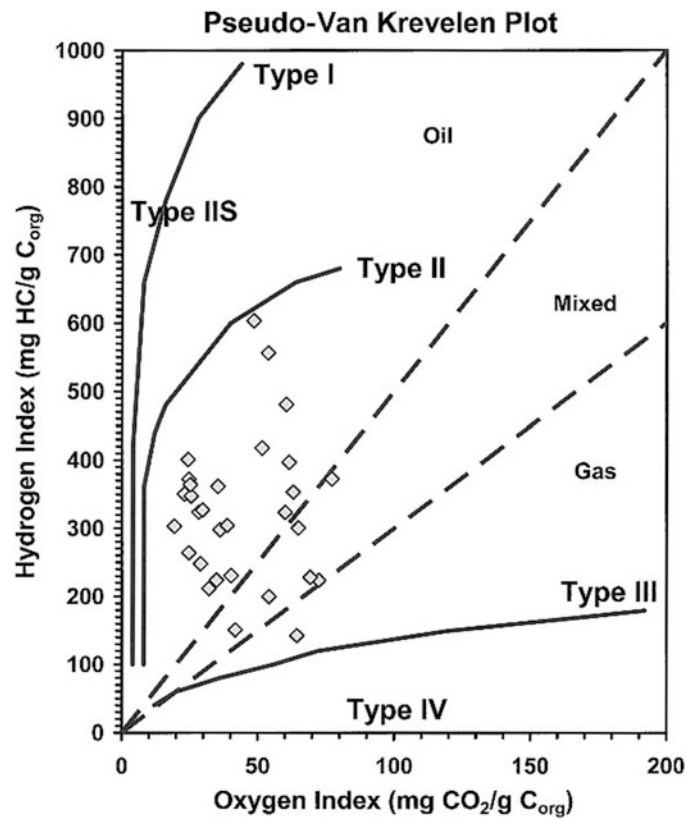


Figure 5.15. Source-rock types are classified by the content of hydrogen (H), carbon (C), and oxygen (O), which changes with maturation and oil and gas generation (photo from AAPG wiki, 2014; available at <http://wiki.aapg.org/File:VanKrevelanDiagram.png>).

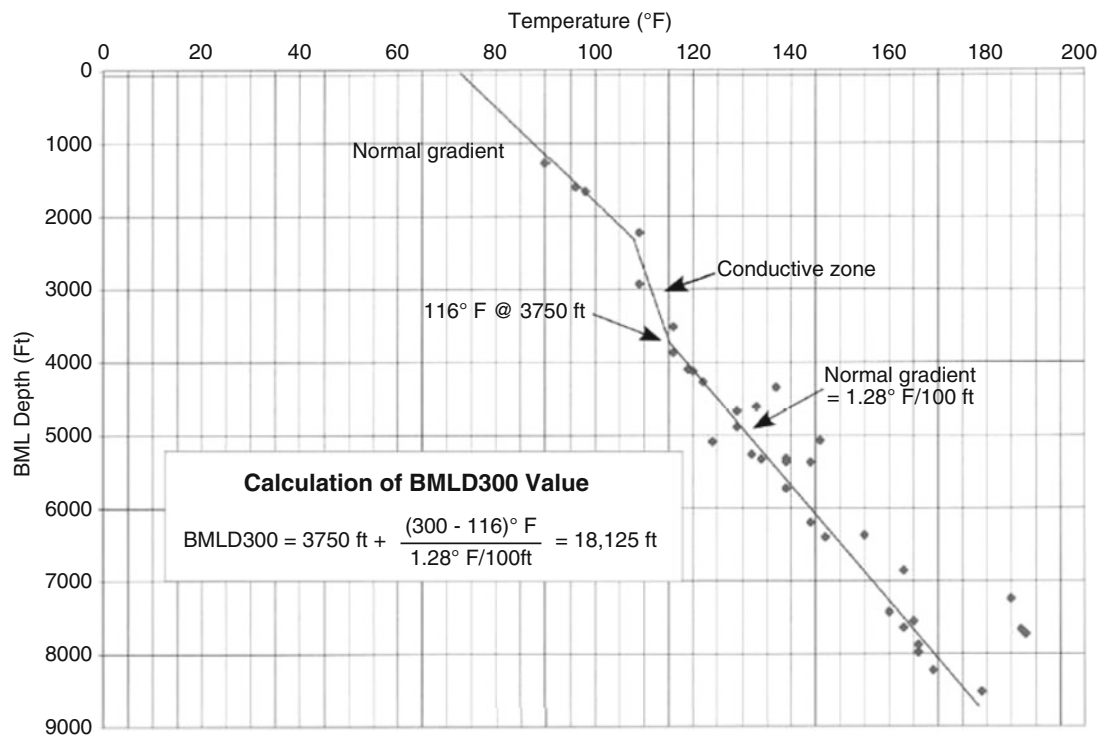


Figure 5.16. Subsurface temperature distributions are the end-result of thermal gradient, thermal conductivity, and heat flow. Subsurface temperature gradients are inversely proportional to the thermal conductivity of sedimentary rocks under conditions of constant heat flow. [BMLD300—below mud-line depth to the 300° isotherm; example from Eugene Island 282 in the Gulf Mexico, data from MMS Atlas of Northern Gulf of Mexico Oil Sands (2001)] Forrest et al. 2007; republished by permission of the Gulf Coast Association of Geological Societies, whose permission is required for further publication use, <http://www.searchanddiscovery.com/documents/2007/07013forrest/images/forrest.pdf>.

Source rocks are organic-rich sediments that have been deposited in a variety of environments including deepwater marine, lacustrine, and deltaic settings that preserve the remains of dead plants and animals. Anoxic or suboxic conditions at the time of deposition are often a requirement for preservation (Hunt 1996). Source rocks are classified by the type of kerogen (organic matter) they contain, which in turn determines the type of hydrocarbons generated as they thermally mature (Hunt 1996). Type I source rocks contain algal remains deposited under anoxic conditions in deep lakes and generate waxy oils. Type II source rocks contain marine planktonic and bacterial remains preserved under anoxic conditions in marine environments and produce both oil and gas. Type III source rocks contain terrestrial plant material that has been decomposed by bacteria and fungi under oxic or suboxic conditions and generate mostly gas and volatiles. Most coals and coaly shales are Type III source rocks. As a primary control on the type of petroleum generated at depth, the source-rock type determines the composition of gases and liquids available to migrate to the surface. Characterization of overlying seeps has been used prior to drilling to infer the presence, maturity, and type of source rocks more deeply buried in a basin.

When source rocks are buried by sediments, temperatures increase, and under suitable conditions the insoluble organic matter (kerogen) in the rock begins to thermally crack or breakdown (Figures 5.15 and 5.16) (Hunt 1996). This breakdown produces hydrocarbons from

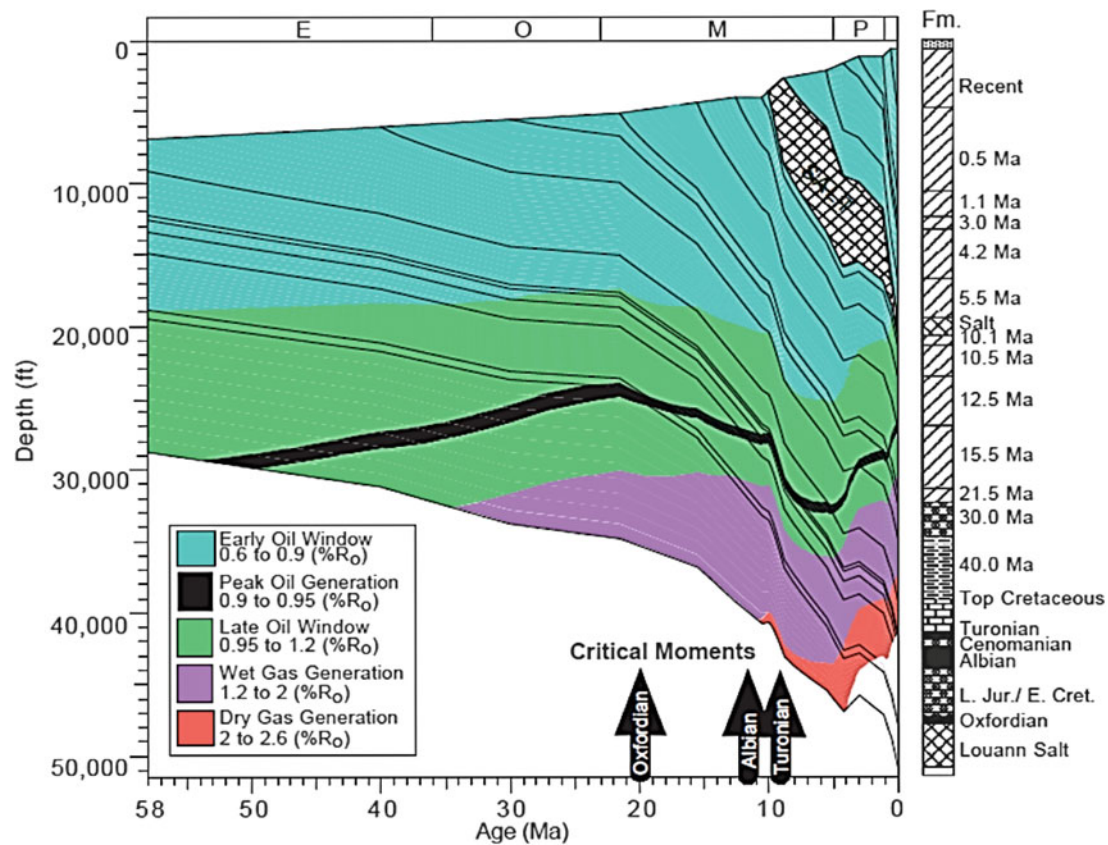


Figure 5.17. Geohistory and burial plot in the north-central Gulf of Mexico (McBride et al. 1999; used with permission of B.C. McBride) (*Ma* million years, *L. Jur.* Lower Jurassic, *E. Cret.* Early Cretaceous; upper scale: *E* Eocene, *O* Ordovician, *M* Miocene, *P* Paleocene; and %*R_o* is Vitrinite Reflectance).

the large and complex biomolecules of kerogen. High temperatures and deep burial can lead to the almost complete cracking of hydrocarbons to methane, producing dry gas (Figure 5.17) (McBride et al. 1999). Wet gas contains significant amounts of C₂ (ethane) to C₅ hydrocarbons (pentanes). Oil and gas generated from thermally mature source rocks are first expelled along with other pore fluids. This expulsion is due to the effects of internal source-rock overpressuring caused by hydrocarbon generation, as well as by compaction and is referred to as *primary migration*. Once released into porous and permeable carrier beds or into fault planes, oil and gas move upward toward the surface because of buoyancy and pressure; this upward movement is referred to as *secondary migration*.

Hood et al. (2002) described the Gulf of Mexico regional geologic framework based on two-dimensional (2D) and three-dimensional (3D) seismic data, identification and mapping of source intervals, and likely migration pathways to reservoirs. The compositions of more than 2,600 produced gas and oil samples and 3,000 seafloor seeps were used to describe source-rock characteristics, including organic matter type, depositional facies, level of maturation, and age. The major offshore hydrocarbon systems in the Gulf of Mexico were identified as the Lower Tertiary, Upper Cretaceous, and Upper Jurassic intervals (Table 5.1 and Figure 5.18). Eocene oil types correlated with source rocks and paleofacies distributions of Eocene deltaic systems. Eocene oils and gases occur on the Texas and Louisiana continental shelf and extend from

Table 5.2. Northern Gulf of Mexico Source Intervals (ages) and Source-Rock Correlations (Hood et al. 2002; AAPG ©2002, reprinted by permission of the AAPG whose permission is required for further use)

Source Interval	Oil Types	Rock Oil Type
Lower tertiary (centered on Eocene) ^a	Tertiary marine	Tie with high maturity cores of south Louisiana multiple-maturity suites and south-central Louisiana offshore Texas (salt sheath)
	Tertiary intermediate	
	Tertiary terrestrial	
Upper cretaceous (centered on Turonian) ^a	Marine—low sulfur—no tertiary influence	Direct ties with mature source rocks: offshore-eastern Gulf of Mexico, onshore Tuscaloosa trend, and Louisiana and Mississippi Giddings trend, Texas
Lower cretaceous	Carbonate—elevated salinity—cretaceous	Direct ties with source rocks: South Florida Basin
Undifferentiated cretaceous		Calcareous—unidentified cretaceous—production from fractured lower cretaceous black shale—south Texas
Uppermost Jurassic (centered on Tithonian) ^a	Marine—high sulfur—Jurassic	Inferred tie to postmature, organic-rich calcareous shales of the eastern Gulf of Mexico and oils in lower cretaceous reservoirs on Florida shelf where the Turonian/Eocene section is immature
	Marine—moderately high sulfur—Jurassic	
	Marine—moderate sulfur—Jurassic	
Upper Jurassic (Oxfordian)	Carbonate—elevated salinity—Jurassic	Tie to postmature, organic-rich carbonates—Mobile Bay
Triassic (Eagle Mills)	Triassic—lacustrine	Tie to postmature, organic-rich cores—northeast Texas (paleontology and palynology confirm nonmarine source character)

^a“Centered on” means that the source is largely within, and may not be restricted to, the designated interval.

onshore to the offshore Texas continental slope. Turonian oils were matched with offshore (east of the Mississippi River Delta) and onshore source rocks (e.g., Tuscaloosa and Giddings trends). Upper Cretaceous Eagle Ford source rocks currently are being developed as prolific shale-oil or gas-shale reservoirs. Based on seismic images, it is known that source rocks thin and ultimately pinch-out toward the basin. Oils and associated gases on the Gulf of Mexico upper slope are interpreted as originating from a Tithonian source. High maturity, organic-rich calcareous shales of the same age in the eastern Gulf of Mexico have been confirmed. Tithonian-sourced oils in Cretaceous reservoirs on the Florida Shelf and the Upper Cretaceous and Tertiary sections are immature. Oxfordian carbonate-sourced oils are common across the northwestern Gulf basin rim. Lower maturity hydrocarbons from this source seep to the surface in deep central Gulf of Mexico.

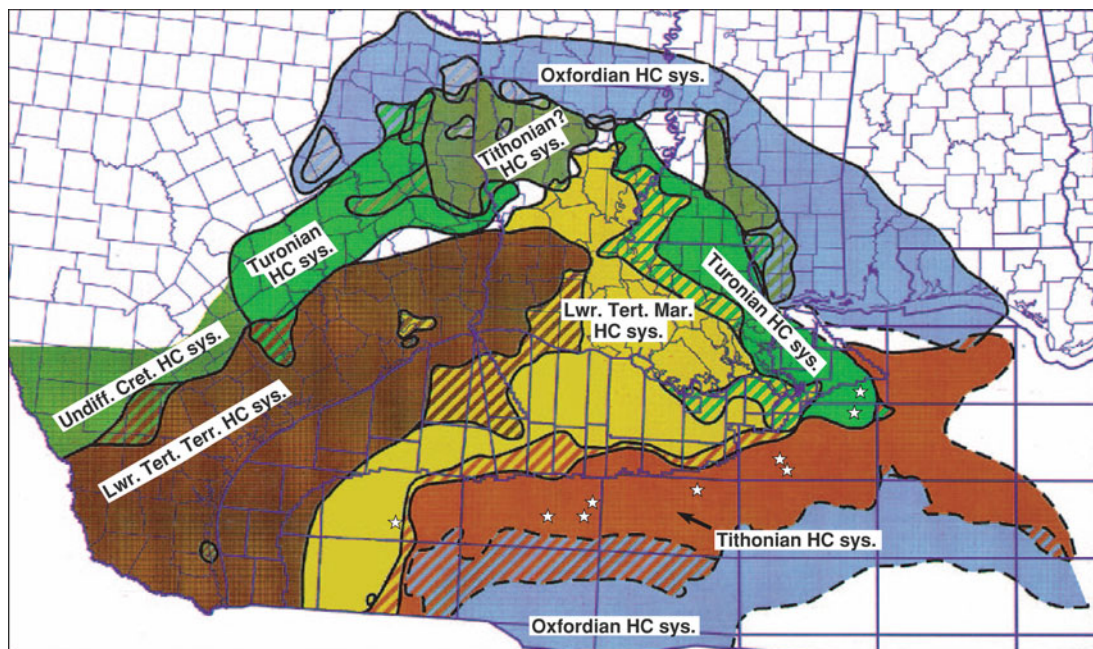


Figure 5.18. Hydrocarbon systems in the northern Gulf of Mexico basin. Each hydrocarbon system comprises a family of oils and gases with similar compositions interpreted as originating from a common source interval. Note that this map extends onshore (Hood et al. 2002; AAPG ©2002, reprinted by permission of the AAPG whose permission is required for further use). [HC sys. hydrocarbon system, *Terr.* terrestrial, *Mar.* Marine, *Undiff. Cret.* Undifferentiated Cretaceous, *Lwr. Tert.* Lower Tertiary].

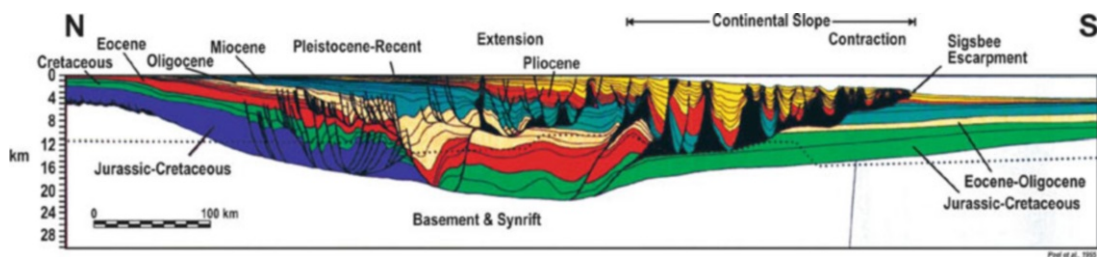


Figure 5.19. A north-south geologic cross section of the northern Gulf of Mexico basin illustrating the complex relationships between sediments and salt (black). The thick intraslope sedimentary basins, salt bodies, and numerous faults of the continental slope provide a geologic framework that favors leakage of subsurface fluids and gases to the modern seafloor. The cross section is an interpretation of two-dimensional seismic data calibrated using well data. From Fisher et al. 2007, citing Peel et al. 1995. Republished with permission of the American Association of Petroleum Geologists from Peel et al. 1995; permission conveyed through Copyright Clearance Center, Inc.

5.4.2 Migration Pathways

Migrating petroleum often crosses strata above deeper source intervals to travel to shallower more porous reservoir rocks or onward to the surface (Figure 5.19) (Peel et al. 1995). Salt movement, faulting or other tectonic activity, depending on geological setting, can create cross-stratum conduits. In the Gulf of Mexico, effective potential migration pathways intersect both the deep source intervals and younger reservoirs. Nearly 70 % of the

world's proven hydrocarbon reserves are found in structures related to salt tectonics (Cao et al. 2013). Migration pathways may form during continued sedimentary loading, without external tectonic influences, due to gravitational instability (e.g., salt is less dense than surrounding rocks). However, active tectonics increases the likelihood of the development of salt structures (Figure 5.20). A salt body pushing through its overburden is known as *diapirism*. Many of the first oil discoveries were associated with salt domes. Salt diapirism is particularly important and prevalent in the Gulf of Mexico and is a major reason for the extensive petroleum seepage observed.

As elsewhere in the world, seepage and subsurface petroleum systems in the Gulf of Mexico are closely correlated. Petroleum seepage patterns and analysis in the offshore Gulf of Mexico have been used to extend mapping of hydrocarbon systems and maturity maps beyond subsurface core data (Hood et al. 2002). As described above, the basic requirements for petroleum to reach the surface are common in the deepwater region of the Gulf of Mexico. Multiple prolific source rocks are present that have been deeply buried by sediment deposition over geologic time. Burial results in maturation contributing to overpressuring that, combined with buoyancy, drives upward fluid migration. The same geological processes produce large sandstone bodies. These bodies serve as excellent high porosity reservoirs where some of the generated liquid and gaseous hydrocarbons are trapped. Salt tectonics involving the underlying Jurassic Louann Salt has created deep subsurface faults. These faults provide conduits for not only migration of petroleum into reservoir rocks but also breaching reservoir seals allowing seepage to the surface.

The Louann Salt is a widespread evaporite formation that formed in the Gulf of Mexico in the Middle Jurassic Epoch (Figure 5.21) (Hudec et al. 2013). The Louann Salt layer formed in a rift as the South American and North American Plates separated forming an embayment in the paleo-Pacific Ocean. The Louann Salt underlies much of the northern Gulf of Mexico from Texas to the Florida panhandle and extends beneath large areas of the Gulf of Mexico coastal plain of Mississippi, Louisiana, and Texas and southward into the deep sea. The geographic distribution of petroleum seeps in the Gulf of Mexico closely correlates with subsurface salt structures that create migration pathways. Salt structures are particularly prevalent in the northwestern Gulf of Mexico from the edge of the continental shelf along the continental slope and into the abyssal Sigsbee Escarpment. This is an area of intensive petroleum seepage. A series of additional salt basins and structures extend to the northeast and toward the basin in the southern Gulf of Mexico offshore of the Campeche Peninsula (Figure 5.21). Seeps have been reported in the southern and southwestern Gulf of Mexico, and major oil and gas accumulations have been found (Figures 5.22 and 5.23). Lava-like flows of solidified asphalt have been reported on the Campeche Knolls (a surface expression of deeper salt diapirs) in 3,000 m (9,843 ft) of water in this area (Figure 5.21) (MacDonald et al. 2004). Gas hydrate, thermogenic gases, biodegraded oil seeps (possibly from an Upper Jurassic source of moderate maturity), and cold-seep communities were reported at this site, confirming asphalt flows seen in a seafloor photograph taken in the 1970s (MacDonald et al. 2004).

5.5 BIOGEOCHEMISTRY

Petroleum seeps in the Gulf of Mexico are a highly variable mixture of chemical compounds reflective of the subsurface source materials and postseepage alteration processes. Seeps exhibit the full spectrum of alterations from pristine (e.g., unaltered) to severely biodegraded. Seeps can be 100 % methane, while in other instances, a complete suite of hydrocarbons typically found in oil is present. The chemical compositions of seeps have been determined by sampling and analysis of air, water, and sediments using seafloor

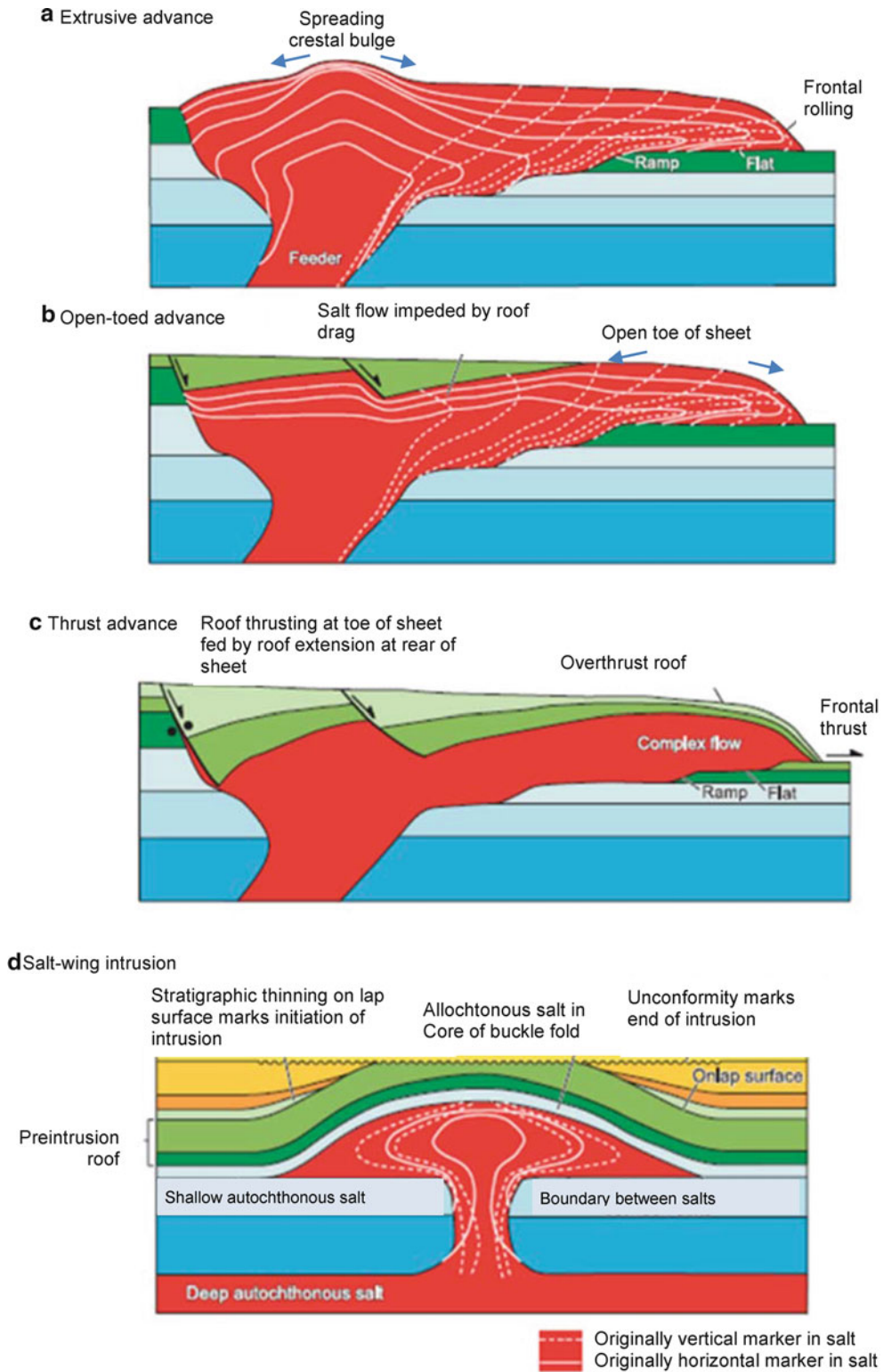


Figure 5.20. Four models of salt-sheet advance. *White lines* in the salt represent deformed markers from an originally rectangular grid. A line flanked with pairs of *black dots* indicates a salt weld (Hudec and Jackson 2006; AAPG © 2006, reprinted by permission of the AAPG whose permission is required for further use).

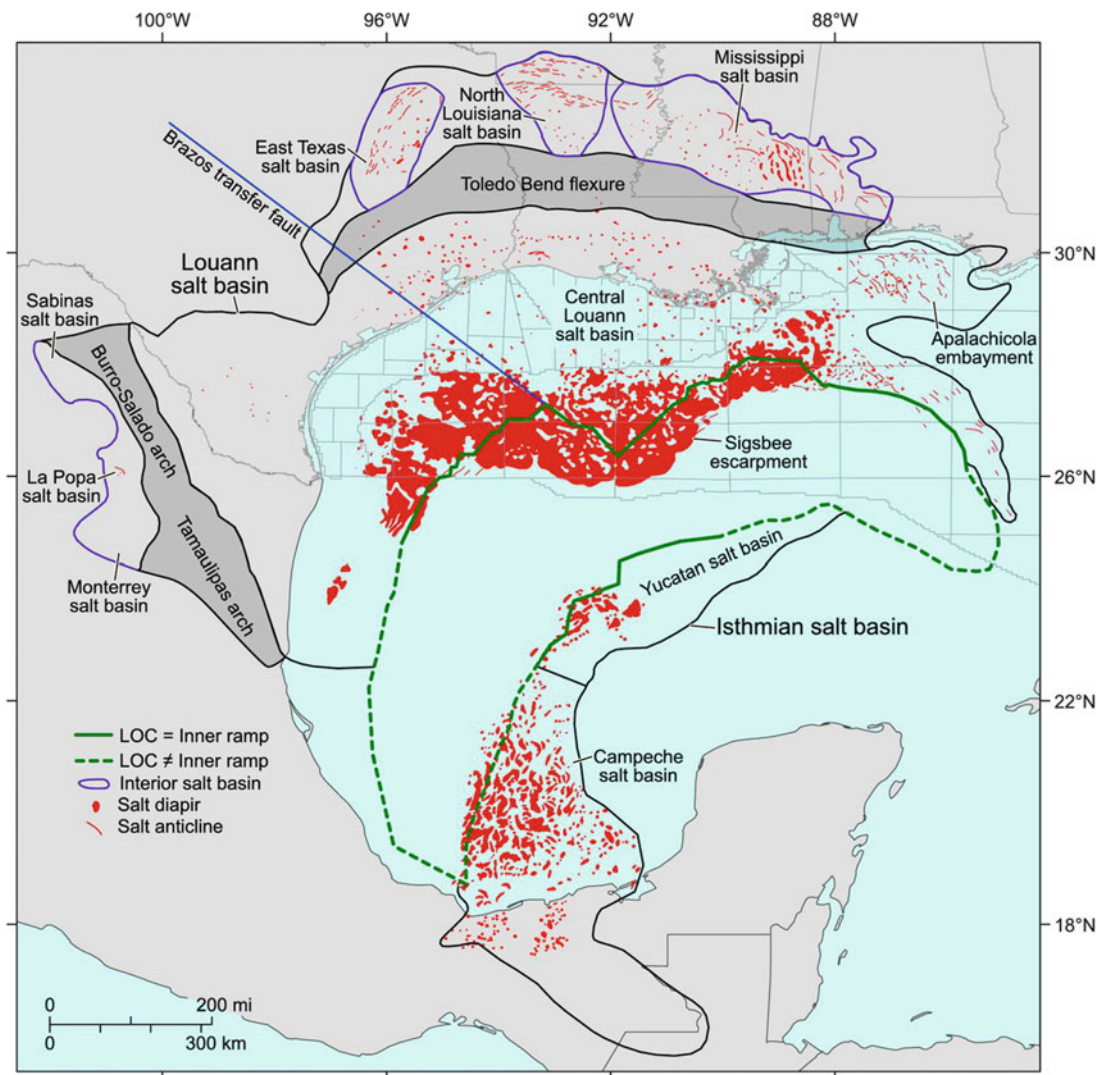


Figure 5.21. Salt basins of the Gulf of Mexico (salt structures are red); Hudec et al. 2013; AAPG©2013, reprinted by permission of the AAPG whose permission is required for further use.

coring devices and remotely operated vehicles and manned submersibles. Sea-surface slicks are collected with adsorbents and screens. Each petroleum seep has its own chemical signature.

5.5.1 Chemistry

Collectively, Gulf of Mexico seeps contain gaseous compounds with 1–5 carbon atoms, volatile compounds with 6–12 carbon atoms, and higher-molecular-weight hydrocarbons with 13 to more than 60 carbon atoms. Seeps can contain alkanes, branched alkanes, cycloalkanes, and aromatic (unsaturated) hydrocarbons. As with petroleum, heteroatomic compounds (containing oxygen, nitrogen and sulfur), resins, asphaltenes, metals and sulfur can be present in oil seeps as well. Complex biochemical-derived compounds that can be linked to known biological

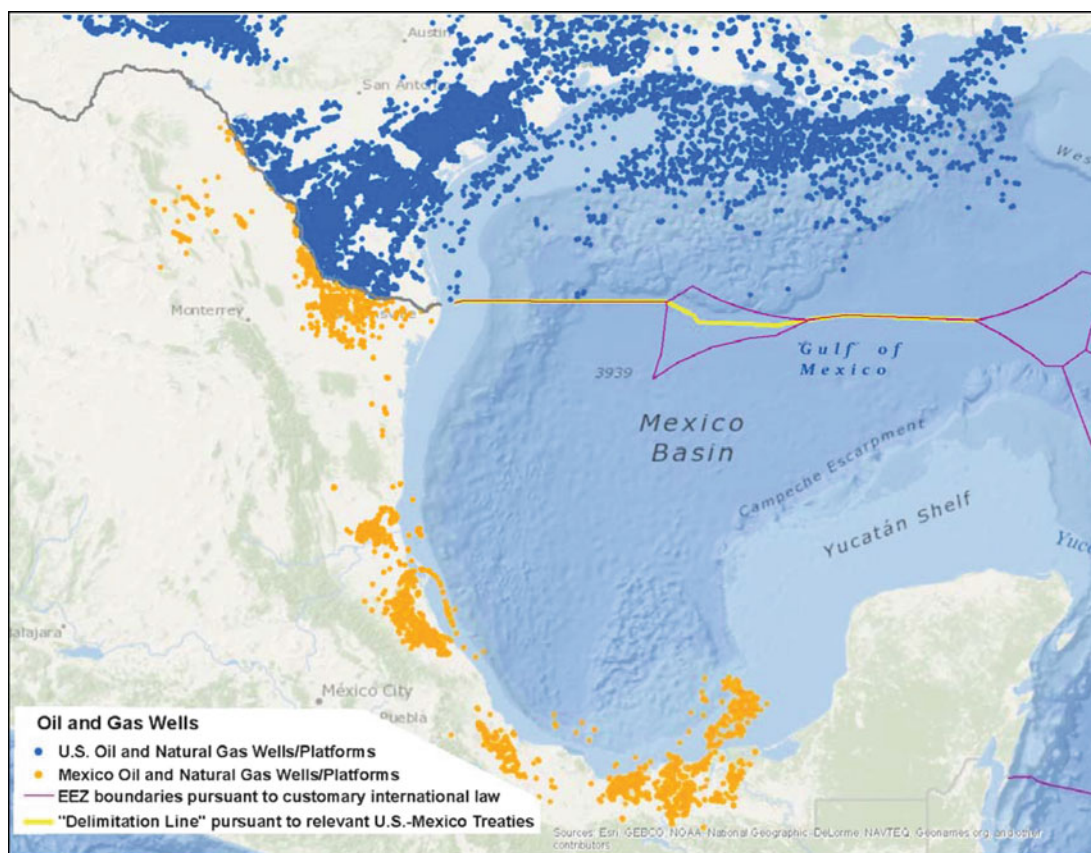


Figure 5.22. The U.S. and Mexico oil and natural gas activity around the Gulf of Mexico (Seelke et al. 2015) <https://www.fas.org/sgp/crs/row/R43313.pdf>.

precursors, the so-called *biological markers* or *biomarkers*, are also commonly present in seeps.

Gas seeps are widespread in the Gulf of Mexico but most have recent, microbiological origins and are often 100 % methane. Seep gases can be unbound (free), bound to mineral or organic surfaces, or entrapped in mineral inclusions (Abrams 2005; Abrams and Dahdah 2011). Gas seeps of microbial methane can be differentiated from deep-sourced thermogenic hydrocarbon gases based on compositional and stable and radiocarbon analyses (Figures 5.24 and 5.25). Microbes produce almost exclusively methane although some have suggested trace amounts of higher-molecular-weight gases may have a microbial origin (Sassen and Curiale 2006). Being of recent origin, biological methane can contain radiocarbon unless fossil organic matter is being metabolized (Figure 5.25). Thermogenic gases, other than highly mature thermogenic methane (dry gas), are often associated with appreciable amounts of ethane to butane gases.

Various compositional ratios of C_1 – C_4 gases have been used to infer origins and maturity. Being derived from fossil carbon, thermogenic gases contain no radiocarbon (Figure 5.25). Thermogenic methane is enriched in ^{13}C relative to microbial-derived methane, with most stable carbon isotopic values ranging from -50 to -35 ‰ (parts per thousand—denoted as ‰—enrichments or depletions relative to a standard of known composition). Microbial gases stable carbon isotopic values vary from -120 to -60 ‰ (Whiticar 1999). Methane hydrogen stable

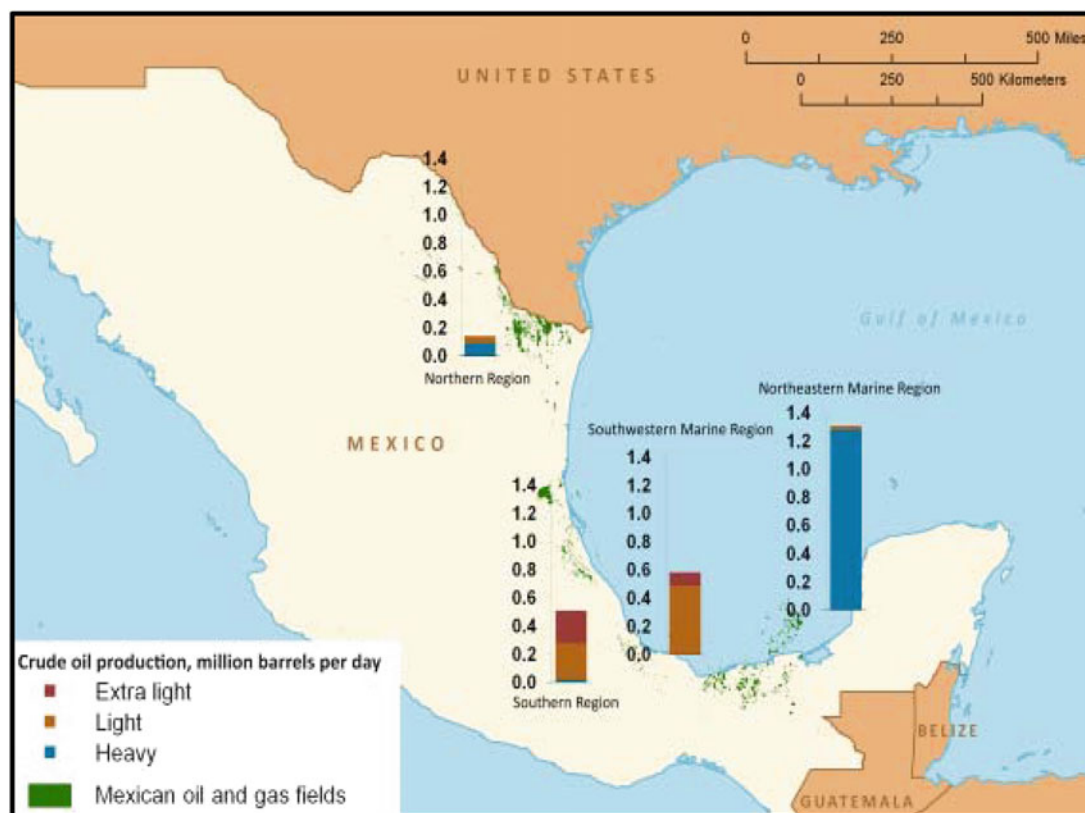


Figure 5.23. Mexico oil production in 2012 (millions of barrels per day; U.S. Energy Information Administration <http://www.eia.gov/todayinenergy/detail.cfm?id=11251>).

isotopic compositions (^1H , ^2H [deuterium]) provide additional information about the origins of gases. The hydrogen isotopic composition of methane derived from bacterial carbonate reduction ranges from -250 to -150 ‰, whereas values for methane derived from bacterial methyl-type fermentation range from -375 to -275 ‰. Thermogenic methane deuterium values range from -300 to -100 ‰ (Schoell 1980). Seep gases can be mixtures of multiple sources, and stable isotopic compositions can be altered by microbial oxidation confounding determination of original compositions.

It has been observed that migrated gasoline-range hydrocarbon compositions can vary from those found in reservoir oils (Abrams et al. 2009). The origins of gasoline-range (volatile) hydrocarbons (C_5 to C_{12}) in near-surface sediments are difficult to determine due to limited knowledge of inputs from recent organic matter. Seep gasoline-range hydrocarbons are often highly altered by microbes as a readily available source of labile reduced carbon.

The chemical and isotopic analyses of Gulf of Mexico oil seeps have been used to infer origins based on individual hydrocarbon concentrations and ratios; sums of homologue concentrations and ratios (e.g., alkanes and polycyclic aromatic hydrocarbons); stable carbon, hydrogen, and sulfur isotopic ratios; sulfur and metal content (e.g., Ni/V ratios); and biomarker compositions. Seep biomarker compounds provide information that can be used to correlate surface seep to subsurface oils and/or source rocks and indicate source-rock maturity and geologic age. Biomarkers commonly analyzed by gas chromatography/mass spectrometry include, but are not limited to, hopanes, steranes, tricyclic/tetracyclic terpanes, diasteranes, monoaromatic steroids, and triaromatic steroids. Low-intensity seeps can be overprinted by

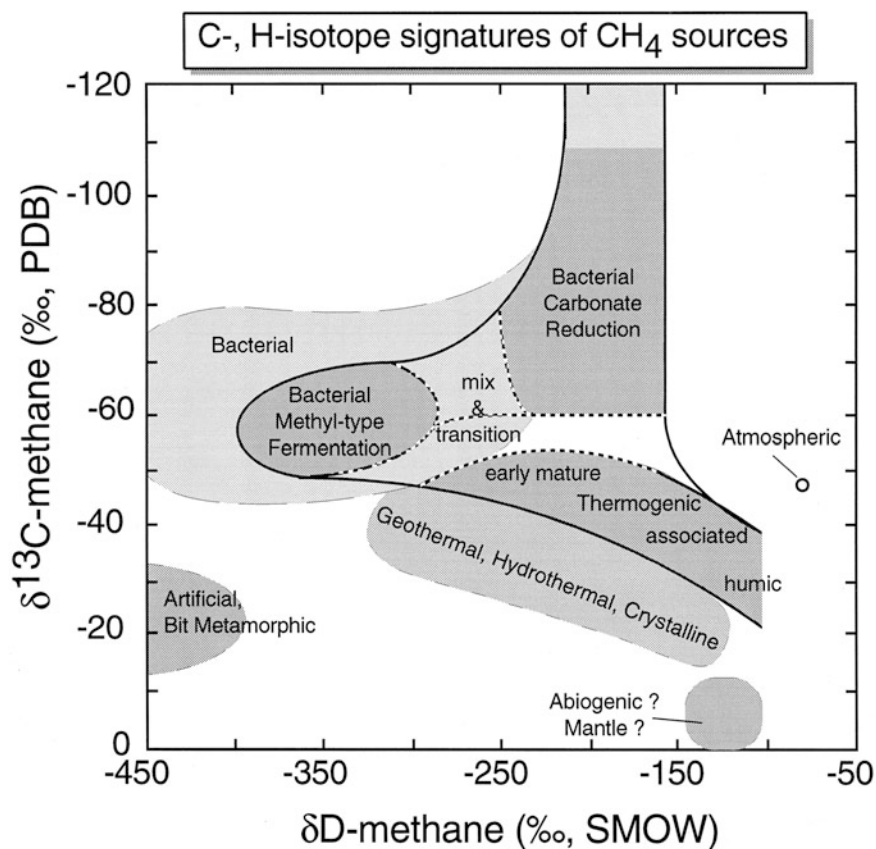


Figure 5.24. Methane stable hydrogen and carbon isotopic compositions vary with source, maturation, and alteration (Whiticar 1999; reprinted with permission from Elsevier).

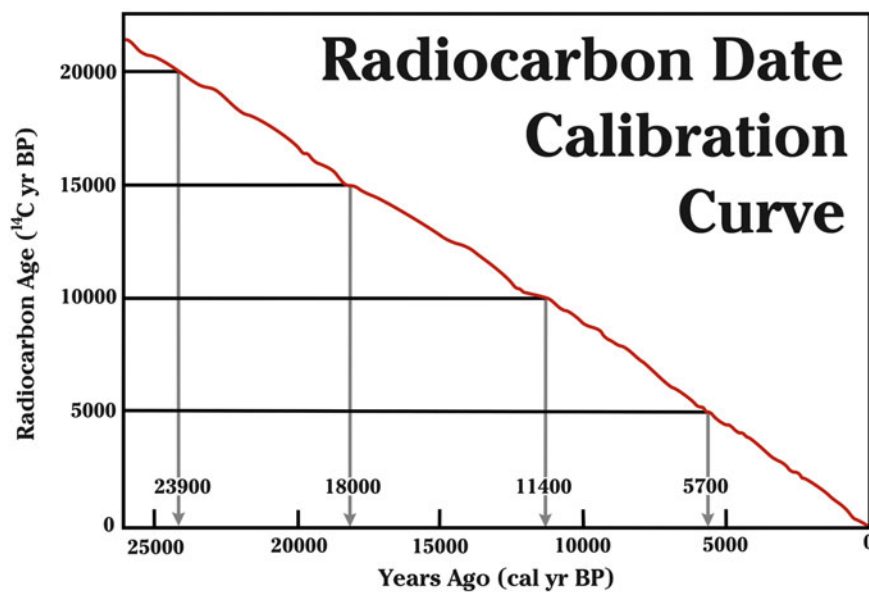


Figure 5.25. Comparison of radiocarbon dates to calendar dates. Actual ages are underestimated because the ratio of ¹⁴C to ¹²C changed over time (Reimer et al. 2004). (*cal yr BP* calibration year Before Present).

recent organic matter, which can obscure origins (Cole et al. 2001). Not all high-molecular-weight thermogenic hydrocarbons in recent sediments are due to oil seepage. Eroded material from surface exposures of thermally mature source rock can be redeposited in recent sediments.

5.5.2 Weathering

Once exposed to the near-surface environment, a range of physical, chemical, and biological processes can alter the physical and chemical properties of a seep from those of the subsurface source (Figure 5.26) (Coleman et al. 2003). Collectively, these processes are referred to as *weathering* and include evaporation, emulsification, dispersion, dissolution, and oxidation. These processes can occur in seafloor sediments, in the water column, at the sea surface, on land, and in the atmosphere. Some processes are mediated by microbiota. In the marine environment, seeping petroleum is also subject to various oceanographic processes including advection and spreading, dispersion and entrainment, sinking and sedimentation, partitioning, biological uptake and utilization, and stranding (Figure 5.27). All of these processes confound estimates of the original volume of seepage and can mask or displace seepage from its site of origin. Depending on the degree and type of alteration, some seep components and properties are preserved. These preserved properties can be used to infer the origin of the seep. Additionally, the progression of some changes in composition is predictable.

Evaporation is an important weathering process if seeping petroleum reaches the air/water or air/land interface. In particular, low-molecular-weight hydrocarbons (C_1 to C_{12}) are subject to evaporative loss (Coleman et al. 2003). Gases can reach the atmosphere with little or no alteration, depending on the physical setting, and compounds with higher molecular weights may be little altered by evaporative losses. Petroleum seeps can be a mixture of hundreds of compounds that vary from location to location and over time, and evaporative losses can be quite complex, variable, and often difficult to predict.

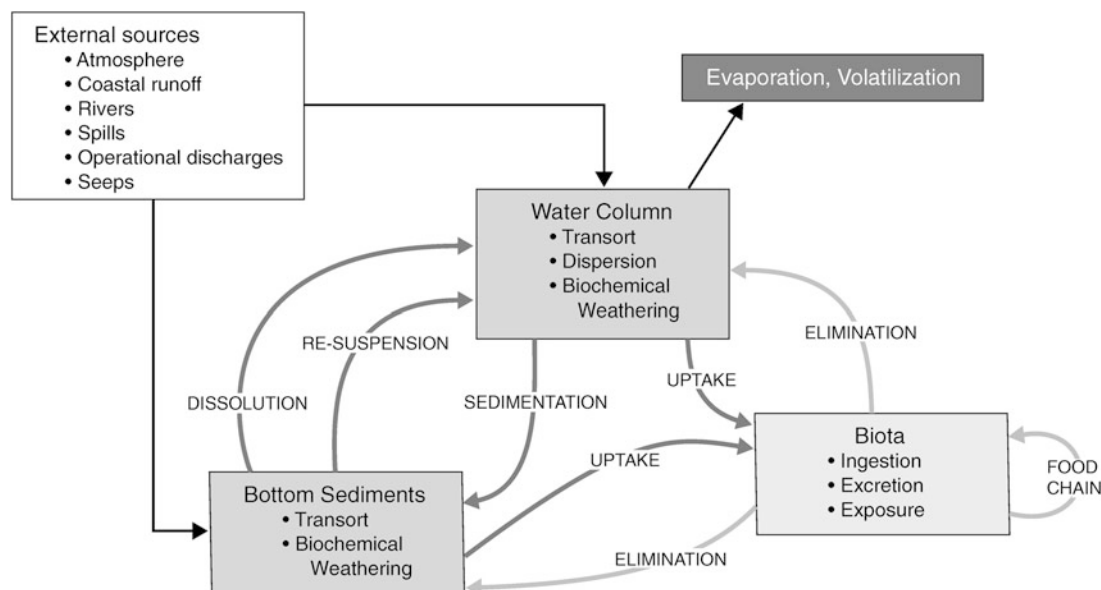


Figure 5.26. Conceptual model for the fate of petroleum in the marine environment (Coleman et al. 2003; republished with permission of Emerald Group Publishing Limited, permission conveyed through Copyright Clearance Center, Inc.)

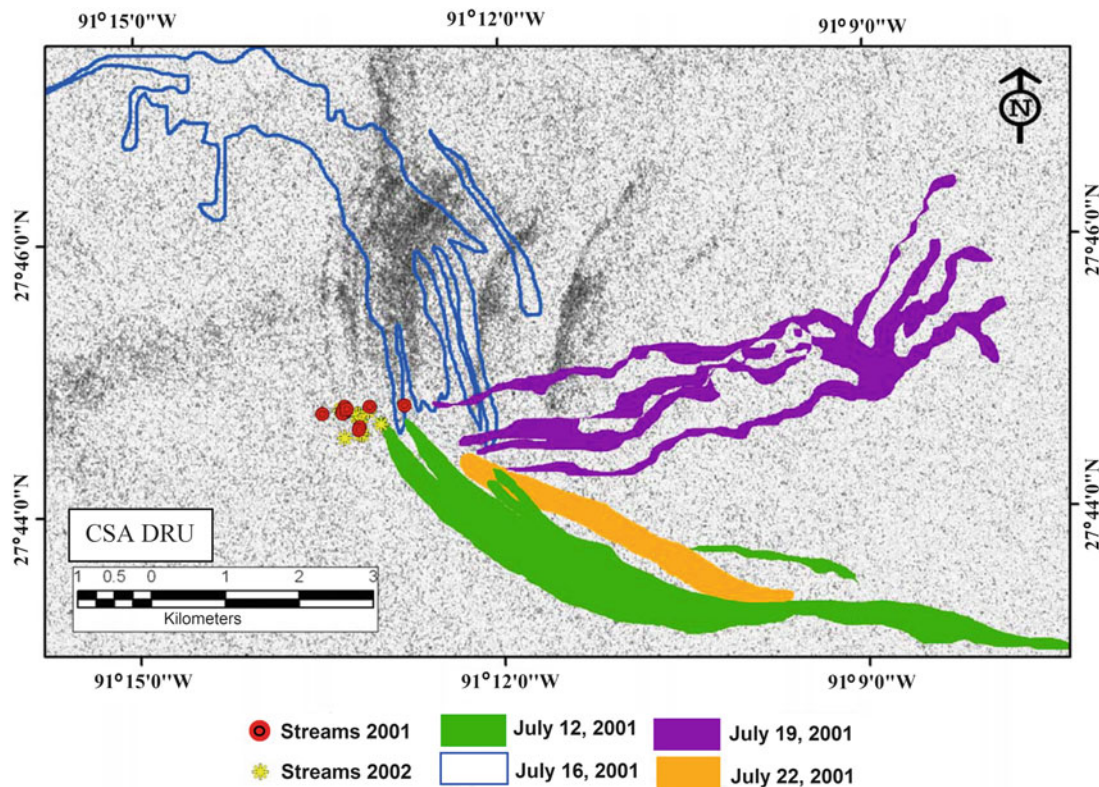


Figure 5.27. Sea-surface oil slicks in the north-central Gulf of Mexico associated with water column streams of gas bubbles detected in acoustic profiles emanating from the seafloor (*red dots*—2001 and *yellow stars*—2002). The *dark gray areas* are oil slicks detected on satellite images on 20 June 2002 (De Beukelaer et al. 2003; reprinted with permission of Springer).

Emulsification is the process where water mixes with oil changing the properties and characteristics of seepage and susceptibility to biodegradation. Additionally, the volume of the seep increases due to the addition of water (Coleman et al. 2003). Emulsification of seeping oil requires turbulent mixing and is therefore mostly restricted to higher energy marine settings. Emulsions do not spread and tend to form lumps or mats. Tar balls, tar mats and pavements, and asphalt flows have been recovered from Gulf of Mexico shorelines, sea surface, and seafloor. These materials can have differing origins including formation in place (due to emulsification), seepage of oil degraded in the subsurface, eruptions of molten asphalt, and formation at the sea surface due to weathering, which can be followed by sinking to the seafloor once their densities exceed that of seawater (Alcazar et al. 1989; MacDonald et al. 2004). In the Gulf of Mexico, natural and anthropogenic tar balls commonly wash up on shorelines and after storm events. Large tar mats and pieces of tar pavements (or reefs) have been observed on beaches (Van Vleet et al. 1983, 1984).

While generally hydrophobic, hydrocarbons have measurable solubility in water. Gases are the most water-soluble constituents of seeps. In most cases, dissolution accounts for only a small portion of oil seep loss but is important because some of the more soluble components of oil, particularly low-molecular-weight aromatic compounds (e.g., benzene, toluene, alkylated benzenes, and naphthalenes), are more toxic to aquatic species than aliphatic hydrocarbons (Coleman et al. 2003). Dissolution can be extensive in marine settings due to long-term exposure to seawater.

Two oxidative processes, photooxidation and biological oxidation, can alter seeps. Photooxidation includes a wide variety of light-catalyzed reactions. Photooxidation binds oxygen to carbon substrates transforming hydrocarbons into functionalized compounds such as alcohols, ketones, and organic acids that are more water-soluble than the original aliphatic hydrocarbons. If oxygen, light, and time are unlimited, the end products of photooxidation are carbon dioxide and water. Photooxidation is usually unimportant from a mass-balance consideration for seeps but may play an important role in the removal of dissolved hydrocarbons in high-light environments (e.g., on land or in shallow water). Some oxidized by-products are more toxic than precursor compounds (Coleman et al. 2003). The chemistry and extent of photooxidation of hydrocarbons can be quite complex. Its course and importance is dependent on a number of compositional and environmental variables.

5.5.3 Biochemistry

Biogeochemical processes are fundamental to, and a critical connection between, commonly expressed phenomena at petroleum seep sites. The primary effects of seeps are the introduction of reduced labile carbon as oil and gas and biological utilization of the labile carbon as an energy source. Other seep effects are those related to the toxicity of some petroleum constituents, and yet other processes involve the by-products (i.e., carbon dioxide and sulfide) and metabolites of hydrocarbon oxidation. Many of these processes are complex, unfold in a stepwise fashion with subsequent processes dependent on the preceding process, have rate-dependent or concentration-threshold limitations and often, these processes are not fully understood. These biogeochemical manifestations of oil and gas seeps have been widely used to recognize the presence of seeps in the absence of direct measurements of hydrocarbons.

A wide range of biota have the capacity to oxidize hydrocarbons, including bacteria, fungi, heterotrophic phytoplankton, and some higher organisms. There are two types of biological oxidation: metabolic detoxification after ingestion and microbial utilization. These two types have markedly differing biochemistries and end products. Metabolic detoxification of hydrocarbons by higher organisms exposed to aromatic hydrocarbons converts them to water-soluble compounds (e.g., alcohols, ketones, phenols, epoxides, and organic acids) that are excreted by the organisms as a protective mechanism. This process is biochemically complex and involves specialized enzymes (e.g., mixed function oxygenases). Not all organisms have the capacity to detoxify hydrocarbons. From a mass-balance perspective, metabolic detoxification of hydrocarbons is unimportant in removing seep hydrocarbons from the environment.

In contrast to metabolic detoxification, microbial oxidation, which occurs commonly, is important in removing hydrocarbons from the environment. Many seeps are highly altered by these processes. Microbial oxidation utilizes hydrocarbons as a carbon source to produce energy from the breaking of carbon bonds and is often referred to as *biodegradation*. Biodegradation causes two important effects: the effect of the by-products/metabolites of hydrocarbon oxidation and change in the residual oil and/or gas. As with photooxidation, the ultimate end products of biodegradation of hydrocarbons can be carbon dioxide and water, but a range of intermediates, such as organic acids, are also formed. The chemical and stable isotopic compositions of residual hydrocarbons are often altered.

Oil and gas seep environments are generally methane and sulfide rich (Joye et al. 2010). When oxygen is available, aerobic microbial oxidation can take place, and in the absence of oxygen, anaerobic microbial oxidation can occur (Figure 5.28) (Valentine and Reeburgh 2000; Coleman et al. 2003). These environmental settings have two distinct types of biogeochemistry and involve different species or consortia of bacteria. Microbial activity at seeps involves two

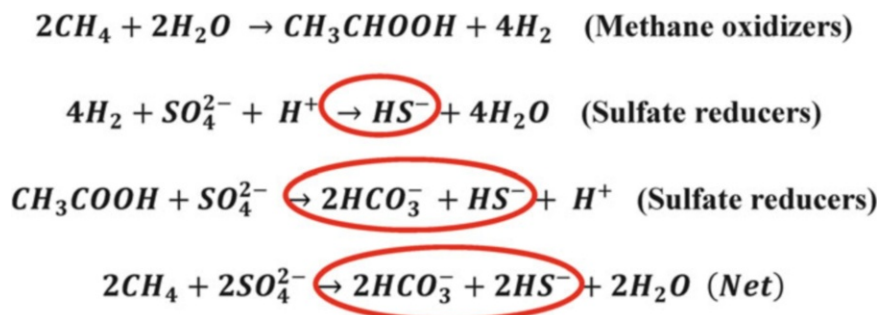


Figure 5.28. Proposed mechanism steps 1–4 for the anaerobic oxidation of methane by archaea and sulfate reducing bacteria (Valentine and Reeburgh 2000).

primary mechanisms: hydrocarbon oxidation and sulfate reduction (Joye et al. 2010). Microorganisms oxidize methane and other hydrocarbons increasing bicarbonate (HCO_3^-) ion concentrations, which increase porewater alkalinity and enhance the precipitation of calcium carbonates and other minerals. Carbonate precipitates form crystals, nodules, and cemented sediments (hard bottom) (Boetius et al. 2000; Joye et al. 2004, 2010). Carbonate precipitation can fill sedimentary veins and fissures restricting or reducing seepage. Hydrocarbon-derived carbonates are common at active sites and are often preserved at past seep sites (Ritger et al. 1987; Greinert et al. 2001; Campbell 2006). Microorganisms reduce sulfate and produce hydrogen sulfide (H_2S) that is used as an energy source for free-living sulfur-oxidizing bacteria and the symbionts of cold-seep community megafauna (Barry et al. 1997; Fisher 1990; Levin 2005). The formation of hydrogen sulfide can also lead to the formation of elemental sulfur (S^0) and sulfur minerals such as pyrite (FeS_2) if iron is present (Sassen 1987; Sassen et al. 1988). This complex biogeochemistry produces characteristic mineral assemblages in sediments at seep sites. Microbial sulfate reduction at seeps sites can be highly temporally and spatially variable, with sites of complete depletion only meters away from sites of little depletion (Formolo and Lyons 2013). Biogeochemical sulfur cycling is complex, nonsteady state, and closely coupled with the availability of reactive iron. Pyrite is an early by-product of seepage close to the sediment–water interface. Rates of biodegradation are influenced by oxygen and nutrient concentrations; temperature, salinity, and pressure; the physical properties and chemical composition of the petroleum oxidized; and the energy level of the seep environment (e.g., replenishment of oxygen and nutrients which can be limiting and dilution and transport of by-products).

The effects of biodegradation on oil and gas chemical and stable isotopic compositions are well known. The effect of biodegradation on methane stable carbon and hydrogen isotopic compositions are illustrated in Figure 5.24. Residual methane becomes progressively enriched in ^{13}C and ^2H as the extent of degradation increases. In more complex mixtures of hydrocarbons, such as oil, the susceptibility of hydrocarbons to microbial oxidation is dependent on structure and molecular weight (Kennicutt 1988). In general, microbes oxidize small molecules with 20 carbon atoms or less before larger ones. Within the same molecular weight range, straight-chain aliphatics (normal alkanes) are more susceptible to oxidation than branched and cycloalkanes, which are more susceptible than aromatic hydrocarbons (Coleman et al. 2003). Microbes metabolize propane and *n*-butane more readily than other hydrocarbon gases. Thermogenic gas seeps that contain biodegraded gas are commonly depleted in propane relative to methane, and *n*-butane relative to isobutane. High-molecular-weight compounds are often preserved, but even these compounds can be altered if biodegradation is severe. This progressive loss of

hydrocarbon types can result in residual oil containing mostly an unresolved complex mixture (UCM) of compounds in gas chromatographic analyses (Figure 5.29) (Abrams 2005; Sassen 1980; Kennicutt 1988). The UCM is largely uncharacterized but is believed to be a highly complex mixture of hundreds of ill-defined hydrocarbons. Unaltered oil seep hydrocarbons are characterized by near equal amounts of long-chained *n*-alkanes (C₁₂₊) and the presence of isoprenoid hydrocarbons (C₁₃–C₂₀ including pristane [C₁₉] and phytane [C₂₀]) (Figure 5.29). The UCM increases in prominence with degree of biodegradation because other components are preferentially removed. Gas chromatographic signatures can be overprinted by recent organic matter, and oil can be biodegraded in the subsurface prior to migration.

Worldwide, white and pigmented filamentous bacterial mats of several undescribed species of *Beggiatoa* have been observed at seep sites. These mats have been sampled at several petroleum seep sites in the Gulf of Mexico (Figure 5.30) (Sassen et al. 1993). Mats typically occur at the interface between reducing sediments and the overlying oxygenated water column. These mats are localized at seafloor seepage features taking advantage of the close proximity of anoxic and oxic conditions, but there is little evidence that these bacteria directly utilize hydrocarbons. Elemental sulfur (S⁰) is often visible within cells of *Beggiatoa*, and mat material is characterized by high sulfur content. Mats are part of a complex bacterial consortium in most sediments that contain oil and gas seepage. *Beggiatoa* spp. can oxidize hydrogen sulfide (H₂S) during the reduction of sulfate produced by the aerobic oxidation of hydrocarbons by other bacteria (Figure 5.31). Oxygen is depleted, and carbon dioxide produced during hydrocarbon oxidation can be incorporated during the biosynthesis of organic matter. These mats appear to retard the loss of hydrocarbons to the water column by creating a physical barrier to flow from the sediments. These processes are partly responsible for the highly biodegraded state of many seep oils.

5.5.4 Geochemistry

The mid-1980s marked the beginnings of extensive studies of unusual geologic characteristics at petroleum seep sites on the continental slope of the Gulf Mexico. Coring, manned submersibles, and remotely operated vehicles have collected seafloor samples for the investigation of the geochemistry, petrography, and structure of authigenic carbonates from the shallow slope to beyond the Sigsbee Escarpment (Figure 5.32) (Roberts and Aharon 1994; Roberts et al. 2009, 2010; Feng et al. 2010). These studies determined the geochemical origins of anomalously high seafloor reflectivity as being primarily due to lithification of sediments by authigenic carbonates (Roberts et al. 2009). Microbe-generated carbon dioxide initiates a cascade of microbe-mediated chemical reactions, including the precipitation of authigenic minerals that produce unique morphologies, mineralogies, and critical habitat for cold-seep fauna at petroleum seep sites.

The stable carbon and oxygen isotopic compositions of carbonates at seep sites confirm their close association with hydrocarbon-sourced carbon dioxide (Roberts et al. 2009, 2010a, b; Feng et al. 2010). The origin of the carbon dioxide incorporated into carbonates is indicated by $\delta^{13}\text{C}$ values and $\delta^{18}\text{O}$ values, which reflect the temperature and fluid source of the carbonates. Potential sources of carbon at seep sites include biogenic and thermogenic gases, oil, seawater carbon dioxide, and methanogenesis (Roberts et al. 2010). Seep carbonate stable isotopic compositions are highly variable indicating various admixtures of these multiple sources (Figure 5.33) (Roberts et al. 2010). Seep site carbonates are generally depleted in ¹³C and enriched in ¹⁸O compared to deep-sea carbonate minerals formed from seawater carbon dioxide. ¹⁸O is enriched in gas hydrate, and the anomalously positive $\delta^{18}\text{O}$ of some seep carbonates suggests an origin related to the decomposition of gas hydrate. Unusually low

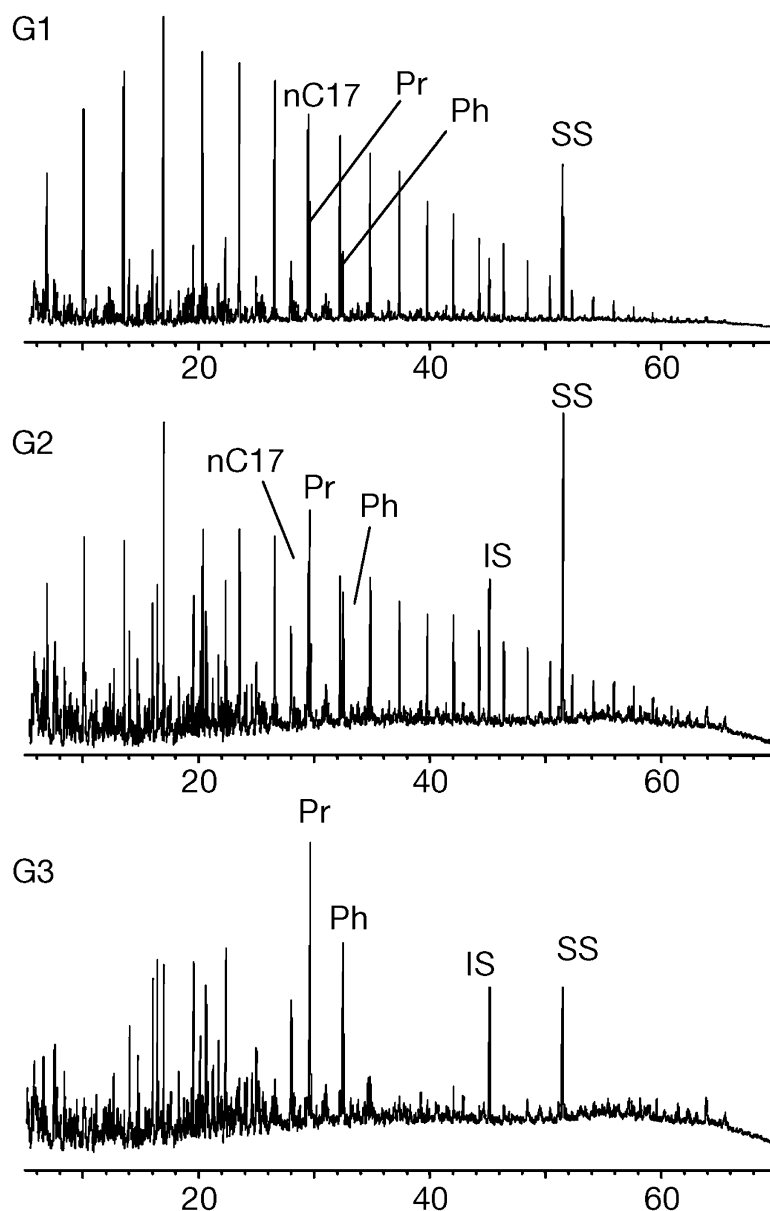


Figure 5.29. Oils of different biodegradation levels (G1, G2, and G3) showing systematic relative removal of *n*-alkanes (e.g., nC17) relative to the isoprenoid alkanes pristane (Pr) and phytane (Ph) (spiked standards are IS and SS) (reprinted by permission from Macmillan Publishers Ltd: Nature [Jones et al. 2008] ©2008). [Times on the chromatograms are displayed from 5 to 70 min from time of injection.]

$\delta^{18}\text{O}$ values (as low as 2.4 ‰ Standard Mean Ocean Water) are likely related to the expulsion of warm fluids at the seafloor during rapid flux events, though other processes also affect carbonate stable isotopic compositions (Bohrmann et al. 1998; Greinert et al. 2001; Sassen et al. 2004; Hesse 2003).

A study of the characteristics of about 100 seep-related carbonate rocks collected on the continental slope of the Gulf of Mexico revealed that the rocks were mostly high in Mg-calcite

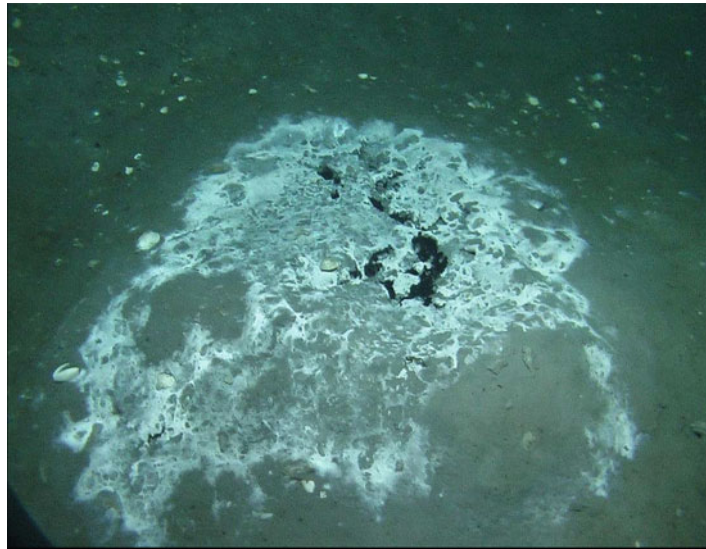


Figure 5.30. Seafloor gas-hydrate mound, seeping oil and brine and associated *Beggiatoa* microbial mat in the north-central Gulf of Mexico (Image courtesy of R. Weiland, BP America).

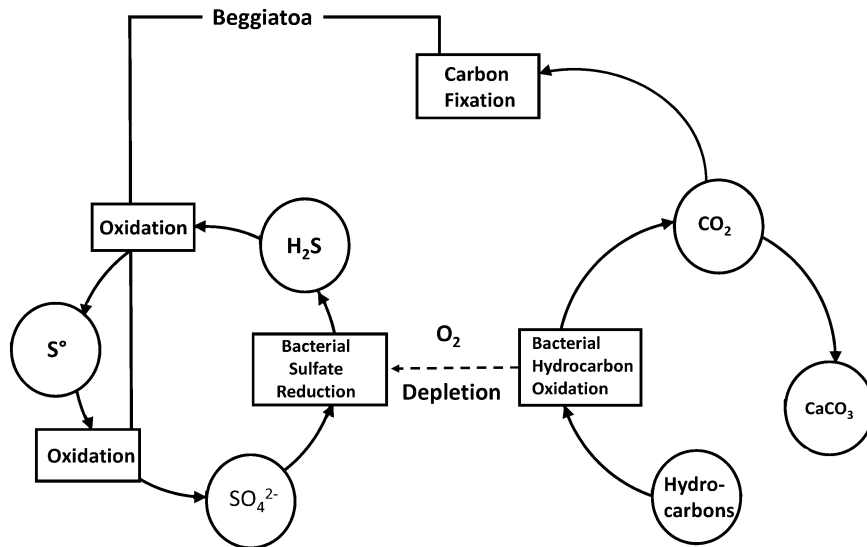


Figure 5.31. Summary of the proposed geochemical role of *Beggiatoa* in cold hydrocarbon seeps (reprinted from Sassen et al. 1993, with permission from Elsevier).

and aragonite and also contained significant amounts of dolomite (Roberts et al. 2009; Feng et al. 2010). These rocks have a range of morphologies including nodules, chimneys, slabs, blocks, mounds, and irregular-shaped aggregations (Figure 5.34) (Roberts et al. 2009).

The local chemical environment and the rate of hydrocarbon seepage control carbonate rock formation. Carbonate nodules of up to about 2 centimeters (cm) (0.8 inches [in.]) in diameter scattered throughout sediments are often incorporated into composite aggregates, occur in association with mussel and tubeworm communities, and form deep in sediments most likely in response to slow hydrocarbon flux rates (Figure 5.34). Chimneys as long 50 cm (19.7 in.)

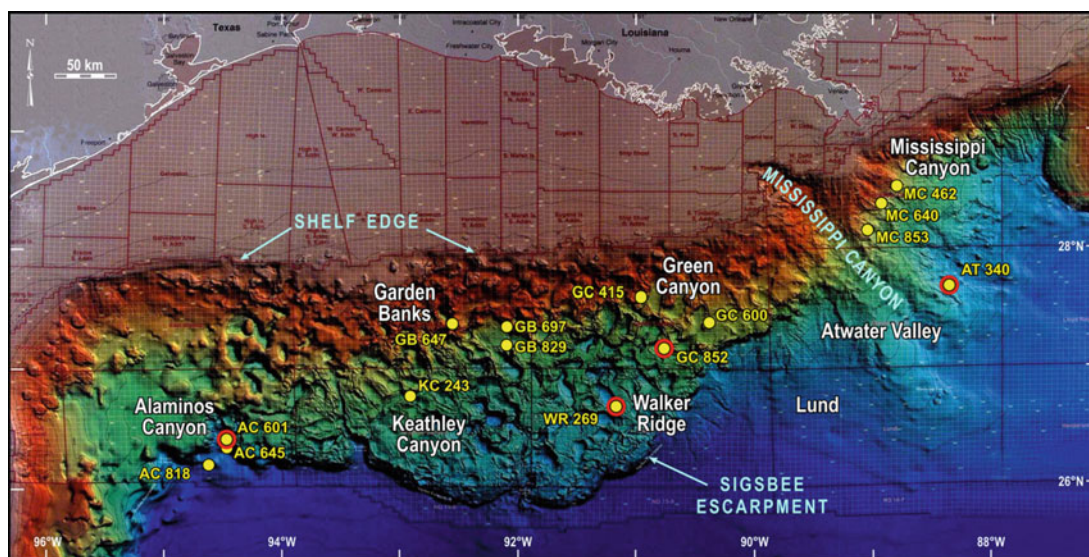


Figure 5.32. Sites on the northern Gulf of Mexico continental slope where manned submersible and remotely operated vehicle dives have been made and seep carbonates were collected. These collections have been extensively supplemented by coring at many other sites across the northern Gulf of Mexico (Roberts et al. 2009; republished by permission of the Gulf Coast Association of Geological Societies, whose permission is required for further publication use).

can occur as broken pipe-like shapes protruding from muddy sediments and may form due to focused vertical migration of hydrocarbon-rich fluids possibly associated with animal burrows. Slabs can be developed with rough surfaces, sometimes multiple layers and mostly composed of aragonite, suggesting precipitation from sulfate-rich porewaters. Carbonate blocks can be heterogeneous and up to several meters in diameter and length and contain void-lining aragonite-splay cements and brecciated structures of unknown origin (possibly related to abrupt expulsion of hydrocarbons or the decomposition of gas hydrate). Carbonate rocks can be rich in mussel and clam shells and contain relics of burrowing activity and occasionally have iron and manganese coatings (Callender et al. 1990, 1992; Feng et al. 2010).

5.6 TERRESTRIAL ENVIRONMENTS

Seeps on land can increase hydrocarbon concentrations in soils and the overlying atmosphere; enhance microbiologic activity; introduce minerals (such as uranium creating radiation anomalies); form calcite, pyrite, elemental sulfur, magnetic iron oxides, and sulfides; bleach red beds; alter clay minerals; affect soil electrochemical properties; and modify biogeochemical and geobotanical processes (Schumacher 2012). Liquid seepage is adsorbed onto soils, while gas seepage can move, mostly unaltered, directly into the atmosphere. Due to the relative lack of water at land sites of seepage compared to marine environments, emulsification is unimportant, but photooxidation can occur on direct exposure to sunlight. The geochemistry of mineral formation mediated by microbiota is similar to that described for marine settings and can encapsulate gases and liquids in mineral interstices. Due to changes in the chemistry of soils and the toxicity of some components of petroleum, land seeps can affect surrounding vegetation health and composition. Soil and air have been analyzed to detect seep-induced surface anomalies on land. Techniques also have been developed to detect these changes using airborne and satellite imagery, spectral reflectance, and other sensors. These surveys typically map

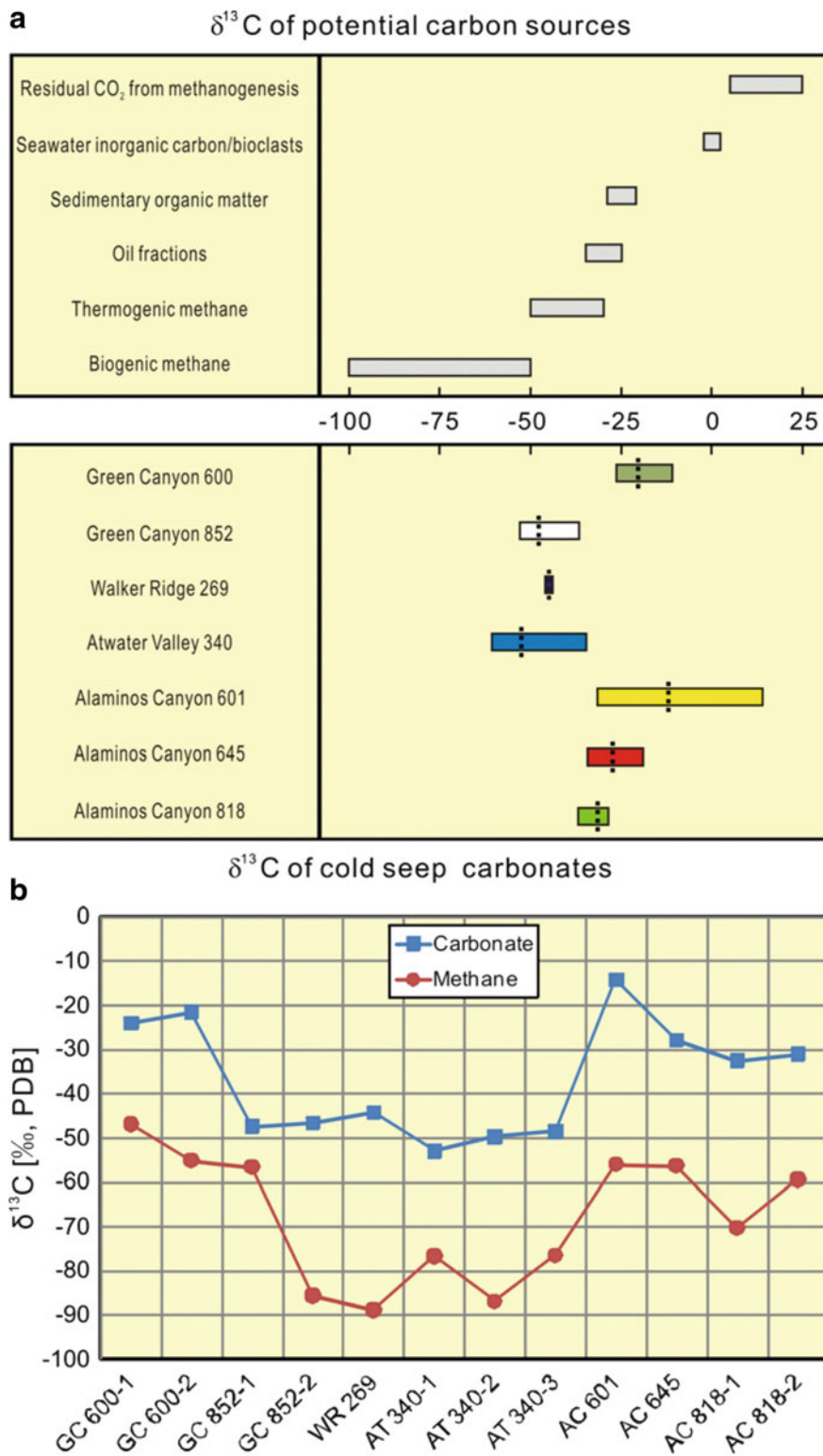


Figure 5.33. Comparisons of Gulf of Mexico $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of: (a) potential carbon sources and carbonates collected in $>1,000\text{-m}$ water depth, (b) carbonates collected in $<1,000\text{-m}$ depth, (c) $>1,000\text{-m}$ water depth, and (d) seep carbonates and methane from sediment cores from the same sites (Roberts et al. 2010 [reproduced with permission of PERGAMON via Copyright Clearance Center, Inc.] and references therein).

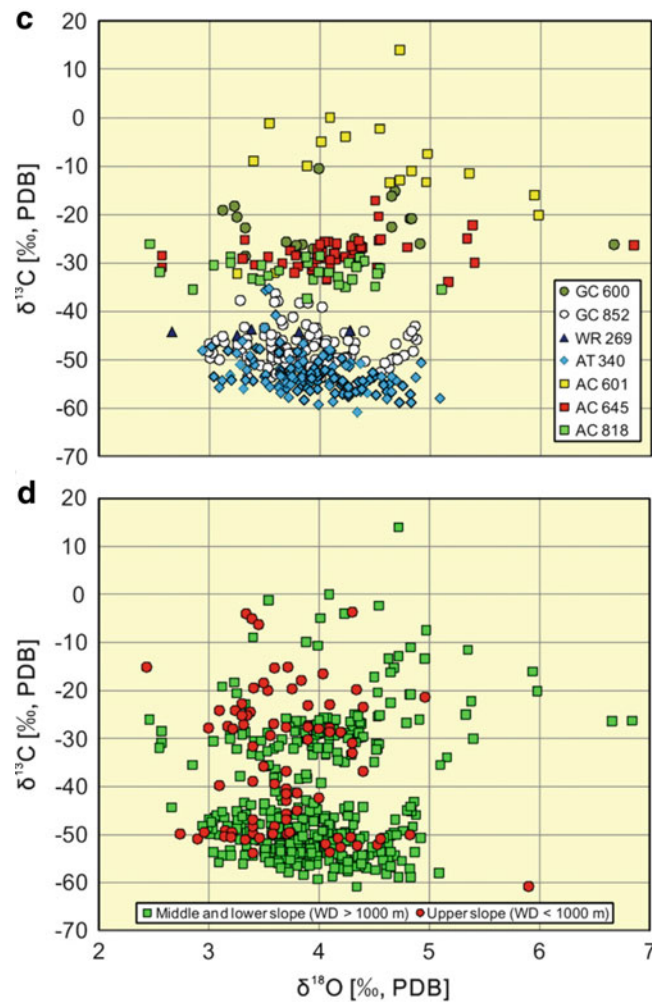


Figure 5.33. (continued)

suspected seep indicators and variations in vegetation health and types. There are various limitations to these methods and ground-truth is essential to confirm correlations with seepage. While there are many prospect-specific examples, few surveys are in the open literature that would allow assessment of the regional occurrence of land petroleum seeps in the Gulf of Mexico region.

The distribution of oil and gas production and potential source rocks suggest that numerous onshore petroleum seeps are to be expected and many individual seeps have been reported in the Gulf of Mexico region (Figures 5.35 and 5.36). These maps also suggest that geographically, oil and gas seepage on land is most likely in the north-central and northwestern Gulf coast. These trends continue southward into the onshore areas of northern Mexico and the southwestern offshore Gulf of Mexico. Sedimentation in the Gulf of Mexico basin is known to have been asymmetrical over its geological history with major rivers mainly located in the north (one exception is the Rio Grande River). Northern Gulf of Mexico source-rock horizons pinch-out toward the center of the basin. However, onshore from the southwestern Gulf of Mexico

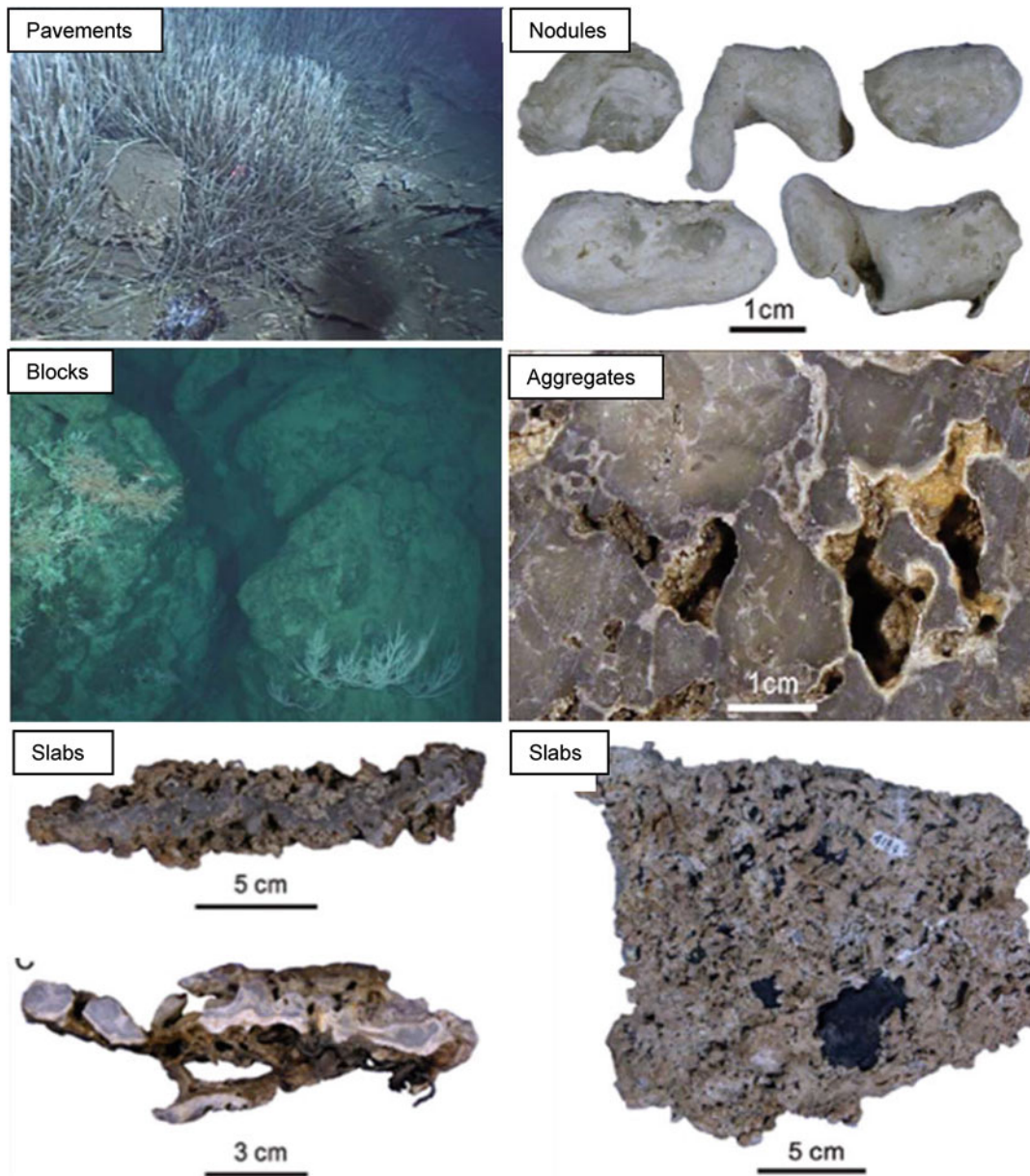


Figure 5.34. The range of morphologies of carbonate rocks collected at seep sites on the continental slope of the northern Gulf of Mexico (Feng et al. 2010; republished by permission of the Gulf Coast Association of Geological Societies, whose permission is required for further publication use).

and along the Campeche peninsula, major oil and gas discoveries have been made, salt basins occur, and petroleum seeps have been reported (Figures 5.21, 5.22, and 5.23).

5.7 MARINE ENVIRONMENTS

In marine environments, petroleum seeps interact with the surrounding environment creating a range of associated phenomena (Kennicutt et al. 1987, 1988a). These phenomena can, but do not always, include bubble streams, acoustic plumes, hydrocarbon concentration

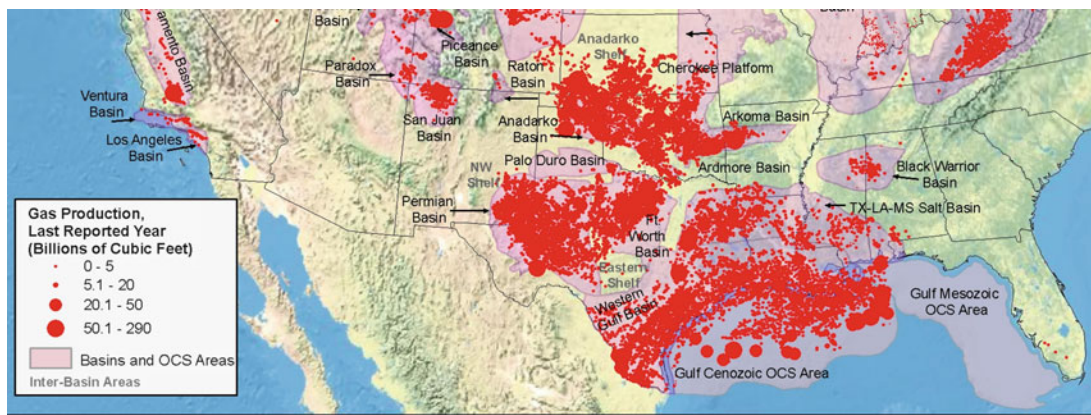


Figure 5.35. Map of Gulf coast onshore and offshore natural gas production in 2009 (Energy Information Administration, 2009 http://www.eia.gov/oil_gas/rpd/conventional_gas.jpg).

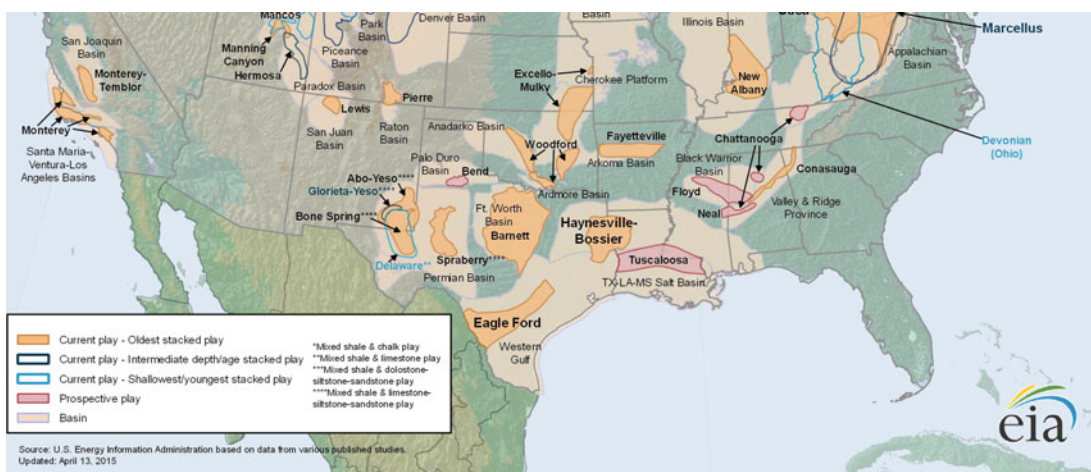


Figure 5.36. Map of potential onshore subsurface shale gas and oil sources (Energy Information Administration, 2015; http://www.eia.gov/oil_gas/rpd/shale_gas.jpg).

anomalies, encircling features (visual, chemical, mineralogical, biological), topographical features, hydrocarbon-derived authigenic minerals, bacterial mats, sea-surface slicks, and methane anomalies in the overlying atmosphere (Figure 5.37) (Foucher et al. 2009; Hovland et al. 2012). The processes manifested at seep sites are controlled by the type and rate of gas and fluid expulsion (Foucher et al. 2009). The presence of overlying seawater, and its dissolved inorganic constituents (i.e., sulfate), has distinct and important effects on the behavior and fate of petroleum seeps in marine environments (see Sections 5.5.3 and 5.5.4).

5.7.1 Sea-Surface Slicks and Water Column Plumes

In the 1960s and 1970s, several authors reported bubbles of gas rising to the surface in the Gulf of Mexico and the first water column concentrations were measured (Bernard et al. 1976; Brooks et al. 1974, 1979; Frank et al. 1970; Geyer 1980; Geyer and Giammona 1980; Swinnerton and Linnenbom 1967). At this time, others reported that bubbles rising from gas seeps could be detected by standard sonar equipment (Figure 5.38) (Pickwell 1967; McCartney and Bary 1965).

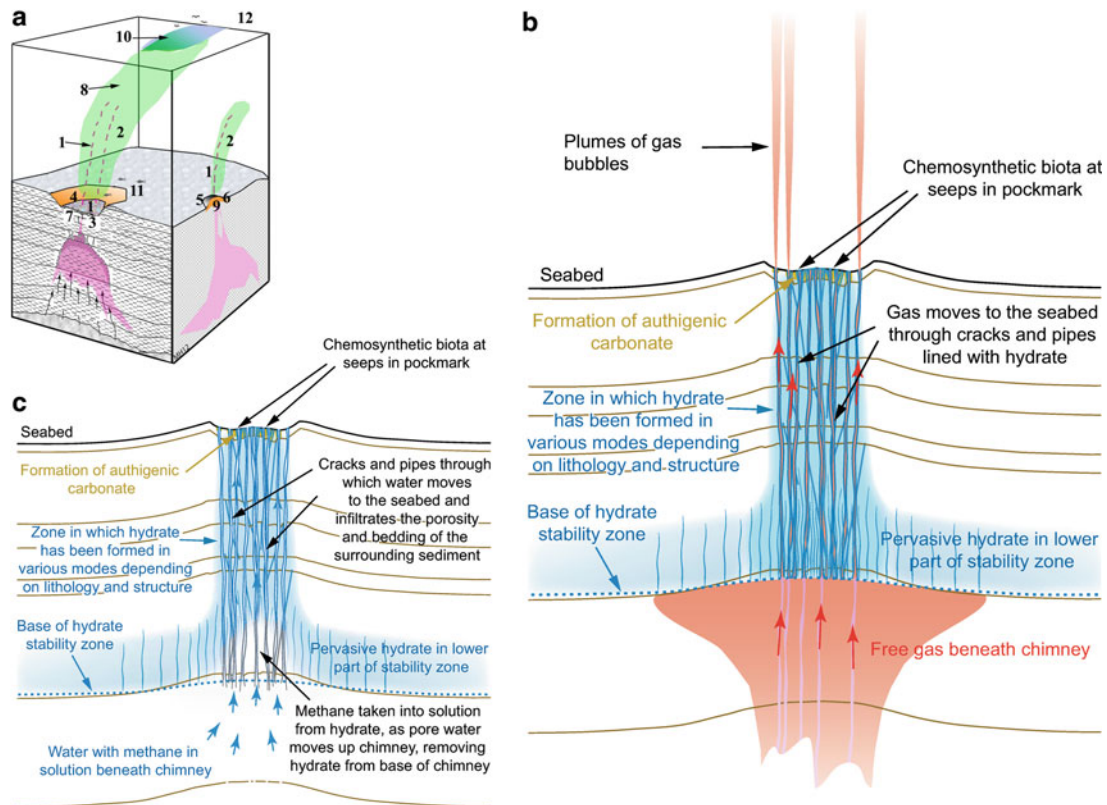


Figure 5.37. Possible processes at an active seep: (a) (1) bubble streams, (2) acoustic plumes, (3) elevated hydrocarbon concentrations, (4) encircling features (visual, chemical, mineralogical, biological), (5) topographic effects, (6) authigenic minerals, (7) bacterial mats, (8) upwelling seawater, (9) entrainment of seawater, (10) sea-surface slicks, (11) attraction of fish and other macrofauna, (12) methane anomalies in atmosphere (not all of these effects occur at all seeps, (reprinted from Hovland et al. 2012 with permission from Elsevier). (b) A pock mark and underlying chimney during active expulsion of free gas and progressive formation of gas hydrate and authigenic carbonates and (c) a pockmark when only methane saturated porewater is migrating through the system and gas hydrate is forming in the underlying sediments (not all of these effects occur at all seeps, Foucher et al. 2009).

Frank et al. (1970) suggested that surveying and mapping of concentrations of hydrocarbons in offshore, near-bottom waters could be used to detect oil and gas seeps. Gas seepage samples were collected at the sea surface by snorkel diving (Bernard et al. 1976). Eleven of the 14 samples collected were mostly methane of microbial origin, but three samples contained significant amounts of ethane and propane of thermogenic origin (Figure 5.39) confirming earlier reports by Brooks et al. (1974). The two gas seeps in this earlier study were 100 % methane, and they were determined to be microbiological in origin based on stable carbon isotopic analysis. These were some of the first studies to use molecular and stable isotopic compositions to differentiate microbial and thermogenic gas seepage in marine environments.

Hydrocarbon gas distributions in seawater have been surveyed by ships that deploy equipment, collectively called *sniffers*, to pump seawater to the surface for analysis. These techniques have found wide use in oil and gas exploration and in the Gulf of Mexico since the 1960s (Dunlap et al. 1960; Lamontagne et al. 1973, 1974; Bernard et al. 1976; Brooks and Sackett 1973; Sackett and Brooks 1973; Sackett 1977). Hydrocarbon sniffers consist of a gas extraction

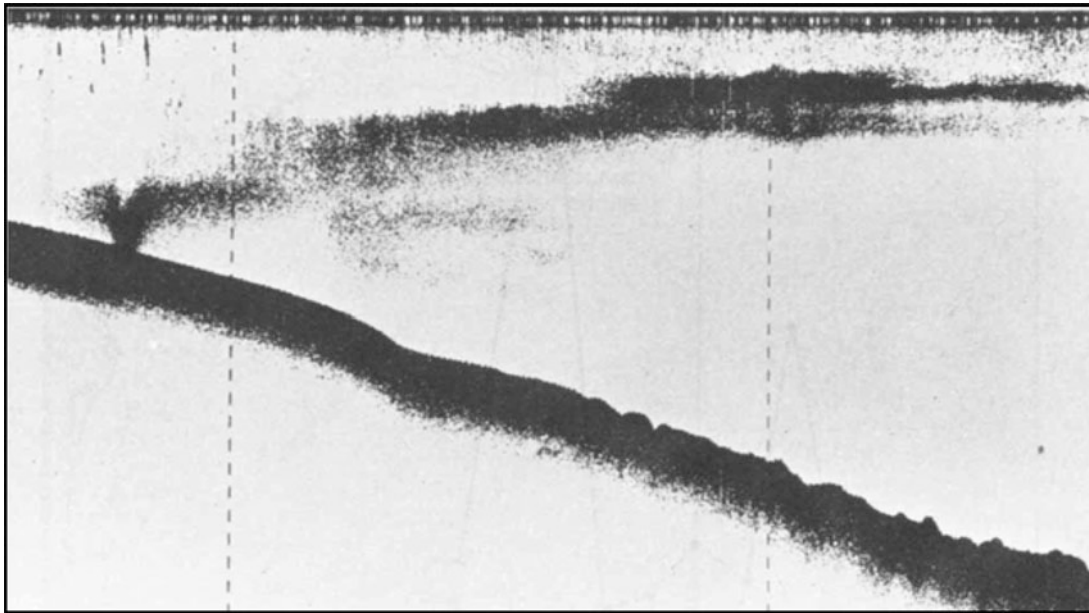


Figure 5.38. Echo sounder evidence of a naturally occurring petroleum seep in the Gulf of Mexico (reprinted from Geyer and Giammona 1980 with permission from Elsevier).

system, adsorbents to concentrate the hydrocarbons, and a gas chromatograph equipped with a flame ionization detector to separate and measure individual hydrocarbon gases. Modern sniffers employ real-time, hydrocarbon detection systems based on various concepts and are deployable on remotely operated and autonomous vehicles. Some sniffers can detect gaseous and liquid hydrocarbons and some have used low-flying airplanes to detect methane in the air overlying the ocean (and land); the use of sniffers in drones has been proposed. Most of the methane detected in the Gulf of Mexico water column is of recent microbiological origin.

When seeping gases and liquids survive transport through the water column, sea-surface slicks are formed above sea-bottom seeps, and on occasion, gas bubbles and oil droplets can be seen bursting at the surface (Figure 5.40) (Sassen et al. 2001a). Removal processes include dissolution in seawater and microbial oxidation. Liquids can become adsorbed on and commingled with particles in the water column (organic and inorganic) and may return to the seafloor (sometimes distant from its origins depending on oceanic currents) once particle density exceeds that of seawater. Gas bubbles rise more rapidly in a water column than do oil droplets, potentially leading to a fractionation of the seeping petroleum (Figure 5.41). Seepage water column plumes are readily detected by sea-bottom acoustic profilers, especially when gases are at concentrations high enough to form bubbles (Figure 5.38). Gaseous bubbles often entrain liquid petroleum creating sea-surface slicks. Most oil slicks form when oil droplets reach the surface and sometimes form pancakes and coalesce. Plumes have been sampled in situ with standard oceanographic water samplers.

Observations of sea-surface slicks were significantly expanded with the advent of remote-sensing (satellite) techniques (Figures 5.42 and 5.43) (MacDonald et al. 1993, 1996; MacDonald (1998); De Beukelaer 2003, De Beukelaer et al. 2003; NASA 2000). Various techniques, such as Landsat Thematic Mapper and Synthetic Aperture Radar, have been used to image hydrocarbon slicks on the sea surface. Hydrocarbons on the sea surface dampen ripples and reduce the reflectivity of water, so that slicks appear as dark patterns on the sea surface in satellite images. Remote-sensing techniques are efficient and repeatable and can cover large areas of the sea

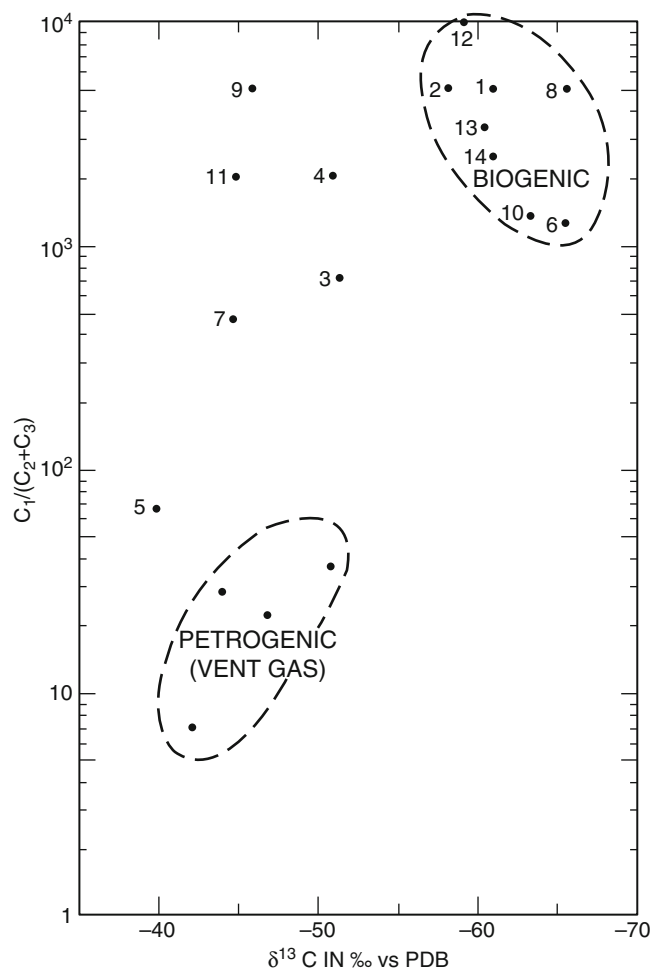


Figure 5.39. Molecular and stable carbon isotopic compositions of microbial and thermogenic seep hydrocarbon gases in the Gulf of Mexico water column (reprinted from Bernard et al. 1976 with permission from Elsevier). (C_1 —methane, C_2 —ethane, C_3 —propane, PDB—Pee Dee Belemnite).

surface. The use of several independent detection techniques and multiple images over time increases confidence in differentiating surface petroleum slicks from other phenomena that create ephemeral organic oil films that form slicks, such as phytoplankton blooms.

5.7.2 Seafloor Sediments

The first reports of retrieval of oil-stained seafloor sediments in the Gulf of Mexico began appearing in the literature in the 1980s. Anderson et al. (1983) noted high concentrations of biodegraded oil, carbonate deposits, and organic sulfur in north-central Gulf of Mexico continental slope sediments recovered by coring. Chemical and stable carbon isotopic compositions indicated that the observed high concentrations of methane to pentane must have been produced thermally at depth beneath the seafloor and had reached the surface through faults and fractures associated with salt diapirs. The authors also noted anomalous seismic reflections that suggested the presence of gas hydrate. Since this first report, the seafloor of the Gulf of

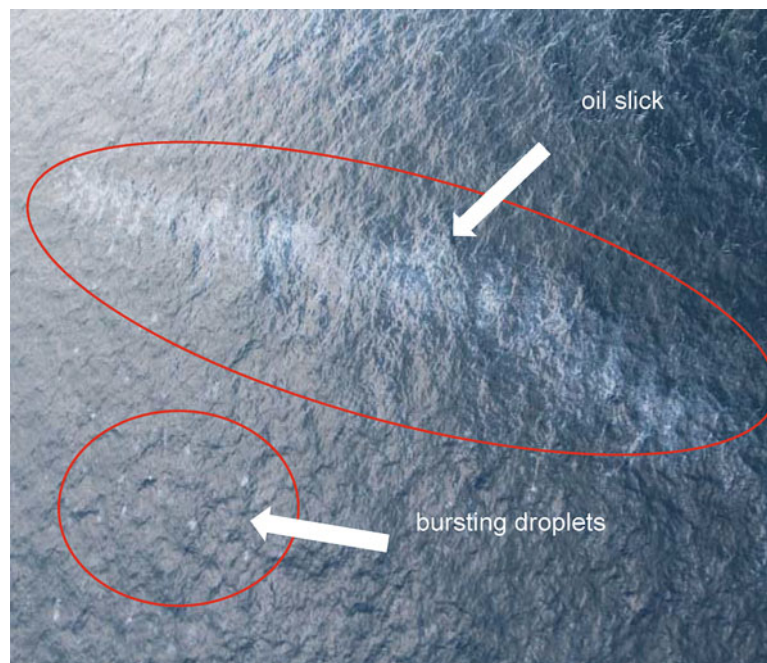


Figure 5.40. Aerial photograph of an oil slick surrounded by a field of individual droplets bursting at the surface to form “pancakes” in the deepwater region of the Gulf of Mexico (no attribution of photo).

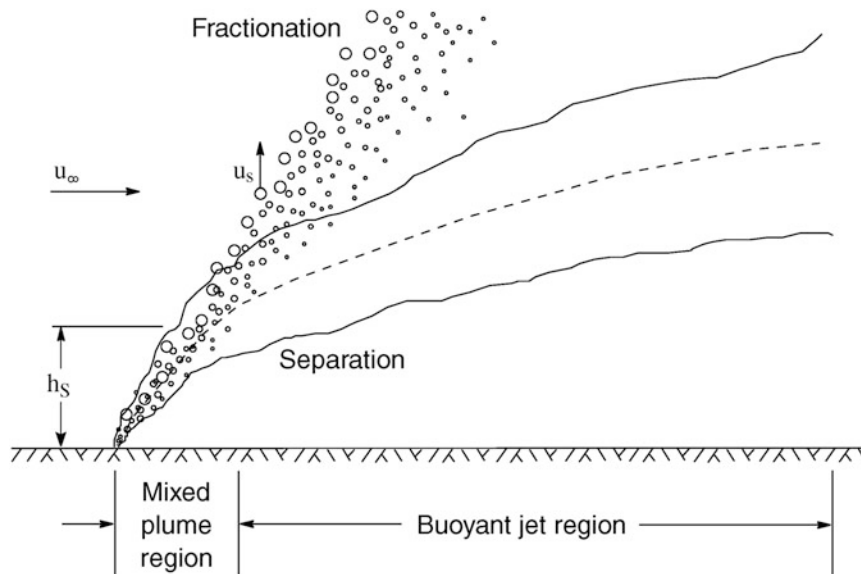


Figure 5.41. A bubble plume in a cross-flowing current. Gas bubbles separate from oil droplets as both rise through the water column (reprinted from Socolofsky and Adams 2002, © International Association for Hydro-Environment Engineering and Research with permission of Taylor & Francis Ltd, www.tandfonline.com, on behalf of International Association for Hydro-Environment Engineering and Research). [h_s —separation height, U_∞ —cross flow velocity, U_s —slip velocity].

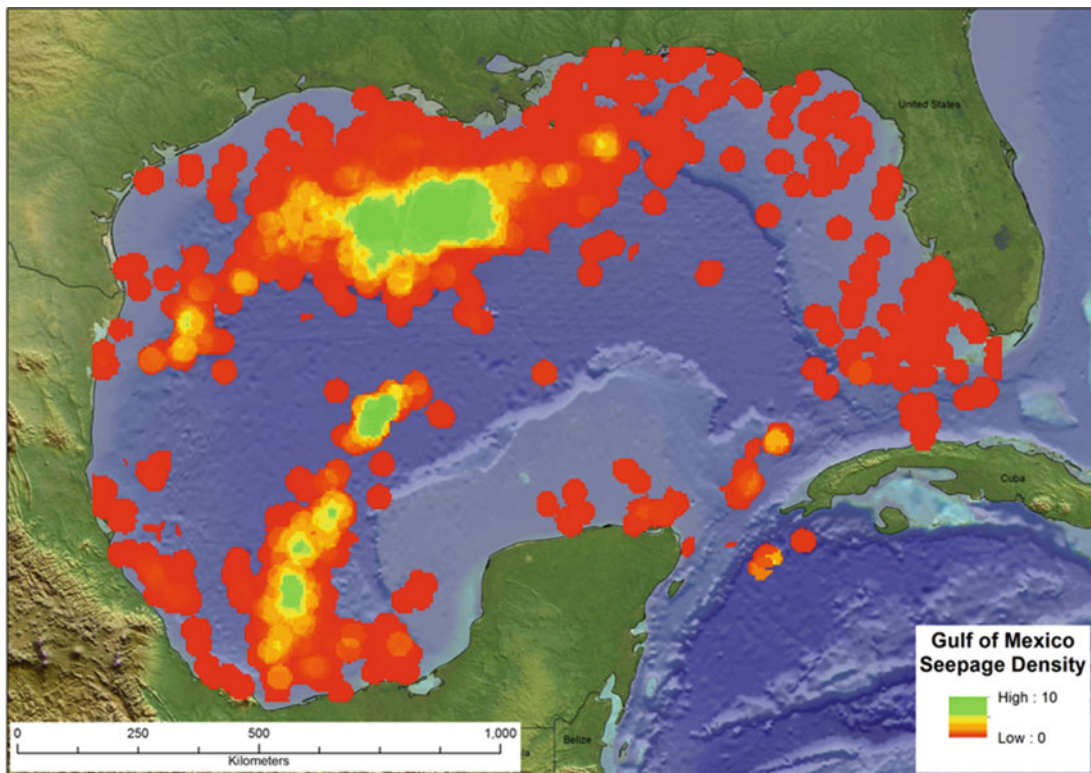


Figure 5.42. Oil and gas seepage in the Gulf of Mexico (determined from analysis of synthetic aperture radar, graphic provided by CGG’s NPA Satellite Mapping, used with permission).

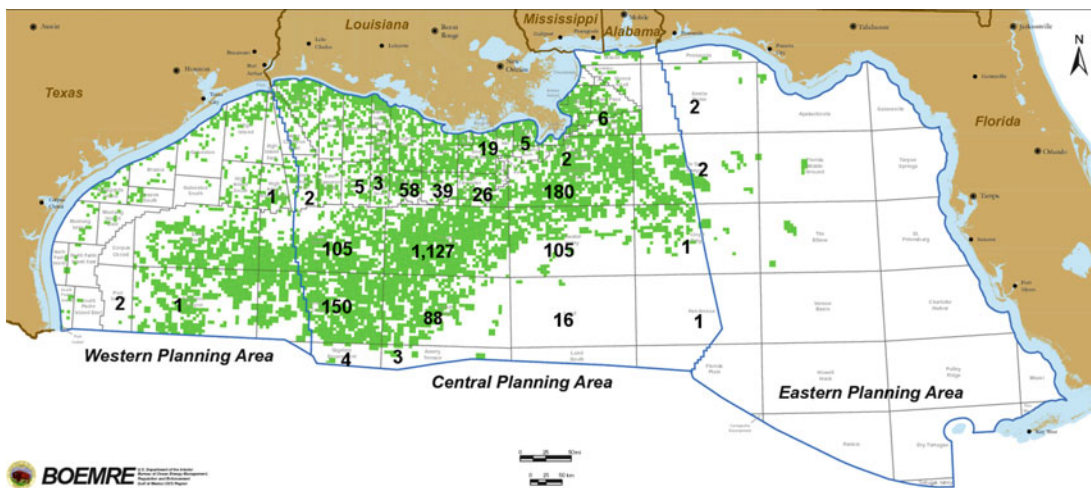


Figure 5.43. Number of persistent sea-surface slicks in lease block areas from 1991 to 2009. Green squares were active leases in 2011 (base map BOMERE <http://img.docstoccdn.com/thumb/orig/79768556.png>); sea slick data (determined from analysis of synthetic aperture radar, graphic provided by CGG’s NPA Satellite Mapping, used with permission).

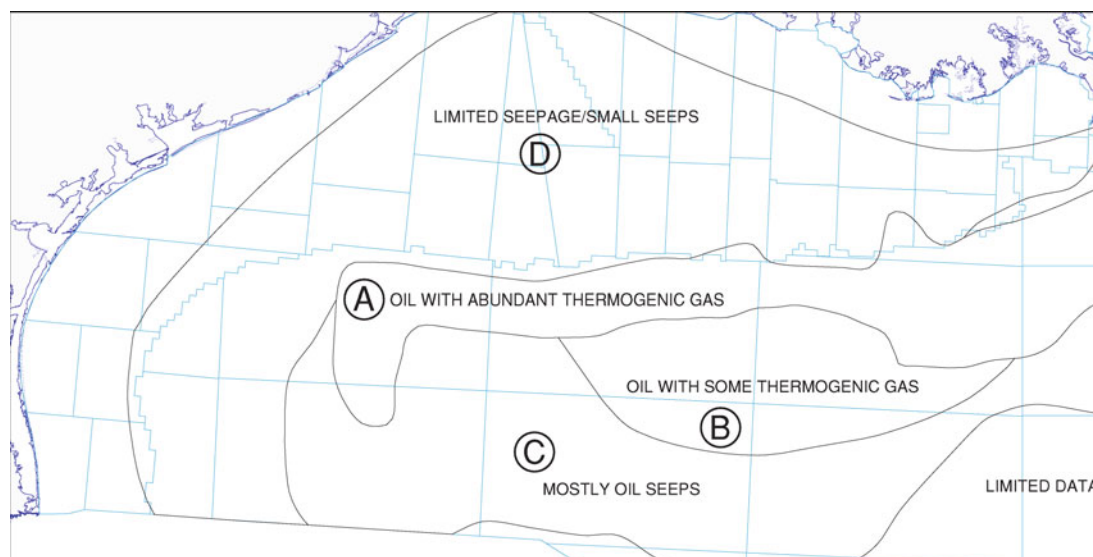


Figure 5.44. Gulf of Mexico seep distributions map based on 5,200 sea-bottom drop cores and sea-surface slicks identified by remote sensing: (a) abundant macroseeps of oil and thermogenic gas, (b) abundant macroseeps of oil with less thermogenic gas, (c) abundant macroseeps of limited thermogenic gas, and (d) limited microseepage (Hood et al. 2002; AAPG ©2002, reprinted by permission of the AAPG whose permission is required for further use).

Mexico has been extensively sampled by various coring devices from ships, remotely operated vehicles, and manned submersibles.

Hood et al. (2002) used data from 3,000 sea-bottom cores to extend hydrocarbon-system maps and predictions of hydrocarbon type and properties beyond data based on subsurface cores. Regions of the northwestern Gulf of Mexico were categorized based on the distribution, type, and intensity of oil and gas seeps (Figure 5.44). In areas (A), (B), and (C) nearly 75 % of sea-bottom samples contained moderate or substantial quantities of oil compared with about 12 % in area (D) (Figure 5.44). In area (A) more than 25 % of the seafloor samples that contained oil had substantial associated thermogenic gas compared to less than 5 % in area (C) (Hood et al. 2002). Seismic records confirmed the associations (migration paths) between source rocks, shallower reservoir rocks, subsurface salt tectonics and faults, near-surface sedimentary wipe-out zones (gas-charged sediments or chimneys), pathways to the seabed, and seabed morphologies such as mounds and mud volcanoes (Figures 5.45 and 5.46) (Hood et al. 2002). Fisher et al. (2007) confirmed the locations of macroseepage in the Gulf of Mexico by mapping seabed cores with unambiguous indications of oil and gas in the upper 5 m (16.4 ft) of sediment, including a few locations in the southern Gulf of Mexico (Figure 5.47).

On a regional basis, a comparison of maps of northern Gulf of Mexico sea-surface slicks (Figures 5.42 and 5.43), seafloor seeps (Figures 5.44 and 5.47), active oil and gas platforms (an indirect indication of deep oil and gas reservoirs) (Figures 5.48 and 5.49), and maximum historical oil and gas production rates (Figures 5.50 and 5.51) illustrates the coincidence of petroleum seeps and deeply buried oil and gas source rocks and accumulations. Of particular note is the geographical coincidence of abundant oil and gas seepage areas (Figures 5.44 and 5.47) and the locations of deepwater oil and gas wells.

Petroleum seepage into seafloor sediments is manifested in a variety of characteristic mineral assemblages and morphologies (Figure 5.37) (Hovland et al. 2012; Boetius and Wenzhofer 2013 and others). Mineralogical changes are closely coupled with microbiological activity

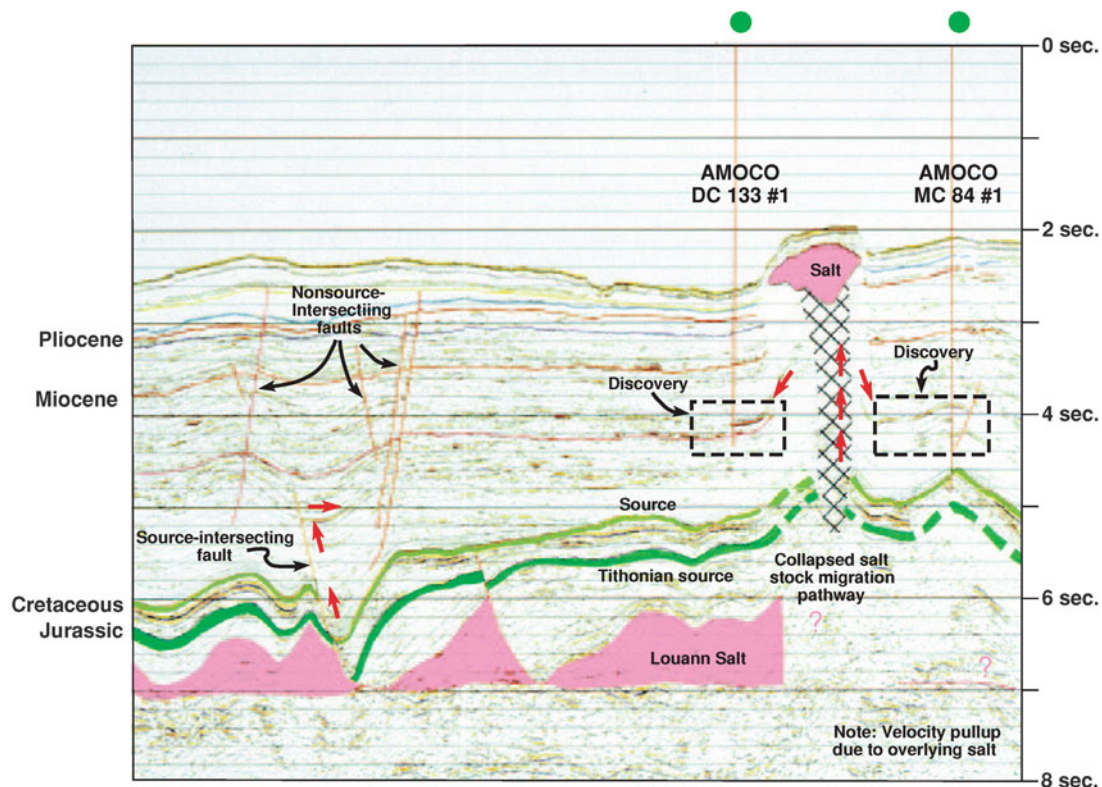


Figure 5.45. Example of a seismic line showing the source intervals and several potential hydrocarbon migration pathways (Hood et al. 2002; AAPG ©2002, reprinted by permission of the AAPG whose permission is required for further use).

that produces excess carbon dioxide and bicarbonate ion favoring the formation of calcium carbonate and other authigenic minerals (see Sections 5.3.3 and 5.3.4). Mud volcanoes are large seabed structures (diameters of 1–10 kilometers [km]; 0.6–6.2 miles [mi]) formed by gas, pore fluid, and mud eruptions with a centrally pointed, flat, or crater-like top (Figure 5.52) (Prior et al. 1989; Milkov et al. 2003). Smaller depressions can form in the seafloor due to gas eruptions (10–1,000 m; 32.8–3,280.8 ft) called *pockmarks* (Figures 5.53 and 5.54) (Foucher et al. 2009). Structures below the seafloor can extend kilometers acting as migration pathways for seepage and are called *gas chimneys* (Foucher et al. 2009). Gas hydrate can form mounds as it expands and accumulates (Fisher et al. 2007; Boetius and Suess 2004). High-energy releases of petroleum can result in the formation of emulsions that mix water and sediments with seeping fluids. This often results in seepage being retained in sea-bottom sediments due to the increased density of the mixture; therefore, not all seafloor seeps result in sea-surface slicks.

High seafloor reflectivity or amplitude responses and acoustic wipe-out zones are caused by the influx of gases and liquids to the seabed, seafloor lithification, physical disruption of internal sediment layering, and gas-hydrate formation and decomposition (Roberts and Aharon 1994, Roberts et al. 1990, 1992, 2007, 2010; Gay et al. 2011). Since 1998, the Bureau of Ocean Energy Management (BOEM) has mapped over 31,000 seafloor acoustic amplitude anomalies in the deepwater northern Gulf of Mexico using 3D time-migrated seismic surveys (Figure 5.55) (Shedd et al. 2012).

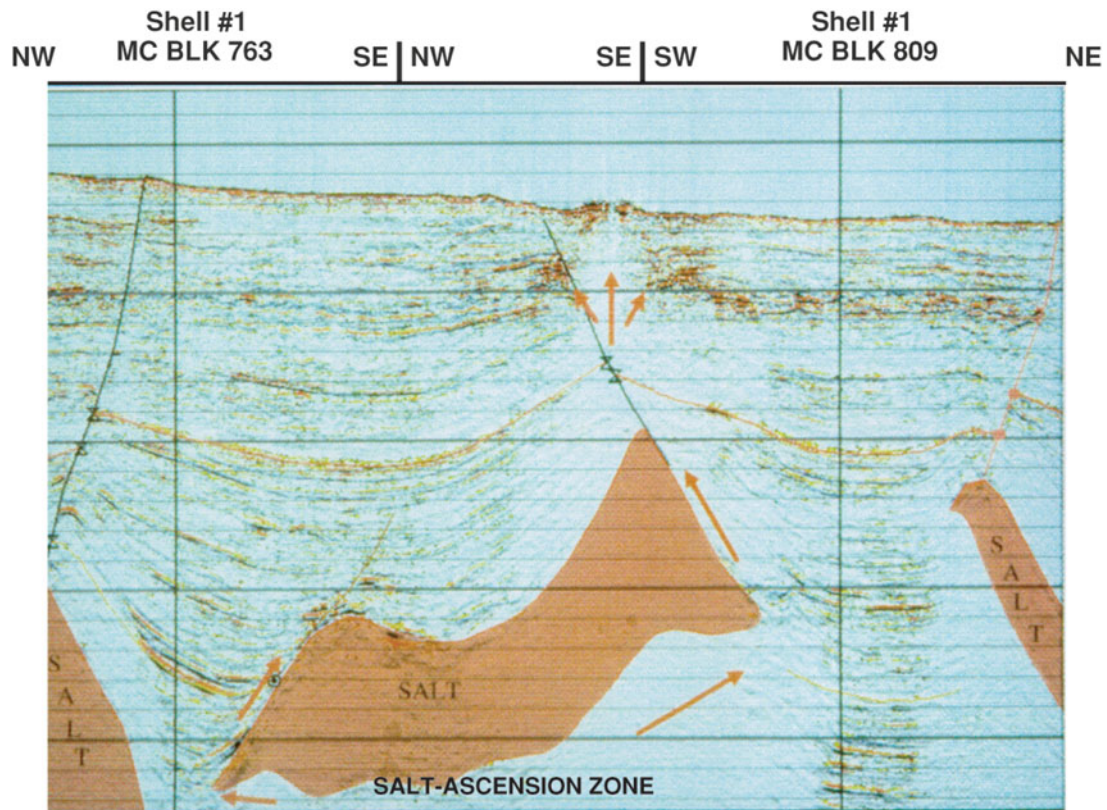


Figure 5.46. A seismic line showing a cross-strata migration pathway to a discovery in the north-central Gulf of Mexico. Hydrocarbon migration occurs up the collapsed salt stock along the salt-sediment interface into smaller faults that reach the seafloor (Hood et al. 2002; AAPG ©2002, reprinted by permission of the AAPG whose permission is required for further use).

5.7.3 Gas Hydrate

Gas hydrates are the largest accumulations of natural gas on Earth and are known to form in outer continental margin sediments and permafrost (Figures 5.56, 5.57 and 5.58) (Collett et al. 2009; Pinero et al. 2013). In the 1930s, gas hydrates were suspected of causing blockages in pipelines but remained unknown in nature until the 1980s when deep-sea drilling recovered cores containing intact gas hydrate from the outer continental shelf/slope, hundreds of meters below the seafloor (Collett et al. 2009). Pinero et al. (2013) noted that gas hydrates “. . . have been recovered in more than 40 regions worldwide and their presence has been deduced from geophysical, geochemical, and geological evidences at more than 100 continental margin sites.” In recent years, near-surface gas hydrate has been recognized as a novel source of gas seepage at some locations, including the Gulf of Mexico.

Most low-molecular-weight gases, including methane, form hydrates when high interstitial porewater concentrations occur at suitable temperatures and pressures. Gas hydrates are crystalline water-based solids that resemble ice, in which small nonpolar molecules (typically gas compounds), or polar molecules with large hydrophobic moieties, are trapped inside “cages” of hydrogen-bonded water molecules (Figure 5.59) (Collett et al. 2009; Boswell et al. 2012). Without the support of the trapped molecules, the lattice structure collapses into ice crystals or liquid water. Gas-hydrate decomposition is a phase change, not a chemical

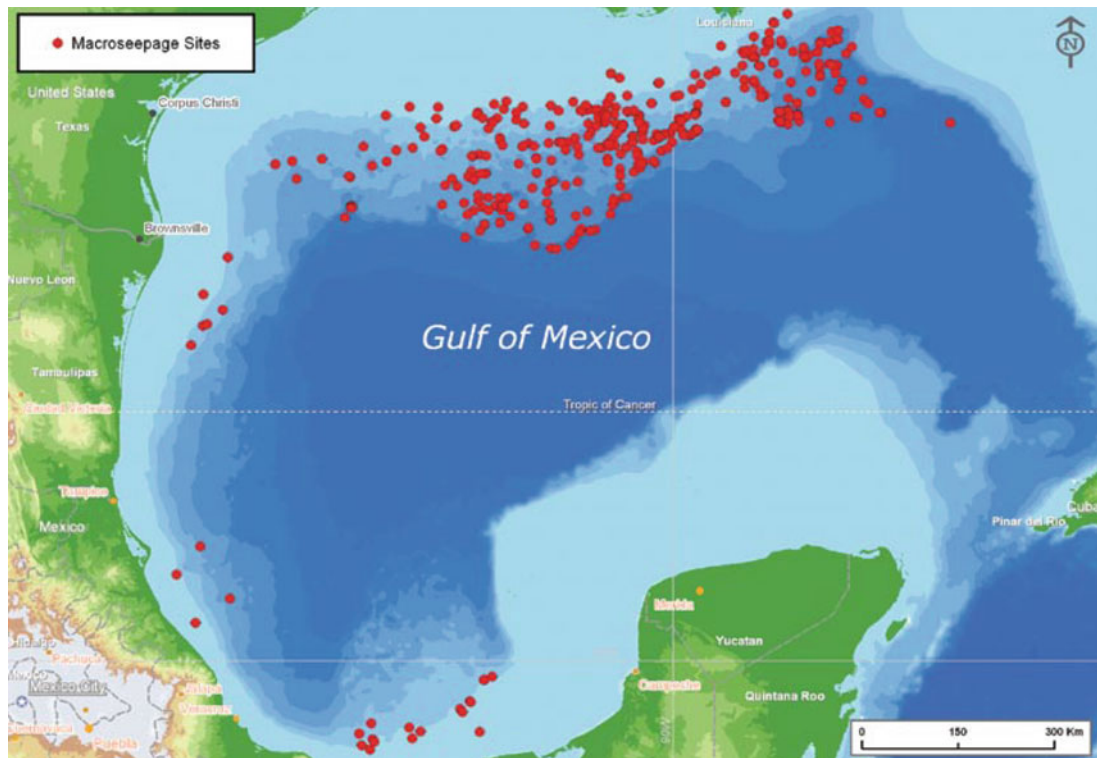


Figure 5.47. Gulf of Mexico locations (*red dots*) of piston cores that have significant levels of oil (greater than 300,000 total Scanning Fluorescence maximum intensity units) or methane (greater than 100,000 parts per million [ppm]) in the top 5 m of sediment (Fisher et al. 2007; Courtesy of TDI-Brooks International).

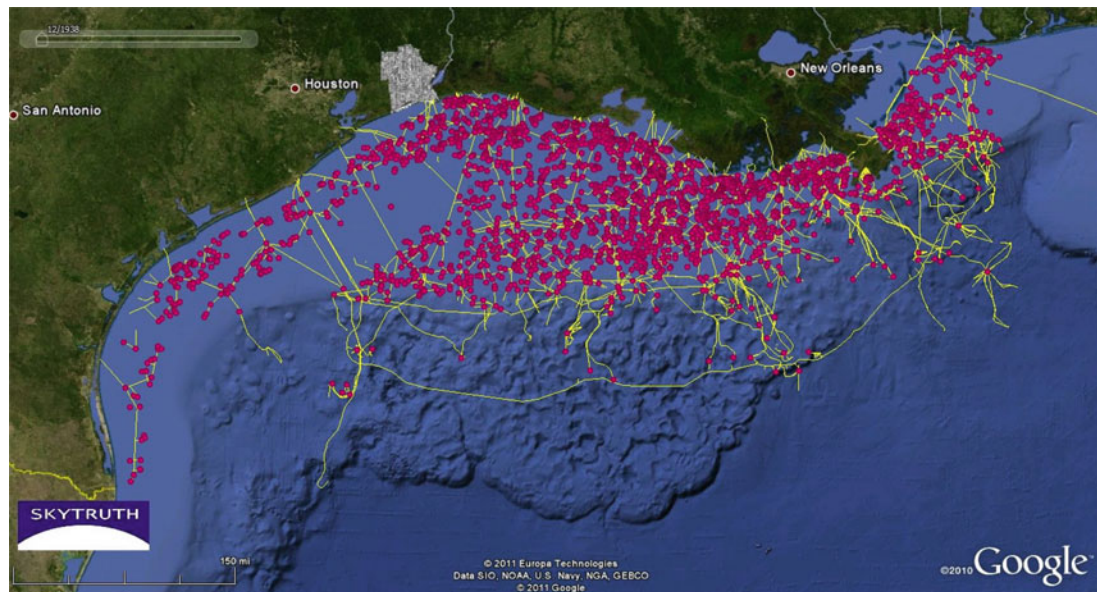


Figure 5.48. Map of active oil and gas platforms (*pink dots*) and pipelines (*yellow*) in 2011, map available at <http://blog.skytruth.org/2011/04/gulf-of-mexico-deepwater-development.html>. (For gas production map see Fig. 5.35).

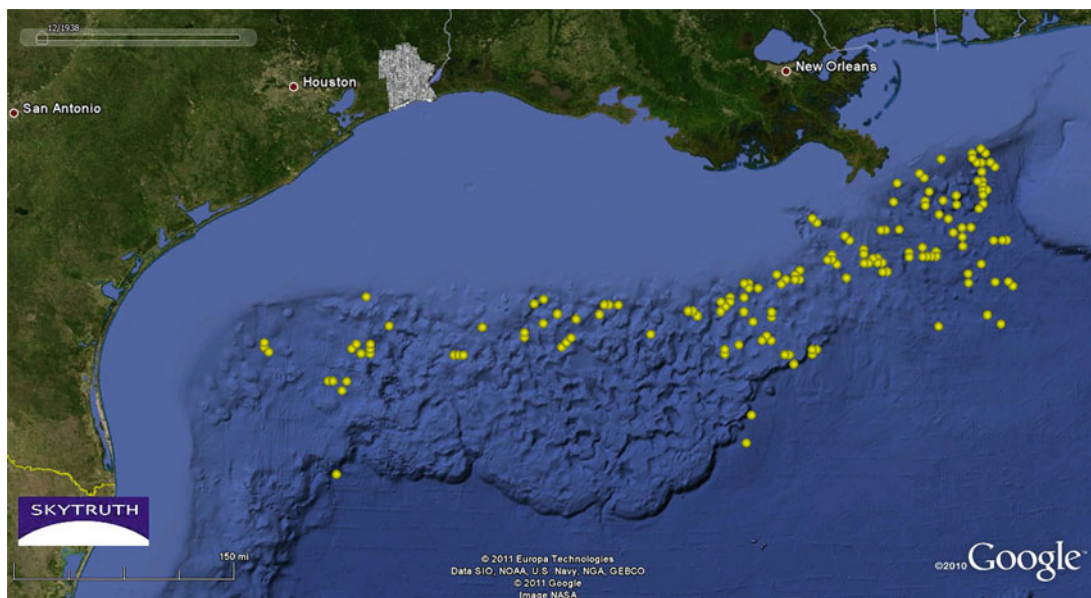


Figure 5.49. Deepwater oil and gas wells in 2011 (yellow dots) map available at <http://blog.skytruth.org/2011/04/gulf-of-mexico-deepwater-development.html>.

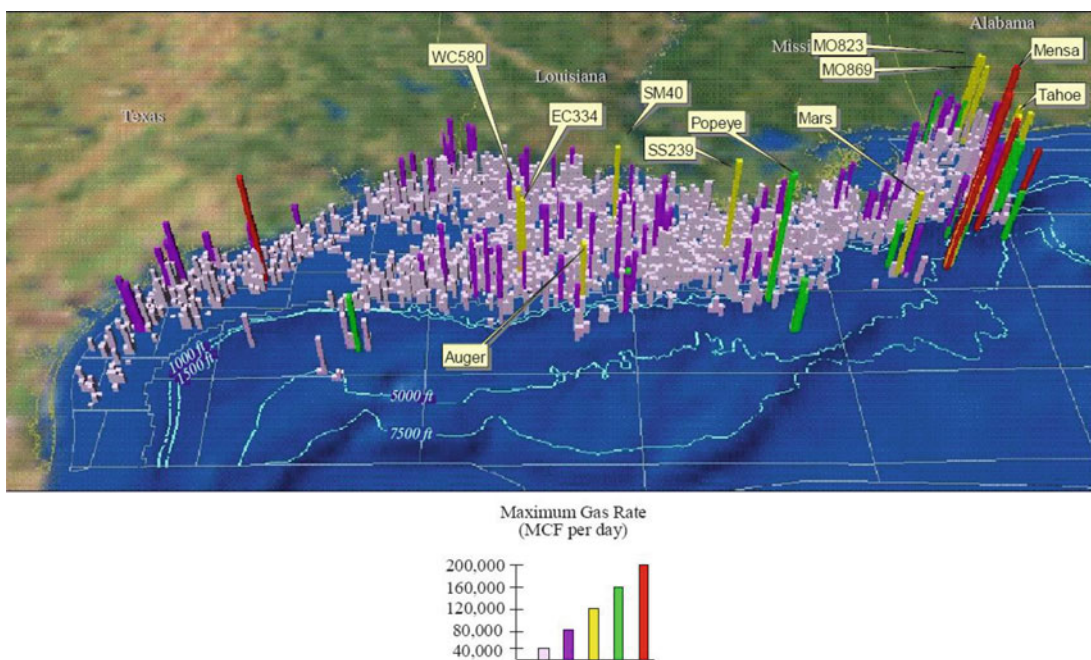


Figure 5.50. Maximum historical gas production rates for Gulf of Mexico wells (U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, 2002; map available at http://www.geographic.org/deepwater_gulf_of_mexico/production_rates.html).

reaction. Recently, the concept of a gas-hydrate petroleum system has been proposed with similar requirements as conventional petroleum systems including (1) gas-hydrate pressure-temperature stability conditions, (2) a source of gas, (3) available water, (4) pathways for gas

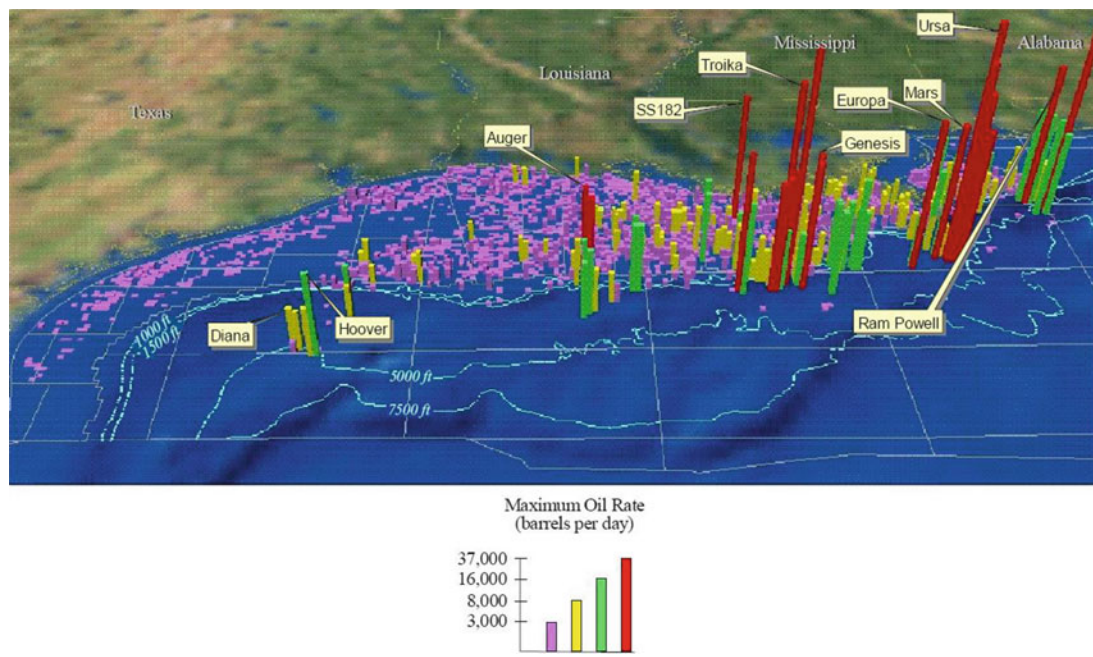


Figure 5.51. Maximum historical oil production rates for Gulf of Mexico wells (U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, 2002; map available at http://www.geographic.org/deepwater_gulf_of_mexico/production_rates.html).

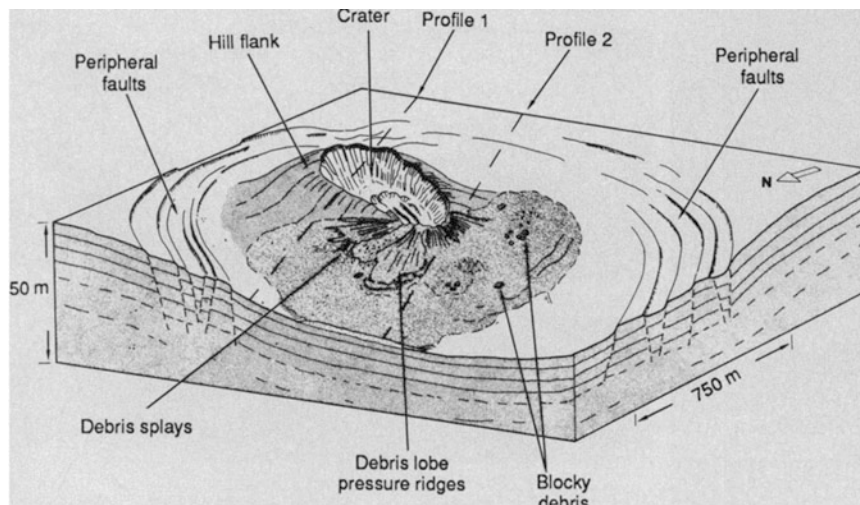


Figure 5.52. Block diagram of a seabed crater in the north-central Gulf of Mexico (Prior et al. 1989; reprinted with permission from the American Association for the Advancement of Science).

migration, (5) a suitable host sediment or reservoir, and (6) the requisite timing among system elements (Collett et al. 2009). A global inventory of methane in gas hydrates has recently been estimated based on theoretical considerations (Figure 5.57) (Pinero et al. 2013).

Until the 1980s, gas-hydrate deposits were believed to occur deep in the subsurface as inferred from seismic records based on bottom simulating reflectors, indicating a phase change

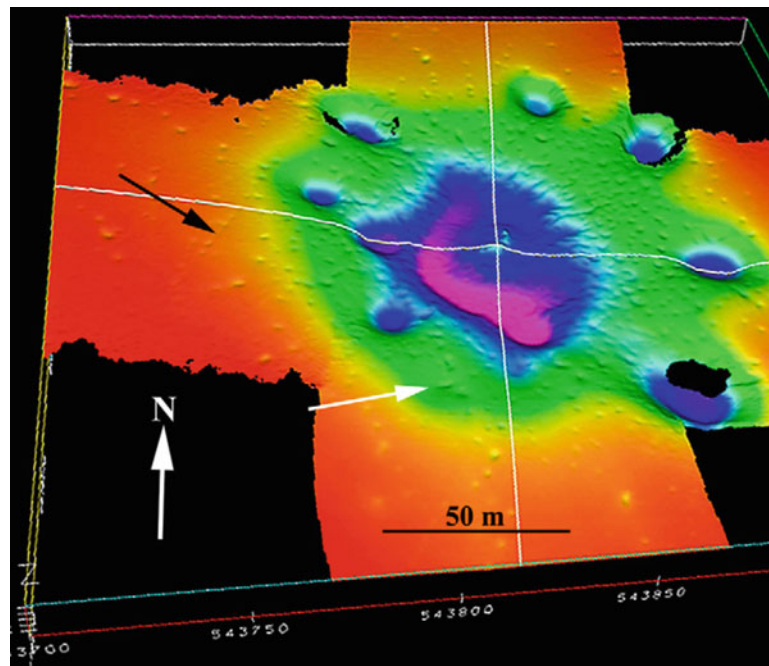


Figure 5.53. Perspective view of a shaded relief digital terrain model from one of a series of pockmarks on the Norwegian seafloor (Hovland et al. 2010; reprinted with permission from Elsevier).

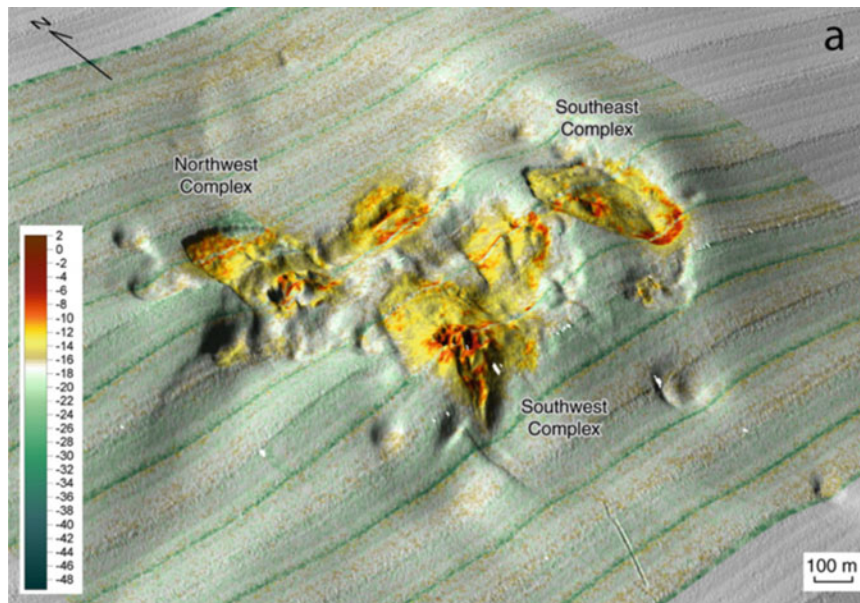


Figure 5.54. Sea-bottom morphological features at a mound in north-central deepwater region of the Gulf of Mexico (bathymetry overlain by acoustic backscatter data) with a scale showing elevation (Macelloni et al. 2010; republished by permission of the Gulf Coast Association of Geological Societies, whose permission is required for further publication use).

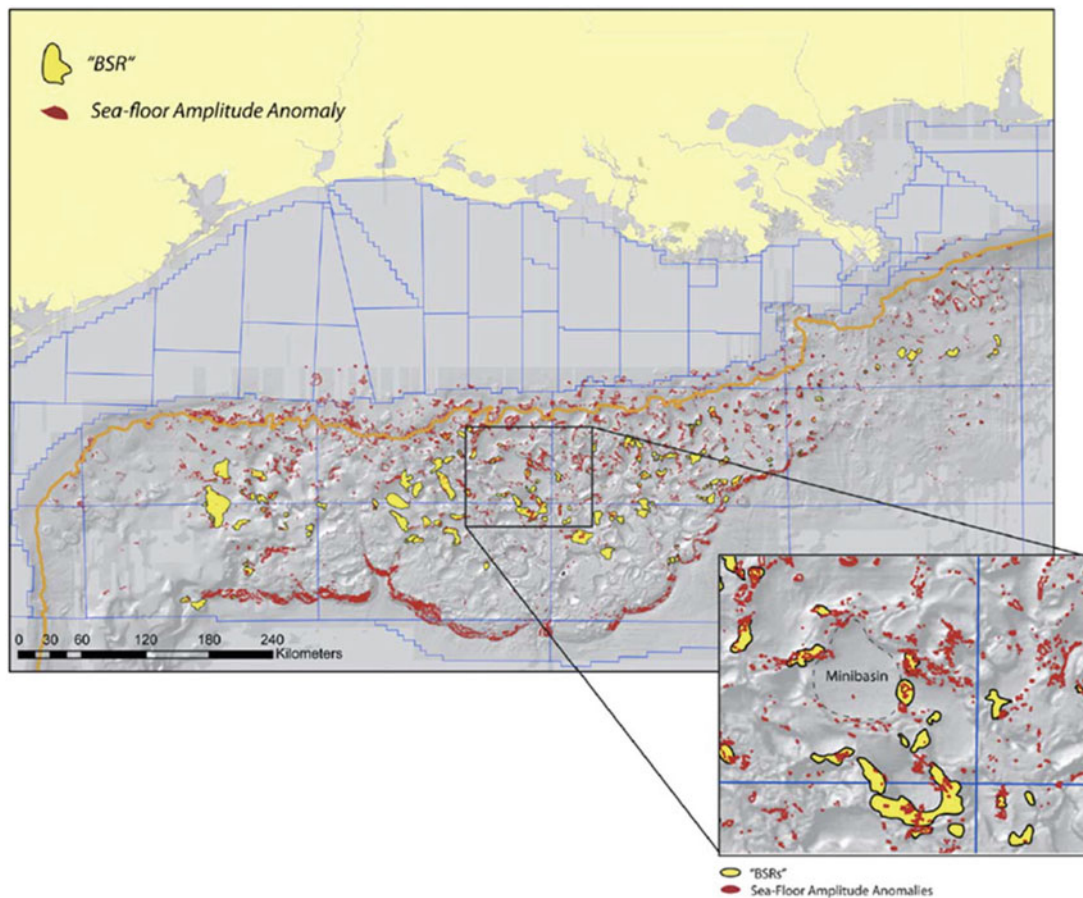


Figure 5.55. Map showing seafloor bathymetry (gray), seafloor seismic amplitude anomalies (red), and mapped bottom simulating reflectors (BSRs) (yellow) (Shedd et al. 2012, reprinted with permission from Elsevier; BOEM, <http://www.boem.gov/Seismic-Water-Bottom-Anomalies-Map-Gallery/>).

from gas to solid hydrate, which crosses subsurface strata (e.g., simulates the seafloor surface). Analyses also indicated that the gas in deep hydrates was solely methane of recent microbiological origin. This view changed when, for the first time, core samples of surface sediments in the Gulf of Mexico recovered thermogenic gas hydrates (Brooks et al. 1984, 1986, 1994) that contained substantial amounts of thermogenic methane and higher-molecular-weight hydrocarbon gases. Following the Gulf of Mexico discoveries, gas hydrates have been recovered from surface sediments cores in the Cascadia continental margin of North America, the Black Sea, the Caspian Sea, the Sea of Okhotsk, the Sea of Japan, and the North and South Atlantic Ocean (Collett et al. 2009).

Seeping hydrocarbon gases can crystallize as gas hydrate in layers, as nodules, and as exposed mounds and vein fillings in sediments (Figure 5.58) (Sassen et al. 2001a, b). Biogenic gas hydrate is white, while thermogenic gas hydrate can be stained with oil or encrusting bacteria giving the hydrate a yellow to orange color (Figure 5.58). Gas-hydrate-derived seepage is largely restricted to occurrences at shallow depths in sediments or outcroppings on the seafloor. In general, gas hydrates tend to accumulate in near-surface sediments, not decompose (Sassen et al. 2001c, 2004). It has been suggested that warmer bottom water temperatures in the

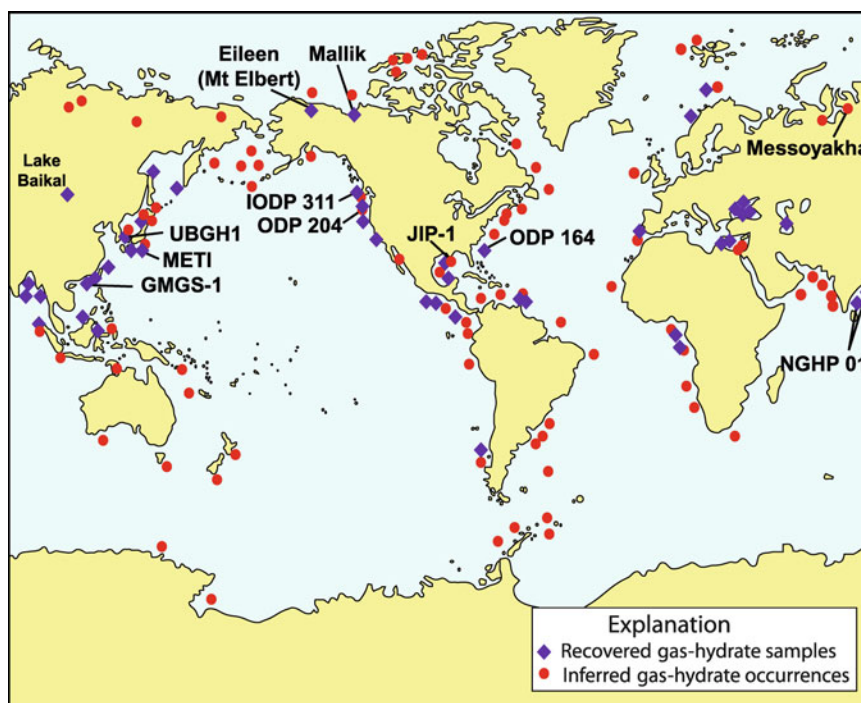


Figure 5.56. Location of sampled and inferred gas-hydrate occurrences in oceanic sediments of outer continental margins and permafrost regions. Most of the recovered gas-hydrate samples have been obtained during deep coring projects or shallow seabed coring operations. Most of the inferred gas-hydrate occurrences are sites at which bottom-simulating reflectors have been observed on available seismic profiles (Collett et al. 2009; AAPG ©2009, reprinted by permission of the AAPG whose permission is required for further use).

ocean can initiate seepage from gas hydrate, which has generated interest in the stability and contribution of gas hydrate to atmospheric greenhouse gases (Sassen et al. 2004). Methane gas hydrate can occur as three different crystalline structures, and all have been observed in nature (Figure 5.59) (Brooks et al. 1984; Sassen and MacDonald 1994; Sassen et al. 2000).

Gas hydrates have been recovered at many sites on the continental slope and abyss in the Gulf of Mexico over the past three decades (Figure 5.60) (Boswell et al. 2012). The first documented physical retrieval of gas hydrate in the shallow subsurface of the Gulf of Mexico was in a Deep-Sea Drilling Project core from the Orca Basin in 1983 when small crystals were determined to be biogenic methane hydrates (DSDP96 in Figure 5.60) (Pflaum et al. 1986). As noted above, in 1984 the first retrieval of near-surface thermogenic gas hydrate in nature was reported in the deepwater region of the Gulf of Mexico (GC 185, Figure 5.60) (Brooks et al. 1984). Thermogenic gas hydrate was recovered from the upper few meters of bottom sediments associated with oil-stained cores in a water depth of 530 m (1,739 ft) close to the limit of gas-hydrate stability. Gas hydrate occurred sporadically associated with sediment seismic wipe-out zones within an area of at least several hundred square kilometers ($100 \text{ km}^2 = 38.6 \text{ mi}^2$). In 1994, the first recovery of structure H gas hydrate in nature was reported in the deepwater region of the Gulf of Mexico (Sassen and MacDonald 1994). In the following years, gas hydrates were shown to be associated with vents, carbonate hard grounds, and shallow fault systems at the margins of salt structures, and hydrate gases were correlated with deeper-reservoired gases (Brooks et al. 1986; Sassen et al. 1999a, b; Milkov and Sassen 2000, 2001; Milkov et al. 2000). In subsequent years, gas hydrate has been recovered many

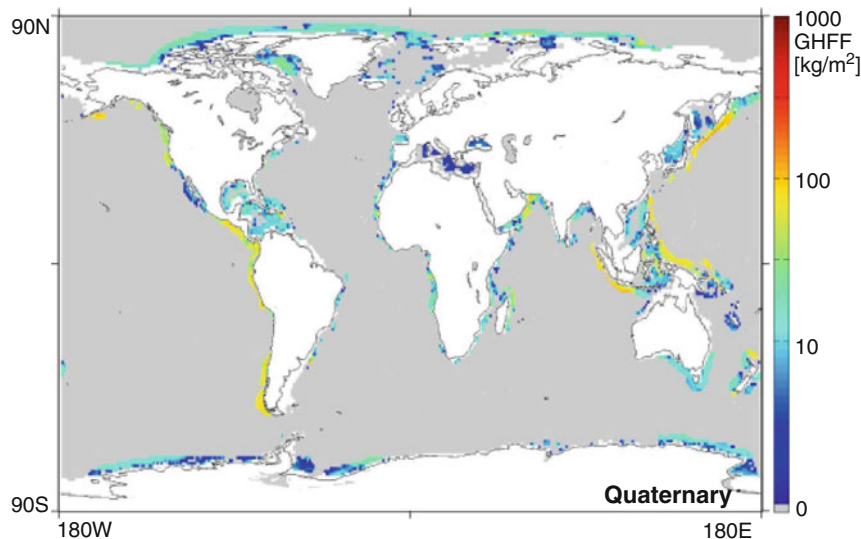


Figure 5.57. Global distribution and estimated quantities of methane gas hydrates based on theoretical steady-state considerations of control parameters (such as sediment organic carbon content, porosity, T/P, heat flow, fluid advection, and others). The “real” gas-hydrate distribution is expected to have a more patchy distribution, and these values are considered minimum estimates (Pinero et al. 2013; Creative Commons Attribution 3.0 License).

times by coring and submersible sampling of the seafloor, and region-wide in-place gas in the form of gas hydrate has been estimated (Figure 5.61) (Frye 2008).

5.7.4 Cold-Seep Communities

In the deep sea, a highly specialized ecology has developed that thrives and depends on petroleum seeps. The discovery of hydrothermal-vent communities in 1977 marked a major change in the understanding of life on Earth and how it might have evolved (Ballard 1977). Until this discovery, it was believed that the primary source of energy available to support life in the oceans was the sun through the process of photosynthesis. Deep-sea hydrothermal-vent communities are supported by alternative sources of energy from reduced chemicals escaping at the deep seafloor. The biological conversion of one or more carbon molecules (usually carbon dioxide or methane) and nutrients into organic matter using the oxidation of inorganic molecules (e.g., hydrogen gas, hydrogen sulfide) or methane as a source of energy is known as *chemosynthesis*. Shortly after these deep-sea discoveries, similar assemblages of organisms were recovered on the continental slope of the north-central Gulf of Mexico at a petroleum seep and at a brine seep at the base of the escarpment off the shore of western Florida (Kennicutt et al. 1985; Paull et al. 1984, 1985; Brooks et al. 1987a, b; Brooks et al. 1989). These unique biological assemblages have become known as cold-seep communities as contrasted to hydrothermal-vent communities.

Since the 1980s cold-seep communities have been discovered worldwide in locations with sufficient inorganic substrates to support life, including the Atlantic Ocean, the Pacific Ocean, the Mediterranean Sea, and recently, Antarctica. The common feature among cold-seep sites is the presence of hydrogen sulfide and methane and an interface with oxygenated water (Figure 5.62). Most sites, outside of the Gulf of Mexico, are associated with microbial methane seeps, gas seeps from gas hydrate, and brine seeps; thermogenic hydrocarbons are mostly absent. Cold-seep communities occur on the ocean’s margins in areas of high primary

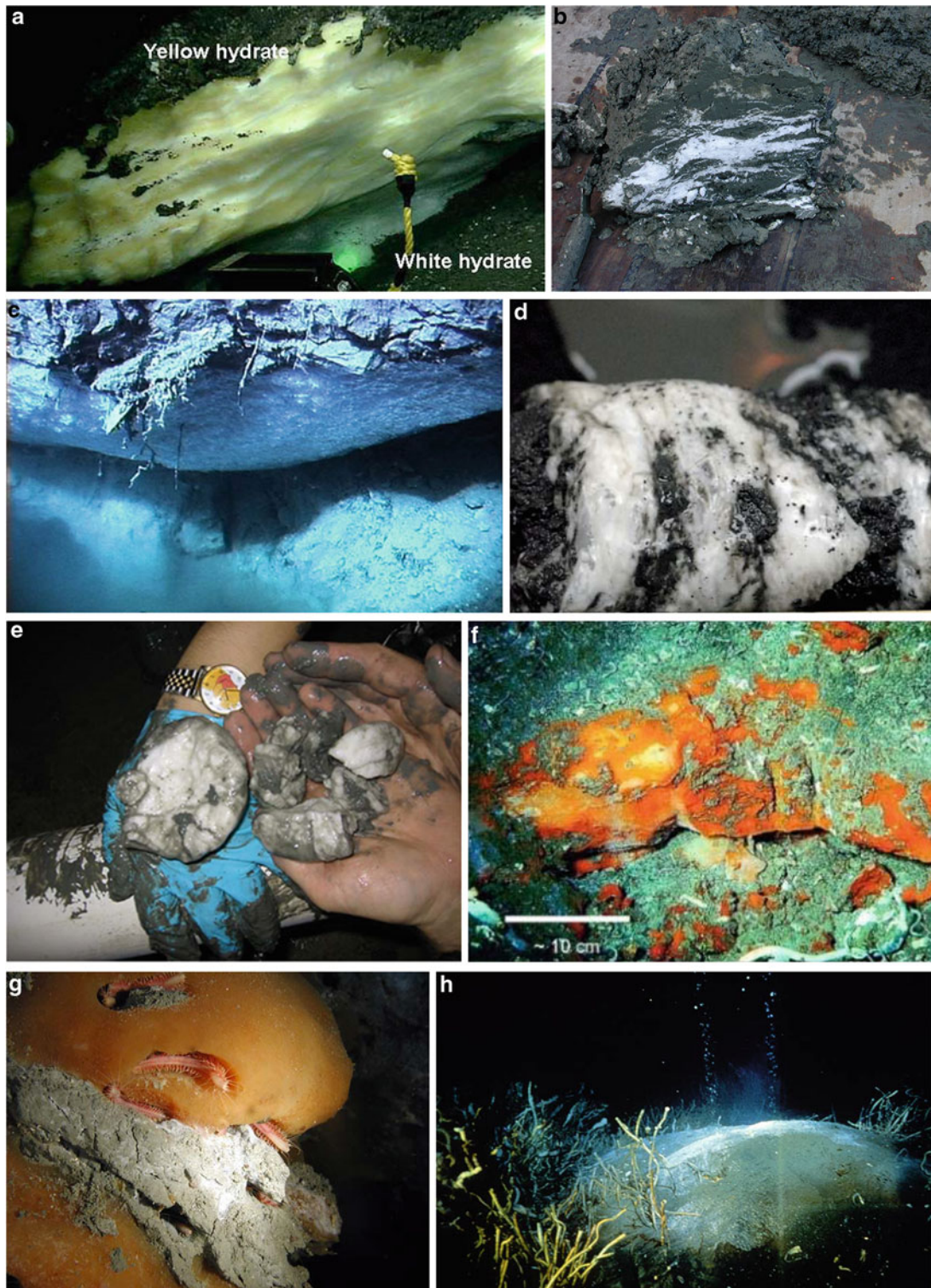


Figure 5.58. Examples of the various forms of gas hydrates in oceanic sediments: (a) Yellow and white hydrates layers (Barkley Canyon off the East Coast of the U.S. photo available at <http://www.nurp.noaa.gov/Spotlight/GasHydrates.htm>); (b) Gas hydrate embedded in the sediment of hydrate ridge, off Oregon, U.S. photo available at http://commons.wikimedia.org/wiki/File:Gashydrat_im_

[Sediment.JPG](#); (c) Gas hydrate beneath a rock overhang (Blake Ridge, East Coast U.S. Image credit NOAA Deep East Exploration 2001) <http://oceanexplorer.noaa.gov/oceanos/explorations/ex1304/background/coldseeps/welcome.html>; (d) Gas hydrates in fractures (Photos: Tim Collett, USGS and 2006–2008 Canada-Japan Mallik Project, <http://www.geoexpro.com/articles/2009/02/gas-hydrates-not-so-unconventional>); (e) Gas hydrate from shallow sediments in the Gulf of Mexico (photograph by B. Winters, USGS). <http://woodshole.er.usgs.gov/project-pages/hydrates/primer.html>; (f) Gas-hydrate outcroppings in the Gulf of Mexico (R. Sassen, pers. comm.); (g) Gas hydrate and *Hesiocaeca methanicola* (Gulf of Mexico, Image courtesy of Deep East 2001, Ian MacDonald, NOAA/OER). <http://oceanexplorer.noaa.gov/explorations/deepeast01/logs/sep23/media/icewormsmed.html>; and (h) Tubeworms surrounding a hydrate mound in the Gulf of Mexico (MacDonald 2002).

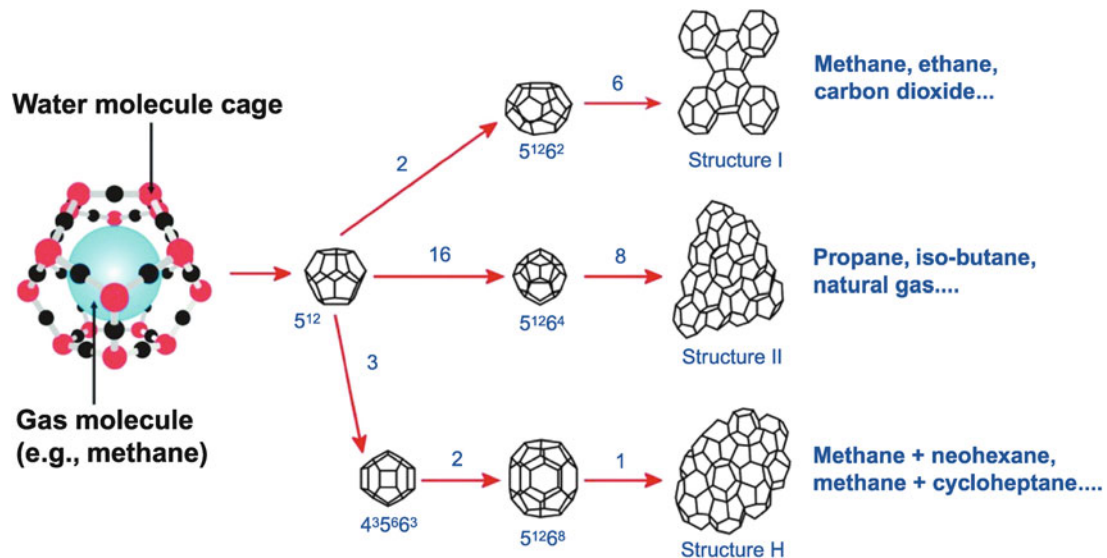


Figure 5.59. Gas-hydrate crystal structures. The three structure types that have been observed as gas hydrates are structures I, II, and H. Guest gas molecules in each hydrate structure are listed (Collett et al. 2009; AAPG © 2009, reprinted by permission of the AAPG whose permission is required for further use). [The five types of water cages that make up the gas-hydrate structures are the pentagonal dodecahedron (512), the tetrakaidecahedron (51262), the hexakaidecahedron (51264), the irregular dodecahedron (435663), and the icosahedrons (51268). Representative guest gas molecules in each hydrate structure are listed].

productivity and tectonic activity where crustal deformation and compaction leads to expulsion of biogenic methane-rich fluids. The primary biota of cold-seep communities are a variety of bacteria and macroinvertebrates, although background deep-sea fauna are often observed (Figure 5.63). Bivalve species with symbionts of the genus *Bathymodiolus* including the families Solemyidae, Lucinidae, Vesicomidae, Thyasiridae, and Mytilidae are commonly present (Callender et al. 1990, Callender and Powell 1992; Oliver et al. 2011). The other megafauna typical of cold-seep communities are tubeworms (Lamellibrachia and pogonophorans).

Since the initial discoveries, extensive surveys and studies have shown that cold-seep communities occur at most, if not all, deep-water macroseeps in the Gulf of Mexico. These sites are the most intensively studied and best understood cold-seep communities in the world (Fisher et al. 2007). By 2007, over 90 cold-seep communities had been discovered from the base of the Florida Escarpment in the east across the northern Gulf of Mexico to offshore southern

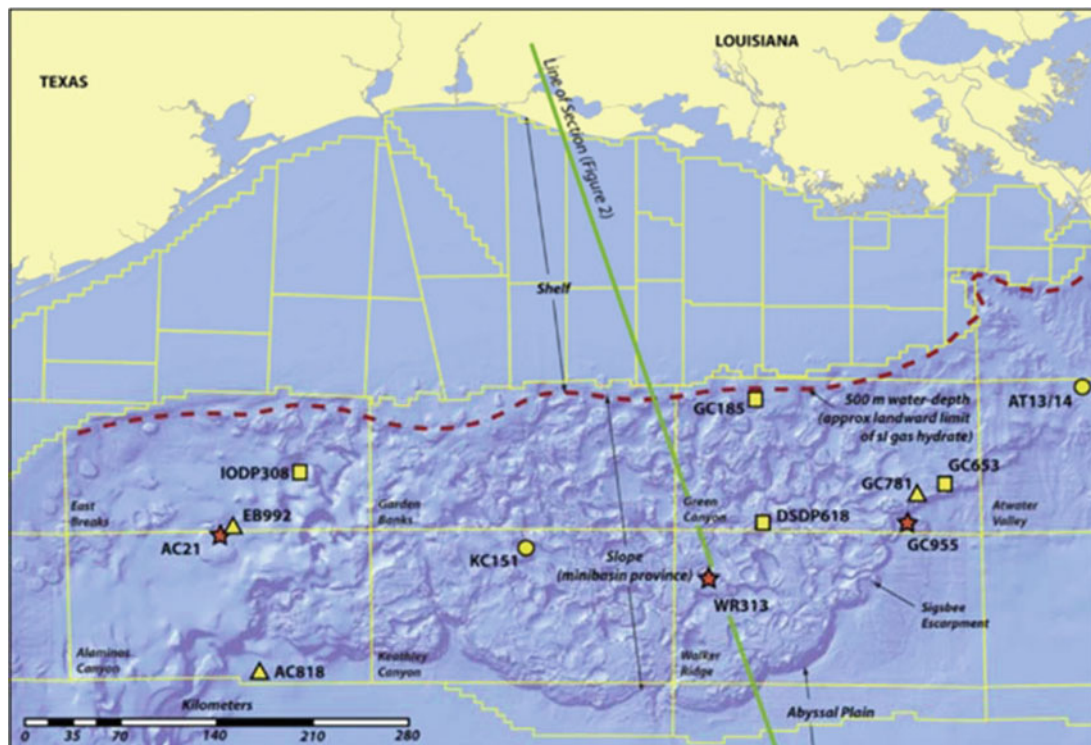


Figure 5.60. Selected sites in the Gulf of Mexico where gas hydrates have been recovered. *Yellow circles* (2005) and *red stars* (2009) denote drilling/coring sites for two joint industry projects. Other known gas-hydrate sites are marked by *yellow squares* and *triangles* (Boswell et al. 2012; reprinted with permission from Elsevier). [DSDP 96 drilled the Orca Basin shown as DSDP Site 618].

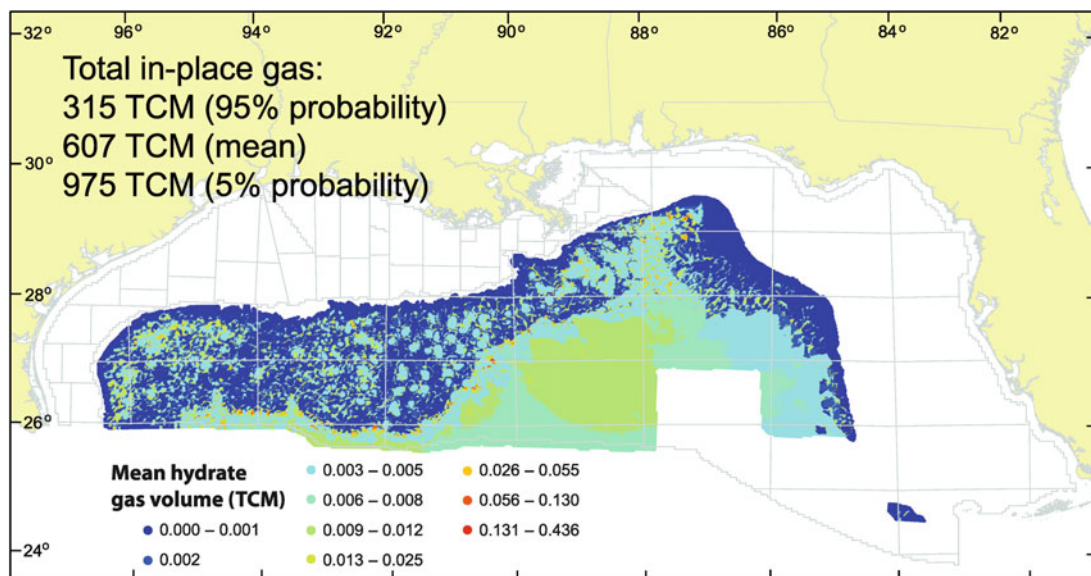


Figure 5.61. An assessment of mean in-place volume of gas (at STP) within hydrates (TCM = trillion cubic meters; $1 \text{ m}^3 = 35.3 \text{ ft}^3$; STP = standard temperature and pressure, 1 atm and $20 \text{ }^\circ\text{C}$ [$69 \text{ }^\circ\text{F}$]; Collett et al. 2009 modified from Frye 2008; AAPG[©]2009, reprinted by permission of the AAPG whose permission is required for further use). The *shoreward boundary* represents the temperature and pressure limits to gas-hydrate stability.

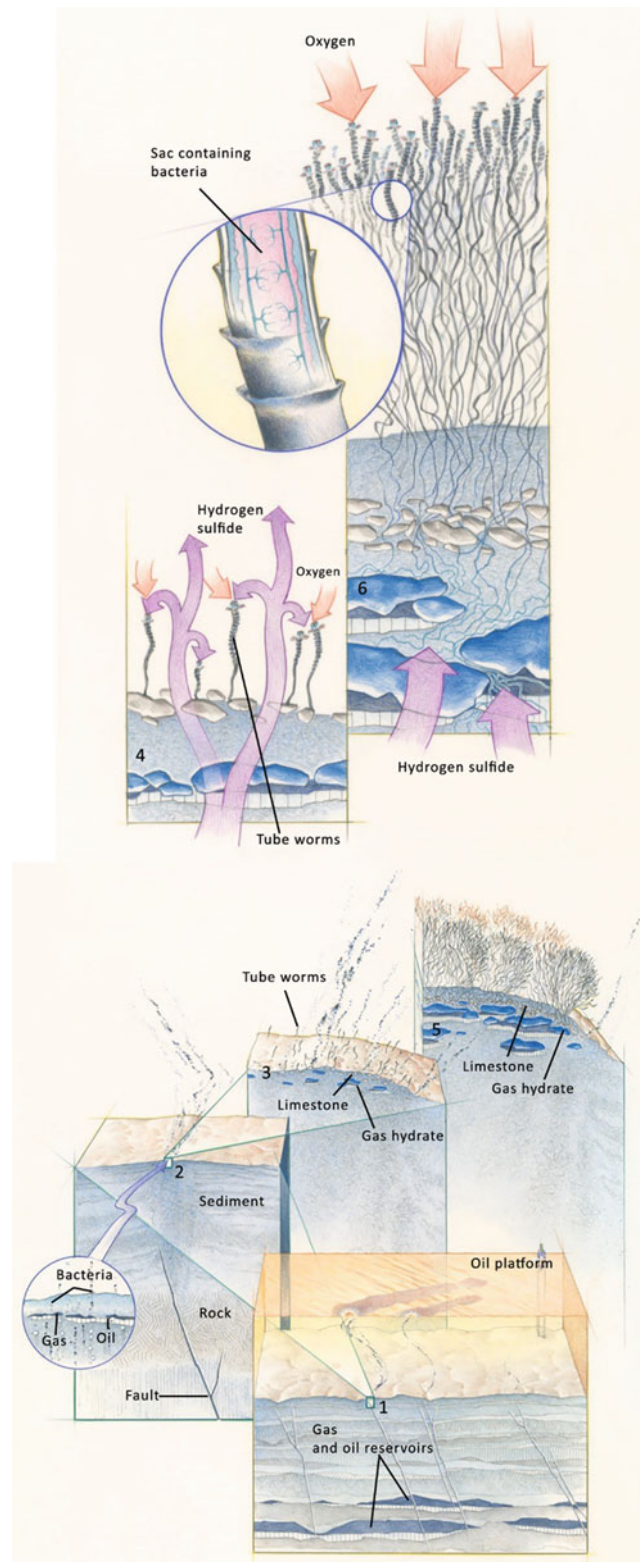
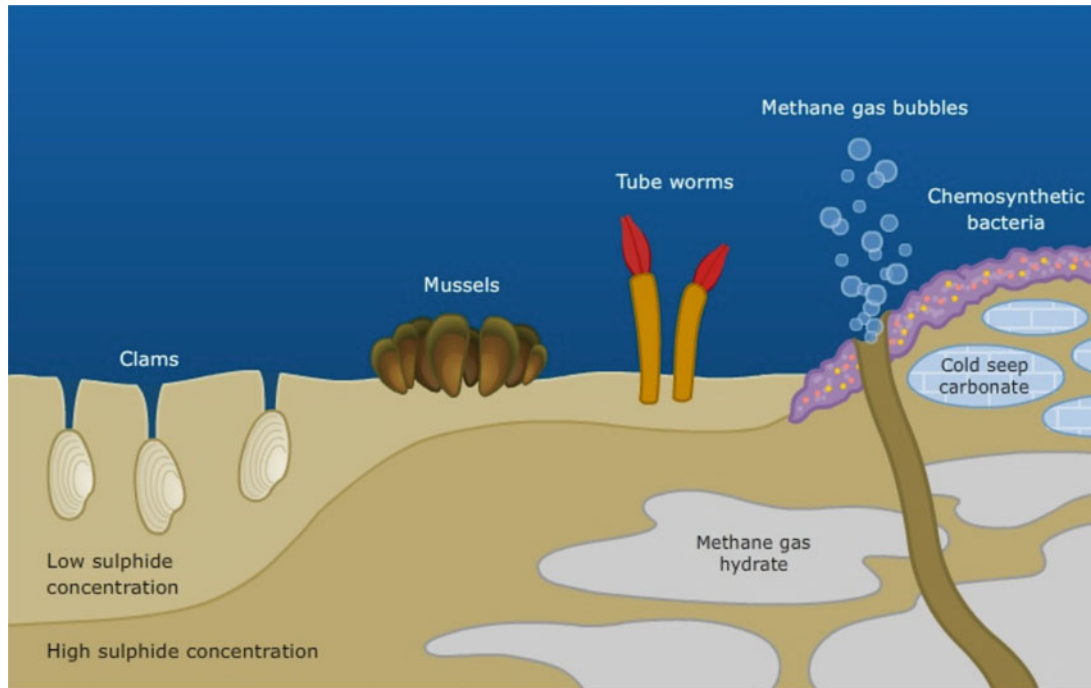


Figure 5.62. Schematic of the progression of the biology/ecology of a typical marine seep location: (1) gas and liquids seep via migration pathways from deep-seated reservoirs to near-surface sediments, (2) bacteria populations are enhanced in the sediments around the seep and may form

bacterial mats that trap oil and gas, (3) bacterial metabolism produces carbon dioxide and hydrogen sulfide which can lead to the formation of carbonate mineral substrates (limestone) that allow tubeworms to colonize the area and the cold temperature and high pressures can create gas hydrate, (4) chemosynthesis-based tubeworms and bivalves flourish in the hydrogen sulfide- and oxygen-rich environment, (5) as the tubeworm colony ages its foundations slowly solidify the sediments blocking the seepage, and (6) eventually the tubeworms acquire most of their nutritional chemicals through extensive root-like systems that extend into the underlying sediments (MacDonald and Fisher 1996; Bruce Morser/National Geographic Creative, used with permission).



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Figure 5.63. A typical biological assemblage associated with cold-seep sites. Image reprinted with permission of the University of Waikato. ©University of Waikato. All Rights Reserved. <https://www.sciencelearn.org.nz/>.

Texas in water depths from 290 to 3,300 m (951–10,827 ft) (Figure 5.64) (Fisher et al. 2007). Other studies extended the biogeographic range of cold-seep communities onto the abyssal plain and into the southern reaches of the Gulf of Mexico (MacDonald et al. 2004).

Surveys and process studies have established that the critical connection between geological and biogeochemical processes that make cold-seep communities viable is the presence of a wide range of microbes (Fisher et al. 2007). Cold-seep communities in the Gulf of Mexico are unique in that the methane that fuels these bacteria is predominantly thermogenic in origin, whereas at other worldwide sites, microbiologic methane is generally more important. Symbionts, microbial mats, and free-living bacteria are ubiquitous, serving as the primary producers of cold-seep food webs (MacAvoy et al. 2005; Fisher et al. 2007). Consortia of bacteria are capable of critical metabolic conversions such as oxidizing methane and reducing sulfate ions, thereby supporting macrofauna communities and producing critical hard substrate via carbonate precipitation (see Sections 5.5.3 and 5.5.4).

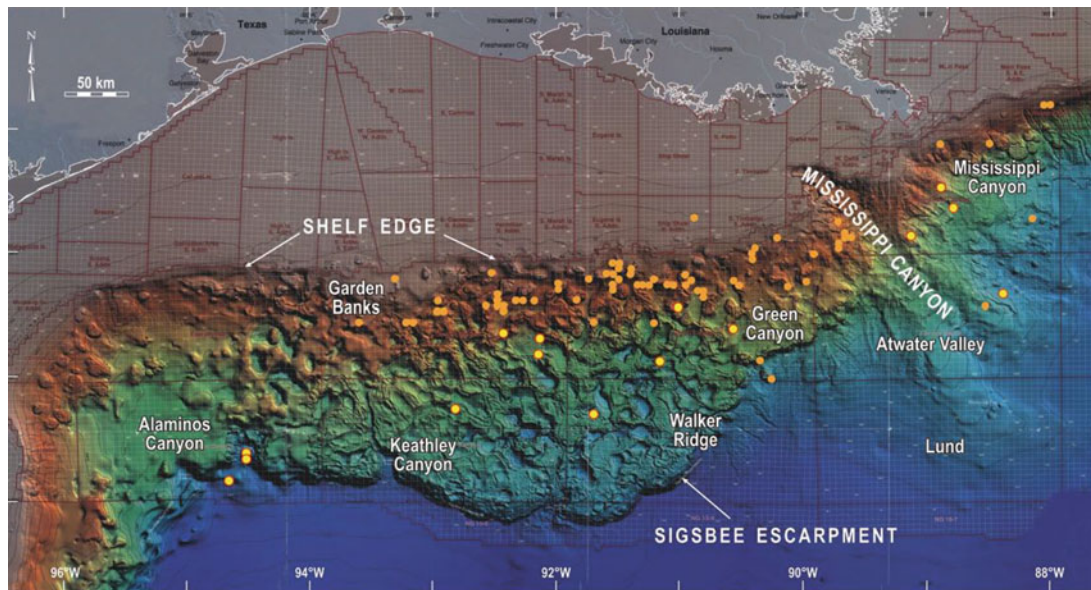


Figure 5.64. Multibeam bathymetric image of the northern Gulf of Mexico showing the location of seep sites where cold-seep communities have been confirmed by remotely operated vehicles or manned submersible dives (Fisher et al. 2007; Figure 1).

Carbonate formation stabilizes sediment and produces the essential substrate necessary for the attachment of various fauna. Sulfide is a required energy source for symbionts in tubeworms and some mussels and for free-living aerobic bacteria (see Sect. 5.5.4) (Joye et al. 2004). The copious and sustained supply of methane and sulfide at seep sites has led to the prevalence of mussels and tubeworms at Gulf of Mexico seeps (Figures 5.65, 5.66, and 5.67) (Kennicutt et al. 1988a, b; Kennicutt and Brooks 1990; MacDonald et al. 1990). Bathymodiolin mussels (*Bathymodiolus childressi*—that contain symbionts that utilize methane) are one of the dominant species, and two species of vestimentiferan tubeworms (*Lamellibrachia lumeyi* and *Seepiophila jonesi*—that contain symbionts that utilize sulfide) are abundant at Gulf of Mexico seep sites (Fisher et al. 2007). Tubeworms have no mouth, gut, or anus and rely on intracellular sulfide absorbing symbionts for the bulk of their nutrition (Nelson and Fisher 1995). Mussel symbionts passively take up methane from the surrounding seawater, whereas tubeworms have specialized blood hemoglobins that bind and actively transport oxygen (from the surrounding water) and sulfide (from sediment porewaters) (Fisher et al. 2007). Individual and aggregations of tubeworms can live for centuries, and the availability of hard substrate can restrict settlement and be growth limiting (Bergquist et al. 2000; Cordes et al. 2007a, b). Tubeworm aggregations begin to senesce and thin out as individuals die, possibly due to carbonate precipitation, resource depletion, and/or old age (Fisher et al. 2007). At some sites, hard and soft corals colonize carbonates; however, direct trophic ties between deep-sea corals and seep primary production have not been demonstrated. Other seep animals such as communities of symbiont containing vesicomyid clams (*Calytogenia ponderosa* and *Vesicomya chordata*) are often present in low densities and were some of the first cold-seep species discovered in the Gulf of Mexico (Kennicutt et al. 1985; Brooks et al. 1987a, b). An unusual community of specialized polychaetes (ice-worms, *Hesiocaeca methanicola*) was found associated with exposed gas hydrate at several sites as well (Figure 5.58g) (Fisher et al. 2000).



Figure 5.65. Typical Gulf of Mexico petroleum seep biological assemblages: (a) mussels, tubeworms, and background fauna closely associated with hard substrate derived from the oxidation of gas and oil (Kennicutt et al. 1988b; Figure 1). (b) Dense clusters of mussels associated with gas seeps (Kennicutt et al. 1988b; Figure 2). (c) Bathymodiolus mussels partly submerged in anoxic brine at the edge of a pockmark. Shells of dead mussel are submerged in the brine at the lower edge of the frame (MacDonald et al. 1990; reprinted with permission from The American Association for the Advancement of Science).

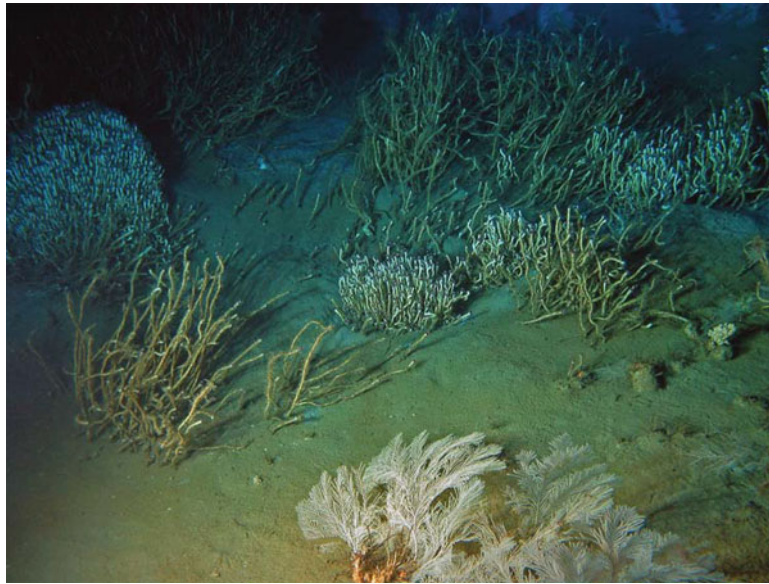


Figure 5.66. Aggregations of the tubeworms *Lamellibrachia luymesii* and *Seepiophila jonesi* (photo courtesy of K. Luley; Cordes et al. 2009, reprinted with permission from Annual Reviews).

Due to the limitations of most manned submersibles to a water depth of 1,000 m (3,281 ft) and difficulties in sampling the deep sea until recently, few seep sites were discovered in water depths greater than 1,000 m (3,281 ft) in the Gulf of Mexico (Brooks et al. 1990; MacDonald et al. 2003, 2004). Previous surveys and the brine-associated community known offshore Florida suggested that cold-seep communities might be present in water depths greater than 1,000 m (3,281 ft). Oil and gas seeps were known to extend to the abyssal plain, and there was no empirical evidence that water depth limited the occurrence of cold-seep communities. In 2006 and 2007, the presence of cold-seep communities was confirmed at 15 sites on the lower Louisiana slope in water depths greater than 1,000 m (3,281 ft), which significantly expanded the geographic range of sites in the Gulf of Mexico (Fisher et al. 2007; Roberts et al. 2010). These sites contained dense communities of tubeworms and mussels, communities of deep-living soft and hard corals, the largest mussel bed known in the Gulf of Mexico, an actively venting mud volcano, asphalt flows, a brine lake, and a variety of new species, including two in the genera *Lamellibrachia* and *Escarpia*. The same species of mussel found at shallower sites, *Bathymodiolus childressi*, was observed in water depths as great as 2,200 m (7,018 ft). Follow-up studies showed that these deeper living populations were genetically isolated from shallower ones (Cordes et al. 2007b). At water depths greater than 1,000 m (3,281 ft), *Bathymodiolus brooksi*, a mussel with both methanotrophic and chemoautotrophic symbionts, was also observed (Fisher et al. 1993), and at sites deeper than 2,200 m (7,018 ft), a third mussel species, *Bathymodiolus heckeri*, with symbionts that utilize reduced sulfur and carbon (methane and perhaps methanol) substrates for energy was the dominant mussel (Roberts et al. 2007, Duperon et al. 2007). At these deeper sites, several other types of biological communities were present including vesicomyid clams in low densities, high-density communities of symbiont containing pogonophoran tubeworms and large aggregations of heart urchins residing in highly reduced sediments (Fisher et al. 2007; Roberts et al. 2010). It is now believed that if the requisite environments are present, cold-seep communities can exist throughout the deep sea regardless of water depth.

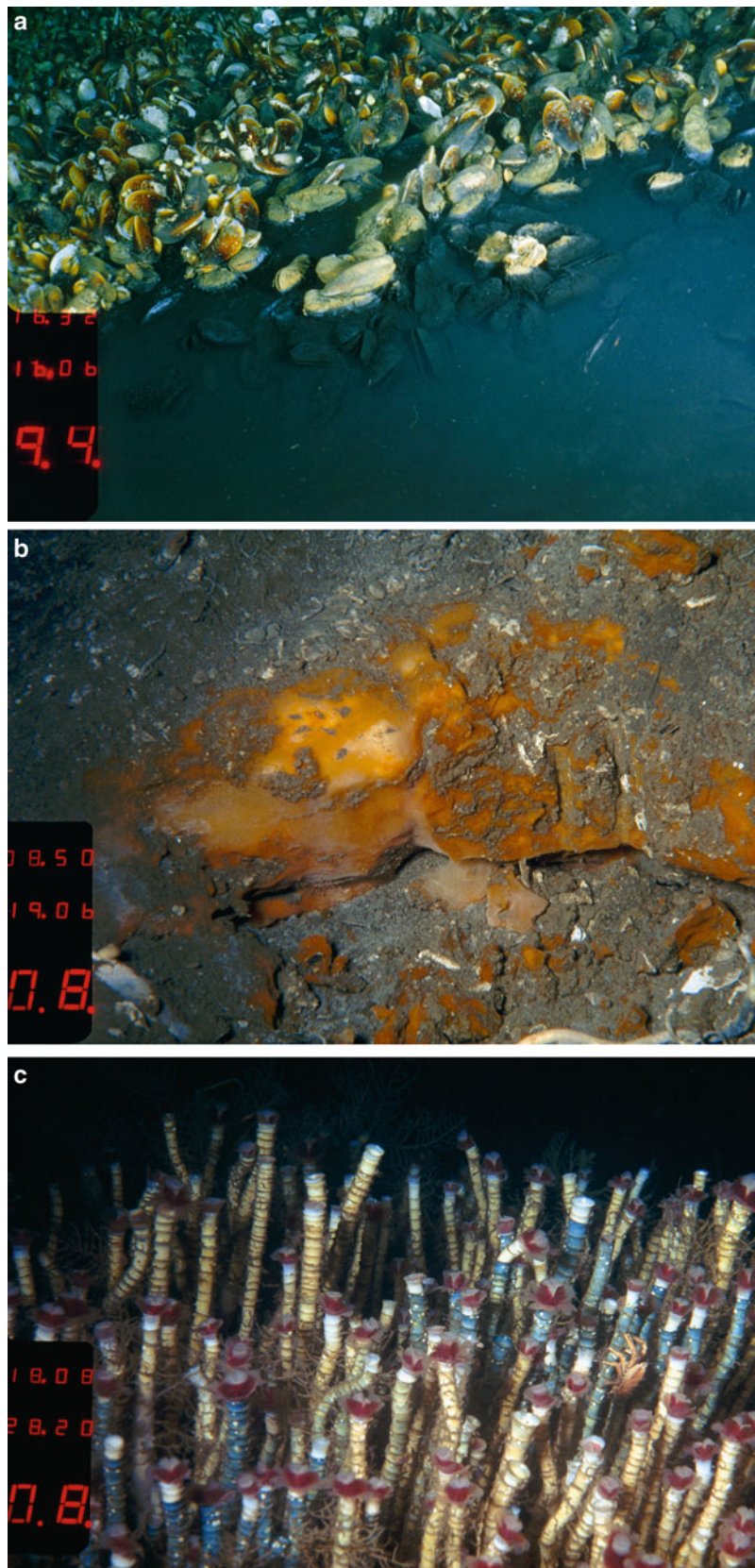


Figure 5.67. Cold seep organisms and outcropping gas hydrate: (a) *Bathymodiolus* mussels closely associated with a methane gas brine pool; (b) outcropping gas hydrate tinged yellow/orange by associated oil; and (c) *Lamellibrachia* tubeworm cluster (MacDonald and Fisher 1996; Jonathan Blair/National Geographic Creative, used with permission).

If there were no oil and gas seeps in the Gulf of Mexico, many of the phenomena described above would be absent and the mass loading of petroleum to the northern Gulf Mexico would be greatly reduced from current estimates. The distribution of methane seeps would be largely the same since the origin of this methane is predominantly microbial reworking of recent organic matter. Liquid hydrocarbons would be exclusively due to anthropogenic inputs and concentrated in the coastal regions rather than the deep sea in the absence of seeps. It could be reasonably expected that tar balls and mats would be substantially reduced on beaches and elsewhere but still be present due to human activities. Shallow gas-hydrate occurrences would likely be absent as sediment gaseous hydrocarbon concentrations would rarely reach supersaturation. It would be expected that hard sea-bottom substrate occurrences would be reduced on average, but relic, shallow water, and erosion-exposed hard bottom would still be present. From an ecological standpoint, the picture is more complex in regard to an absence of seeps.

The predominant megafauna at cold-seep communities require elevated sulfide concentrations associated with seeps to support endosymbiosis. It is known that these communities have ceased to exist when seepage is no longer present. Since many cold-seep species are *endemic* (i.e., found only at seeps), Gulf of Mexico biodiversity would be decreased. Studies have shown that cold-seep communities are largely oases of life in an otherwise relatively uniform deep-sea environment. MacAvoy et al. (2005) concluded that some heterotrophic fauna collected in close association with cold-seep communities most likely obtain the bulk of their nutrition from chemosynthetic production through a combination of grazing on free-living bacteria and directly consuming faunal biomass. However, other background deep-sea fauna have been shown to contain little evidence of the utilization of cold-seep primary production, so the broader ecological importance of cold-seep communities to the deep sea remains largely a mystery (Carney 2010). On the other hand, Boetius and Wenzhofer (2013) concluded that, on a global basis, seep sites on continental slopes sustain some of the richest ecosystems in the deep sea and that cold-seep communities utilize about two orders of magnitude more oxygen per unit area than non-seep communities. Other studies have shown that cold-seep ecosystems contribute substantially to the microbial diversity of the deep sea. Hydrocarbon seeps have been described as “. . . geologically driven hot spots of increased biological activity on the seabed. . .” (Foucher et al. 2009), and it has become increasingly recognized that biological hot spots are critical to sustaining biodiversity. The differences in the larger Gulf of Mexico ecosystem that might be expected if there were no seeps is difficult to predict given the present state of knowledge but the effects are expected to be limited, as most Gulf of Mexico biomass and diversity occurs in coastal regions beyond the influence of seeps. However, oil and gas seeps are an intrinsic feature of the region and are expected to persist as long as oil and gas remains deep within the basin and finds its way to the surface.

5.7.5 Exemplar Sites

The prevalence, persistence, number, and volumes of petroleum seeps in the Gulf of Mexico have established the conditions for the common occurrence of sites that display a spectrum of characteristics typical of marine oil and gas seeps. The number of confirmed cold-seep communities in the Gulf of Mexico exceeds the combined number of all other sites identified in the world's ocean, and it is likely hundreds of other sites are yet to be discovered (Fisher et al. 2007). Extensive studies of Gulf of Mexico oil and gas seep sites over the last three decades have clarified some of the complex interactions of physical, chemical, biological, and ecological processes. The geological and biological manifestations of petroleum seeps on the seafloor are related not only to the composition of released gases and fluids but also the rate and history of seepage (Fisher et al. 2007). Seeps release oil, gas, brines, and occasionally

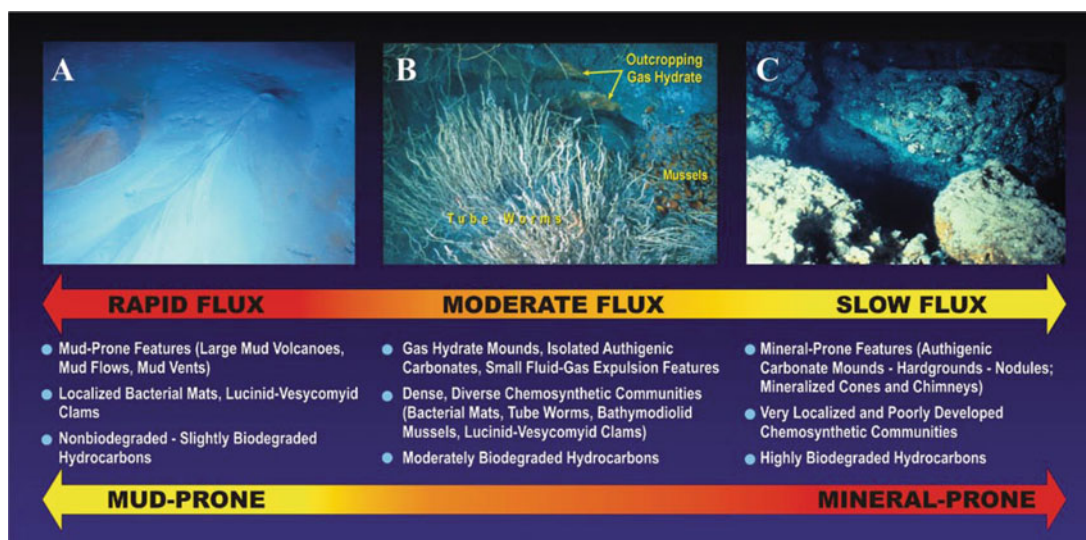


Figure 5.68. Relationships between rates of petroleum seepage features. (a) Rapid flux may produce mud volcanoes, mud vents, mudflows, and sparse cold-seep communities, (b) Moderate flux is commonly associated with surficial exposures of gas hydrate or gas hydrate in the shallow subsurface and well-developed cold-seep communities; and (c) Slow flux systems are likely to produce authigenic carbonates and other mineral assemblages; the supply of reduced chemicals is generally low and insufficient to support cold-seep communities (Fisher et al. 2007; Figure 4).

fluidized sediment. The rates of these releases vary from slow seepage to rapid venting (Figure 5.68). As fluxes of fluids and gases vary over time, the associated communities are distinct and evolve, and when seepage ceases, these communities do as well (Fisher et al. 1997, 2007).

One of the most detailed studies of petroleum seep sites in the Gulf of Mexico is that of Roberts et al. (2010). Seep-related seafloor features, mineralogical assemblages, and associated biological communities were characterized using 3D seismic survey data complemented by observations and the collection of shallow subsurface samples by manned submersible and remotely operated vehicles at 15 sites (Figure 5.69) (Roberts et al. 2010). These studies confirmed the close links between highly positive seafloor reflectivity, hard bottoms, hydrocarbon seeps or vents, authigenic minerals, gas hydrate, anoxic surface sediments, brine pools and flows, and cold-seep communities. Four exemplar sites from this study are presented to illustrate and describe the characteristics of the seafloor at petroleum seeps on the Gulf of Mexico continental slope (Figure 5.69 is a location map for the following summaries).

The Alaminos Canyon site, located in lease block 601 (AC601), exhibited surface amplitude anomalies in 3D seismic data that identified a brine lake and fluid-gas expulsion features associated with faults (Figure 5.70) (Roberts et al. 2010). The brine lake was circular (about 180 m [591 ft] in diameter) and averaged about 4 m (13 ft) deep (Figure 5.71). Terraced areas surrounding the brine lake contained small outcrops of authigenic carbonate suggesting lake levels were higher in the past. A clear interface was present between the brine lake surface and the surrounding seawater. The salinity of the lake was about twice that of seawater. White flocs floating within the brine were determined to be barite. Lake brine sulfate levels were about half that of seawater, but porewaters in lake-bottom cores contained no sulfate, and chloride-to-sodium ratios suggested halite was the source of the brine (Roberts et al. 2007a, b). The water column directly above the lake was supersaturated with methane. The brine itself had no animal

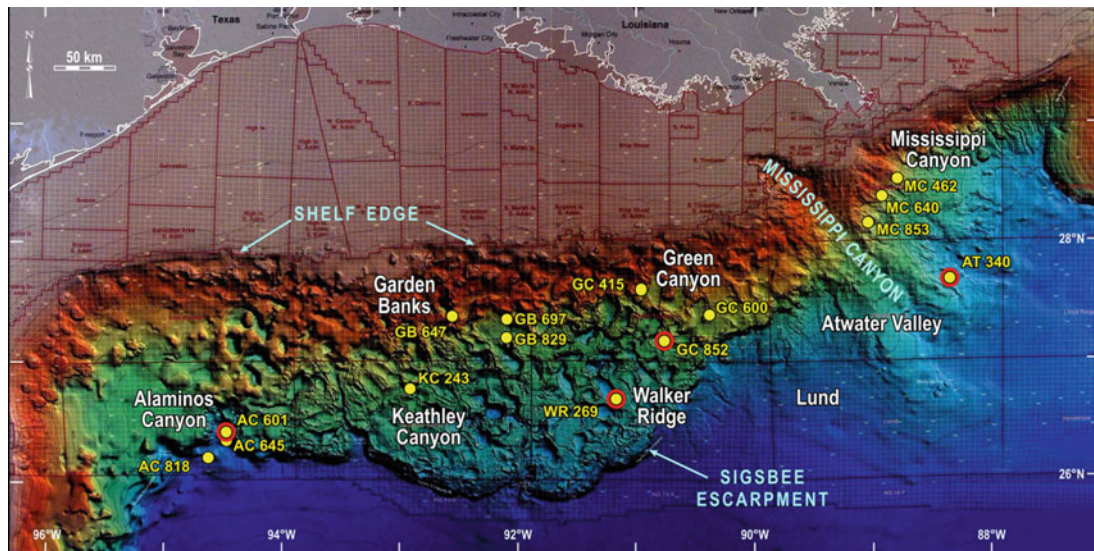


Figure 5.69. Shaded multibeam bathymetry relief map of the northern Gulf of Mexico continental slope with the locations of sites discussed below in red circles (BOEMRE oil and gas lease areas are in white lettering; Roberts et al. 2010 [reproduced with permission of Pergamon via Copyright Clearance Center, Inc.]).

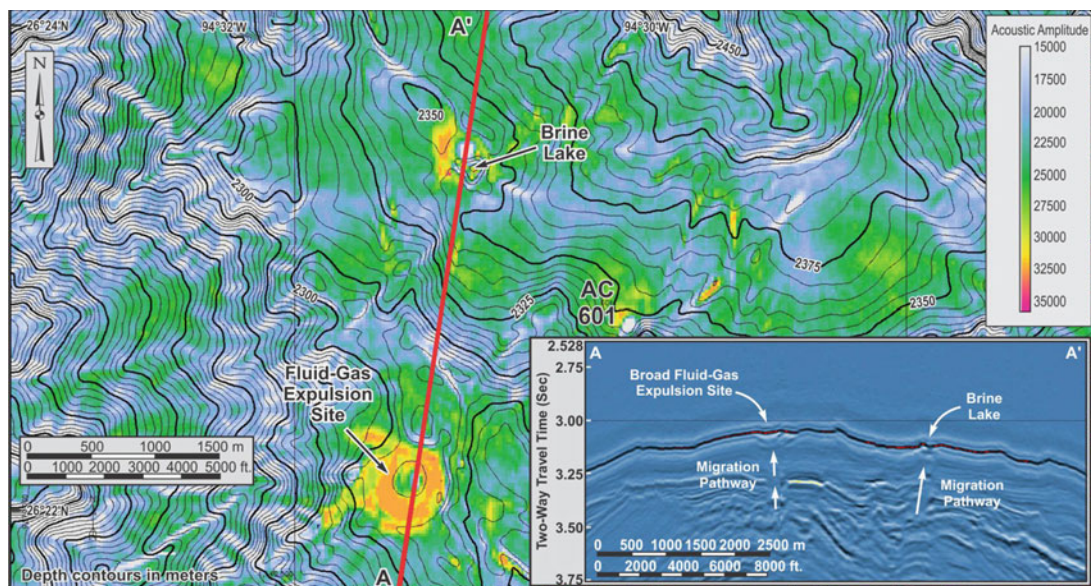


Figure 5.70. 3D seismic surface amplitude and bathymetry map illustrating a large fluid-gas expulsion area and a brine lake. The seismic profile (*inset*) shows that these features are above a breached subsurface anticlinal structure and faults that are migration pathways from the deep subsurface (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

life, but there were scattered clumps of mussels, a few tubeworms, and numerous urchin trails around the lake about 5–15 m (16.4–49.2 ft) from the lake shoreline (Figure 5.71). On higher ground further away from the lake, larger vestimentiferan tubeworm communities and

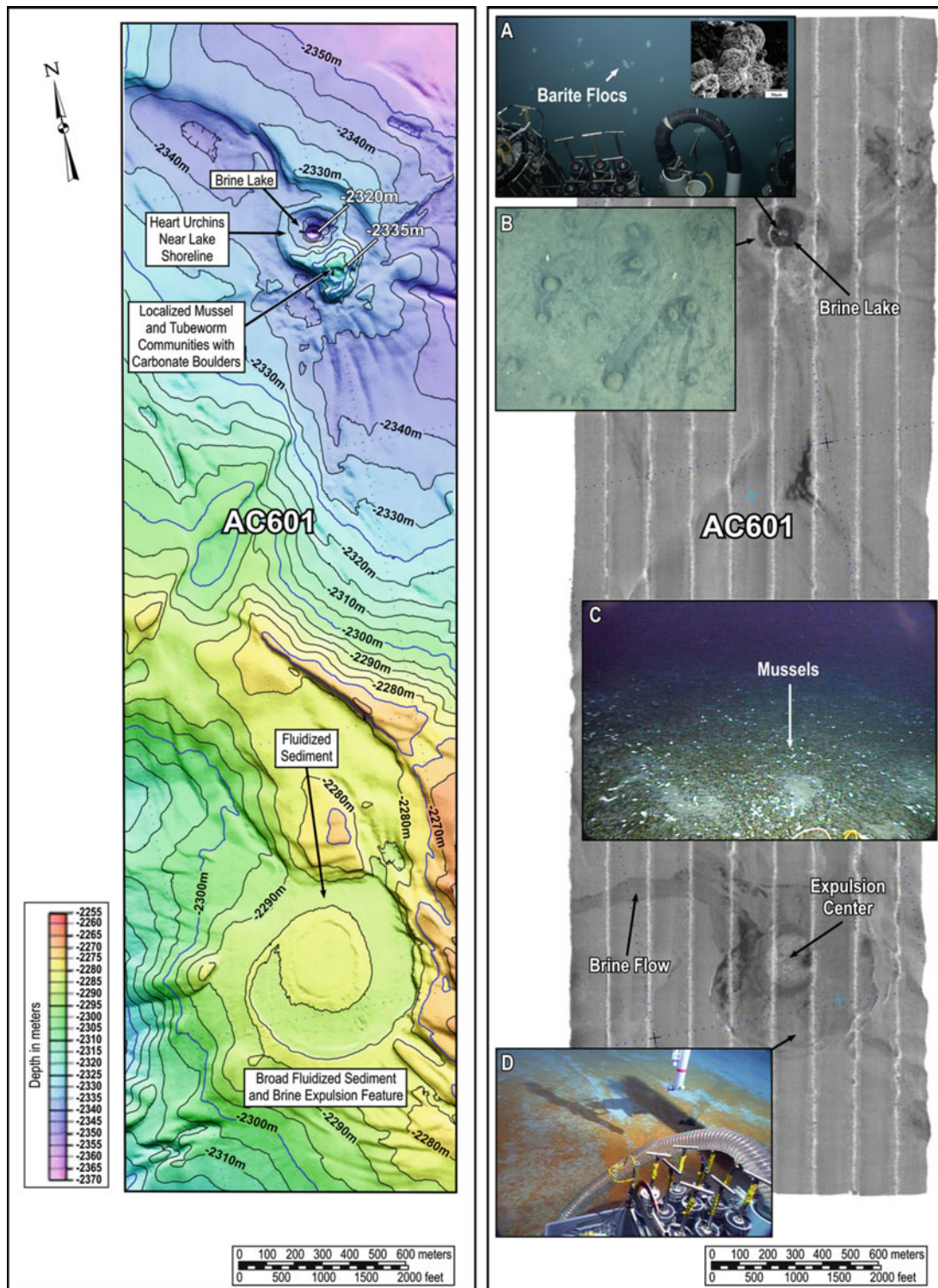


Figure 5.71. High-resolution autonomous underwater vehicle (AUV)-acquired multibeam bathymetry (*left*) and associated backscatter data (*right*) of the brine lake and large fluid-gas expulsion site in AC601. *Dark* areas on the backscatter image are highly reflective surfaces. (a) White flocs of barite are floating on the brine of the lake. (b) Heart urchins were observed above the brine shoreline on the lake's margin. (c) The high reflectivity (*dark*) on the backscatter image of the large, circular expulsion center is beds of living mussels. (d) Samples being collected of soft orange-stained mud in the southern part of the circular expulsion feature (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

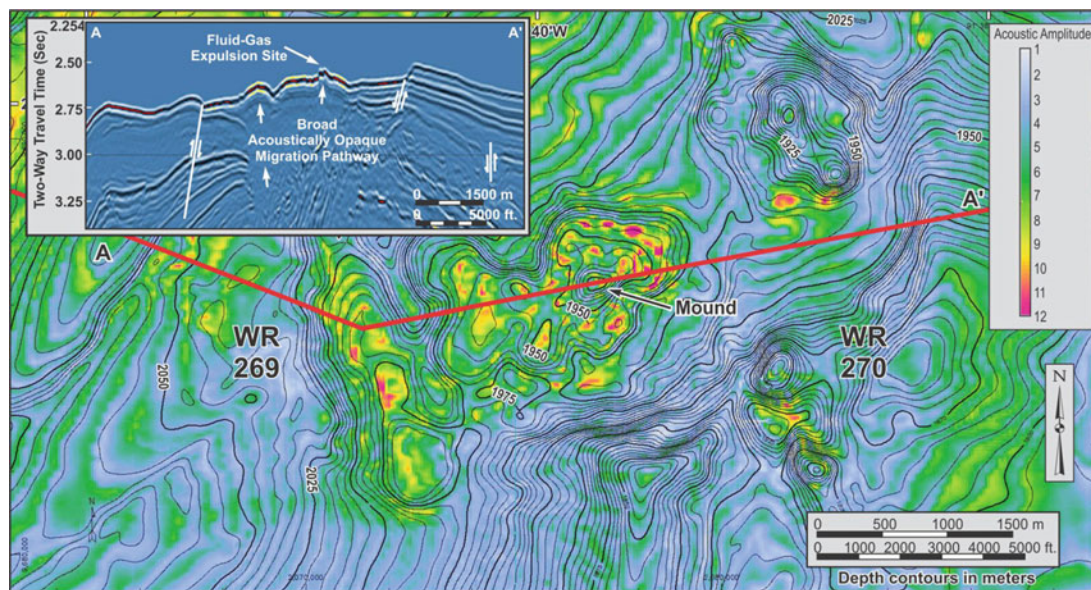


Figure 5.72. 3D seismic surface amplitude and bathymetry map of a series of mounds exhibiting high-positive surface amplitudes. The seismic profile (*inset*) shows a broad, acoustically transparent migration pathway beneath the mounds and above a salt diapir (not shown) in the shallow subsurface (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

extensive exposures of authigenic carbonate were observed. High-amplitude areas, representing zones of lithified seafloor, surround the lake (Figure 5.70). The reflective and high-positive amplitude area about 3 km (1.9 mi) south of the brine pool was a well-defined vertical migration pathway from the crest of an underlying breached anticline. Surficial brine flows, large areas of dark reduced mud, scattered clumps of living mussels, and light-gray fluidized mud suggested recent extrusions of sediment. Additional observations identified broad areas of red-stained sediment, a large mudflow along the southern rim of the feature, scattered clamshells, and a large bed of living mussels. The mussel bed was along the north-northwest rim of a circular expulsion feature. Carbonate outcrops were not obvious in the vicinity of the expulsion feature. High-positive 3D seismic surface amplitudes within the western and southern parts of the feature and apparent flow paths out of the feature suggested that mussel and clam beds may have developed on the surface of mudflows and were subsequently buried.

The Walker Ridge site, located in lease block 269–270 (WR269-270), exhibited a series of mounded features (Figure 5.72) (Roberts et al. 2010). The mounds are on the margin of an uplifted and compressed mini basin filled with Plio-Pleistocene turbidites, fans, and hemipelagic sediments. A north-south trending salt diapir underlies the uplifted eastern side of the basin, and migration pathways are linked from the seabed to the subsurface. Three mounded areas displayed a high surface amplitude response in 3D seismic data, and indications were that these areas are composites of smaller mounded features. The highest seafloor amplitudes were at the tops of the mounds (Figure 5.72). The easternmost mound in this grouping had the highest relief in the mound group. At the highest relief zones of the feature gas that was 99 % methane was observed venting. A broad and acoustically opaque area and the presence of bubble-phase gas and communities of pogonophorans, holothurians, and crustaceans (primarily crabs) were observed (Figure 5.73, inset). Large patches of dark, reducing sediments were observed on the mound's eastern flank (Figure 5.73). Scattered mussel shells and shell fragments were observed

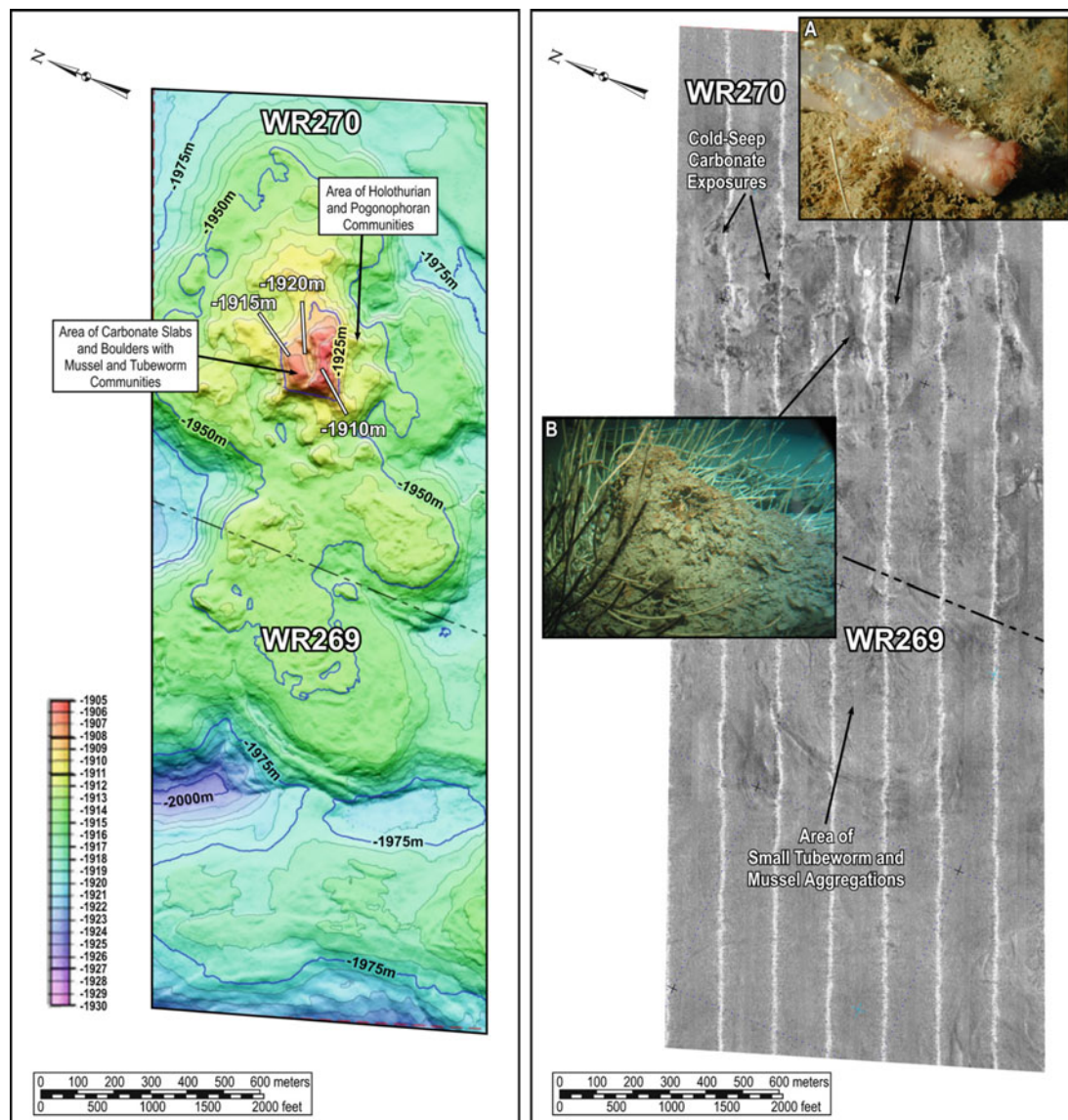


Figure 5.73. Multibeam bathymetry (left) and backscatter images (right) of the highest relief mound at the study site included (a) pogonophorans and holothurians communities on the east flank of the mound and (b) carbonates, vestimentiferan tubeworms, and mussels rimmed a slight depression at the crest of the mound (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

on the steep slope leading to the crest of the mound. There was a shallow depression on the crest of the mound (2–5 m [6.7–16.4 ft] deep) with a well-defined rim. Beds of large living mussels, vestimentiferan tubeworm colonies, slabs of carbonate and small gas seeps were also found. The carbonates and tubeworm colonies were mainly confined to the rim of the shallow depression, whereas mussels were at the rim and toward the middle of the depression.

The Green Canyon site, located in lease block 852 (GC852), exhibited a ridge crest and large cold-seep carbonate blocks and slabs (Figure 5.74). The ridge was supported by salt within a

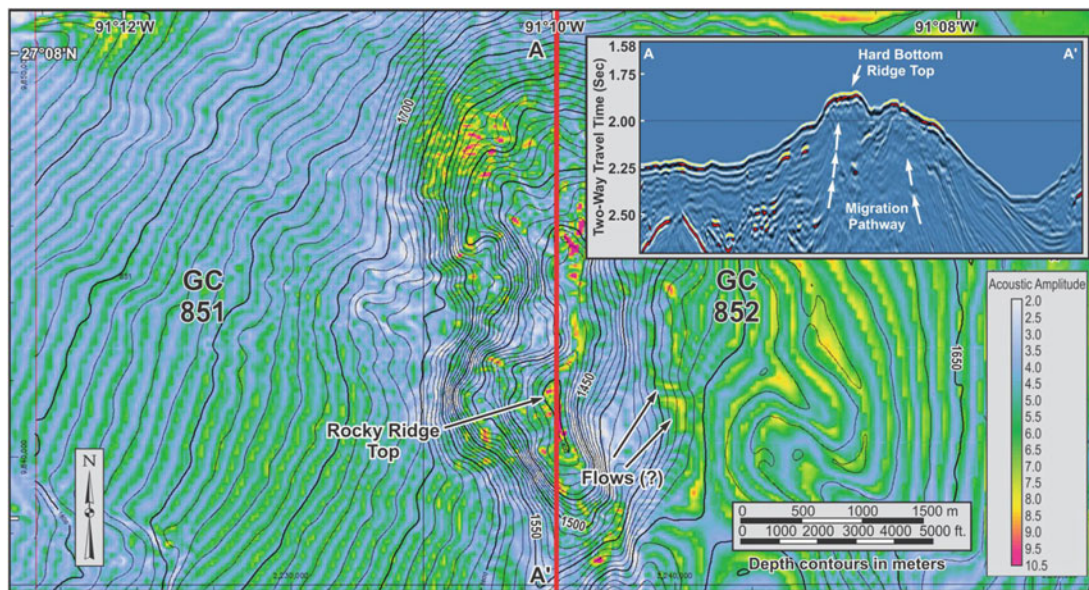


Figure 5.74. 3D seismic surface amplitude and bathymetry map illustrating high-positive amplitude anomalies on the top and on the flanks of a north-south-oriented submarine ridge. Highly reflective areas of the ridge included widespread hard-bottom areas composed of cold-seep carbonate slabs and large blocks. A seismic profile across the ridge (*inset*) defines migration pathways for the transport of hydrocarbons (oil and gas) to the seafloor (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

well-developed basin. The 3D seismic seafloor reflectivity and surface amplitude data suggested localized hard seabed conditions, flow deposits, and cold-seep communities on top of the ridge. The cross-sectional shapes of the ridge and fluid-gas migration pathways to the surface of the ridge crest are shown in Figure 5.74 (*inset*). The crest of the ridge varied in width from about 100 to 300 m (328–984 ft). Sea-surface oil slicks were observed above the ridge. Hard bottoms of authigenic carbonate slabs and mound-like structures of large cold-seep carbonate blocks were observed on the southern ridge crest. Mussel beds were scattered among the carbonate slabs and boulders and vestimentiferan tubeworms were widespread along the southernmost ridge crest (Figure 5.75). Prolonged hydrocarbon seepage was indicated by abundant authigenic carbonates at the southern ridge crest. Brine seepage was found throughout the area and several small gas seeps were observed in mussel beds but no oil seepage was observed. Gorgonians and scattered bamboo corals were widespread throughout the southern ridge crest area. Huge carbonate blocks and a dense and diverse hard coral community were observed at the shallowest point on the ridge (Figure 5.74). There was little evidence of active seepage on the ridge.

The Atwater Valley site, located in lease block 340 (AT340) exhibited a cluster of high-positive amplitude features (Figure 5.76) (Roberts et al. 2010). The low relief mound, east of the Mississippi Canyon, transitions from a canyon to a submarine fan complex caused by an underlying salt body in the shallow subsurface. The area included numerous small-scale surface mounds, and bubble-phase gas was evident along the migration pathway. The 3D seismic surface amplitude (reflectivity) maps showed high-positive surface amplitude features associated with mounds of up to 20 m (65.6 ft) relief (Figures 5.77 and 5.78). Abundant bathymodiolid mussel shells were cemented into authigenic carbonate. The diverse fauna at the site included numerous bathymodiolid mussel beds, vestimentiferan tubeworm colonies, and sea urchins and anemones were scattered among the carbonate blocks. Areas of brine seepage

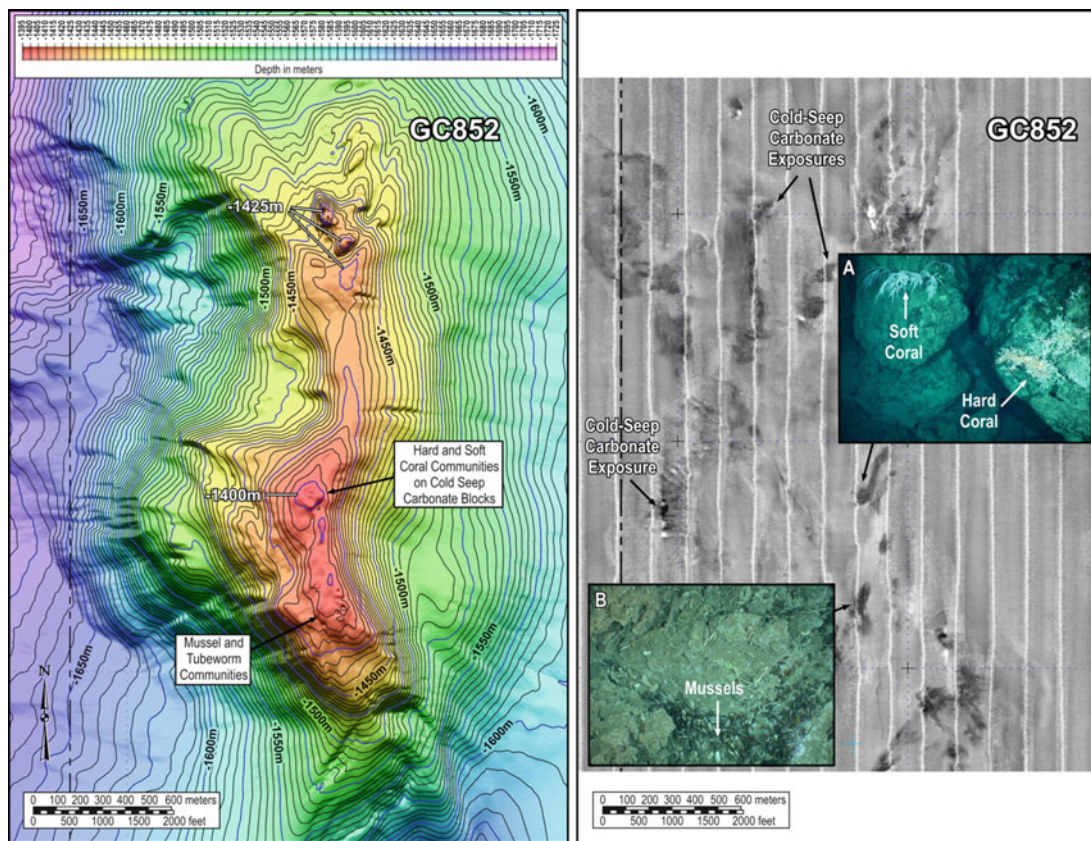


Figure 5.75. Multibeam bathymetry (*left*) and associated backscatter data (*right*) illustrates variable and small-scale relief along a ridge crest. Communities of mussels and tubeworms were found on the southern ridge crest and its upper flanks. At the highest point along the ridge, deepwater coral communities were found in association with a large area of cold-seep carbonate blocks. The most active seepage sites and cold-seep communities were on the southern ridge area. (a) Soft and hard coral communities on large cold-seep carbonate blocks (b) Beds of mussels between the cold-seep carbonate slabs and blocks of the southern ridge crest area (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

adjacent to the mound contained large communities of heart urchins in dark reducing sediments (Figures 5.77 and 5.78).

5.8 SUMMARY

Petroleum seepage is a prevalent, natural worldwide phenomenon that has occurred for millions of years and is especially widespread in the deepwater region of the Gulf of Mexico. As one of the most prolific oil and gas basins in the world, the Gulf of Mexico has abundant deep-seated supplies of oil and gas to migrate to the surface. The deepwater region of the Gulf of Mexico is an archetype for oil and gas seepage, and most of our knowledge of petroleum seeps is based on studies of the region. The essential geological conditions for seepage are met in many areas of the deepwater region of the Gulf of Mexico region including multiple deeply buried mature source rocks and migration pathways to the surface. The northern Gulf of Mexico basin has been a depocenter for massive amounts of sediments over geologic time, and salt tectonics are prevalent, setting boundaries on the geographic patterns of petroleum

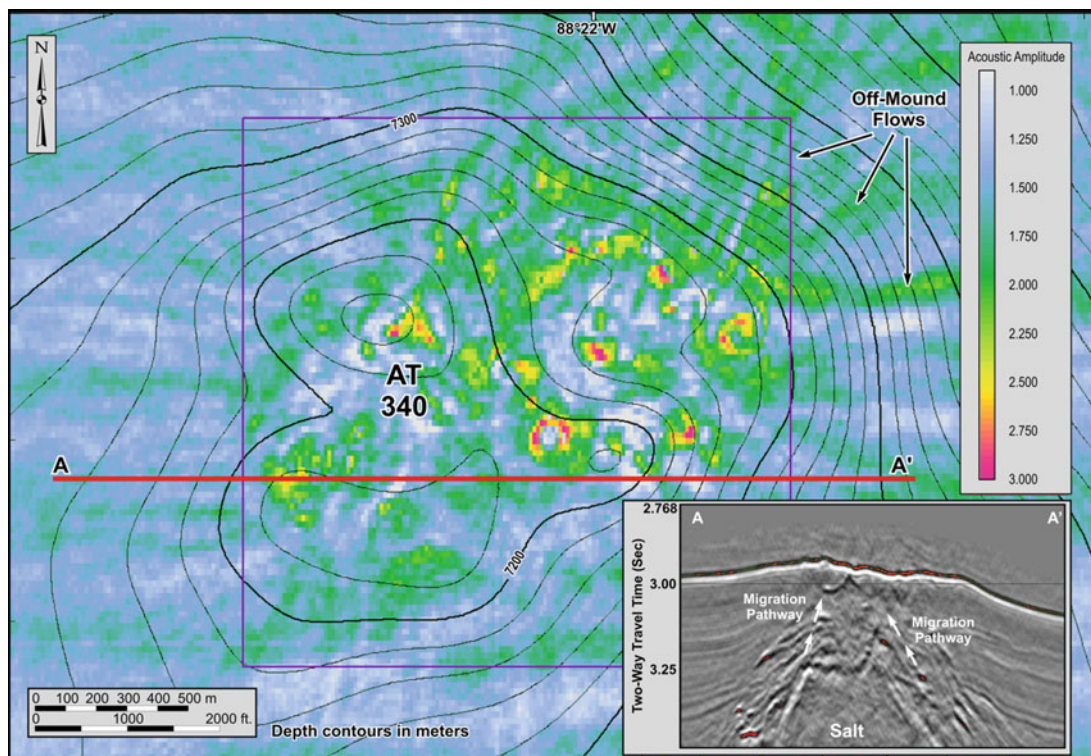


Figure 5.76. 3D seismic surface amplitude and bathymetry map showing a low-relief regional mound with surficial high-positive seafloor amplitude anomalies. Seafloor amplitude data showed apparent flows originating from the mound crest and extending to deeper water. An east-west seismic profile across the regional mound (*inset*) shows supporting by salt in the shallow subsurface and fluid-gas migration routes at the salt margins of the mounded seafloor (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

seepage. Gulf of Mexico seeps are highly variable in composition and volume and include gases, volatiles, liquids, pitch, asphalt, tars, water, brines, and fluidized sediments. Seeps are dynamic over a range of temporal scales and can be ephemeral or persist for many years. In the Gulf of Mexico, seeps annually release vast amounts of oil and gas to the environment. In the Gulf of Mexico region, seeps occur on land; however, most petroleum seepage is in the northwest and north-central offshore regions. Collectively, petroleum seeps in the Gulf of Mexico are sources of highly variable mixtures of hydrocarbons, which are often altered by the weathering processes that occur after seepage. Seeps can be pristine to severely biodegraded. The prevalence, persistence, number, and volumes of petroleum seeps in the Gulf of Mexico display a spectrum of characteristics typical of petroleum seeps. Biogeochemical processes are the critical connections between commonly expressed phenomena at petroleum seep sites, including topographic features and authigenic minerals. The Gulf of Mexico continental slope and abyss are complex topographically with areas of high seafloor reflectivity and acoustic wipe-out zones caused by the active influx of gases and fluids, lithification, physical disruption of sediments, and gas-hydrate formation and decomposition. Gas seeps are widespread in the Gulf of Mexico and most have microbiological origins, but thermogenic gas seeps are also common. Gas hydrate occurs in near-surface sediments at water depths below about 500 m (1,640 ft), which defines their upper stability limit. Surveys and studies have shown that cold-seep chemosynthetic communities are common at macroseeps Gulf-wide, including on the

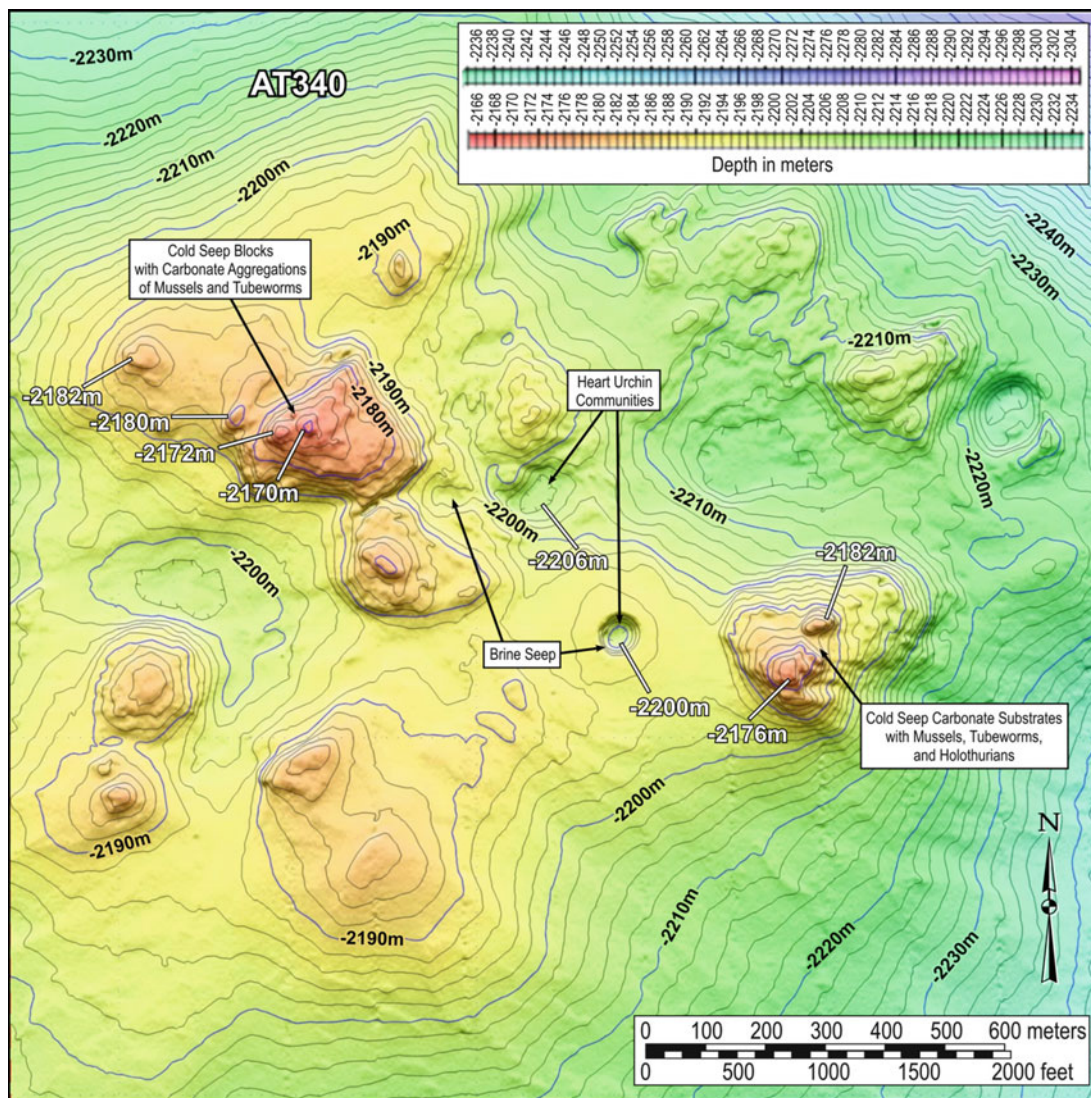


Figure 5.77. A multibeam bathymetry map showing small-scale relief features (mounds and depressions) composed of cold-seep carbonate slabs and blocks and brine seeps in the depressions (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

abyssal plain and in the southern Gulf of Mexico. Geological and biological manifestations at petroleum seeps on the seafloor are controlled by the composition of released gases and fluids and the rate and history of seepage. The rates of seepage of oil, gases, brines, and fluidized sediment vary from slow seepage to rapid venting. As these fluxes vary over time, cold-seep community assemblages evolve, and when seepage ceases, seep communities disappear. In the offshore Gulf of Mexico, the geographic distributions of source-rock horizons, salt basins, oil and gas production platforms, satellite and air-borne images of sea-surface oil slicks, regional oil and gas reserves, cold-seep communities, and gas hydrates illustrate the close association of petroleum seepage and these phenomena. Petroleum seepage in the Gulf of Mexico has occurred for millions of years and is widespread and active today.

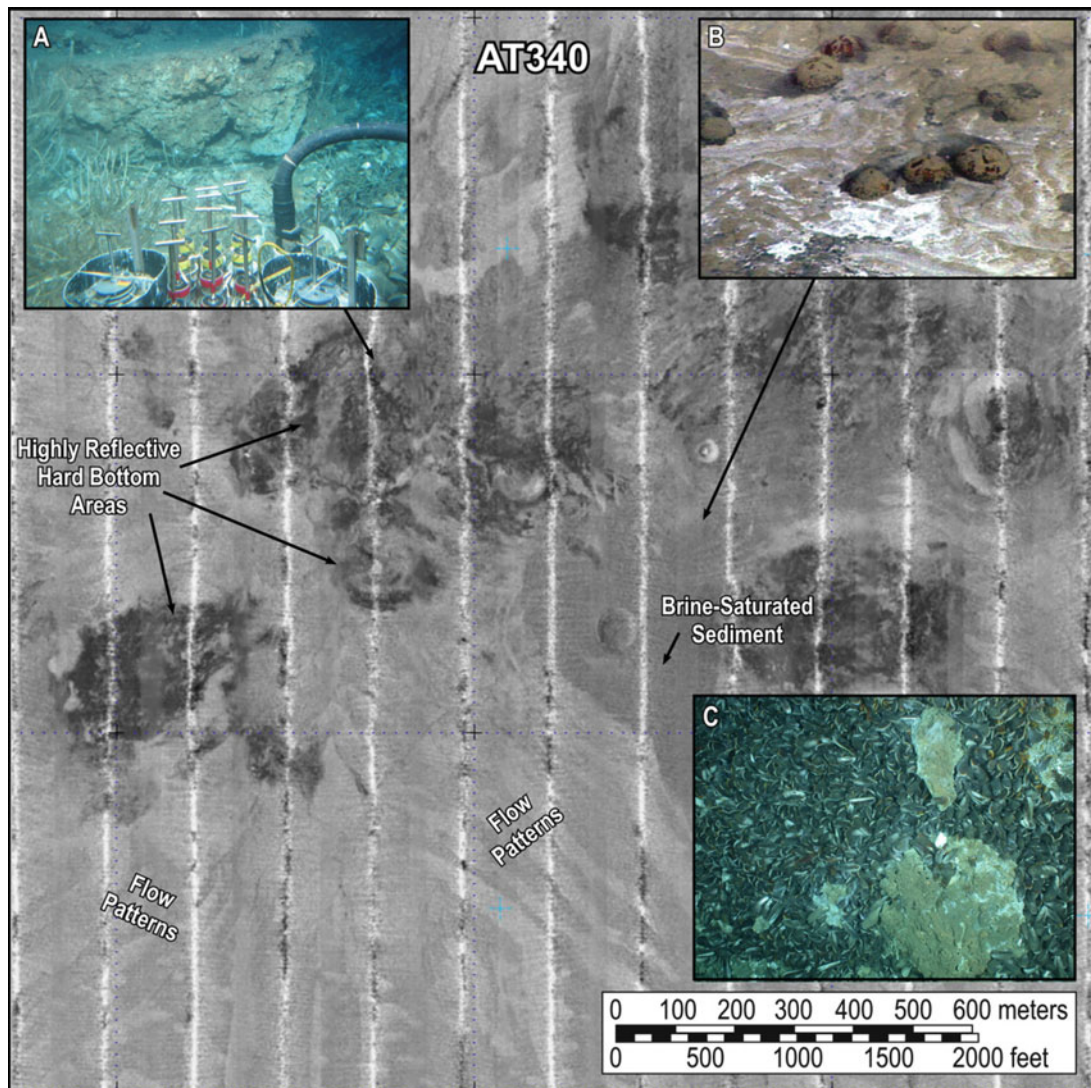


Figure 5.78. A backscatter image showing highly reflective hard-bottom and mounded areas. Active gas seepage associated with these mounds, numerous (a) living mussel beds, (b) urchin communities in areas of brine seepage, and (c) tubeworm communities among the carbonate blocks and slabs were observed. Flow lines in this backscatter image are brine flows associated with active fluid-gas expulsion (Roberts et al. 2010; reproduced with permission of Pergamon via Copyright Clearance Center, Inc.).

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APPENDIX A: GEOCHEMICAL DEFINITIONS

Table A.1. Geochemical Definitions (from Miles 1989)

Item	Definition
$\delta^{13}\text{C}$	<ul style="list-style-type: none"> • ^{13}C is an isotope of carbon with six protons and seven neutrons. Microbes preferentially reject ^{13}C with the result that microbial gas and carbonates are depleted in ^{13}C • The standard established for carbon-13 work was the Pee Dee Belemnite (PDB) and was based on a Cretaceous marine fossil, <i>Belemnitella americana</i>, which was from the Pee Dee Formation in South Carolina. This material had an anomalously high $^{13}\text{C}:^{12}\text{C}$ ratio (0.0112372), and was established as $\delta^{13}\text{C}$ value of zero. Use of this standard gives most natural materials a negative $\delta^{13}\text{C}$. The calculation is: $\delta^{13}\text{C}_{\text{sample}} = \left(\frac{^{12}\text{C}/^{13}\text{C}_{\text{sample}}}{^{12}\text{C}/^{13}\text{C}_{\text{PDB}}} - 1 \right) \times 1000$ • The standards are used for verifying the accuracy of mass spectroscopy; as isotope studies became more common, the demand for the standard exhausted the supply. Other standards, including one known as VPDB (for Vienna PDB) have replaced the original • Methane has a very light $\delta^{13}\text{C}$ signature: biogenic methane of about -60‰; thermogenic methane about -40‰ • More commonly, the ratio is affected by variations in primary productivity and organic burial. Organisms preferentially take up light ^{12}C, and have a $\delta^{13}\text{C}$ signature of about -25‰, depending on their metabolic pathway
^{14}C , carbon dating	<ul style="list-style-type: none"> • Carbon-14, ^{14}C, or radiocarbon, is a radioactive isotope of carbon with a nucleus containing six protons and eight neutrons. Its presence in organic materials is the basis of the radiocarbon dating method pioneered by Willard Libby and colleagues (1949) to date archaeological, geological, and hydrogeological samples • Three naturally occurring isotopes of carbon are on earth: 99 % of the carbon is ^{12}C, 1 % is ^{13}C, and ^{14}C in trace amounts, i.e., making up about 1 part per trillion (0.000000001 %) of the carbon in the atmosphere. The half-life of ^{14}C is $5,730 \pm 40$ years. ^{14}C decays into ^{14}N through beta decay. The primary natural source of ^{14}C on Earth is cosmic ray action upon nitrogen in the atmosphere, and it is therefore a cosmogenic nuclide. However, open-air nuclear testing from 1955 to 1980 contributed to this pool • Radiocarbon dating is a radiometric dating method that uses ^{14}C to determine the age of carbonaceous materials up to about 60,000 years old. Willard Libby and his colleagues developed the technique in 1949 during his tenure as a professor at the University of Chicago. Libby estimated that the radioactivity of exchangeable ^{14}C would be about 14 disintegrations per minute (dpm) per gram of pure carbon, and this is still used as the activity of the modern radiocarbon standard • One of the frequent uses of the technique is to date organic remains from archaeological sites. Plants fix atmospheric carbon during photosynthesis, so the level of ^{14}C in plants and animals when they die approximately equals the level of ^{14}C in the atmosphere at that time. However, it decreases thereafter from radioactive decay, allowing the date of death or fixation to be estimated. The initial ^{14}C level for the calculation can either be estimated, or else directly compared with known year-by-year data from tree-ring data (dendrochronology) up to 10,000 years ago (using overlapping data from live and dead trees in a given area), or else from cave deposits (speleothems), back to about 45,000 years before the present. A calculation or (more accurately) a direct comparison of ^{14}C levels in a sample, with tree ring or cave-deposit ^{14}C levels of a known age, then gives the wood or animal sample age-since-formation • Oils and gases are always much older than 50,000 years and so are made of the so-called dead carbon

Item	Definition
Alkane C ₁₂ nC ₁₂	<ul style="list-style-type: none"> An alkane is a saturated hydrocarbon. Alkanes consist only of hydrogen and carbon atoms, all bonds are single bonds, and the carbon atoms are not joined in cyclic structures but instead form an open chain. They have the general chemical formula C_nH_{2n+2}. Alkanes belong to a homologous series of organic compounds in which the members differ by a molecular mass of 14.03u (mass of a methanediyl group, -CH₂-, one carbon atom of mass 12.01u, and 2 hydrogen atoms of mass ≈ 1.01u each). There are two main commercial sources: crude oil and natural gas Each carbon atom has four bonds (either C-H or C-C bonds), and each hydrogen atom is joined to a carbon atom (H-C bonds). A series of linked carbon atoms is known as the carbon skeleton or carbon backbone. The number of carbon atoms is used to define the size of the alkane (e.g., C2-alkane, C18-alkane, and C28-alkane). Other terms include the addition of the term <i>normal</i> as in nC₂, nC₁₈, nC₂₈, etc.
Isoprenoids Pristane Phytane	<ul style="list-style-type: none"> Isoprenoids are hydrocarbons that contain double bonds. Their general chemical formula is C_nH_{2n+2}. A common origin for pristane (C₁₉H₄₀) and phytane (C₂₀H₄₂) is the phytyl side chain of chlorophyll <i>a</i> in phototrophic organisms and bacteriochlorophyll <i>a</i> and <i>b</i> in purple sulfur bacteria. Reducing or anoxic conditions in the sediments promote the cleavage of the phytyl side chain to yield phytol, which undergoes reduction to dihydrophytol and then to phytane. Oxic conditions promote the competing conversion of phytol to pristane. A common precursor for both pristane and phytane is inferred by the similarity of their δ¹³C values, which commonly differ by no more than 0.3 ‰ (Peters et al. 2007) Pristane and phytane are resistant to biodegradation. The ratios between pristane/nC₁₇ and phytane/nC₁₈ are established in non-biodegraded samples. As biodegradation intensifies, nC₁₇ and nC₁₈ are preferentially depleted and the value of the ratio increases In addition, the boiling points of pristane/nC₁₇ and phytane/nC₁₈ are very close so if an oil is subject to evaporation the ratios will stay constant. It is possible therefore to distinguish evaporation and biodegradation mechanisms in partially depleted oils
Biomarker	<ul style="list-style-type: none"> Compounds, or characteristics of compounds, found in petroleum or rock extracts that indicate an unambiguous link with a natural product are known as biological markers, biomarkers for short. Diagenetic changes that occur in sediment may alter functional groups and bonds in the natural compound, but the carbon skeleton of the compound remains the same. The simplest compounds that are biomarkers are normal alkanes derived from plant waxes and fatty acids, isoalkanes, and isoprenoids. Chlorophyll decomposes to porphyrin and to pristane and phytane from the side chain

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