The Origin of Petroleum in the Marine Environment

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All figures are available on the companion website in color (if applicable).

26.1 **INTRODUCTION**

In coastal upwelling areas, the underlying sediments are enriched in organic matter due to high biological productivity in the surface waters and relatively shallow water depths. Given appropriate environmental conditions, diagenesis and catagenesis can convert the sedimentary organic matter to petroleum over time scales of tens of millions of years. This process has been likened to "cooking" in the geologic "kitchen." Overall the production of petroleum is highly inefficient due to the remineralization of organic carbon during microbial respiration. As shown in Figure 25.1, most of the sedimentary carbon is in the form of biogenic carbonate.

Humans are rapidly returning the petroleum carbon reservoir to the atmosphere through the burning of fossil fuels. This perturbation of the crustal-ocean-atmosphere carbon cycle is the source of the gas (CO_2) primarily responsible for the anthropogenic contribution to global warming. Nevertheless, petroleum remains the major source of energy fueling the world economy.

Although most petroleum is used to generate energy, primarily for transportation, it is also an important feedstock for the manufacture of petrochemicals used in the creation of synthetic rubber, synthetic fibers, drugs, detergents, and plastics. Components of petroleum also serve as lubricating oils and solvents. Because of these valuable uses, many have suggested that we are wasting a valuable feedstock resource by continuing to burn it for energy.

Considerable effort continues to be directed at determining how and where petroleum has formed. As we are depleting the easily recoverable deposits of petroleum, interest is being increasingly directed at locating and recovering coal and natural gas. In this chapter, we discuss the biogeochemical conditions required for the formation of large petroleum deposits. Because these requirements are numerous, finding large petroleum deposits is akin to searching for a needle in a haystack. Whether we have found and depleted all of the large reservoirs is a matter of great controversy.

Petroleum prospecting represents one of the most successful applications of the molecular biomarker approach. Ten to 20% of the organic compounds in crude oil

were formed directly from hydrocarbons synthesized by organisms. Thus, hundreds of biomarkers are present in petroleum, although they collectively represent less than 2% of the total mass of the organic carbon. These biomarkers have been use to identify: (1) the source of organic matter in petroleum deposits, (2) the environmental conditions present during deposition of the organic matter, and (3) the nature of subsequent diagenetic, catagenetic, and metagenetic transformations. Although some controversy still exists regarding the source of the organic carbon in petroleum, the presence of biomarkers provides strong evidence for a largely biotic origin.

Petroleum geochemists use the molecular biomarker approach and other diverse kinds of data to evaluate the production potential of sediments in an effort to minimize the drilling of costly exploratory wells. This approach requires knowledge of the timing and locations of past conditions under which organic matter production and preservation were favored. This knowledge, in turn, relies on an understanding of the role of marine organisms in the production and destruction of organic matter and the role of the ocean-atmosphere system in controlling water circulation as the latter determines the rates of O_2 and nutrient delivery. Since the processes leading to the formation of large petroleum deposits occurred tens and even hundreds of millions of years ago, understanding them is truly a paleoceanographic endeavor. In other words, this chapter, in describing the formation of petroleum in the marine environment, provides a synthesis and practical application of most of the topics previously covered in this text.

26.2 WHAT IS PETROLEUM?

Petroleum is operationally defined as any hydrocarbon mixture that can be recovered through a drill pipe. It is composed of a great variety of molecules that range in molecular weight from methane (16 g/mol) to the asphaltenes (tens of thousands of g/mol). Compounds can be present as gases, liquids, and condensates. The condensates are hydrocarbons retrieved as gases or liquids that upon cooling change into liquids or solids. The gas phase includes low-molecular-weight hydrocarbons ($\leq C_4$). These *natural gases* include methane, ethane, propane, and butane. The liquid phase is commonly referred to as a *crude oil*. Although petroleum is primarily composed of hydrocarbons, trace amounts of other chemicals are present. These include (1) gases, such as N_2, CO_2, H_2S, and He; (2) trace metals, particularly V, Zn, Ni, and Hg; and (3) organic compounds that contain N, S, and O.

The liquid, or *crude oil*, portion of petroleum is transformed into commercial form via distillation. This process removes impurities and enables production of various fractions, such as gasoline, kerosene, and oil. The boiling point ranges of these fractions are given in Figure 26.1. These fractions are mixtures of compounds whose structure and size are similar as these factors determine their boiling points. For example, the gasoline fraction is composed of hydrocarbons that contain four to 10 carbons.

The major classes of hydrocarbons found in petroleum are the *paraffins*, *isoparaffins*, *cycloparaffins*, *aromatics*, and *olefins*. Sample structures are provided in Figure 26.2 as skeletal formulae in which a carbon atom is present at each end or kink
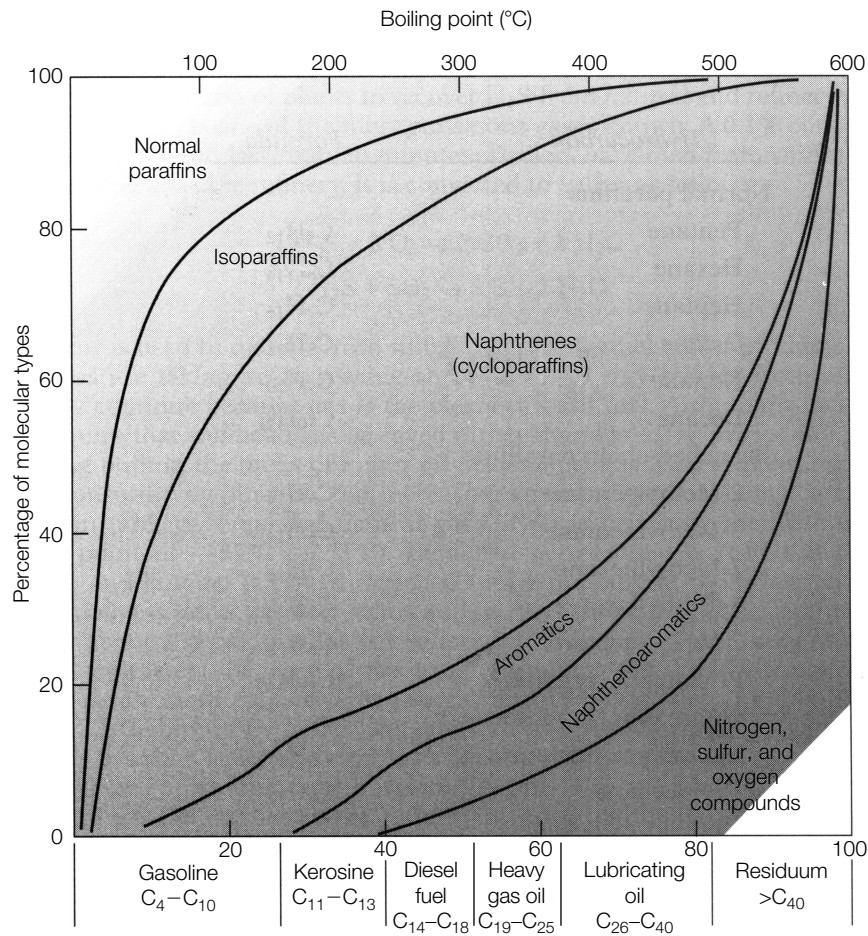
FIGURE 26.1

Chemical composition of a crude oil. *Source*: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition, W. H. Freeman and Co., New York, p. 39.

of a chain and the hydrogen atoms are not shown. The paraffins (also called alkanes) are straight-chain (nonaromatic) hydrocarbons. Because they do not contain any double or triple bonds, they are also categorized as "saturated" hydrocarbons. These molecules contain the maximum amount of hydrogen atoms possible given their number of carbon atoms. Their stoichiometry is thus C_nH_{2n+2}. Paraffins with greater than 20 carbon atoms are solids, called *paraffin waxes*. The high-molecular-weight paraffins can contain as many as 80 carbon atoms. The isoparaffins have at least one branch in their carbon chain, which leads to an increased boiling point.

The cycloparaffins, or naphthenes, are rings that contain 5 or 6, and sometimes 7, carbons. Napthenes compose about half of average crude oil. The high-molecular-weight
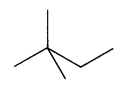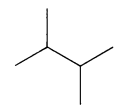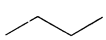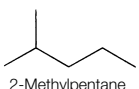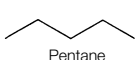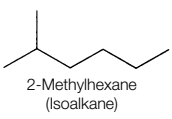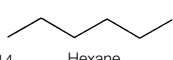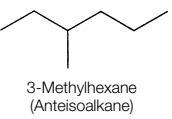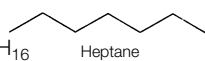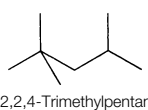
(a) Normal paraffins

(b) Branched-chain paraffins

		Boiling point
CH_4	Methane	$-161°C$
C_2H_6	Ethane	$-89°C$
C_3H_8	Propane	$-42°C$
C_4H_{10}	Butane	$-0.5°C$
C_5H_{12}	Pentane	$36°C$
C_6H_{14}	Hexane	$69°C$
C_7H_{16}	Heptane	$98°C$

		Boiling point
C_4H_{10}	2-Methylpropane (Isobutane)	$-12°C$
C_6H_{14}	2,2-Dimethylbutane	$50°C$
C_6H_{14}	2,3-Dimethylbutane	$58°C$
C_6H_{14}	2-Methylpentane	$60°C$
C_7H_{16}	2-Methylhexane (Isoalkane)	$90°C$
C_7H_{16}	3-Methylhexane (Anteisoalkane)	$92°C$
C_8H_{18}	2,2,4-Trimethylpentane (Iso-octane)	$99°C$

FIGURE 26.2 *(Continued)*

napthenes are made up of fused multiple rings. The stoichiometry of the napthenes is C_nH_{2n}, reflecting a lower hydrogen content than in the aliphatic paraffins.

Olefins are hydrocarbons that contain one or more carbon-carbon double bonds. They are unsaturated and, hence, have a stoichiometry of C_nH_{2n-2}. Many biomolecules, such as the terpenoids, are olefins. This class of compounds is uncommon in crude oil because of their high chemical reactivity. During petroleum formation, the double bonds tend to become reduced by incorporation of hydrogen or sulfur atoms, thereby generating either paraffins or nonhydrocarbons, respectively, both of which are thermodynamically very stable.

(d) Naphthenes (Cycloparaffins)
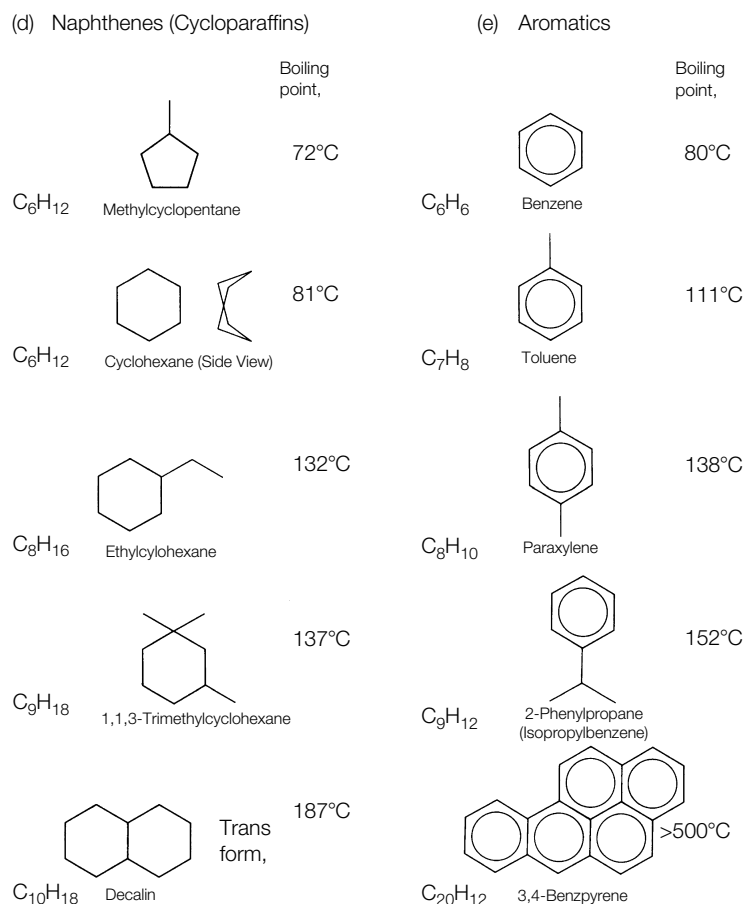
(e) Aromatics

FIGURE 26.2

Molecular structures of (a) paraffins, (b) branched paraffins, (c) olefins, (d) cycloparaffins, and (e) aromatics. *Source*: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition, W. H. Freeman and Co., New York, p. 28 and 31.

The higher boiling-point fraction of petroleum contains hydrocarbons that tend to have high molecular weights and high degrees of unsaturation. They include the aromatics and mixed structures, such as the napthenoaromatics. The aromatics are molecules that contain benzene rings and, hence, are highly unsaturated because they contain multiple carbon-carbon double bonds. Their stoichiometry is C_nH_{2n-6}. The highest molecular-weight aromatics have fused rings and are termed *polynuclear aromatic hydrocarbons* (PAHs). These compounds tends to be very carcinogenic.

The residue left at the end of the distillation process is composed of very high molecular-weight hydrocarbons, called *asphaltenes*, and nonhydrocarbons, called *asphaltics*. The latter contain varying amounts of either oxygen, nitrogen, or sulfur. The

Table 26.1 Percent Elemental Composition of Oil, Asphalt, and Kerogen.

	Gas	**Oil**	**Asphalt**	**Coal**	**Kerogen**
Carbon	76	84.5	84	83	79
Hydrogen	24	13	10	5	6
Sulfur	0	1.5	3	1	5
Nitrogen	0	0.5	1	1	2
Oxygen	0	0.5	2	10	8
	100	100	100	100	100

Source: *From Hunt, J. M. (1996).* Petroleum Geochemistry and Geology, *2nd edition. W. H. Freeman and Co., New York, p. 24.*

structures of asphaltenes typically have lots of fused hexane and benzene rings along with paraffin side chains. The distillation residue can range from resinous to solid at room temperature. Solid residues are termed *asphalts* and can be somewhat liquefied with heating. The term *asphalt* is also used to describe the solid residue created in a geologic deposition during the formation of petroleum. The collective mass of organic matter represented by the petroleum and asphalt in a geologic deposit is referred to as *bitumen*.

Commercially desirable fractions of petroleum are nearly pure mixtures of hydrocarbons and contain little sulfur, nitrogen, and oxygen. Sulfur and nitrogen are undesirable because their combustion generates nitric and sulfuric acid, both of which contribute to acid rain. As shown in Table 26.1, all of the petroleum fractions have a much higher hydrogen content than coal. (Coal is a highly combustible rock containing more than 50% by weight organic material of biogenic origin.) This difference reflects the chemical composition of their source materials. As discussed further in the next section, the source matter for petroleum is marine and aquatic organic matter, whereas coal is generated from the remains of terrestrial plants. These source materials can be identified from unique molecular biomarkers preserved in petroleum and coal. As with petroleum, the most desirable coals are the ones with the lowest nitrogen and sulfur contents. These levels are highly dependent on the depositional history and cooking conditions and, hence, vary from deposit to deposit.

26.3 **CARBON SOURCES AND BIOMARKERS**

About 10 to 20% of petroleum is composed of hydrocarbons either synthesized by organisms or generated from biogenic organic matter during diagenesis. The rest is formed via the catagenesis and metagenesis of the residual biogenic organic matter. (A minor amount may have formed abiogenically from CO_2 or methane). Thus, living

organisms are the ultimate source of petroleum (and coal). Since plants produce most of the biomass, they are the largest source of organic matter to the soils and sediment. Their biomolecules are predominantly proteins, carbohydrates, and lipids. Although the kinds of organisms present on Earth have evolved over time, the fundamental metabolic pathways appear to have been rather constant, making the modern-day biomolecules similar to those that gave rise to petroleum and coal.

As shown in Table 26.2, the biomolecules with the highest degree of chemical similarity to petroleum are the lipids. They have a high hydrogen content and are low in sulfur, nitrogen, and oxygen. The lipid content of representative marine and terrestrial biota is shown in Table 26.3. As compared to terrestrial vascular plants, marine plankton have high lipid contents. Another striking difference is the high percentage of lignin in terrestrial plants, which is absent in marine plankton. Because lignins have low hydrogen contents, they generate coal, whereas organic matter derived from aquatic or marine plankton yields gas and oil. As discussed in Chapter 23.6.6, vascular plants use lignin and cellulose as structural materials. These biomolecules are relatively stable and, hence, are well preserved in soils and sediment.

Petroleum deposits typically contains hundreds of compounds that can serve as biomarkers. Some examples are shown in Table 26.4. Although the biomarkers collectively compose a small mass fraction of the petroleum hydrocarbons, they provide information on the source of the organic matter in the deposit, its depositional environment, and its cooking and migration histories. For example, odd-numbered short-chain (C_{15} to C_{21}) paraffins are characteristic of marine organisms, whereas land plants tend to generate longer odd-numbered chains (C_{25} to C_{37}). The longer chains tend to be waxes. These compounds help land plants control water loss from their leaves and provide protection from mechanical and parasite damage. The shorter chains are generally liquids (fats) and are used by marine organisms for energy storage, insulation, and buoyancy. Plants tend to generate hydrocarbons with odd numbers of carbons, whereas bacteria and higher organisms do not exhibit this selectivity. Another

Table 26.2 Average Chemical Composition of Biochemicals as Compared to Petroleum.

	Elemental Composition in Weight Percent				
	C	H	S	N	O
Carbohydrates	44	6			50
Lignin	63	5	0.1	0.3	31.6
Proteins	53	7	1	17	22
Lipids	76	12			12
Petroleum	85	13	1	0.5	0.5

Source: *From Hunt, J. M. (1996).* Petroleum Geochemistry and Geology, *2nd edition. W. H. Freeman and Co., New York, p. 63.*

Table 26.3 Elemental Composition of Living Matter.

Substance	Weight Precent of Major Constituents			
	Proteins	**Carbohydrates**	**Lipids**	**Lignin**
Plants				
Spruce wood	1	66	4	29
Oak leaves	6	52	5	37
Scots-pine needles	8	47	28	17
Phytoplankton	23	66	11	0
Diatoms	29	63	8	0
Lycopodium spores	8	42	50	0
Animals				
Zooplankton (mixed)	60	22	18	0
Copepods	65	25	10	0
Oysters	55	33	12	0
Higher invertebrates	70	20	10	0

Note: *Dry ash-free basis. There is great variability for different species of each organism. For example, Blumer et al. (1964) reported* Calanus *copepods to contain 27 to 57% lipids. Lipid variability is partly due to the nutrient availability and health of the organisms. If the food supply is limited or there is crowding during growth, the organism will increase its lipids. For example,* Chlorella *grown in a favorable environment contains 20% lipids, but in an unfavorable environment, 60% lipids (Blumer, M., M. M. Mullin, and D. W. Thomas. (1964). Pristane in the marine environment.* Helgolander Wissenschaftliche Meeresuntersuchungen *10: 187–200). Source*: *From Hunt, J. M. (1996).* Petroleum Geochemistry and Geology, *2nd edition. W. H. Freeman and Co., New York, p. 64.*

readily identifiable set of biomarkers are the degradation products of chlorophyll. As illustrated in Figure 26.3, diagenesis acts to remove the phytyl side chain. Under anoxic conditions the phytyl side chain is released as phytane and under oxic conditions, as pristane. The central magnesium atom in the porphyrin ring is replaced by metals such as V, Ni, Fe, Cu, or Mn. These metals are present in high concentrations in the organic-rich sediments as they have high enrichment factors (EFs) in planktonic biomass (Table 11.5).

The most useful terpenoid biomarkers are the steroids, carotenoids, and hopanoids (Figures 22.19 and 22.8f). As described in Chapter 22.4.3, some steroids are unique metabolites, such as fucosterol (brown algae), dinosterol (dinoflagellates), sitosterol (higher plants), and stigmasterol (terrestrial plants). Steroids generate degradation products that reflect the redox conditions under which diagenesis took place. These degradation products are readily identifiable as stanols, sterenes, and steranes.

The most commonly used biomarkers are the hopanoids, with several hundred of these compounds having been isolated from bacteria and sediments. The hopanoids are highly resistant to degradation and, hence, are well preserved molecular fossils. This is also true for the six-ring terpenoid, gammacerane (Figure 22.19c), which is thought to be synthesized by cyanobacteria and protozoans. Even the sulfur content of the organic matter is diagnostic of diagenetic redox conditions as reduction of the carbon-carbon double bonds in olefins by reaction with H_2S produces unique and stable products.

Table 26.4 Biological Markers as Source and Paleoenvironmental Indicators.

Biomarker	C Range	Indication
n-Alkanes		
CPI>5	C_9–C_{21}	Marine, lacustrine algal source, C_{15}, C_{17}, C_{19} dominant
	C_{25}–C_{37}	Terrestrial plant wax source, C_{27}, C_{29}, C_{31} dominant
CPI<1	C_{12}–C_{24}	Bacterial source: oxic, anoxic, marine, lacustrine
	C_{20}–C_{32}	Saline, anoxic environment: carbonates, evaporites
Acyclic isoprenoids		
Head to tail		
Pristane	C_{19}	Chlorophyll, α-tocopherol, oxic, suboxic environments
Phytane	C_{20}	Chlorophyll, phytanylethers of methanogens, anoxic, saline
Head to head	C_{25}, C_{30}, C_{40}	Archaebacteria, bacterial cell-wall lipids
Botrycoccane	C_{34}	Lacustrine, brackish
Sesquiterpenoids		
Cadalene, eudesmane	C_{15}	Terrestrial plants
Diterpenoids		
Abietane, pimarane, kaurane, retene	C_{19}, C_{20}	Higher plant resins
Tricyclic terpanes	C_{19}–C_{45}	Diagenetic products of bacterial and algal cell-wall lipids
Tetracyclic terpanes	C_{24}–C_{27}	Degradation of pentacyclic triterpenoids
Hopanes	C_{27}–C_{40}	Bacteria
Norhopanes	C_{27}–C_{28}	Anoxic marine
2- and 3-methylhopanes	C_{28}–C_{36}	Carbonate rocks
Benzohopanoids	C_{32}–C_{35}	Carbonate environments
Hexahydrobenzohopenoids	C_{32}–C_{35}	Anoxic, carbonate-anhydrite
Gammacerane	C_{30}	Hypersaline environments
Oleananes, lupanes	C_{30}	Late Cretaceous and Tertiary flowering plants
Bicadinane	C_{30}	Gymnosperm tree resins
β-Carotane	C_{40}	Arid, hypersaline

(Continued)

Table 26.4 *(Continued)*

Biomarker	C Range	Indication
Steranes	C_{19}–C_{23}	Eukaryote organisms, plants, and animals
	C_{26}–C_{30}	
24-*n*-Propylsterane	C_{30}	Restricted to marine sediments
4-Methylsteranes	C_{28}–C_{30}	Marine and lacustrine dinoflagellates
Dinosteranes	C_{30}	Marine, Triassic or younger

Source: *From Hunt, J. M. (1996).* Petroleum Geochemistry and Geology, *2nd edition. W. H. Freeman and Co., New York, p. 107.*
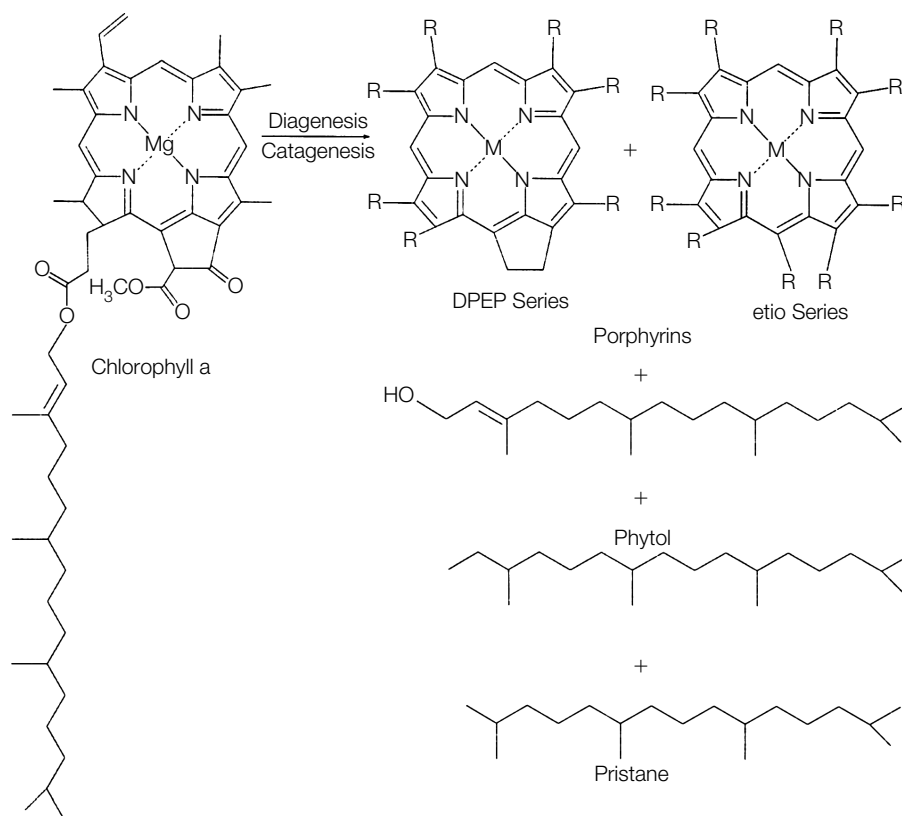

FIGURE 26.3

Early diagenesis of chlorophyll. Loss of the phytyl side chain can occur prior to or after the removal of the central magnesium atom. R = H or an alkyl group, M = V, Ni, Fe, Cu or Mn. *Source*: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition. W. H. Freeman and Co., New York, p. 81.

Unfortunately these catagenetic sulfurization reactions are very pervasive and lead to the formation of "dirty" petroleum and coal.

26.4 **DEPOSITIONAL ENVIRONMENT**

The formation of petroleum from marine organic matter first requires creation of a source bed. Productive source beds have high organic carbon contents and are enriched in compounds with high H/C ratios, such as lipids. Productive source beds were created in environments that supported the accumulation and burial of large quantities of organic-rich sediments. This required high plankton productivity in the surface waters with most of the organic matter being generated by diatoms, dinoflagellates, and coccolithophorids. Accumulation in the sediments was highest where water depths were shallow, bottom-water O_2 concentrations were low, and burial rates were high. The shallow water depths ensure a quick trip to the seafloor, reducing the likelihood that the sinking detrital POM will be consumed or remineralized. When bottom-water O_2 concentrations are low, benthic microbes are less effective at completely oxidizing sedimentary organic carbon to CO_2. This is also promoted by rapid burial, which isolates the sedimentary organic matter from the bottom waters and the bioturbating benthos. To ensure a high organic content, high burial rates had to be a consequence of the rapid accumulation of organic-rich sediment. Even under the most favorable conditions, most of the POM created in the surface waters is remineralized prior to burial. Thus, even the most organic-rich marine sediments have preserved only a small fraction of the overlying production.

The organic carbon content of source beds that have generated large petroleum deposits ranges from 0.5 to 5%, with a mean of 1.5%. Conditions promoting this high a level of organic carbon are generally found in coastal waters beneath upwelling zones or within marginal seas and fjords where sills restrict circulation and lead to permanent or semipermanent anoxia. For example, the organic content of Black Sea sediments is greater than 15%, whereas sediments located in suboxic environments are typically 1 to 3% OC. Modern coastal upwelling areas with high deposition rates of organic matter are located in Walvis Bay and along coastal Peru. At these locations, a permanent O_2 minimum zone (OMZ) is present and extends to the seafloor (Figure 8.4). During interglacials and periods of fast seafloor spreading, rising sea level causes the OMZ to migrate landward, spreading low-O_2 conditions over a wide expanse of continental shelf (Figure 26.4). Thus, periods of transgression have served to promote the formation of large petroleum depositions.

Most of the economically useful petroleum deposits were deposited during the Phanerozoic. This is thought to reflect the lower rate of organic carbon production and burial in the earlier eons. Another problem is that excessive time after burial can lead to loss of petroleum through "overcooking," which eventually converts the carbon to CO_2 and graphite. As a side note, the depositional environments that led to coal formation were the coastal swamps located near areas of high vascular vegetation. The
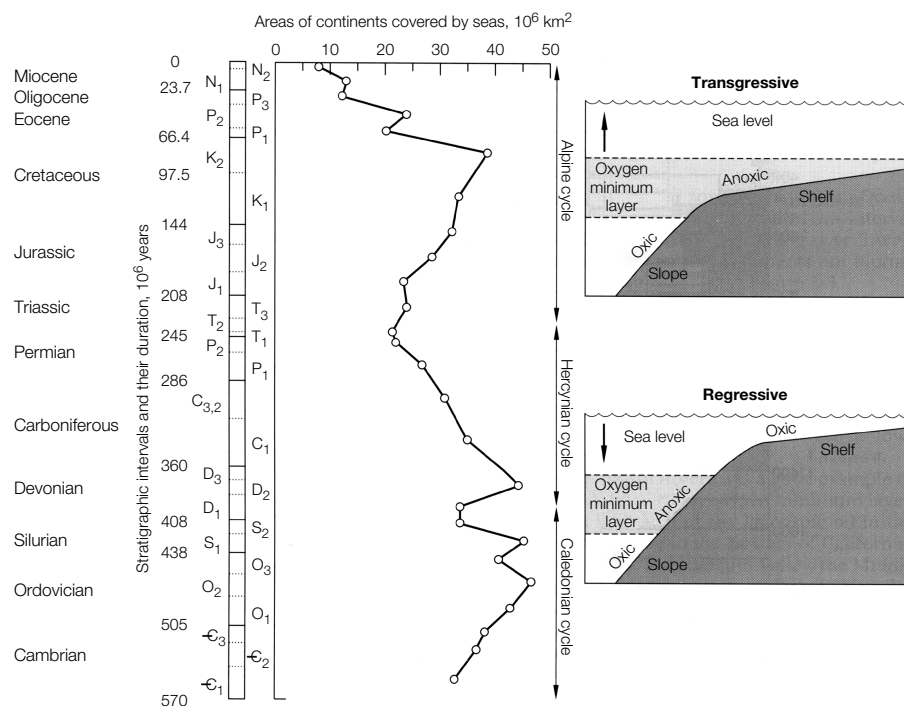
FIGURE 26.4

Transgressions and regressions of the seas on the continents during the Phanerozoic. Also shown are areas of slope and shelf covered by an OMZ during transgressive and regressive cycles.
Source: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition, W. H. Freeman and Co., New York, p. 122.

rate of organic matter input was large enough to create anoxic conditions that supported formation of peat beds. After burial, the peats were transformed, via diagenesis, catagenesis, and metagenesis, into coal. At least some coal deposits were formed as a result of coastal forests that were "drowned" during periods of rising sea level.

26.5 **DIAGENESIS**

Maturation is the process by which biomolecules are converted into petroleum. As illustrated in Figure 26.5, this occurs over tens of millions of years as sediments first undergo diagenesis, followed by catagenesis. During this cooking process, the original organic compounds are transformed into a far more complex mixture of hydrocarbons and asphaltics. Diagenesis is defined as the chemical reactions that occur in the first few thousand years after burial at temperatures less than 50°C. As previously described in Chapter 12, most diagenetic reactions involving organic matter are mediated by
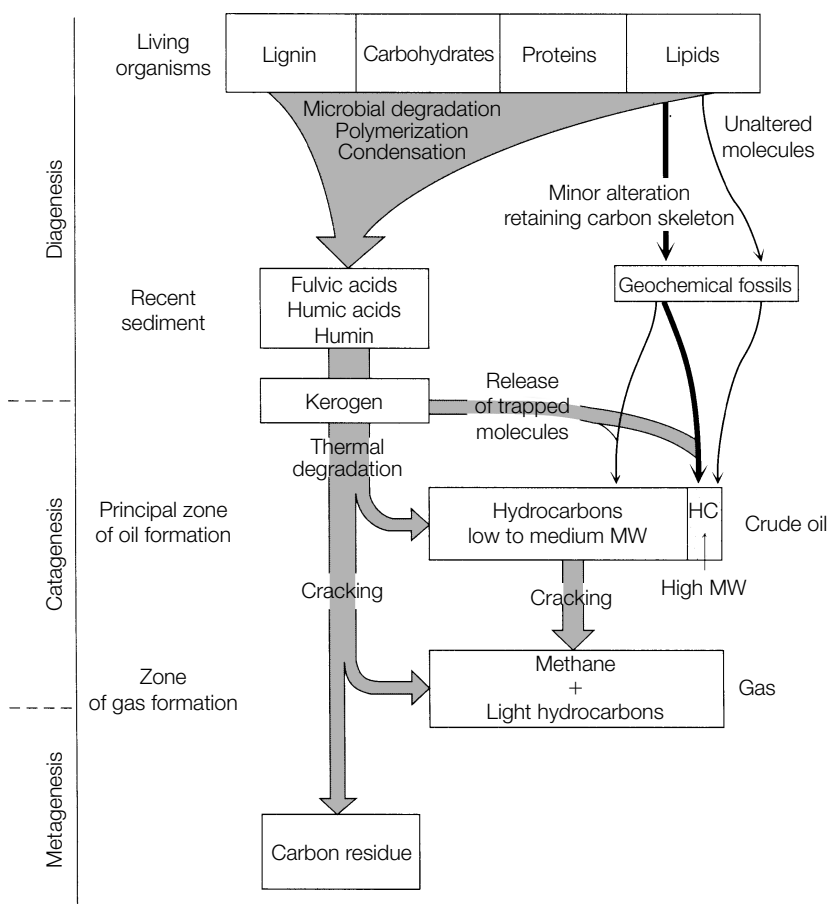
FIGURE 26.5

The petroleum maturation process. *Source*: From Tissot, B. P., and D. H. Welte (1978). *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, Springer-Verlag, p. 93.

microbes. Under anoxic conditions, which should have prevailed in the organic-rich sediments, the dominant diagenetic reactions are denitrification (including the annamox pathway), sulfate reduction, and methanogenesis.

During diagenesis, oxygen is removed from the organic matter as water, nitrogen as N_2, and sulfur as H_2S. In removing O, N, and S, the hydrogen content of the sedimentary organic matter is increased. If iron is present in the deposit, the H_2S leads to precipitation of pyrite. Long-term burial converts these iron sulfides into oolitic ironstones, which are common in shales. This mode of sulfur removal enhances the economic worth of the petroleum as otherwise H_2S, or *sour gas*, would remain in the deposit. Methanogenesis produces biogenic methane, which is termed *dry gas*.

As the anaerobic metabolisms proceed, biopolymers are degraded into biomonomers. Some of these biomonomers are preserved along with resistant low-molecular-weight biomolecules. Some undergo further reactions. For example, free-radical reactions transform some paraffins into isoparaffins. Some of the biomonomers polymerize into complex high-molecular-weight compounds called *geopolymers*. Still others undergo vulcanization reactions in which sulfur atoms are incorporated into the hydrocarbon structures, creating sulfur-rich macromolecules that are extremely resistant to further degradation. The resulting mixture of biopolymers, biomonomers, and geopolymers is called *kerogen*. If marine or aquatic organic matter is the source material, the resulting kerogen is termed a *sapropel*. If the source materials is from terrestrial plants, a humic-type kerogen is formed. Because of differences in the chemical composition of their molecular sources, the sapropelic kerogens tend to be have a higher hydrogen content than the humic kerogens.

Some classes of compounds are not substantially altered during diagenesis and, thus, serve as molecular fossils. Other biomarkers are generated during the diagenetic reactions. These include the degradation products of chlorophyll (Figure 26.3) and hopanoids with shorter side chains than their microbial precursors.

26.6 **CATAGENESIS AND METAGENESIS**

As time passes, surface sediments which have undergone diagenesis become more deeply buried due to the continuing accumulation of particles on the seafloor (Figure 12.6). The deeply buried sediments undergo abiotic chemical reactions that take place at elevated temperatures and pressures. The reactions that occur between 60 and 200°C are considered to be catagenetic in nature. Metagenesis takes place at temperatures over 200°C and is considered to be a type of very low-grade metamorphism.

Sediment temperatures increase with depth below the seafloor due to compaction as the resulting friction is dissipated in the form of heat. Some of the geothermal heat is supplied via conduction from Earth's core of heat generated by nuclear reactions. Compaction also compresses the deposit, transforming it into a sedimentary rock. Most kerogen-bearing deposits also contain clay and are transformed into sedimentary rocks called black shales.

In marine sediments, the geothermal gradient is on the order of 15 to 50°C/km (Figure 25.3). Thus, temperatures exceeding 60°C are attained at depths ranging from 1 to 4 km. Cooking at temperatures from 60 to 150°C transforms kerogen into bitumen (petroleum + asphalt). Because shale is porous, the bitumen is found dispersed in the rock and as interbedded layers. As shown in Figure 26.6, oil production occurs at burial depths of 3 to 5 km. Further burial exposes the bitumen to temperatures greater than 200°C, which favors the conversion of organic carbon into CO_2 and graphite.

During catagenesis, the organic compounds undergo a variety of thermal degradation reactions including: (1) reduction of double bonds by incorporation of hydrogen or sulfur atoms, (2) cracking reactions, and (3) condensation reactions. The net effect of
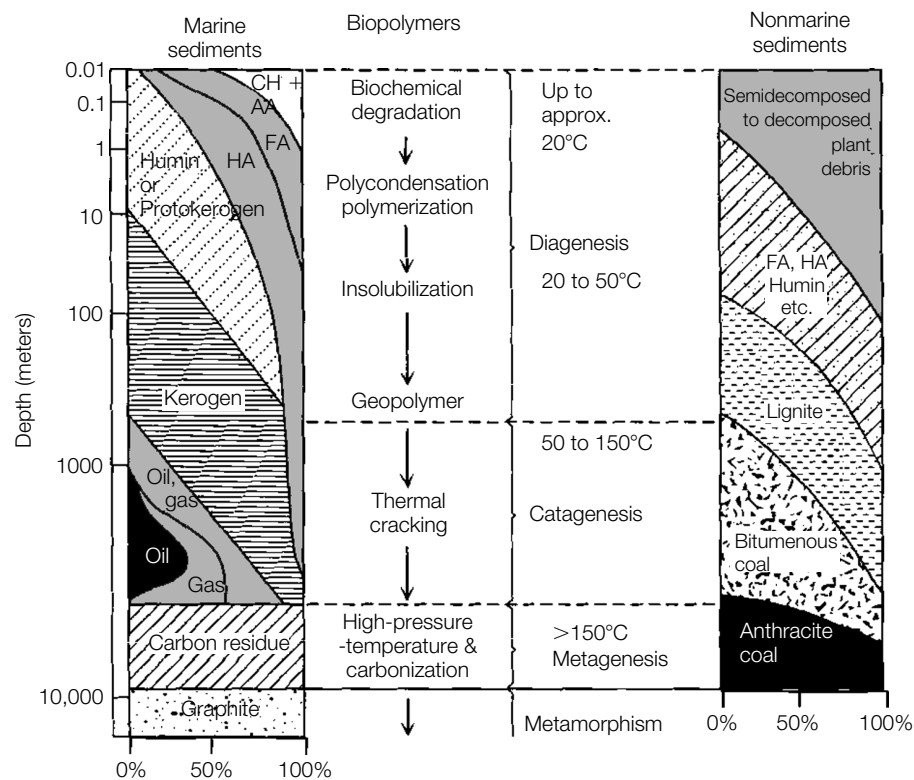
FIGURE 26.6

A general outline of the changes that occur in organic matter during diagenesis, catagenesis, and metamorphism. The relative abundances of the various forms of organic matter are shown on the *x*-axis. CH, chlorophyll; AA, amino acids; FA, fulvic acids; HA, humic acids. *Source*: After Tissot, B. P. and D. H. Welte (1978). *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, 2nd ed. Springer-Verlag, Heidelberg, Germany, p. 70.

these reactions is a kind of disproportionation during which the hydrogen content of the forming petroleum is increased at the expense of the residual kerogen. As shown in Figure 26.7, this causes the elemental H/C ratio of kerogen to decrease with increasing degree of maturation.

Examples of the chemical reactions that take place during maturation are provided in Figure 26.8. These include *cracking reactions* in which short-chain hydrocarbons are broken off larger parent molecules. In the example shown in Figure 26.8a, two types of hydrocarbons are generated, one that is saturated and the other that is unsaturated. Another example of a disproportionation reaction is shown in Figure 26.8b in which the H atoms needed to create saturated hydrocarbons via cracking reactions are supplied by the parent kerogen. Removing H atoms from the kerogen causes it to undergo condensation reactions in which rings are formed. Further removal of H atoms requires the rings to aromatize. This causes the elemental H/C ratio of the kerogen to decline as maturation
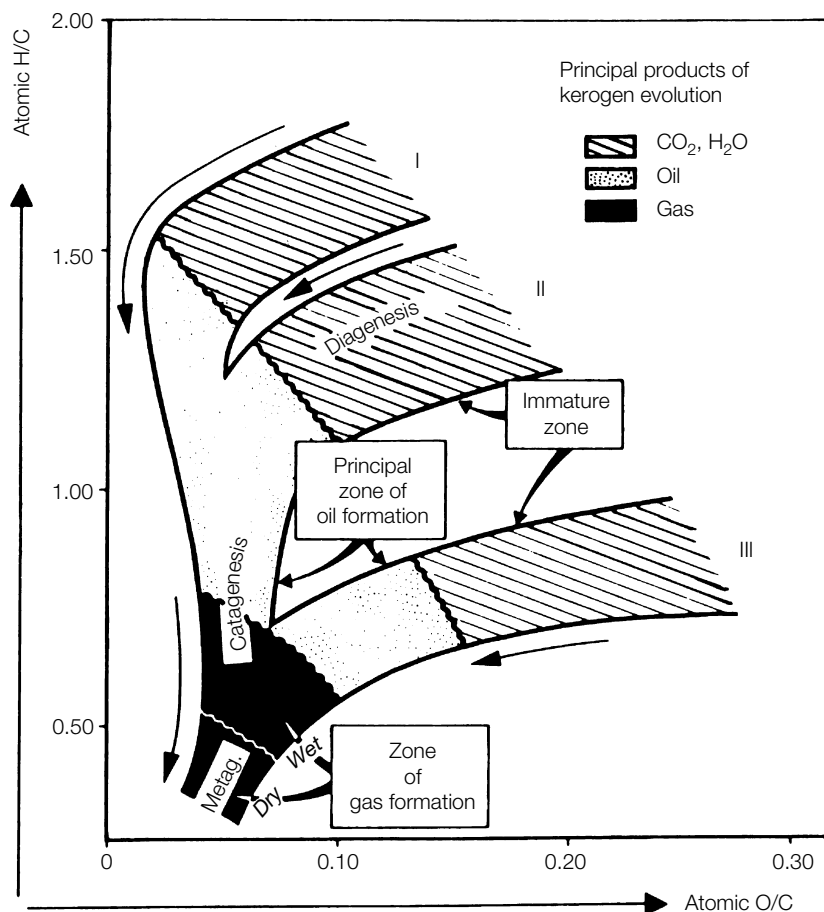
FIGURE 26.7

General scheme of kerogen evolution as depicted by a van Krevelen diagram. Three types of kerogen are shown with type I being marine in origin. *Source*: From Tissot, B. P., and D. H. Welte (1984). *Petroleum Formation and Occurrence*: *A New Approach to Oil and Gas Exploration*, 2nd ed. Springer-Verlag, Heidelberg, Germany, p. 216.

proceeds as does the chain length of the saturated hydrocarbons. Other transformations characteristic of catagenesis include loss of the odd carbon predominance in the paraffins and loss of the isoparaffins. These trends are illustrated in Figure 26.9.

At least some of the H atoms required for the formation of petroleum hydrocarbons are supplied by water. The leftover oxygen atoms contribute to evolution of CO_2 (Figure 26.10). The maturation reactions are also likely catalyzed by various minerals, such as the clays and ironstones. Limestone is thought to play an important role in maturation reactions because it can react with CO_2 and hence shift the position of equilibrium reactions in favor of production of additional petroleum hydrocarbons. Other
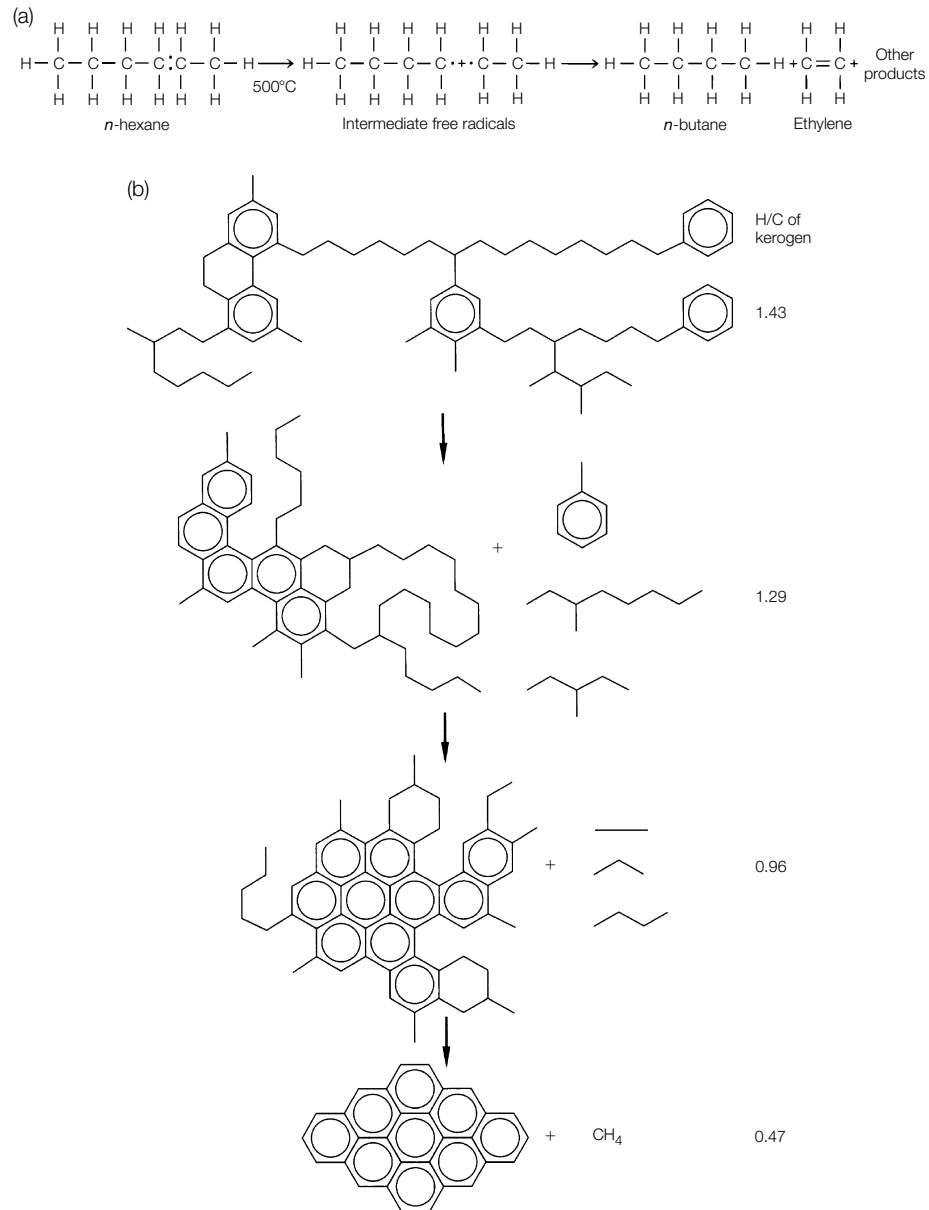
FIGURE 26.8

Mechanisms of cracking reactions in (a) paraffins and (b) kerogen. *Source*: After Rashid, M. A. (1985). *Geochemistry of Marine Humic Compounds*, Springer-Verlag, Heidelberg, Germany, p. 206. Reprinted by permission; and Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition, W. H. Freeman and Co., New York, p. 208.
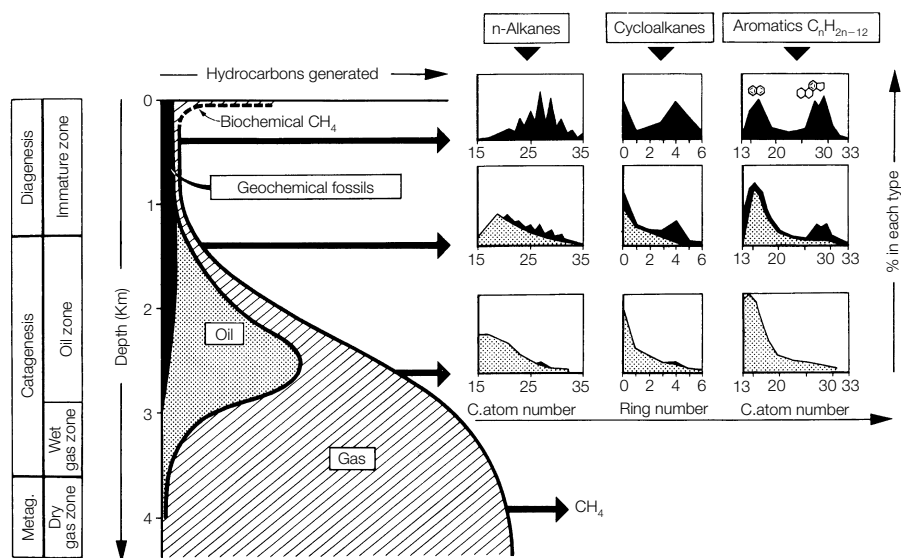
FIGURE 26.9

Relative quantities of hydrocarbons produced in fine-grained sediments. The areas under the curves are proportional to masses as carbon. Depths are only indicative and may vary according to the actual geological situation. Wet gas is comprised of ethane, butane, and propane. *Source*: From Tissot, B. P., and D. H. Welte (1984). *Petroleum Formation and Occurrence*: *A New Approach to Oil and Gas Exploration*, 2nd ed. Springer-Verlag, p. 215.

likely maturation reactions involve the oxidation of petroleum hydrocarbons by the reduced trace metals found in abundance in the organic-rich deposits.

The types of hydrocarbons generated during maturation are dependent on the chemical composition of the source biomolecules and the cooking conditions. Figure 26.6 illustrates that catagenesis of sapropelic kerogens generates oil, whereas humic kerogens are converted into coal. Both kerogens produce gas but differ in their yields and chemical composition. As shown in Figure 26.10, humic kerogens produce more carbon dioxide because their carbon source (terrestrial organic matter) is more oxidized than marine organic matter. The sapropelic kerogens generate more abiotic methane (dry gas). Note that biogenic methane is produced from both sources during diagenesis, but at much lower yields than that generated during catagenesis. Marine sapropels tend to generate more H_2S because seawater contains a large supply of sulfate, enabling sedimentary sulfate reduction.

Cooking conditions also determine the chemical composition of the maturation products. Slow burial with low geothermal gradients generates a different suite of petroleum hydrocarbons than does fast burial with high gradients. The time scales involved are on the order of tens of millions of years. Burial to the 1-km depth threshold required to initiate catagenesis takes 10 million y assuming sedimentation rates characteristic of marginal seas (10 cm per 1000 y). As shown in Figure 26.11, the maturation process
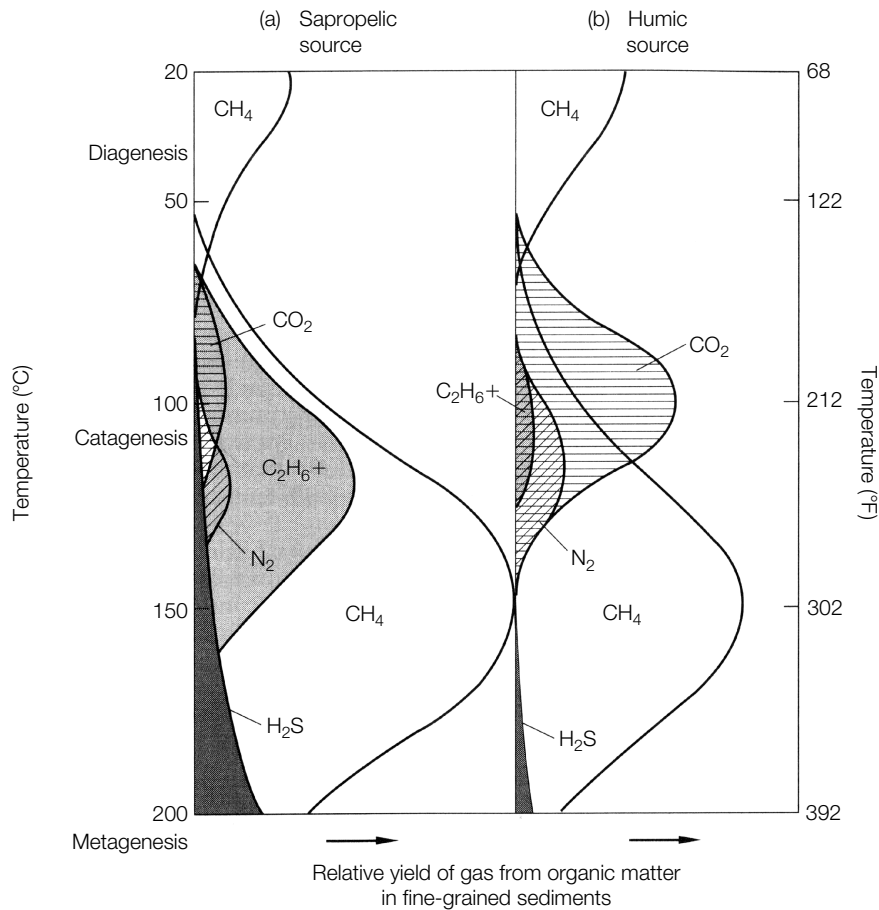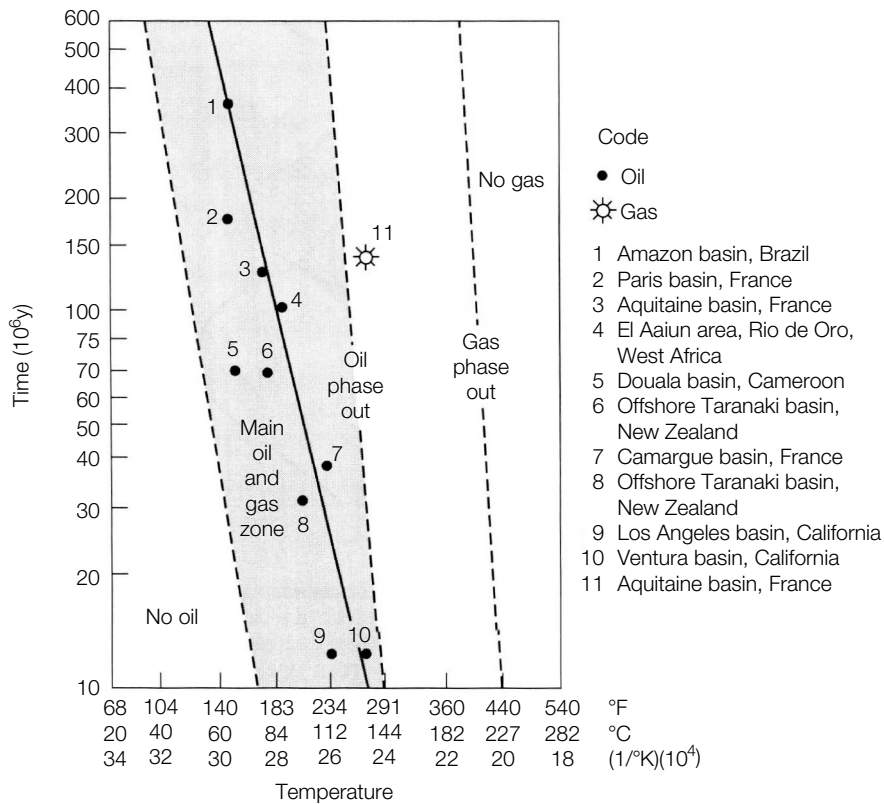
FIGURE 26.10

Relative gas yields from organic matter buried in fine-grained sediments as a function of temperature: (a) Sapropelic source and (b) humic source. The $C_2H_6^+$ represents hydrocarbon gases heaver than methane and is collectively referred to as "wet gas." From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition, W. H. Freeman and Co., New York, p. 187.

can take anywhere from 10 to several hundred million years. Exceptions to this include petroleum hydrocarbons generated in relatively recent sediments as a result of heating near active plate boundaries, such as in the Besshi deposits found in the Guaymas Basin. These deposits tend to have high levels of PAHs and sulfur.

Figure 26.11 shows that the time required for oil and gas production is shorter at higher temperatures. This effect is due to faster reaction rates. There is an upper limit to this enhancement as very high temperatures and pressures favor the conversion of organic carbon into carbon dioxide, methane, and graphite. Thus, deposits that have been subjected to metagenesis and metamorphism for extended periods are unlikely

FIGURE 26.11

Time-temperature dependence of petroleum genesis. *Source*: From Connan, J. (1974).
Time-temperature relation in oil genesis, *American Association of Petroleum Geologists Bulletin*, 58,
2516–2521, Figure 3, p. 25.

to have significant amounts of petroleum hydrocarbons. Even at lower temperatures
and pressures, petroleum production will eventually cease as the source bed becomes
depleted in labile organic carbon. Petroleum deposits can also be degraded by exposure
to surface water and O_2. This can happen if fracturing of the source rock permits infil-
tration of oxygenated water from above. The degradation process is biotic and involves
the oxidation of hydrocarbons by aerobic and anaerobic microbes. Thus the formation
of large petroleum deposits requires an intact, isolated source bed.

26.7 GAS HYDRATES

As in described in Chapter 25.1.1, methane can accumulate in marine sediments in the
form of gas hydrates. Some of this methane is biotic in origin, arising from diagenesis,

and some is abiotic, being produced during catagenesis, and metagenesis. Other gas hydrates form from CO_2, H_2S, ethane, propane, and isobutane.

The gas hydrates are crystalline solids in which the ice structure of water is distorted to form cages that contain the gas molecules. In the methane hydrates, each gas molecule is generally surrounded by six to seven water molecules. Hydrates form at sufficiently high pressures in the sediment if temperatures are less than $20°C$. The depth range within the sediments over which hydrates are stable depends on the length of the water column, the temperature gradient in the sediment, and the pore-water salinity (Figure 25.3). For example, at $0°C$ methane hydrates are stable at total depths (water column + sediment) greater than 300 m. At $20°C$, total depths must exceed 2000 m. In the sediments, the geothermal heat gradient causes the $20°C$ threshold to be exceeded 500 m below the seafloor, so methane hydrates are limited to the top 500 m of the sediment. At depths in the sediment below the zone of methane hydrate stability, the gases are present in free form. The other gases (CO_2, H_2S, ethane, propane, and isobutane) form hydrates at lower pressures and, hence, shallower depths than methane, but their abundances are much lower than that of methane.

The typical methane hydrate contains $40\,m^3$ of CH_4 (STP) per m^3 of deposit with values as high as 160 being reported. Thus, methane hydrates may collectively represent the largest remaining petroleum resource. The locations of these gas hydrate deposits are shown in Figure 26.12. Efforts are now underway to develop the technology for mining this deposits. As noted in Chapter 25.5.5, warming of marine sediments and the permafrost in the arctic tundra could lead to the decomposition of the hydrates and release of methane into the oceans and atmosphere. This could cause a positive feedback increasing global warming. This feedback is thought to have played a role in past global warming events during the Phanerozoic eon.

26.8 MIGRATION INTO A RESERVOIR

During diagenesis and catagenesis, compaction lithifies the source bed into a source rock, usually an organic-rich shale or limestone. The production of petroleum increases pressure within the rock because oils and gas are less dense than solids and, hence, take up more volume. The overpressure fractures the source bed, enabling *migration* of the gas and oil into adjacent permeable rocks. Most fractures are 1 to 3 mm in diameter. Migration occurs vertically and laterally through the fractures and faults until an impermeable barrier is reached. Migration can also take place through the pore spaces in the sedimentary rocks. But this involves only small hydrocarbons (fewer than 26 carbon atoms), because the pores are generally less than 10 nm in diameter.

Migration acts to separate the petroleum from its asphalt, making this process critical to the formation of economically attractive deposits of oil and gas. Migration occurs in two stages. Primary migration takes place within the source rock following its pressure fracturing. Thus, an important requirement for a productive source rock is that it be easily fractured. During primary migration, the gas and oil travel together as a single liquid phase due to the high pressures (generally greater than 270 atm) in the source rock.
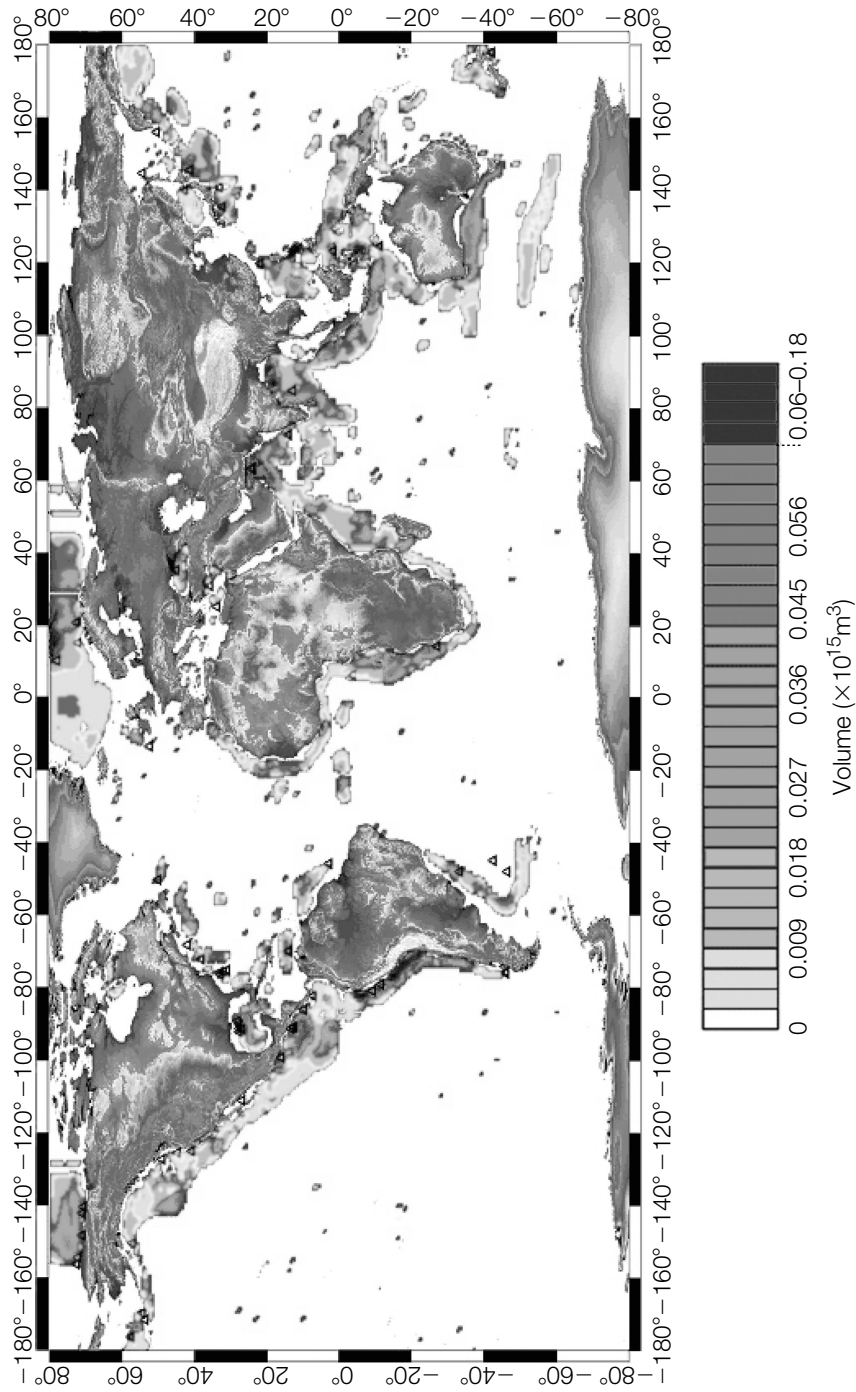
FIGURE 26.12

Predicted distribution of methane hydrates in marine sediments. The total mass of methane hydrates is estimated as 7.44×10^4 Gt. (This is an order of magnitude higher than the estimate in Figure 25.1.) *Source*: After Klauda, J. B., and S. I. Sandler (2005). Global distribution of methane hydrate in ocean sediment. *Energy & Fuels* 19, 459–470. (See companion website for color version.)

Expulsion from the source rock probably occurs in pulses in which continuing generation of petroleum creates enough pressure to reopen fractures and pores. After the pressure is released by migration, the fractures and pores close. Once the petroleum migrates out of the source rock, pressures decline, especially if the migration is vertical. The movement of petroleum outside of the source rock and into a *reservoir bed* is termed *secondary migration.* Siltstones, sandstones, fractured shales, limestones, chalks, dolomites, and fractured or weathered igneous and metamorphic rocks make good reservoir beds because of their high porosity.

During secondary migration, the gas and oil separate with the gas traveling out ahead of the oil. Rates are on the order of centimeters per year. Lateral migration can occur over hundred of miles and vertical migration over thousands of kilometers. The largest petroleum deposits are the result of lateral migration because this provides drainage from a larger volume of source rock than does vertical migration. Migration pathways can change over time as chemical reactions, such as pressure solution, recrystallization, and cementation, can alter permeability.

If migration continues, the oil and gas will become highly dispersed, producing deposits of little economic value. Most petroleum is present in such a dispersed state (although economic value is a moving target determined in part by market demand). If the migrating petroleum encounters a relatively impermeable barrier, further movement is inhibited. The oil and gas pool behind this barrier, forming a concentrated deposit. The part of the reservoir bed where the petroleum pools is called a *trap*. Petroleum migrates laterally into *stratigraphic traps* and vertically into *structural traps*. Examples are illustrated in Figure 26.13.

In most cases, differences in permeability between adjacent stratigraphic layers inhibit migration. This causes petroleum to flow within geologic units. For petroleum to accumulate in a trap, it must encounter a *cap rock* or *seal*. Gas hydrates make the best seals due to their low permeability. Evaporites are second best. They are found in deeply buried sediments as vertical pillars called *diapirs*. These salt pillars form because halite is more easily deformed by overlying pressure than other sedimentary rocks. Thus, the salt pillars flow through fractures and faults much like toothpaste squeezed out of its tube. Though not all diapirs have associated petroleum deposits, their frequent co-occurrence reflects similar depositional environments, i.e., shallow-water basins with restricted circulation.

As the oil undergoes primary and secondary migration, it can continue maturing. If it travels into shallow enough sediments, temperatures will be low enough ($<80°C$) to permit microbial degradation to take place. This is commonly seen in foreland basins, such as the Atlantic margin basins of Africa, South America, Canada, and the Gulf of Mexico. As the petroleum migrates upward, anaerobic bacteria preferentially degrade the low-molecular-weight hydrocarbons, leaving behind heavy oils. These oils pool in sandstones to form tar sands (Figure 26.14). They represent the largest reservoir of oil on the planet. The degradation is promoted by the presence of water and occurs over time scales of millions of years. Likely microbial reactions are anaerobic and include iron reduction, methanogenesis, and sulfate reduction. Because of these continuing biotic and abiotic reactions, as well as the ongoing physical separation process, each migratory
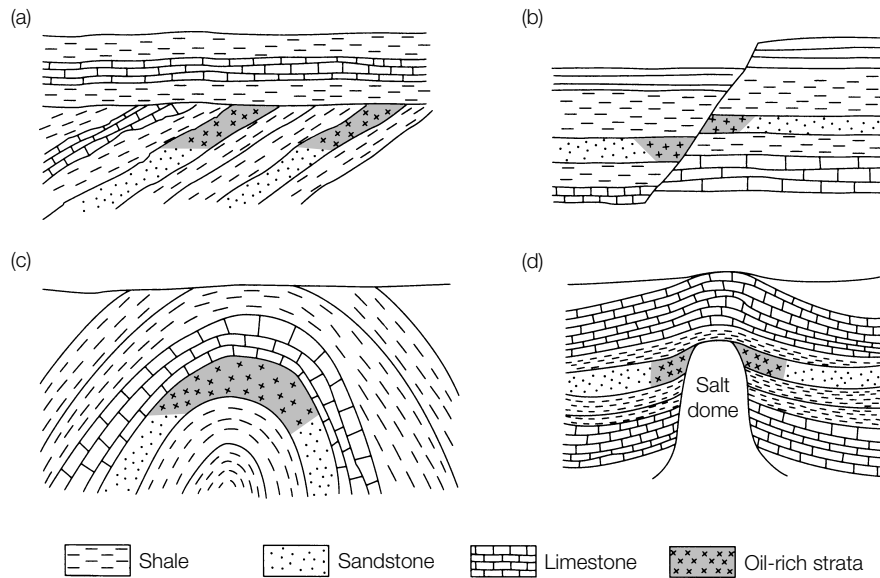
FIGURE 26.13

Different possible types of (a–c) stratigraphic and (d) structural oil traps. For simplicity, the reservoir beds are always indicated as sands. *Source*: From Ross, D. A. (1988). *Introduction to Oceanography*, 4th ed., Prentice Hall, Inc., Englewood Cliffs, NJ, p. 350.
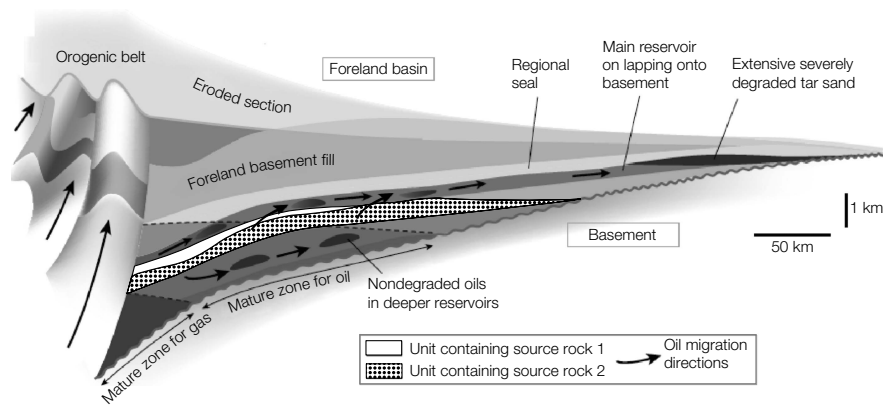
FIGURE 26.14

An idealized foreland basin petroleum system with source rocks in the platform sediments, a regionally extensive reservoir sandstone sequence and a regionally extensive seal. During migration into and through the reservoir beds, the oils biodegrade and tar sands accumulate. Continuing biodegradation and the lower temperatures in the shallower reservoirs increase the oil's viscosity, helping trap it. *Source*: From Head, I. M., D. Martin Jones, and S. R. Larter (2003). Biological activity in the deep subsurface and the origin of heavy oil. *Nature* 426, 344–352. (See companion website for color version.)

pathway creates a unique mixture of petroleum hydrocarbons as it moves along its flow path. The chemical composition of the mixtures can be used to trace the locations of the source bed and trap. This also explains why each petroleum deposit has a unique hydrocarbon "fingerprint" (Figure 22.4).

If the stratigraphic trap or cap rock is breached, usually as a result of tectonic activity, petroleum can leak out of the reservoir. Some of these leaks cause petroleum to seep onto the sea floor or out onto the land. Most reservoirs leak to some extent. This has proven useful as nearly all of the important oil-producing regions were discovered as surface seeps of oil or gas. As discussed in Section 28.6.6, once in the ocean or on land, some of the seeped petroleum evaporates and some undergoes chemical weathering. As much as 40% of the world's petroleum resources are estimated to have been lost to natural seeps.

26.9 **LOW-TEMPERATURE ORES**

Petroleum tends to have high concentrations of trace metals as shown in Figure 26.15. This is problematic when the petroleum is used as fuel because burning mobilizes
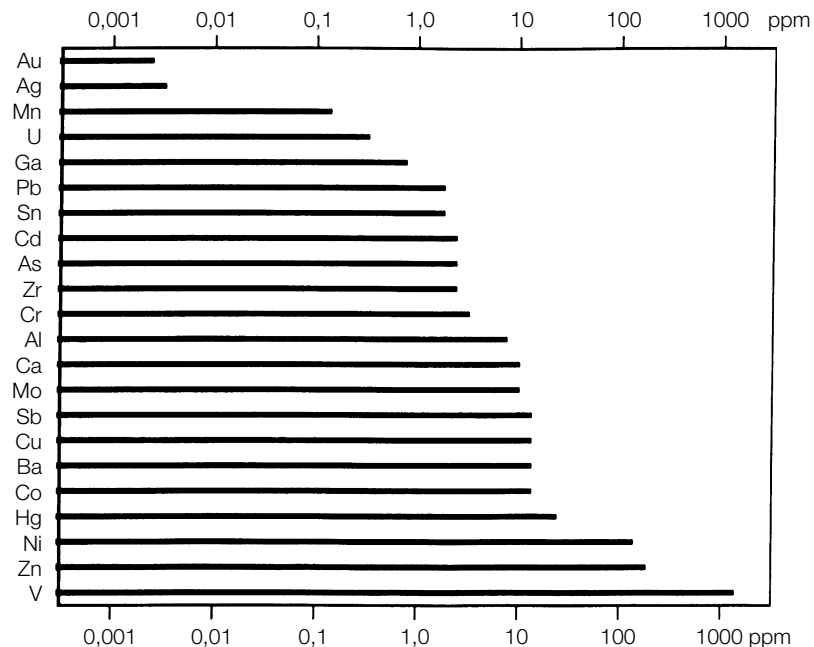
FIGURE 26.15

Maximum values reported for selected elements in petroleum. *Source*: From Jones, P. (1975). Trace metals and other elements in crude oil—a literature review. British Petroleum Co. Ltd, Sunbury, 40 pp.

the trace metals. On the other hand, the trace metal enrichments in petroleum enable the natural formation of metalliferous ore deposits. Low-temperature ores commonly associated with black shales include the sulfides [PbS (galena), ZnS (sphalerite), FeS (pyrite), $CuFeS_2$ (chalcopyrite) and NiS (millerite)], barite ($BaSO_4$), and fluorite (CaF_2). Some of these deposits represent economically important sources of metals.

These metalliferous ores seem to form through a set of processes similar to that of petroleum: (1) the trace metals are mobilized from a source deposit, (2) migration transports them to a suitable reservoir, and (3) precipitation generates a solid mineral phase. Petroleum and kerogen play several important roles in the formation of these ore bodies. First, their organic matter represents a source of metals due to natural enrichment by plankton. Second, metals delivered to the sediments in their oxidized particulate forms are converted to soluble species under the reducing conditions created during diagenesis of the organic matter. Third, the organic compounds in petroleum and kerogen are effective chelating agents. The metals that bind with the liquid petroleum can then be transported via migration. The interactions between organic matter and trace metals that lead to the formation of low-temperature metal ores are illustrated in Figure 26.16.
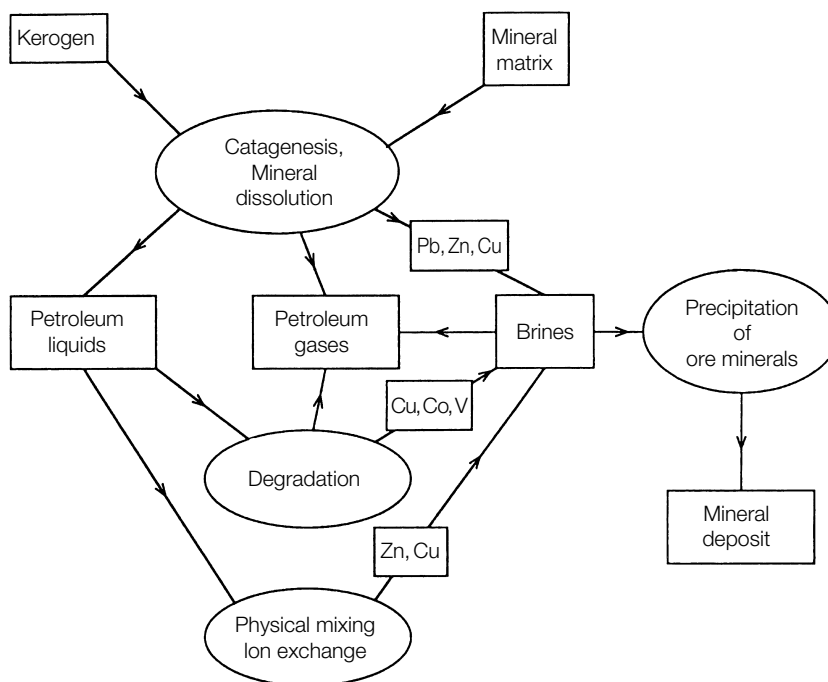

FIGURE 26.16

Geochemical pathways in which organic matter participates in the low-temperature formation of ore minerals. *Source*: From Gize, A. P., and D. A. C. Manning (1993). Aspects of the organic geochemistry and petrology of metalliferous ores. In *Organic Geochemistry: Principles and Applications*, M. H. Engel and S. A. Macko, eds, pp. 565–580, 561.

26.10 **PROSPECTING FOR MARINE PETROLEUM**

The lengthy set of requirements for the formation of large petroleum deposits is summarized in Table 26.5. As this list suggests, formation of petroleum is a pretty inefficient process as most of the organic matter is lost to remineralization, overcooking, dispersal, microbial degradation, or seepage. Thus, petroleum is a relatively small geological reservoir. The "giant" fields are rarer still, comprising only 1% of the total number of producing fields. The largest is the Ghawar Field in Saudi Arabia, which has an estimated recoverable oil reserve of 66 to 100 billion barrels of oil. Although rare, the giant fields contain about half of the known reserves. The proven reserves of oil and gas by country are shown in Table 26.6 along with an estimate of the total world reserves. The world oil demand is presently (2007) on the order of 85 million barrels per day. Assuming no growth in annual consumption, which is not very realistic, we will deplete the proven reservoirs within 43 years. Thus, considerable effort is being expended in locating and exploiting new large oil and gas fields.

Geochemists play an important role in petroleum prospecting because they are able to assess the depositional, maturation, and migration history of a potential field from geological, geophysical, and geochemical data. These assessments help identify the most likely sites of large petroleum deposits; thereby minimizing the amount of expensive exploratory well drilling required. Marine settings most likely to have large deposits are ancient silled marine basins of the right age and burial depth. Even with this specificity, petroleum prospecting is still a bit like searching for a needle in a haystack as 900 such sedimentary basins exist worldwide, of which 600 have the other required conditions for large petroleum deposits. Of these, 160 are presently commercially productive, 240 are partially explored, and the remaining 200 (mostly offshore) are as yet unexplored.

Table 26.5 Essential Requirements for Favorable Petroleum Prospects.

1. A sufficient source of the proper organic matter
2. Conditions favorable for the preservation of the organic matter—rapid burial or a reducing environment
3. An adequate blanket of sediments to produce the necessary temperatures for the conversion of the organic matter to fluid petroleum
4. Favorable conditions for the movement of the petroleum from the source rocks and the migration to porous and permeable reservoir rocks
5. Presence of accumulation traps, either structural or stratigraphic
6. Adequate cap rocks to prevent loss of petroleum fluids
7. Proper timing in the development of these essentials for accumulation and a postaccumulation history favorable for preservation

Source: *From Hedberg, H. D., J. D. Moody, and R. M. Hedberg (1979). Petroleum prospects of the deep offshore.* American Association of Petroleum Geologists Bulletin *63, 286–300, p. 288.*

Table 26.6 World's Proven Reserves of (a) Oil, (b) Natural Gas, and (c) Coal. Also shown are the national distributions of these reserves.

(a) OIL

Rank	Country	Proven Reserves (bbl oil)	%
NA	World	1,349,000,000,000	NA
1	Saudi Arabia	262,700,000,000	19%
2	Canada	178,900,000,000	13%
3	Iran	133,300,000,000	10%
4	Iraq	112,500,000,000	8%
5	United Arab Emirates	97,800,000,000	7%
6	Kuwait	96,500,000,000	7%
7	Venezuela	75,590,000,000	6%
8	Russia	69,000,000,000	5%
9	Libya	40,000,000,000	3%
10	Nigeria	36,000,000,000	3%
11	Mexico	33,310,000,000	2%
12	Kazakhstan	26,000,000,000	2%
13	Angola	25,000,000,000	2%
14	United States	22,450,000,000	2%
15	China	18,260,000,000	1%
16	Qatar	16,000,000,000	1%
17	Brazil	15,120,000,000	1%
18	Algeria	12,460,000,000	1%
19	Norway	9,859,000,000	1%
20	European Union	7,294,000,000	1%

(b) NATURAL GAS

Rank	Country	Proven Reserves (bbl oil equivalent)	%
NA	World	1,123,552,123,552	NA
1	Russia	306,113,256,113	27%
2	Iran	171,299,871,300	15%
3	Qatar	165,830,115,830	15%
4	Saudi Arabia	42,110,682,111	4%
5	United Arab Emirates	38,648,648,649	3%
6	United States	34,446,589,447	3%
7	Algeria	29,157,014,157	3%
8	Nigeria	28,970,398,970	3%
9	Venezuela	26,969,111,969	2%
10	European Union	20,952,380,952	2%
11	Iraq	20,045,045,045	2%
12	Kazakhstan	19,305,019,305	2%

Table 26.6 *(Continued)*

Rank	Country	Proven Reserves (bbl oil equivalent)	%
13	Indonesia	16,454,311,454	1%
14	Australia	16,402,831,403	1%
15	China	16,280,566,281	1%
16	Malaysia	13,667,953,668	1%
17	Norway	13,629,343,629	1%
18	Turkmenistan	12,934,362,934	1%
19	Egypt	12,226,512,227	1%
20	Uzbekistan	12,065,637,066	1%
21	Netherlands	11,299,871,300	1%
22	Canada	10,765,765,766	1%
23	Kuwait	10,115,830,116	1%
24	Libya	8,500,643,501	1%
25	Ukraine	7,213,642,214	1%

(c) COAL

| Rank	Country	Proven Reserves (tonnes)	Proven Reserves (bbl oil equivalent)	%
NA	World	847,488,000,000	4,315,933,491,072	NA
1	USA	242,721,000,000	1,236,085,576,299	29%
2	Russian Federation	157,010,000,000	799,592,109,190	19%
3	China	114,500,000,000	583,104,875,500	14%
4	Australia	76,600,000,000	390,094,615,400	9%
5	India	56,498,000,000	287,722,788,262	7%
6	South Africa	48,000,000,000	244,445,712,000	6%
7	Ukraine	33,873,000,000	172,502,283,387	4%
8	Kazakhstan	31,300,000,000	159,398,974,700	4%
9	Serbia	13,885,000,000	70,711,014,815	2%
10	Poland	7,502,000,000	38,204,827,738	1%
11	Brazil	7,068,000,000	35,994,631,092	1%
12	Colombia	6,959,000,000	35,439,535,621	1%
13	Germany	6,708,000,000	34,161,288,252	1%
14	Canada	6,578,000,000	33,499,247,782	1%
15	Czech Republic	4,501,000,000	22,921,878,119	1%
16	Indonesia	4,328,000,000	22,040,855,032	1%

bbl = barrels of oil
1 ton oil = 7.3 bbl = 42 GJ
*1 ton coal = 29.3 GJ*

Estimates are circa 2002 to 2005 depending on the country. Source of estimates: (a and c) U.S. Federal Government (2007) 2007 CIA World Factbook – Updated Guide to the World, with Country Profiles, Flags, Maps, and Data, https://www.cia.gov/cia/publications/factbook/rankorder/217Brank.txt and (b) World Energy Council (2007) 2007 Survey of Energy Resources, http://www.worldenergy.org/documents/ser2007_final_online_version_1.pdf.

Other settings where large deposits are likely to be found include: (1) ancient platforms (continental shelves) and (2) intracratonic sags or depressions.

Within a sedimentary basin, numerous fields may be present. Each field can be considered as a separate petroleum system in which all the required elements enumerated in Table 26.5 must be established as present to justify the cost of exploratory drilling. A typical approach to organizing this information is illustrated in Figure 26.17, which is called an *events chart*. In addition to listing the required elements, it shows the timing of important events in the field's history. This is critical because system events
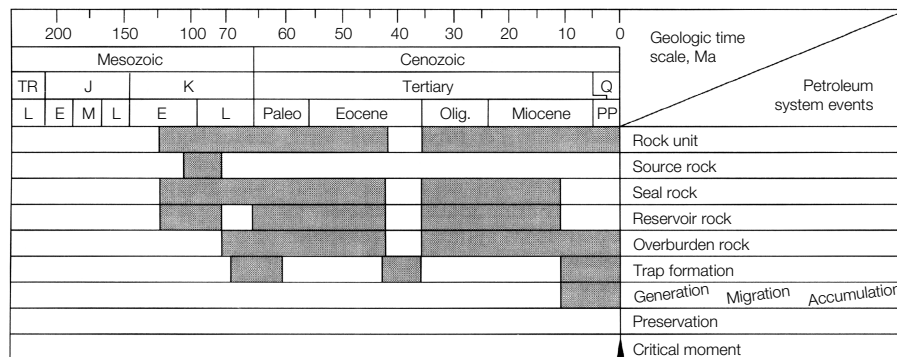
A
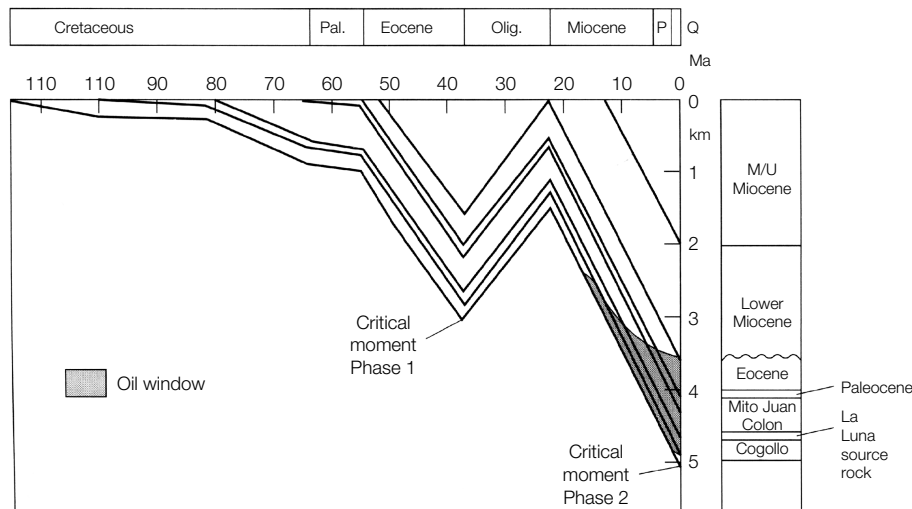
B

FIGURE 26.17

Events chart for a petroleum system located in the Maracaibo Basin, Venezuela. The critical moment is the time when most of the petroleum in the system is forming and accumulating in its primary trap. *Source*: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition. W. H. Freeman and Co., New York, p. 594.

must happen in the correct sequence. Three-dimensional geophysical mapping is also used to define spatial relationships of the essential elements. Another important tool is construction of a mass balance for the system in which estimates are made of the percentage of petroleum lost to dispersal and seepage versus the percentage present as oil accumulations.

The two most important predictors of the size of a deposit are the size and quality of the source bed and its mode of entrapment. The most productive source rocks are ones that still retain a high organic carbon and hydrogen content and are relatively thick. The most favorable entrapment conditions involve lateral migration into a reservoir rock with high impedance to dispersion. The latter requires a good trap and cap rock (seal).

Interestingly, over 90% of the known and estimated petroleum reserves are located in only six stratigraphic intervals that are concentration in the mid-to-late Mesozoic era (Figure 26.18). Most are derived from sediments that were deposited during marine transgressions and which have since been lithified into black shales. Two thirds are located between 0 to 45° latitude. Most are trapped in carbonate reservoirs with evaporite seals.

No systematic time trends are present in the deposition of source rocks. The episodic nature of petroleum generation suggests that it is driven by factors that favor the
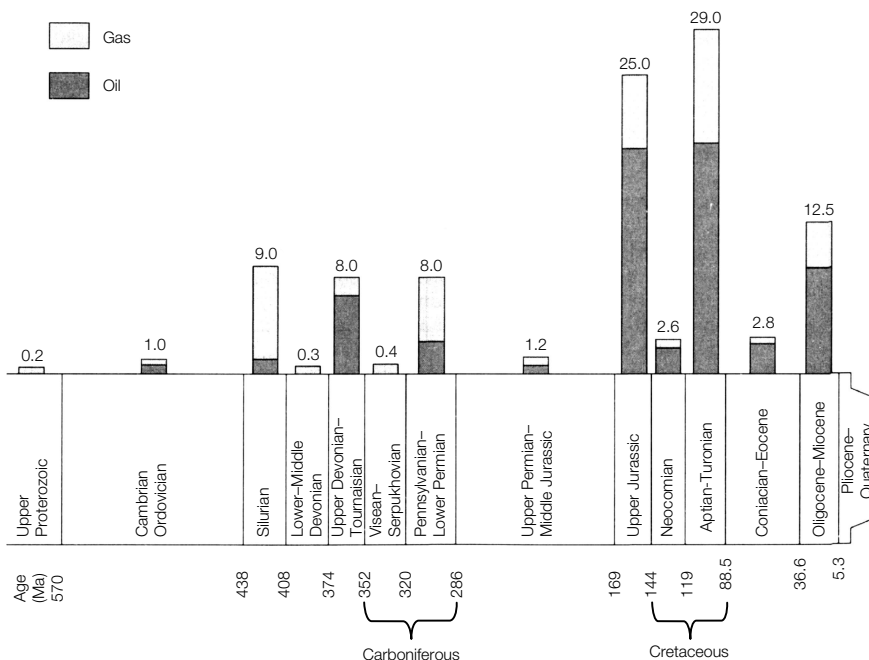

FIGURE 26.18

Stratigraphic distribution of effective source rocks given as a percentage of the world's original petroleum reserves generated by these rocks. *Source*: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology*, 2nd edition. W. H. Freeman and Co., New York, p. 621.

preservation and maturation of sedimentary organic matter, namely plate tectonics and climate. Another interesting observation is that 80% of the recoverable reservoirs were generated and trapped within the past 100 million years, although in many cases, deposition occurred hundreds of millions of years earlier. This suggests a delayed delivery to the hydrocarbon kitchen.

As discussed earlier, most deposits of marine petroleum are located in marginal seas. These sites are conducive to the formation of sizable petroleum deposits because they are characterized by high rates of primary production, shallow water depths, and restricted circulation. As a result, marginal seas have large POM fluxes and anoxic sediments. Both favor the burial of large quantities of organic matter at rapid rates. Their close proximity to land ensures a supply of sand, which can form clean sandstone reservoir beds. Since marginal seas are likely to have been isolated from the ocean during periods of lower sea level, they tend to have diapirs. But production of a substantial amount of petroleum also requires that enough time has elapsed for burial, maturation, and migration. In the United States, the largest such deposits occur in the Gulf of Mexico. In 2006, a new field was discovered in the Gulf. It is thought to hold 3 to 15 billion barrels of oil, making it one of the rare "supergiant" fields. This amount of oil would boost U.S. proven oil reserves by as much as 50%. This field is also unusual as it lies at a great depth beneath the seafloor (7000 m) under a 2300-m water column. This find supports the hypothesis that a lot of as yet undiscovered, but recoverable, petroleum may lie at great depths beneath the seafloor.

Abyssal plains are unlikely sites for large petroleum deposits as they lack an abundant source of POM and their sediments are too old. The continental margins that lie outside a marginal sea are also not promising. Because of rapid current motion, the sediments are more oxidizing at these sites and, hence, do not favor the burial of organic matter. Nevertheless, the U.S. government has subdivided the seafloor of its continental shelf and sold some leases to oil prospectors. Test wells drilled along the East Coast have not yielded substantial amounts of petroleum. In the late 1980s, several large tanker spills occurred in coastal waters. As a result of concern over the environmental impact of increased ocean drilling, an open-ended moratorium on leasing was declared by the federal government in 1990. The current crisis in petroleum availability has led to a reconsideration of this moratorium.

The sole exceptions to the unpromising nature of most continental shelves are areas located beneath coastal upwelling areas. For example, the oil wells of Southern California are pumping petroleum created from sedimentary organic matter that accumulated beneath an ancient upwelling area. A similar and very large deposit is thought to lie beneath the Grand Banks. The intense upwelling that presently occurs at this site supports one of the world's largest fisheries. Though this area has been leased, environmentalists and fishermen have halted attempts to drill at this site.

Using this kind of assessment of where petroleum is likely to be found, the U.S. Geological Survey has recently estimated the world's undiscovered oil reserves that are likely to be discovered between 1995 and 2025 (Figure 26.19). These estimates are of new conventional resources, i.e., new fields that can be exploited with current technology implemented at the same profit margin. A substantial amount of "undiscovered" resources are also estimated to lie in existing fields. Past history has shown that the
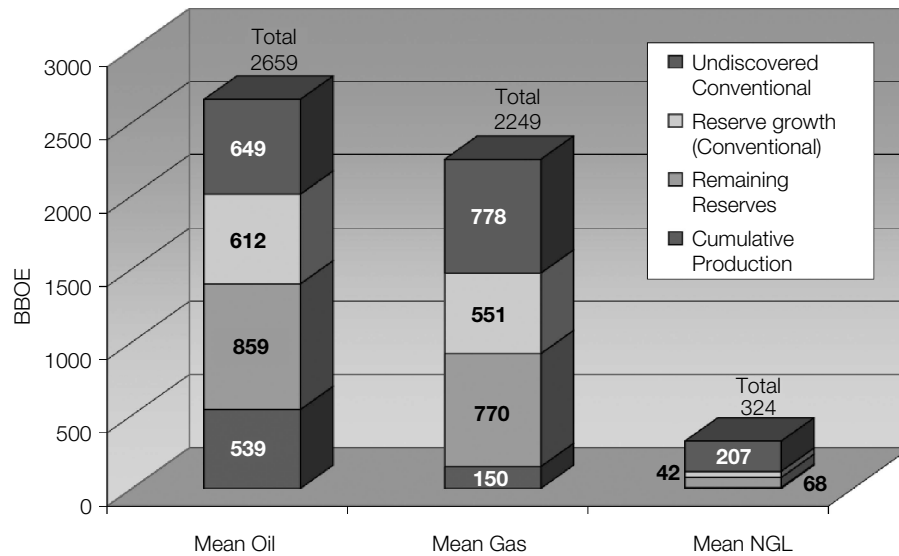
FIGURE 26.19

Mean estimate of the world grown conventional endowment of oil, gas, and natural gas liquids (NGL) in billion barrels of oil equivalent (BBOE). This includes cumulative production, remaining reserves, and, in conventional accumulations, mean estimates of reserve growth and undiscovered resources. Production and reserve data are circa January 1996. Estimates of growth and undiscovered resources are a 30-year forecast for 1995 to 2025. *Source*: After USGS World Energy Assessment Team (2000). U.S. Geological Survey World Petroleum Assessment 2000: Description and Results. U.S. Geological Survey Digital Data Series—DDS-60.

sizes of existing fields tend to be underestimated, causing them to appear to "grow" as they are harvested. This reserve "growth" is nearly as large as the estimates of the undiscovered new field resources and suggests that 75% of the world's oil and 55% of its gas have already been discovered. By the end of 1995, 20% of the oil and 7% of the gas had already been produced. It may seem that a lot is left, but the remaining resources are located in more challenging locations and are of lower purity than those already produced and, thus, will be harder to harvest. The greatest volumes of undiscovered conventional oil are thought to be located in the Middle East, the northeastern Greenland Shelf, the West Siberian and Caspian areas of the former Soviet Union, and the Niger and Congo delta areas of Africa. The greatest volumes of undiscovered gas are likely to be found in the West Siberian Basin, the Barents and Kara Sea shelves of the former Soviet Union, the Middle East, and the Norwegian Sea.[1]

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[1] In November 2007, Brazil's state oil company announced that it had discovered an offshore oil deposit in their Tupi field that contains between 5 and 8 billion barrels of recoverable light oil. This would satisfy world oil needs for 16 y (using a consumption rate circa 2007). This deposit is located 250 km offshore in water depths of 2 to 3 km and 5 to 7 km below the ocean floor.