Generation and Migration
of Petroleum

The preceding chapters discussed the physical and chemical properties of crude oil and natural gas and the behavior of fluids in the subsurface. The object of this chapter is to discuss the genesis, migration, and maturation of petroleum. We now have a good understanding of what oil and gas are made up of and plenty of empirically derived data that show how they occur. Thus, we know how to find and use oil and gas. However, the precise details of petroleum generation and migration are still debatable. Recent advances in geochemistry, especially in analytical techniques, have resulted in rapid progress on this front, but many problems remain to be solved. Any theory of petroleum generation must explain two sets of observations: geological and chemical.

A theory of petroleum genesis must explain the following *geological facts*:

1. Major accumulations of hydrocarbons characteristically occur in sedimentary rocks (Table 5.1). In the words of Pratt (1942): "I believe that oil in the earth is far more abundant and far more widely distributed than is generally realized. Oil is characteristic of unmetamorphosed marine rocks of shallow water origin. In its native habitat in the veneer of marine sediments that came with time to be incorporated into the earth's crust, oil is a normal constituent of that crust; a creature of the direct reaction of common earth forces on common earth materials." Half a century later, few geologists would disagree with this statement, except perhaps to note in passing that continental and deep marine sediments are also petroliferous.
2. Numerous examples of hydrocarbon accumulations in sandstone and limestone reservoirs are totally enclosed above, below, and laterally by impermeable rocks. The Devonian reefs of Alberta and the Cretaceous shoestring sands of the Rocky Mountain foothill basins are examples of this phenomenon.
3. Other geological occurrences to consider are
   a. Commercial accumulations of hydrocarbons have been found in basement rocks, but a young geologist's career is not enhanced by recommending that management drill such prospects.
   b. Traces of indigenous hydrocarbons have been found in igneous and metamorphic rocks. Commercial accumulations in basement, however, are always in lateral fluid continuity with sedimentary rocks.
   c. Traces of hydrocarbons occur in stony chondritic meteorites.

TABLE 5.1   Amount of Organic Matter in Sedimentary Rocks

	Mass in (10^8 g)	
Organic sediments	1	
Petroleum	0.5	
Asphalts		
Coal		
Lignite	15	
Peat		
Organic matter disseminated in sedimentary rock		16.5
Hydrocarbons	200	
Asphalts	275	
Kerogen (nonextractable organic matter)	12,000	
		12,475
Total		12,491.5

From: Hunt (1979). Used with permission.

A theory of petroleum genesis must also explain the following *chemical facts*:

1. Crude oils differ from shallow hydrocarbons in 2014.
   a. They show a preference for even-numbered carbon chains (modern hydrocarbons tend to occur in odd-numbered chains).
   b. They contain >50% light hydrocarbons, which are rare or absent in modern sediments.
2. Crude oils show the following affinities with modern organic hydrocarbons:
   a. Young oils show levorotation. This property of optical activity is characteristic of hydrocarbons produced biosynthetically.
   b. They contain certain complex molecules that occur either in modern organic matter or as a product of their degradation (e.g., the porphyrins and steroids).
   c. It is possible to use biomarkers to "fingerprint" the depositional environment within which a particular petroleum originated (Volkman, 1988).
3. Correlation between source rock and reservoir oil can be carried out by fingerprinting using gas chromatography (Bruce and Schmidt, 1994).

In discussing theories that seek to explain the preceding geological and chemical facts, it is very important to make several distinctions. Whether petroleum is of organic (biological) or of inorganic (cosmic or magmatic) origin has been debated often. How petroleum is formed from its parent material has also been debated. Origin and mode of formation are two related but quite distinct problems. Most geologists are clear in their own minds that oil is organic in origin, although most have only the vaguest ideas as to how it forms. Ignorance of the mode of formation of oil need not invalidate the fact that its nature is organic. In an appropriate analogy, ignorance of the principles of brewing need not prevent one from knowing that beer can be made from yeast, hops, and malted barley.

The next section discusses whether petroleum is organic or inorganic in origin. This section is followed by a discussion of the mode of formation of petroleum.

5.1 ORIGIN OF PETROLEUM: ORGANIC OR INORGANIC

Early theories of petroleum generation postulated an inorganic origin (e.g., Berthelot, 1860; Mendele'ev, 1877, 1902). Jupiter, Saturn, and some of the satellites of the outer planets are known to contain methane. A particular class of meteorites, the carbonaceous chondrites, contains traces of various hydrocarbons, including complex amino acids and the isoprenoids phytane and pristane (Mueller, 1963; Epstein et al., 1987; Pillinger, 1987; Chyba, 1990). Extra-terrestrial hydrocarbons are believed by most authorities to have formed abiogenically (Studier et al., 1965). The opposite view has been argued by Link (1957) and Zahnle and Grinspoon (1990) who suggest that the presence of cosmic hydrocarbons provides evidence of extraterrestrial life.

Some astronomers have argued that the earth's oil was of cosmic origin. Thus, in 1955, Professor Sir Frederic Hoyle wrote: "The presence of hydrocarbons in the bodies out of which the Earth is formed would certainly make the Earth's interior contain vastly more oil than could ever be produced from decayed fish—a strange theory that has been in vogue for many years…. If our prognostication that the oil deposits have also been squeezed out from the interior of the Earth is correct, then we must, I think, accept the view that the amount of oil still present at great depths vastly exceeds the comparatively tiny quantities that man has been able to recover" (Hoyle, 1955).

Let us return to earth to examine this theory. Until the turn of the century, many distinguished scientists believed in the magmatic origin of hydrocarbons. Among the earliest and greatest of these scientists were the geographer Alexander von Humboldt and the great chemist Gay-Lussac (Becker, 1909). This theory was adopted by Mendele'ev, who suggested that the mantle contained iron carbide. This iron carbide could react with percolating water to form methane and other oil hydrocarbons (Mendele'ev, 1902), which is analogous to the reaction in which acetylene is produced by carbide and water:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)^2$$
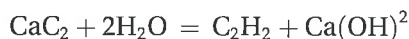
There is little evidence for the existence of iron carbide in the mantle. Yet the belief in a deep, inorganic origin for hydrocarbons has been widely held by many scientists, chemists, and astronomers, but not, however, by geologists (see Dott and Reynolds, 1969; for a historical review). Vestigial traces of this belief still survive today in Russia (Porfir'ev, 1974) and even in the United States. If this theory is true, one would expect hydrocarbons to be commonly associated with igneous rocks and areas of deep crustal disturbance and faulting. We now examine evidence for the exhalation of hydrocarbons from volcanoes, their occurrence in congealed magma, and their association with faults.

Gaseous hydrocarbons have been recorded to emanate from volcanoes in many parts of the world. White and Waring (1963) have reviewed some of these occurrences. Methane is the most commonly found gaseous hydrocarbon, generally present at <1%, although readings of ≥15% are noted. In all these instances, however, the volcanoes erupt through a cover of sedimentary rocks, from which methane may have been derived by the heating of organic

matter. Data have accumulated over the years describing the occurrence of hydrocarbons within igneous rocks. Three genetic types of igneous hydrocarbons may be classified:

1. Hydrocarbon gases, bitumens, and liquids occurring within vesicles andicroscopic inclusions and as irregular disseminated masses within igneous and metamorphic rocks
2. Hydrocarbons trapped where igneous rocks intrude sediments
3. Hydrocarns in weathered igneous basement trapped beneath unconformits

Solid and liquid hydrocarbons of the first type have been widely reported in Precambrian basement rocks in Karelia and the Kola peninsula of northern Russia (Filippov, 1995; Gottikh, 1995; Morakhovsky, 1995; Pushkarev, 1995). One of the most celebrated cases occurs in the Khibiny massif of the Kola peninsula in northern Russia (Petersil'ye, 1962; Ikorskiy, 1967). Here, alkaline intrusives penetrate a series of volcanic and volcaniclastic sediments. Ninety percent of the intrusives are composed of nepheline syenite. Gaseous and liquid hydrocarbons occur within inclusions in the nepheline crystals. Some 85—90% of the hydrocarbons consist of methane, but there are traces of ethane, propane, and n-butane and isobutane, together with hydrogen and carbon dioxide. Traces of bitumens have also been recorded, with long-chain alkanes and aromatics. Even though the quantity of hydrocarbons present in the Khibiny intrusives is infinitesimal, their diversity is impressive.

Further Russian occurrences of igneous oil are reviewed by Porfir'ev (1974). There is an ongoing debate as to whether these occurrences formed from abiogenic mantle sources, or whether they are metamorphosed late Precambrian organic-rich sediments. The debate is not an idle one, as deep (>5530-m) wells in the Republic of Tarastan have located extensive fracture systems below 5000 m (Nazipov and Iskanderov, 1995). Deep wells have been drilled in Russia in an endeavor to locate commercial accumulations of hydrocarbons in Precambrian basement.

A second celebrated case of igneous oil has been described by Evans et al. (1964) from Dyvika in the Arendal area of Norway. Here, oil occurs in vesicles in a dolerite dyke. The vesicles are rimmed with crystals of calcite, analcite, chalcedony, and quartz. Paraffinic hydrocarbons occur in the center of the vesicles. The dolerite dyke intruded Precambrian gneisses and schists.

Somewhat different to the examples just discussed are the widespread reports of subcommercial quantities of hydrocarbons in Phanerozoic intrusives (Robinson et al., 1986). The Cornubian granites of southwest England are one of many instances where subcommercial quantities of bitumen and free oil have been reported (Selley, 1992). These granites are extensively mineralized. Field evidence shows that the petroleum was emplaced at a late stage in the cooling of the magma together with lead—zinc sulfide ores at temperatures of some 150 °C. It is suggested that the petroleum and the mineralizing fluids were transported into the granites by convective flow from sedimentary cover rocks that have since eroded (Fig. 5.1).

The second type of occurrence of hydrocarbons in basement is far more common and contains many commercial accumulations of oil and gas. Oil sometimes occurs where sediments, especially organic shales, have been intruded by igneous material. Instances occur, for example, in the Carboniferous oil shales of the Midland Valley of Scotland. Commercial accumulations of this type occur in the Jatibonico field of Jatibonico, Cuba, and in the interior coastal plain of Texas (Collingwood and Rettger, 1926). In these instances, oil occurs in various hydrothermally altered basic intrusions. Such fields lack water and,
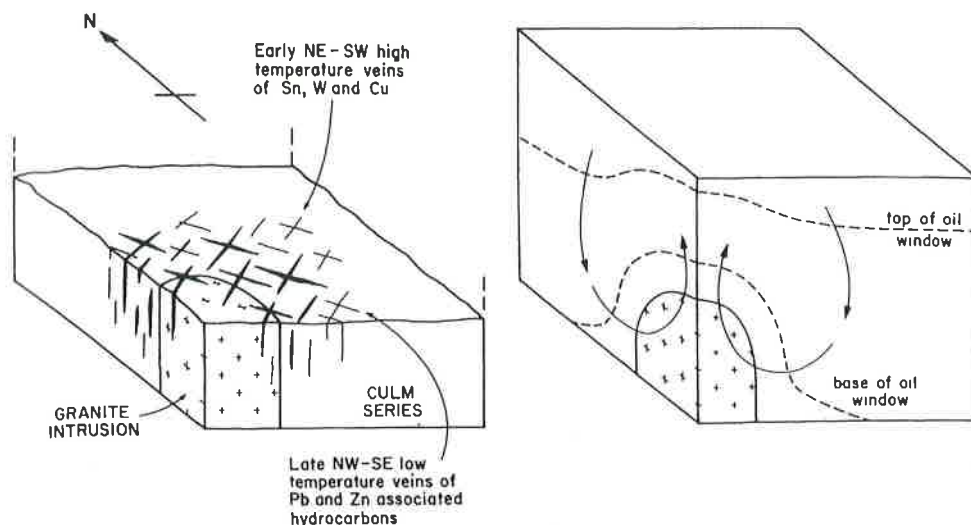
FIGURE 5.1   Illustrations showing how hydrocarbons may have been emplaced into the Cornubian granites of southwest England by convective flow during late mineralization. Subsequent erosion has removed the sedimentary cover that provided the source for the hydrocarbons and, most probably, the minerals. This mechanism has been advanced to explain many, though not all, occurrences of hydrocarbons in igneous rocks. *Reprinted from Selley (1992). Copyright 1992, with kind permission from Elsevier Science Ltd.*

although they may show very high initial production rates because of oil or gas expansion drive, often deplete rapidly. The Texas intrusives, of which >17 fields have been found, intrude Cretaceous limestones and shales (Fig. 5.2).

The third type of oil accumulation in igneous rock is frequently commercially significant. This type is where oil or gas occurs in fractures and solution pores within igneous and metamorphic rocks beneath unconformities. The porosity is obviously due to weathering. The basement rocks are overlain and onlapped by sediments that include organic-rich clays. This occurs, for example, in the oil and gas fields of offshore Vietnam (Schnip, 1992; Dmitriyevsky, 1993), in the Augila-Nafoora fields of Libya, and in northern China (Guangming and Quanheng, 1982).

Let us now consider the origins of these three genetic types of oil in igneous rock. For the first type, where hydrocarbons occur in vesicles or inclusions, there are two possible explanations. These occurrences could have originated from abiogenic hydrocarbons derived from the mantle. Alternatively, they could have resulted from the metamorphism of late Precambrian organic-rich sediments. Contamination of magma as it intruded Phanerozoic organic sediments could be postulated in some cases, but not in those where sedimentary rocks are absent.

The second type of occurrence, where hydrocarbons occur at the margin of igneous intrusives, is genetically equivocal. It could be argued that either the oil was genetically related to the magma or it was formed by thermal metamorphism of kerogen in the intruded sediments. Geochemical fingerprinting, however, demonstrates that the petroleum could be correlated with petroleum extracted from kerogen in adjacent sediments.
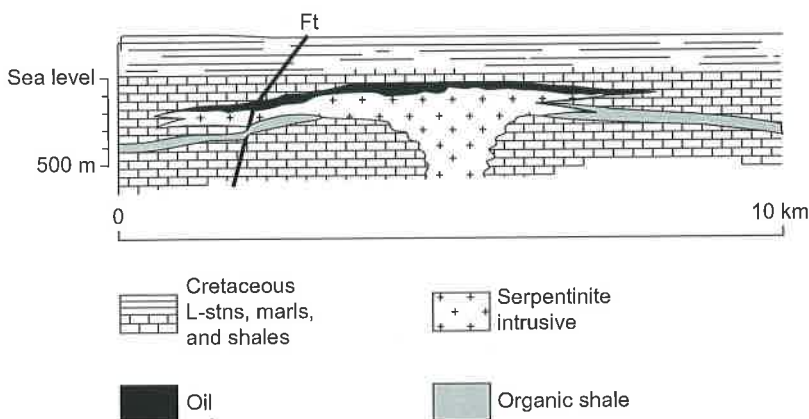
FIGURE 5.2 Cross-section of the Lytton Springs oil pool, Caldwell County, Texas. Oil occurs in the crest of a circular serpentinite plug. There is no free water. Note the adjacent organic shale. *Modified from Collingwood and Rettger (1926), reprinted by permission of the American Association of Petroleum Geologists.*

The third type, where oil occurs in weathered basement beneath unconformities, can best be explained as being caused by emigration from the enveloping sediments. Genesis synchronous with intrusion is hard to accept, because oil emplacement must have postdated both the weathering of the basement and the deposition of the sediments that provide the seal. Again, geochemical fingerprinting demonstrates that the petroleum correlates with petroleum extracted from kerogen in adjacent sediments.

In both of the preceding instances, it is probable that the petroleum was transported into the granites by convective flow from sedimentary cover rocks, as discussed in Chapter 4.

5.1.1 Hydrocarbons from the Mantle

As discussed earlier, faults play an important part in the migration and entrapment of petroleum. Although some faults are impermeable and act as seals to petroleum migration, thus causing fault traps, others allow the upward movement of oil and gas. Some faults exhale flammable gases at the surface of the earth during earthquakes. Exhalation is preceded by bulging of the ground and accompanied by loud bangs, flashing lights, and visible ground waves. An ensuing evil smell is sometimes noted, due to the presence of hydrogen sulfide gas. These phenomena are all well documented and certainly demonstrate that some faults are conduits for flammable gas (Gold, 1979). Detailed analyses of these gases reveal the presence of methane, carbon dioxide, hydrogen sulfide, and traces of noble gases (Sugisaki et al., 1983). Peyve (1956), Subbotin (1966), and Gold and Held (1987) have argued that subcrustal abiogenic hydrocarbon and other gases migrate up major faults to be trapped in sedimentary basins or dissipated at the earth's surface. Porfir'ev (1974) cited the flanking faults of the Suez, Rhine, Baikal, and Barguzin grabens as examples of such petroleum feeders.

This school of thought has been supported in the West (Gold, 1979, 1984; Gold and Soter, 1982). Gold has argued that earthquake outgassing along faults allows methane to escape

from the mantle. This process gives rise to deep gas reservoirs and, by polymerization, to oil at shallower horizons. To most geologists, these ideas seem improbable and are largely rejected out of hand. Gold's earthquake outgassing theory implies that to find limitless quantities of oil and gas, all that needs to be done is to drill adjacent to faults deep enough and often *enough*.

The classic geologist's response has been cogently argued by North (1982). Because porosity and permeability decrease with depth, there can be no deep reservoirs to contain and disburse any gas that might exist. On a global scale, gas reservoirs are closely related to coal-bearing formations of Late Carboniferous (Pennsylvanian) and Cretaceous to Paleocene ages (the gas-generating potential of humic kerogen is discussed later).

Note that many of the most dramatic reports of earthquake outgassing occur in faulted basins with thick sequences of young sediments. These loosely packed sands are bound to be charged with biogenic methane and hydrogen sulfide. A seismic shock will cause the packing of the sand to tighten, resulting in a decrease in porosity and a violent expulsion of excess pore fluid. It is possible, however, to differentiate biogenic from abiogenic methane. Carbon has two isotopes: C^{12} and C^{13}. The $C^{12}:C^{13}$ ratio varies for different compounds, and this ratio is especially large for the different types of methane. Biogenic methane is enriched in C^{12}; abiogenic methane contains a higher proportion of C^{13} (Hoefs, 1980). The $C^{12}:C^{13}$ ratios of methane from the "hot spots" of the Red Sea, Lake Kivu (East Africa), and the East Pacific Rise suggest an abiogenic origin (MacDonald, 1983).

Gold's theory has been tested by wells drilled on the Siljan ring, a meteorite impact structure in Sweden dated at some 360 mybp. This structure occurs in Precambrian basement. Within the impact crater, there are Ordovician and Silurian limestones and shales that contain petroleum (Fig. 5.3). Gold argued that this was just the place to drill for oil, because the impact of the meteorite would have shattered the crust, thus allowing the petroleum to escape to the surface, as proved by the seeps. The first well was drilled to 6957 m. Drilling problems were encountered due to lost circulation and due to drilling mud being lost into the formation. This indicates the existence of deep porosity and permeability. Gaseous and liquid hydrocarbons were encountered, and up to 85 barrels of oil were produced (Vlierbloom et al., 1986). Unfortunately, however, when the well lost circulation, diesel oil was added to the drilling mud system. It is argued, however, that the recovered oil is different from diesel. Enthusiasts for the abiogenic theory were disappointed to learn, however, that the black gelatinous hydrocarbons recovered from the bottom of the well were actually an artifact of the drilling process, due to the mixing of diesel with caustic soda (Jeffrey and Kaplan, 1988, 1989).

5.1.2 Genesis of Petroleum by Fischer—Tropsch Synthesis

There is a third theory for the origin of petroleum that is intermediate between the abiogenic mantle theory, just discussed, and the shallow biogenic theory. The Fischer—Tropsch reaction is a well-known industrial process that is used to produce synthetic hydrocarbons. It was used by Germany in World War II, and more recently by South Africa to produce petroleum and related products. In the Fischer—Tropsch reaction, carbon dioxide and
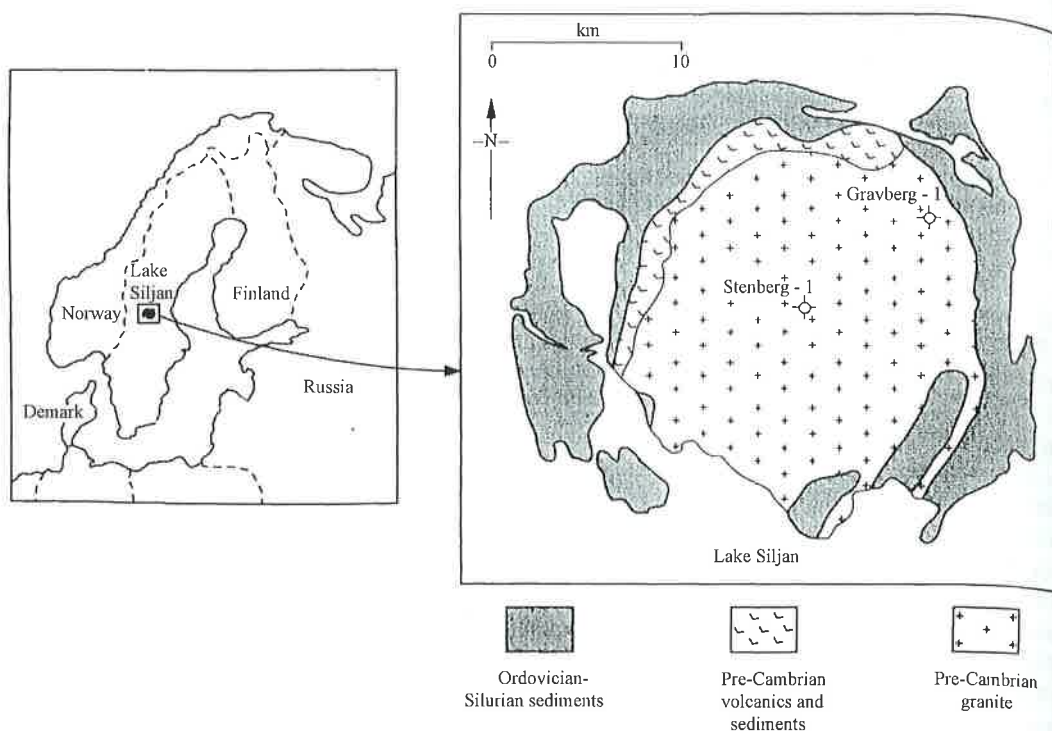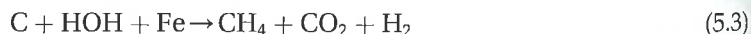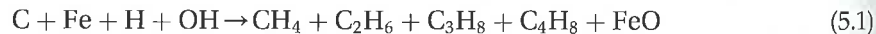
FIGURE 5.3   Map of the Siljan ring meteorite impact crater, Sweden. This was drilled in 1986 to test the abiogenic mantle-derived theory of petroleum genesis. It proved the existence of deep porosity and permeability and recovered oil and gas. The oil proved to have been produced by the alteration of diesel in the mud system caused by the action of the drill bit on hot rock.

hydrogen are passed over a catalyst of hematite and magnetite at temperatures of $>500\,°C$. According to Gould (1991), the reactions involved are probably as follows:

$$C + Fe + H + OH \rightarrow CH_4 + C_2H_6 + C_3H_8 + C_4H_8 + FeO \tag{5.1}$$

$$CO_2 + HOH + Fe \rightarrow CH_4 + FeO \tag{5.2}$$

$$C + HOH + Fe \rightarrow CH_4 + CO_2 + H_2 \tag{5.3}$$

$$CO_2 + H_2 \rightarrow CH_4 + H_2O \tag{5.4}$$

Robinson (1963) suggested that this process could produce methane and liquid petroleum in nature. More recently, Szatmari (1986, 1989) discussed this process in the light of plate tectonics. He argued that hydrocarbons could be generated by the Fischer–Tropsch process at convergent plate boundaries where sedimentary rocks and oceanic crust undergo subduction. The carbon dioxide could be formed from the metamorphism of carbonates, and the hydrogen by the serpentinization of ophiolites. The latter would provide the iron oxides necessary to catalyze the reaction. A critique of this theory can be found in Le Blanc (1991).

5.1.3 Abiogenic versus Biogenic Genesis of Petroleum: Conclusion

In concluding this review of theories for the abiogenic origin of petroleum hydrocarbons, it must be stressed that the apparently unquestionable instances of indigenous oil in basement are rare and not commercially important. Not only are the volumes of hydrocarbons trapped this way insignificant but the "reservoirs" are impermeable unless fractured.

Commercial accumulations of hydrocarbons in igneous rocks only occur where the igneous rocks intrude or are unconformably overlain by sediments.

There is now clear evidence for the origin of abiogenic hydrocarbons in the deep crust or mantle, and for its emergence along faults and fractures, notably in midoceanic ridges and intracontinental rifts. Geologists will not fail to note, however, that commercial accumulations of oil are restricted to sedimentary basins. Petroleum seeps and accumulations are absent from the igneous and metamorphic rocks of continental shields, both far from and adjacent to faults. It is now routine to use gas chromatography (fingerprinting) to match the organic matter in shales with the petroleum in adjacent reservoirs (Flory et al., 1983; Hunt, 1996). Geologists thus conclude that commercial quantities of petroleum are formed by the thermal maturation of organic matter. This thesis is now examined, beginning with an account of the production and preservation of organic matter on the earth's surface and then charting its evolution when buried with sediments.

5.2 MODERN ORGANIC PROCESSES ON THE EARTH'S SURFACE

The total amount of carbon in the earth's crust has been estimated to weigh 2.65×10^{20} g (Hunt, 1977). Some 82% of this carbon is locked up as CO^3 in limestones and dolomites. About 18% occurs as organic carbon in coal, oil, and gas (Schidlowski et al., 1974). The key reaction is the conversion of inorganic carbon into hydrocarbons by photosynthesis. In this reaction, water and atmospheric carbon dioxide are converted by algae and plants into water and glucose:

$$6CO_2 + 12H_2O = C_6H_{12}O_6 + 6H_2O + 6O_2$$

Glucose is the starting point for the organic manufacture of polysaccharides and other more complex carbon compounds. This polysaccharide production may happen within plants or within animals that eat the plants. In the natural course of events, the plants and animals die and their organic matter is oxidized to carbon dioxide and water. Thus, the cycle is completed (Fig. 5.4). In certain exceptional circumstances, however, the organic matter may be buried in sediments and preserved, albeit in a modified state, in coal, oil, or gas. Gas chromatography can be used to "fingerprint" petroleum and to correlate it with the source rock from which it was derived (Bruce and Schmidt, 1994) and to determine the type of organism and depositional environment in which it lived (Volkman, 1988).

To trace the evolution of living organic matter into crude oil and gas, it is necessary to begin with an examination of its chemistry. The major groups of chemicals that occur in organic matter are proteins, carbohydrates, lipids, and lignin. The proteins are found largely in animals and to a lesser extent in plants. They contain the elements hydrogen, carbon, oxygen, and nitrogen, with some sulfur and phosphorus. This combination of
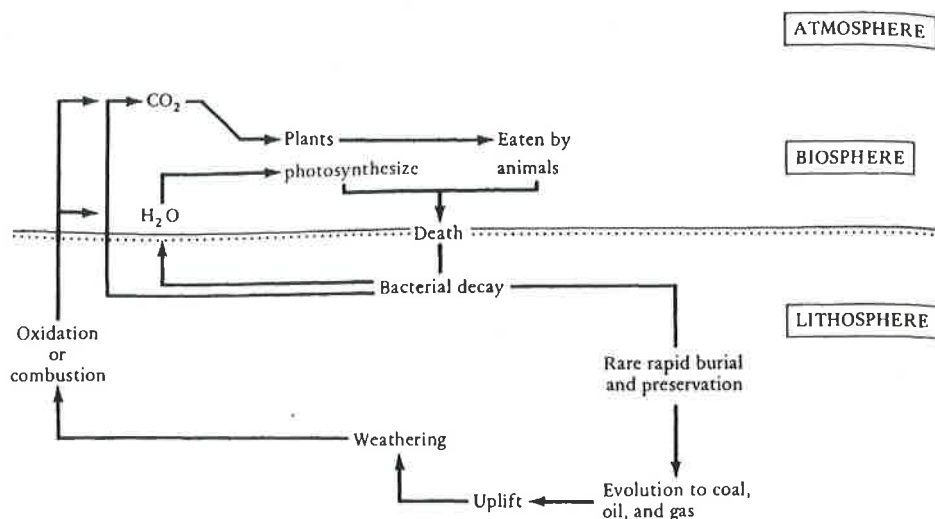
FIGURE 5.4   The cycle of organic carbon within the earth's crust. The primary source for the carbon is from the weathering of crustal rocks, together with mantle-derived carbon dioxide and methane.

elements occurs in the form of amino acids. The carbohydrates are present in both animals and plants. They have the basic formula $C_n(H_2O)_n$ and include the sugars, such as glucose, and their polymers—cellulose, starch, and chitin. The lipids are also found in both animals and plants. They are basically recognized by their insolubility in water and include the fats, oils, and waxes. Chemically, the lipids contain carbon, hydrogen, and oxygen atoms. The basic molecule of the lipids is made up of five carbon atoms (C_5H_8). From this base, the steroids are built. The last of the four major groups of organic compounds is lignin, which is found only in the higher plants. Lignin is a polyphenol of high molecular weight, consisting of various types of aromatic carbon rings. Figure 5.5 shows the distribution of these four groups of compounds in living organisms and in recent shallow sediments. Table 5.2 shows their abundance in different groups of animals and plants.

5.2.1 Productivity and Preservation of Organic Matter

As previously discussed, the amount of organic matter buried in sediments is related to the ratio of organic productivity and destruction. Generally, organic matter is destroyed on the earth's surface, and only minor amounts are preserved. The deposition of an organic-rich sediment is favored by a high rate of production of organic matter and a high preservation potential. These two factors are now discussed. Determining production and preservation for the present day is relatively easy; extrapolating back in time is harder. This problem is especially true for continental environments, whose production—destruction ratio of organic matter is largely related to the growth of land plants. Therefore, marine and continental environments should be considered separately.
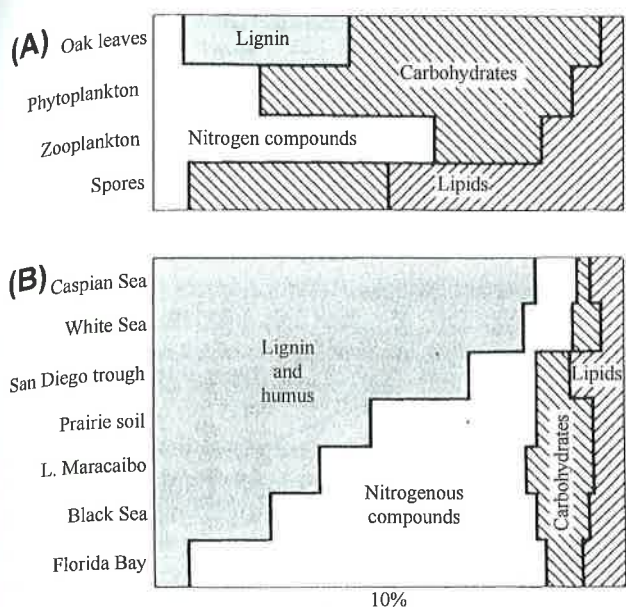
(A) Oak leaves
Phytoplankton
Zooplankton
Spores

(B) Caspian Sea
White Sea
San Diego trough
Prairie soil
L. Maracaibo
Black Sea
Florida Bay

10%

FIGURE 5.5 Composition of organic matter in (A) organisms and (B) shallow Recent sediments. *From: Hunt (1979). Used with permission.*

TABLE 5.2   Chemical Composition of Various Groups of Animals and Plants

Substance	Weight percent of major constituents (ash-free)			
	Proteins	Carbohydrates	Lignin	Lipids
Plants				
Spruce	1	66	29	4
Oak leaves	6	52	37	5
Pine needles	8	47	17	28
Phytoplankton	23	66	0	11
Diatoms	29	63	0	8
Lycopodium spores	8	42	0	50
Animals				
Zooplankton	60	22	0	18
Copepods	65	25	0	10
Higher invertebrates	70	20	0	10

From: Hunt (1979). Used with permission.

5.2.1.1 Organic Productivity and Processes in Seas and Oceans

In the sea, as on the land, all organic matter is originally formed by photosynthesis. The photosynthesizers in the sea are pelagic phytoplankton and benthic algae. The biological productivity of these plants is related to both physical and chemical parameters. Of the former, temperature and light are of foremost significance. The amount of light is dependent on the depth, latitude, and turbidity of the water. The amount of organic productivity is the highest in the shallow photic zone and decreases rapidly with increasing water depth and decreasing light and temperature.

Chemical conditions favoring organic productivity include the abundance of phosphates and nitrates. These chemicals are essential for the growth of plants and animals. Oxygenation is not important for the phytoplankton themselves, but is vital for the existence of animals that later form links in the food chain. Because oxygen is a by-product of photosynthesis, phytoplankton increases the oxygen content of the sea.

Figure 5.6 shows the biological productivity in the present-day oceans of the world. Three major areas of organic productivity can be recognized. Large zones, where <50 g/m^2/year are produced, are found in the polar seas and in the centers of the large oceans. Two belts of higher productivity (200–400 g/m^2/year) encircle the globe along the boundaries between the polar and equatorial oceans. These are attributable to high-latitude upwelling (Hay, 1995). Three zones of above average organic productivity occur off the western coasts of North America, South America, and Africa. These zones are where deep, cold ocean currents well up from great depths (the California, Humboldt, and Benguela currents, respectively). The nutrients that these currents contain, principally nitrates and phosphates, are responsible for the high organic productivity of these zones.

It is important to stress that the areas of high oceanic productivity are not necessarily the areas where organic matter is best preserved. The preservation of organic matter is favored by anaerobic bottom conditions and a rapid sedimentation rate. Johnson Ibach (1982) described a detailed study of the relationship between rate of sedimentation and total organic carbon (TOC) in cores recovered from the ocean floors by the Deep Sea Drilling Project. The samples ranged in age from the Jurassic to Recent. Figure 5.7 illustrates the results. Black shale, siliceous, and carbonate sediments are shown separately. For all three sediments, however, the TOC content increases with sedimentation rate for slow rates of deposition, but

FIGURE 5.6 Production of organic matter in the present-day world oceans. Note the low productivity in polar regions and the high productivity along eastward sides of the oceans. *For sources, see Debyser and Deroo (1969), Degens and Mopper (1976), Calvert (1987), and Hay (1995).*
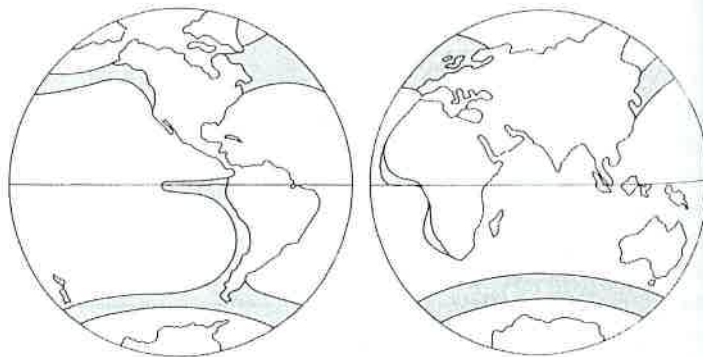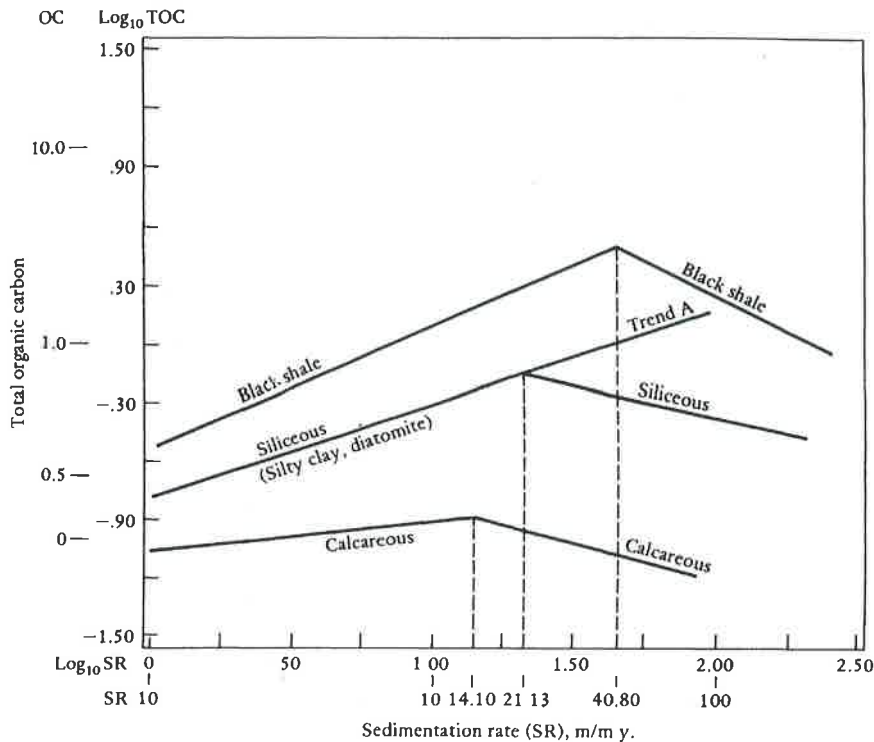
FIGURE 5.7 Graph showing the relationship between total organic carbon and sedimentation rate for Jurassic to Recent cores recovered by the Deep Sea Drilling Project. The graph shows that each different type of sediment has an optimum sedimentation rate for the maximum preservation of organic matter. At too slow a rate, oxidation occurs; at too high a rate, organic carbon is diluted by sediment. *Modified from Johnson Ibach (1982), reprinted by permission of the American Association of Petroleum Geologists.*

decreases with sedimentation at high rates of deposition. The switchover occurs at slightly different sedimentation rates for the three lithologies. Johnson Ibach interprets these results as showing that at slow sedimentation rates organic matter is oxidized on or near the seabed. Rapid deposition effectively dilutes the organic content of the sediment. For each lithology, there appears to be an optimum rate for the preservation of organic matter; this rate is a balance between dilution and destruction of the organic fraction. Nonetheless, more recent studies of both modern and ancient organic-rich sediments have led to the conclusion that organic productivity is the dominant controlling factor in its preservation (Pederson and Calvert, 1990; Parrish, 1995).

Another important condition favoring the preservation of organic matter is the presence of stratification within the waters from which sedimentation occurs. Demaison and Moore (1979, 1980) recognize four major settings for the formation of organic-rich sediments in anoxic environments (Fig. 5.8).

The first of these settings is the freshwater lake, in which thermally induced stratification of water develops, with warm water near the surface and cooler, denser water deeper down
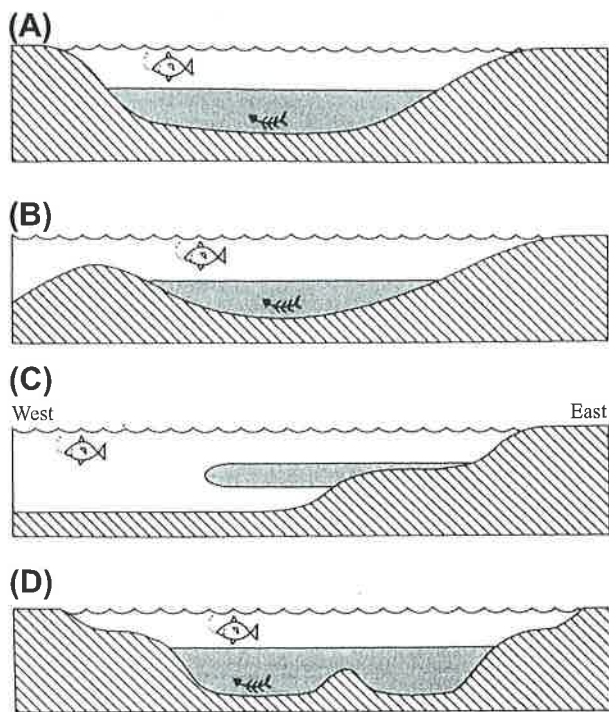
FIGURE 5.8 Illustrations of the four main settings for anoxic environments favorable for the preservation of organic matter in sediments as classified by Demaison and Moore (1980): (A) a lake (thermally induced stratification), (B) a barred basin (stratification due to salinity contrast), (C) a continental shelf with upwelling, and (D) an ocean basin anoxic event.

(Fig. 5.8(A)). Life will thrive in the upper zone, with phytoplankton photosynthesizing and oxygenating the photic zone. In the deeper layer, oxygen, once used up, will not be replenished because photosynthesis does not occur in the dark, and the density layering inhibits circulation. Sporadic storms may stimulate water circulation and cause mass mortality by asphyxiation of life throughout the lake, enhancing the amount of organic detritus deposited in the lake bed (Fleet et al., 1988). This situation is well known in modern lakes, such as those of East Africa (Degens et al., 1971, 1973). Similar lakes in ancient times include the series of Tertiary lakes of Colorado, Utah, and Wyoming, in which the Green River formation oil shales were deposited (Bradley, 1948; Robinson, 1976; Katz, 1995).

A second setting for the deposition of organic matter and its preservation in an anoxic environment occurs in barred basins (Fig. 5.8(B)). In this setting, seawater enters semirestricted lagoons, gulfs, and seas. In arid climates, evaporation causes the water level to drop and salinity to increase. Less dense water from the open sea enters across the bar and floats on the denser indigenous water. The same bar prevents the escape of the denser water to the sea. Thus, a water stratification analogous to that of the freshwater lake develops. But in this case, the density layering is due to differences not of temperature, but of salinity. Similar anoxic bottom conditions develop, however, and organic matter

may be preserved. The Black Sea is a recent example of an anoxic barred basin (Deuser, 1971; Degens and Ross, 1974). The organic-rich Liassic shales of northwest Europe may have been deposited in this type of barred basin (Hallam, 1981; Bessereau et al., 1995).

A third situation favorable to the deposition and preservation of organic matter occurs today on the western sides of continents in low latitudes. The high productivity of these regions has already been described, and attributed to the upwelling of waters rich in nutrients in general, and phosphates in particular (Fig. 5.8(C)). In these settings, the seawater is commonly oxygen-deficient between 200 and 1500 m (650 and 5000 ft) (Fig. 5.9). The Phosphoria formation (Permian) and the Chattanooga–Woodford shales (Devonian–Mississippian) were probably deposited in analogous settings (Claypool et al., 1978; Duncan and Swanson, 1965; Parrish, 1982, 1995). Both are relatively thin, but laterally extensive, formations that cover ancient continental shelves. The deposition of such organic-rich sediments is favored by a rise in sea level, possibly caused by a global temperature rise, so that the anoxic zone rises to extend across the continental shelves. Thus, this type of source rock commonly blankets an unconformity and occurs during the high stand phase of the sequence stratigraphic cycle. Specifically, it overlies the maximum flooding surface and occurs within the lower part of the high stand system tract (Creaney and Passey, 1993; Bessereau et al., 1995).

The fourth setting for the deposition of organic sediment is in an anoxic ocean basin. There is no known Recent instance of this situation. Most modern ocean floors are reasonably well oxygenated. Deep oceanic circulation is caused by density currents, where cold polar waters flow beneath warmer low-latitude waters. It has been argued, however, that deep oceanic circulation may not have existed in past periods when the earth had a uniform, equable climate without the polar ice caps of today; this seems to have been particularly true of
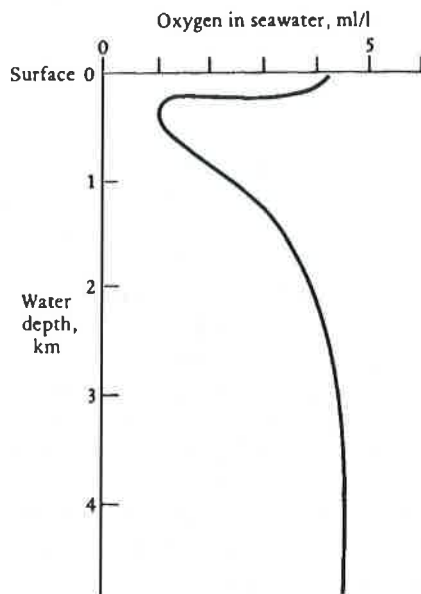

FIGURE 5.9   Variation of oxygen content against depth in modern oceans. *After Emery (1963), and Dietrich (1963).*
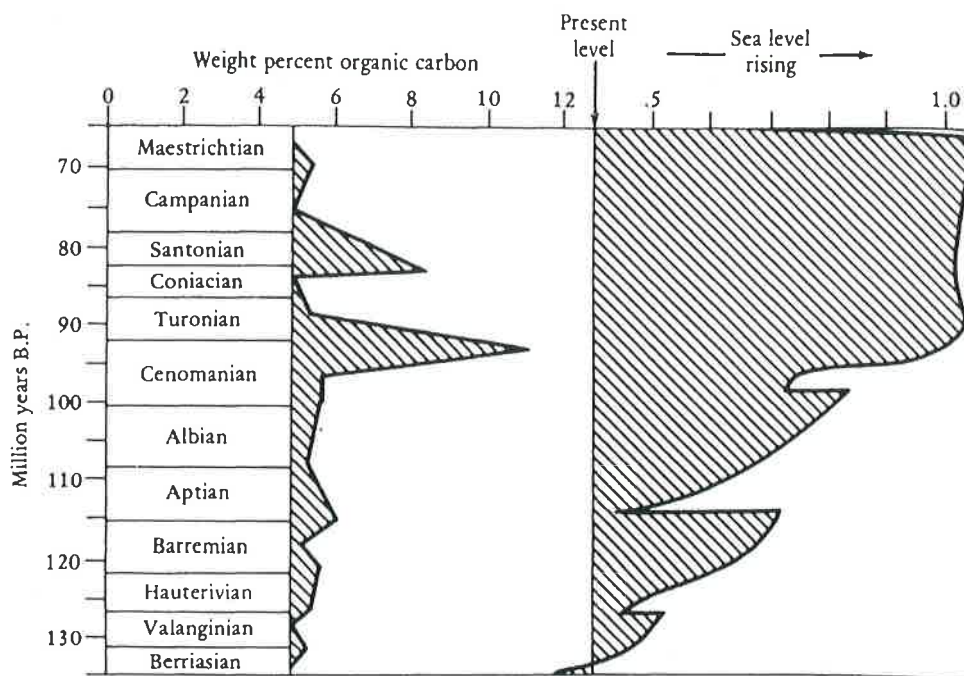
FIGURE 5.10   Relationship between source rocks and estimated sea level. Left: Graph of average values of organic carbon in Deep Sea Drilling Project cores in the North Atlantic. *(After Arthur and Schlanger (1979).)* Right: Global sea level curve. Modified from Vail et al. (1977), reprinted by permission of the American Association of Petroleum Geologists.

the late Mesozoic Era (Allen et al., 1994). At such times, global "anoxic" events may have been responsible for the worldwide deposition of organic-rich sediment (Fig. 5.8(D)). This mechanism has been proposed to explain the extensive Upper Jurassic–Lower Cretaceous black shales that occur in so many parts of the world, notably in the Atlantic Ocean and its environs (Arthur and Schlanger, 1979; Schlanger and Cita, 1982; Stein, 1986; Summerhayes, 1987). Tissot (1979) has shown that about 85% of the world's oil was sourced from Late Jurassic to Early Cretaceous formations. Figure 5.10 shows the correlation between organic sedimentation and sea level, thus supporting the thesis that transgressions favor anoxic environments. Waples (1983), however, has disputed the existence of a global anoxic event in the early Cretaceous, pointing out that the evidence mainly comes from the Atlantic Ocean and its borderlands. During this time, the Atlantic was but a narrow seaway in which local restriction of water circulation was to be expected.

5.2.1.2 *Organic Productivity and Preservation in Continental Environments*

The productivity and preservation of organic matter in the continental realm are rather different from those in the oceans, seas, and lakes. Oxygen content is constant. Important variables are water and the number of growing days per year, which is a function of temperature and daylight hours. Thus, the organic productivity of the polar regions is low. Given

adequate humidity, it increases with increasing temperature and daylight toward the equator.

Significant destruction of organic matter does not occur in upland areas below a mean temperature of approximately 10 °C and, in swamps, of approximately 15 °C (Gordon et al., 1958). Since any sediment with or without organic matter is unlikely to be preserved in upland environments, only swamp deposits need concern us. Gordon et al. (1958) also showed that the rate of production versus decay of organic matter increases from polar temperatures up to about 25 °C. At this point, organic productivity begins to decline, although the rate of decay continues to increase. Thus, the preservation potential of organic detritus declines above 25 °C. These data are of relatively little importance as far as the generation of fluid hydrocarbons are concerned, but are of considerable interest regarding the formation of coal. The same conclusion is reached for continental realms as for oceans, namely, that the rate of decay of organic matter is more significant than its rate of formation.

5.2.2 Preservation of Organic Matter in Ancient Sediments

Extrapolating these data from the present day back in geological time is very difficult. Whereas the oceans appear to have contained diverse plant and animal life since way back in the Precambrian, plants only began to colonize the land toward the end of the Silurian Period, and extensive coal formation did not begin until the Carboniferous Period. In addition to the possibility of fluctuation of the rate of production of organic matter in the past, the chemical composition of the various plants may have changed as well. In particular, the amount of lignin may have increased in proportion to lipids, carbohydrates, and proteins.

Similarly, many paleontologists have traced the abundance of different groups of fossils back through geological time. Most studies use the number of species of a particular group as a criterion for their abundance. Although extrapolating from this information to actual numbers and biomass is hard, studies such as that by Tappan and Loeblich (1970) on phytoplankton may be particularly significant. They postulate a gradual increase in phytoplankton abundance from the Precambrian to 2014, with major blooms in the late Ordovician to early Silurian, and in the late Cretaceous.

This review shows that the preservation of organic matter in sediments is favored by high organic productivity; by an optimum, though not necessarily slow, sedimentation rate; and by anoxic conditions. These conditions may occur in diverse settings, from localized lakes to whole oceans. Gas chromatography can be used to fingerprint petroleum and to correlate it with the source rock from which it was derived (Bruce and Schmidt, 1994) and to determine the type of organism and depositional environment in which it lived (Volkman, 1988).

Many geologists have documented the distribution of organic-rich sediments in space and time (North, 1979, 1980; Grunau and Gruner, 1978; Grunau, 1983; Klemme and Ulmishek, 1991). Tissot (1979) and Klemme (1993) have pointed out the concentration of source rocks in Late Jurassic to Early Cretaceous sediments (Fig. 5.11).

Three old-established themes of geological research can now be brought together. Since the days of Du Toit and Wegener, geologists have been reconstructing the movement of the continents through time. It is now possible to use computers to model not only the wanderings of the continents but also the patterns of water circulation in the ancient oceans through

FIGURE   5.11 Histograms showing the distribution of the world's currently discovered oil and gas reserves through geological time. Note the concentration in rocks of Late Jurassic to Early Cretaceous ages, times of known organic-rich sediment deposition. *After Klemme and Ulmishek (1991).*
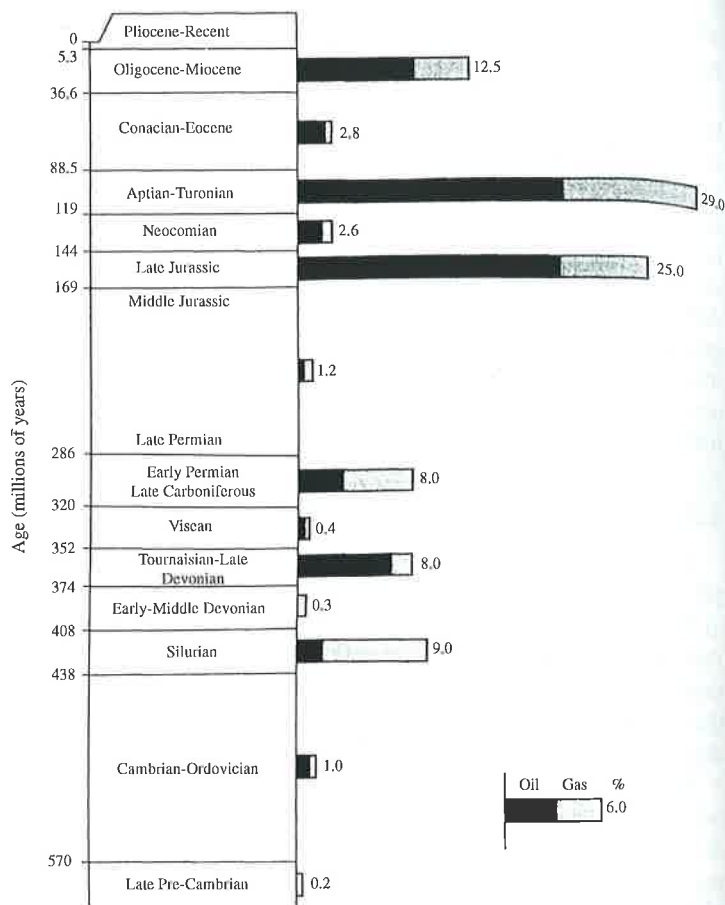
which they drifted, together with climatic variations. These can be integrated to map the global distribution of petroleum source rocks through the history of the earth (Huc, 1995).

5.3 FORMATION OF KEROGEN

Having now discussed the generation and preservation of organic matter at the earth's surface, it is appropriate to consider what happens to this organic matter when buried in a steadily subsiding sedimentary basin. As time passes, burial depth increases, exposing the sediment to increased temperature and pressure.

Tissot (1977) defined three major phases in the evolution of organic matter in response to burial:

1. *Diagenesis*: This phase occurs in the shallow subsurface at near normal temperatures and pressures. It includes both biogenic decay, aided by bacteria, and abiogenic reactions. Methane, carbon dioxide, and water are given off by the organic matter, leaving a

complex hydrocarbon termed *kerogen* (to be discussed in much greater detail shortly). The net result of the diagenesis of organic matter is the reduction of its oxygen content, ling the hydrogen:carbon ratio largely unaltered.

2. *Catagenesis*: This phase occurs in the deeper subsurface as burial continues and temperature and pressure increase. Petroleum is released from kerogen during catagenesis—first oil and later gas. The hydrogen:carbon ratio declines, with no significant change in the oxygen:carbon ratio.

3. *Metagenesis*: This third phase occurs at high temperatures and pressures verging on metamorphism. The last hydrocarbons, generally only methane, arxpelled. The hydrogen:carbon ratio declines until only carbon is left in the form of graphite. Porosity and permeability are now negligible.

The evolution of surface organic matter into kerogen and the ensuing generation of petroleum are discussed in detail in the following section.

5.3.1 Shallow Diagenesis of Organic Matter

The pH and Eh adjacent to the sediment:water interface are controlled by chemical reactions in which bacteria play an important role. In the ordinary course of events, circulation continually mixes the oxygenated and oxygen-depleted waters. As previously discussed, stratified water bodies inhibit this circulation. An oxygenated zone (+Eh) overlies a reducing zone (−Eh). Depending on circumstances, the interface between oxidizing and reducing conditions may occur within the water, at the sediment:water interface, or, if the sediments are permeable, below the sea bottom. In the lower reducing zone, anaerobic sulfate-reducing bacteria of the genus *Desulfovibrio* remove oxygen from sulfate ions, releasing free sulfur. In the upper oxygenated zone, the bacteria *Thiobacillus* oxidize the sulfur again:

$$SO_4 \xleftrightarrow[\text{Thiobacillus}]{\text{Desulfovibrio}} S + 2O_2$$
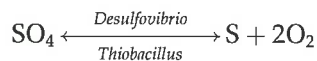
In the reducing zone, the sulfur may combine with iron in ferrous hydroxide to form pyrite:

$$Fe(OH)_2 + 2S = FeS_2 + H_2O$$
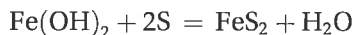
Sulfate ions may also react with organic matter to form hydrogen sulfide:

$$SO_4 + 2CH_2O = 2HCO_3 - +H_2S$$
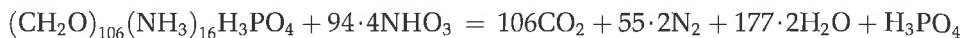$$\underset{\substack{Organic \\ matter}}{}$$
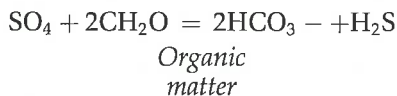
This formula for organic matter is very simple, and it may be more appropriate to assume that the average content of marine organic matter has a carbon: nitrogen:phosphorus ratio of 106:16:1 (Goldhaber, 1978).

The first stage of biological decay is oxidation, which generates water, carbon dioxide, nitrates, and phosphates:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 = 106CO_2 + 16NHO_3 + H_3PO_4 + 122H_2O$$
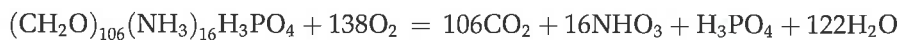
In the next stage, reduction of nitrates and nitrites occurs:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 94\cdot 4NHO_3 = 106CO_2 + 55\cdot 2N_2 + 177\cdot 2H_2O + H_3PO_4$$

This process is followed in turn by sulfate reduction, which results in the generation of hydrogen sulfide and ammonia:

$$(CH_2O)_{106}(NH_3), 6H_3PO_4 + 52SO_4^{2-} = 106HCO_3^- + 53H_2S + 16NH_3 + H_3PO_4$$
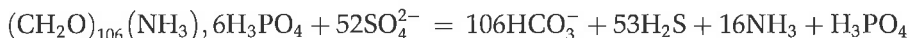
These equations are, of course, very simplified. As has been shown earlier, the organic compounds that are the starting point of this sequence of reactions are diverse and complex, consisting essentially of proteins, carbohydrates, lipids, and lignin; the relative rate of decay being in this order, with proteins being the least stable and woody lignin the most resistant. These compounds are all acted on by the enzymes of microbes to produce various biomonomers. For example, carbohydrates, such as starch and cellulose, are broken down to sugars. Cellulose is also converted into methane and carbon dioxide:

$$(C_6H_{10}O_5)_n \rightarrow CO_2 + CH_4$$
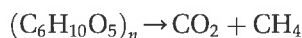
Methane is a major by-product of the bacterial decay of not only cellulose but also many other organic compounds. As this biogenic methane moves upward from the decaying organic matter, it may cross the −Eh:+Eh surface and be oxidized:

$$3CH_4 + 6O_2 = 3CO_2 + 6H_2O$$

In environments where the deposition of organic matter and its rate of decay are rapid, free methane may seep to the surface as bubbles of marsh gas. This gas occasionally ignites spontaneously, giving rise to the will o' the wisp phenomenon, which terrifies the uninformed in bogs and graveyards.

The proteins in decaying organic matter are degraded into amino acids and peptides. The lipid waxes and fats degrade to glycerol and fatty acids. The lignin of woody tissues breaks down to phenols, aromatic acids, and quinones. Plant material is degraded into fulvic acids, humic acids, and humin. These changes all take place within the top few meters of sediment. With gradually increasing burial depth, the physical environment of the sediment changes, and chemical reactions alter in response to these changes. The increase in overburden pressure results in compaction of the sediment. Numerous studies of compaction have been made and are discussed elsewhere. At this point, it is sufficient to state that within the first 300 m of burial, the porosity of a clay typically diminishes from some 80% down to only about 30 or 40%. During compaction, water escapes. Part of this water is primary pore water, but some of it is of biogenic origin. It contains in solution carbon dioxide, methane, hydrogen sulfide, and other organic compounds of decay, loosely termed *humic acids.*

At this time, several important inorganic reactions may be taking place, causing the formation of early authigenic minerals. The generation of pyrite has already been discussed, but in carbonate-rich clays siderite ($FeCO_3$) is also common. Early calcium carbonate cementation may occur by direct precipitation or, in evaporitic environments, by the interreaction of calcium sulfate and organic matter (Friedman, 1972). Sulfate ions react with organic matter

to produce hydrogen sulfide (as previously discussed) and HCO_3. The latter reacts with the calcium to form calcite, water, and carbon dioxide. Essentially,

$$CaSO_4 + 2CH_2O \rightarrow CaCO_3 + H_2O + CO_2 + H_2S$$
$$\textit{Organic}$$
$$\textit{matter}$$
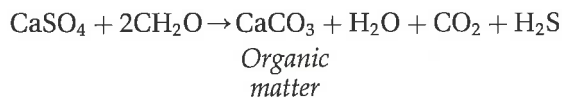
With increasing depth of burial, the ambient temperature increases and the role of bacteria in biogenic reactions gradually declines as they die out (although some thiophilic bacteria can occur deep in the subsurface). At the same time, however, increasing temperature allows inorganic reactions to accelerate. The generation of hydrocarbons now declines as the production of biogenic methane ceases. There are occasional reports of the shallow occurrence of biogenic hydrocarbons other than methane. One of the best known is the occurrence of up to 200 ppm of aromatics and paraffinic naphthenes in sand less than 10,000 years old and only 30 m deep off the Orinoco delta (Kidwell and Hunt, 1958). More recently, lipid-rich liquid hydrocarbons have been recorded from ocean floor samples. This protopetroleum is formed by the minor breakdown of organic oils. It is chemically distinct from crude oil, has not undergone thermal maturation, and does not appear to be present in commercial accumulations (Welte, 1972). Important changes continue to take place, however, within the preserved organic matter. Water and carbon dioxide continue to be expelled as the formation of kerogen begins.

Figure 5.12 illustrates the transformation of living material into kerogen and various types of hydrocarbons.

5.3.2 Chemistry of Kerogen

The etymology and original definition of kerogen as recognized in oil shale is discussed in Chapter 9. In 2014, kerogen is the term applied to disseminated organic matter in sediments that is insoluble in normal petroleum solvents, such as carbon bisulfide. This insolubility distinguishes it from bitumen. Chemically, kerogen consists of carbon, hydrogen, and oxygen, with minor amounts of nitrogen and sulfur (Table 5.3).

Three basic types of kerogen are generally recognizable. The differences are chemical and are related to the nature of the original organic matter. Because these three kerogen types generate different hydrocarbons their distinction and recognition are important (Tissot, 1977; Dow, 1977). Figure 5.13 illustrates the three kerogen types and depositional environments.

Type I kerogen is essentially algal in origin (Plate 5.6). It has a higher proportion of hydrogen relative to oxygen than the other types of kerogen have (H:O ratio is about 1.2−1.7). The H:C ratio is about 1.65 (Table 5.3). Lipids are the dominant compounds in this kerogen, with derivates of oils, fats, and waxes. This kerogen is particularly abundant in algae such as *Bottryococcus*, which occurs in modern Coorongite and ancient oil shales. Similar algal kerogen is characteristic of many oil shales, source rocks, and the cannel or boghead coals. The basic chemical structure of type I algal kerogen is shown in Fig. 5.14(A).

Type II, or liptinitic, kerogen is of intermediate composition (Plate 5.6). Like algal kerogen, it is rich in aliphatic compounds, and it has an H:C ratio of >1. The chemical structure is shown in
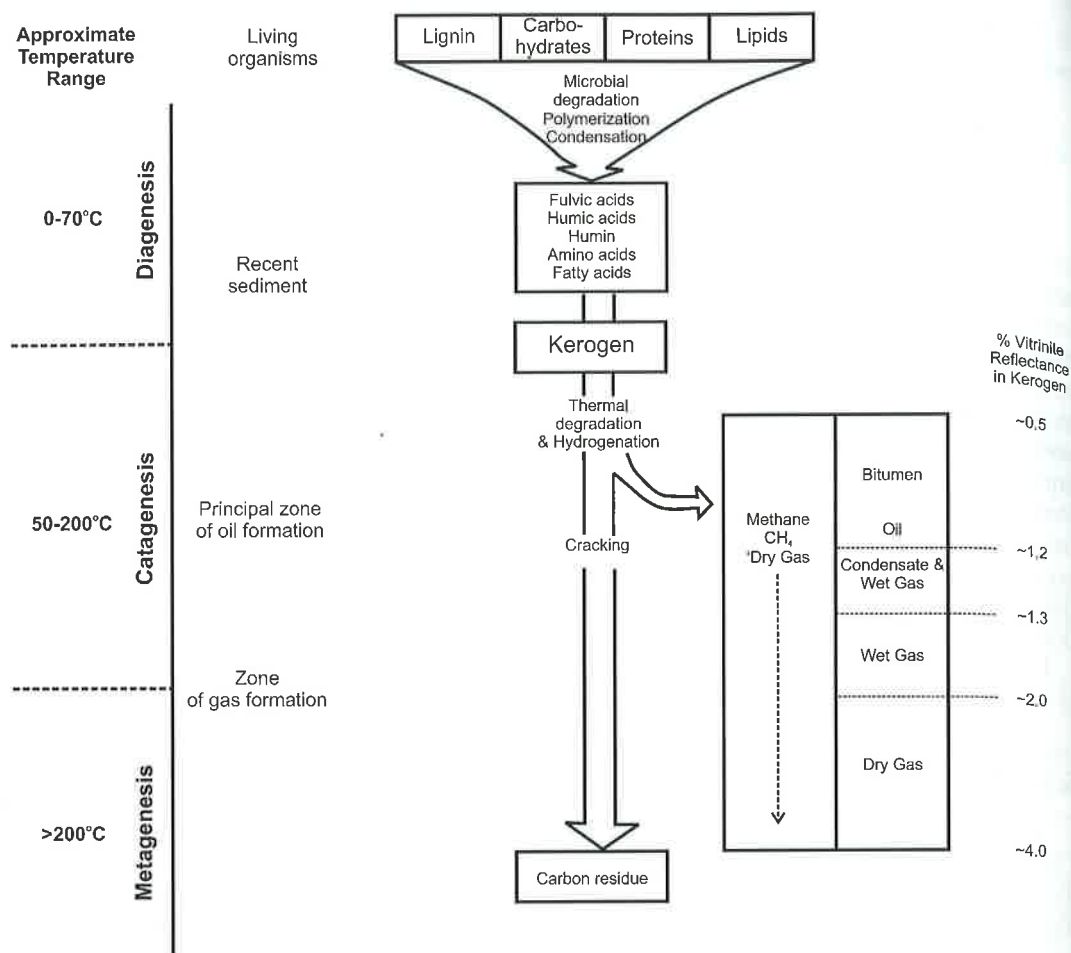
FIGURE 5.12 Alteration of organic matter in the subsurface. *Modified from Tissot and Welte (1984) and Meissner (1991).*

Fig. 5.14(B). The original organic matter of type II kerogen consisted of algal detritus, and also contained material derived from zooplankton and phytoplankton. The Kimmeridge clay of the North Sea and the Tannezuft shale (Silurian) of Algeria are of this type.

Type III, or humic, kerogen has a much lower H:C ratio (<0.84). Chemically, it is low in aliphatic compounds, but rich in aromatic ones (Plate 5.6). The basic molecular structure is shown in Fig. 5.14(C). Humic kerogen is produced from the lignin of the higher woody plants, which grow on land. It is this humic material that, if buried as peat, undergoes diagenesis to coal. Type III kerogen tends to generate largely gas and little, if any, oil. Nonmarine basins were once thought to be gas prone because of an abundance of humic kerogen, whereas marine basins were thought to be oil provinces because of a higher proportion of algal kerogen. This type of generalization is not valid. Many continental basins contain

TABLE 5.3   Chemistry of Kerogens

	Weight percent					Ratios		
	C	H	O	N	S	H–C	O–C	Petroleum type
Type I Algal	75.9 (7 samples)	8.84	7.66	1.97	2.7	1.65	0.06	Oil
Type II Liptinic	77.8 (6 samples)	6.8	10.5	2.15	2.7	1.28	0.1	Oil and gas
Type III Humic	82.6 (3 samples)	4.6		2.1	0.1	0.84	0.13	Gas

Weight percent data from Tissot and Welte (1978), ratios from Dow (1977). Reprinted with permission from Springer-Verlag.

ORGANIC FACIES IS DETERMINED MAINLY BY:
1. ORIGIN OF ORGANIC REMAINS (AQUATIC PLANTS VS LAND PLANTS)
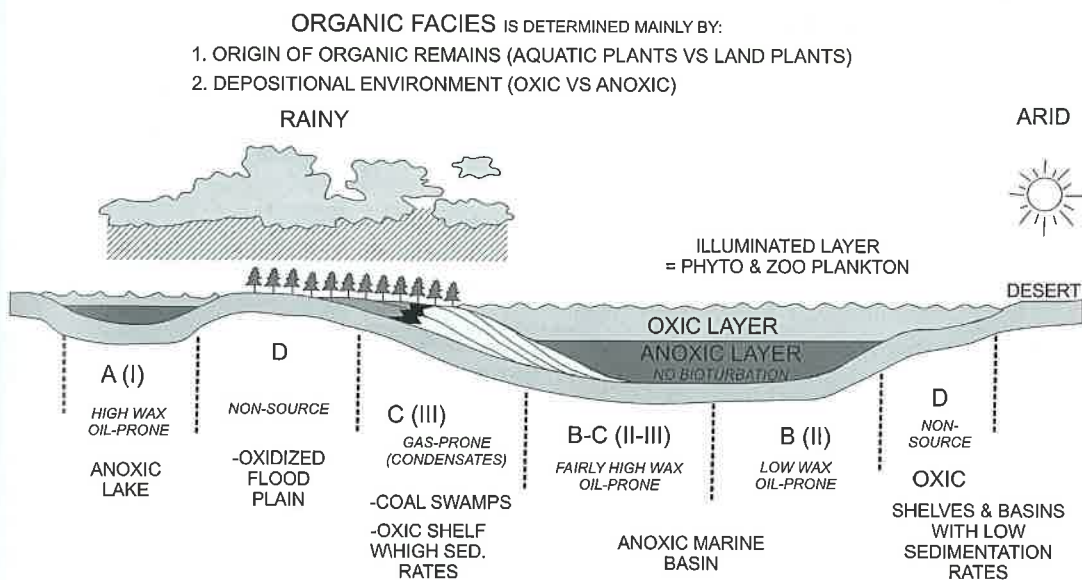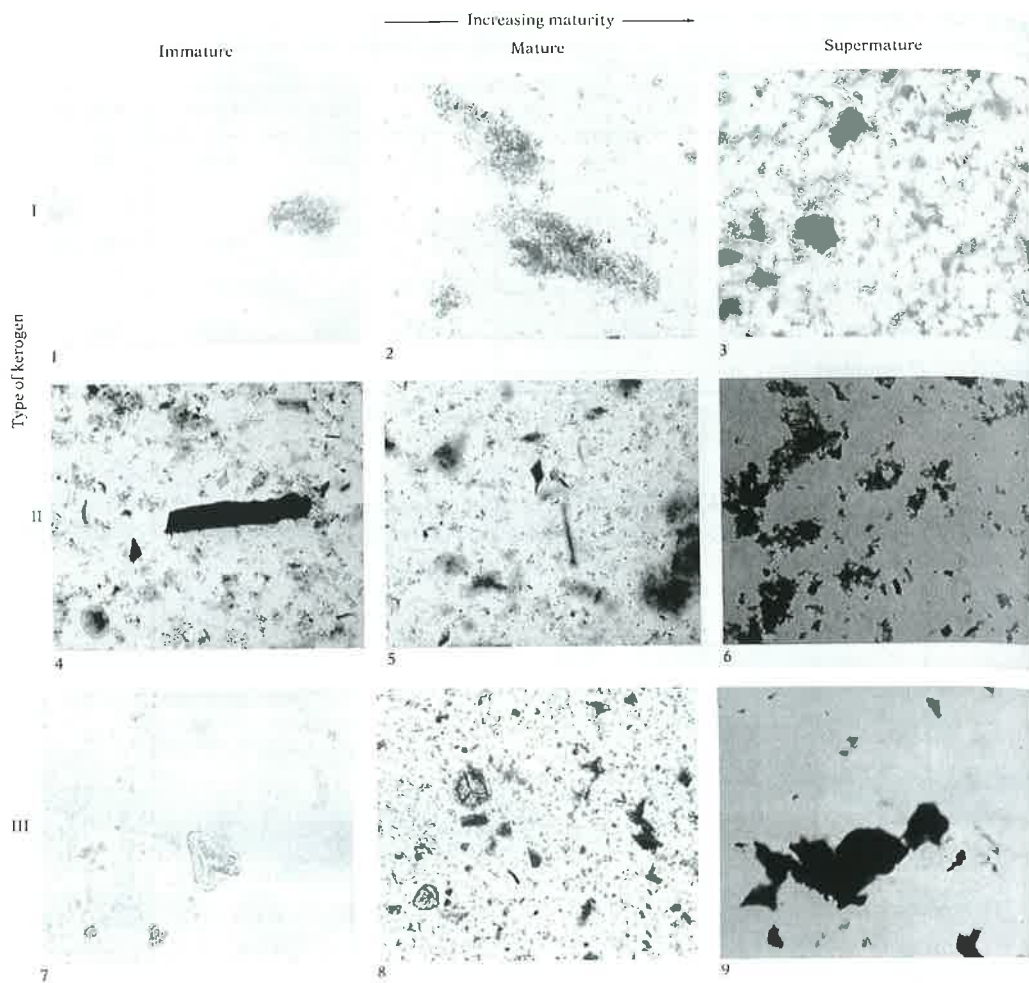2. DEPOSITIONAL ENVIRONMENT (OXIC VS ANOXIC)

FIGURE 5.13   Organic facies and kerogen type. *Modified from Jones and Demaison (1980).*

lacustrine shales rich in algal kerogen. The Green River formation of Colorado, Utah, and Wyoming is a noted example; other examples occur in China (Li et al., 1982). Further details on kerogen can be found in Tissot and Welte (1978), Hunt (1996), Katz (1995), Brooks and Fleet (1987), and Durand (1980).

This review of the three basic types of kerogen shows the importance of identifying the nature of the organic matter in a source rock so as to assess accurately its potential for generating hydrocarbons. A second important factor to consider is not only the quality of kerogen but also the quantity necessary to generate significant amounts of oil and gas suitable for

Photograph Number	1	2	3	4	5	6	7	8	9
Locality	Gurpi Fm Zagros, Iran	Kazdumi Fm, Zagros, Iran	Garau Fm Zagros, Iran	Kimmeridge Clay Dorset, UK	Kimmeridge Clay Dorset, UK	Sembar Fm, Lower Indus, Pakistan	Shamsi Fm, Alborz, Iran	Coal Measures South Wales	Coal Measures South Wales
Type of Kerogen	I	I	I	II	II	II	III	III	III
Maturation Level	Immature	Mature	Supermature	Immature	Mature (just)	Supermature	Immature	Mature	Supermature
R_o(%)	0.4	0.9	2.0	0.4	0.5	2.0	0.4	1.2	3.0
Magnification	X25	X25	X62	X25	X25	X62	X25	X25	X50

PLATE 5.6   Photomicrographs of different types of kerogen at various maturation stages (See the color plate). *Courtesy of Kinghorn and Rahman.*
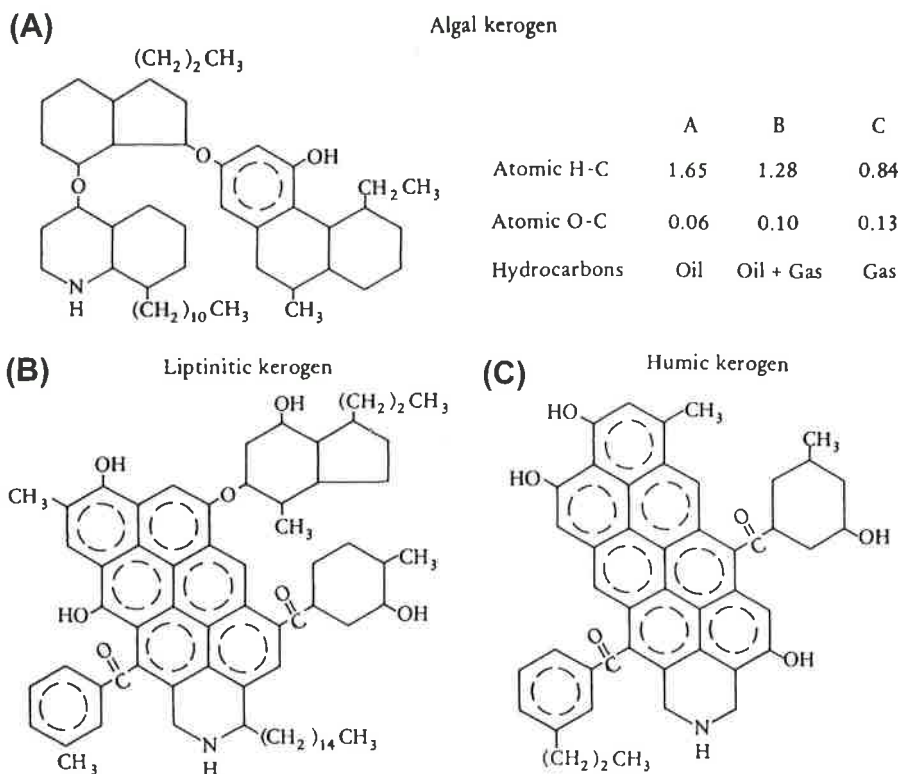
FIGURE 5.14   The molecular structure of (A) type I, or algal, kerogen; (B) type II, or liptinitic, kerogen; and (C) type III, or humic, kerogen. *Reprinted from Dow (1977), with kind permission of Elsevier Science, The Netherlands.*

commercial production. Several separate items are to be considered here, including the average amount of kerogen in the source bed, the bulk volume of the source bed, and the ratio of emigrated to residual hydrocarbons. The total organic matter in sediments varies from 0% in many Precambrian and continental shales to nearly 100% in certain coals. A figure of 1500 ppm TOC is sometimes taken as the minimum requirement for further exploration of a source rock (Pusey, 1973a).

5.3.3 Maturation of Kerogen

During the phase of catagenesis, kerogen matures and gives off oil and gas. Establishing the level of maturation of kerogen in the source rocks of an area subject to petroleum exploration is vital. When kerogen is immature, no petroleum has been generated; with increasing maturity, first oil and then gas are expelled; when the kerogen is overmature, neither oil nor gas remains. Figure 5.15 shows the maturation paths for the different types of kerogen. The maturation of kerogen can be measured by several techniques to be described shortly. The rate of maturation may be dependent on temperature, time, and, possibly, pressure.
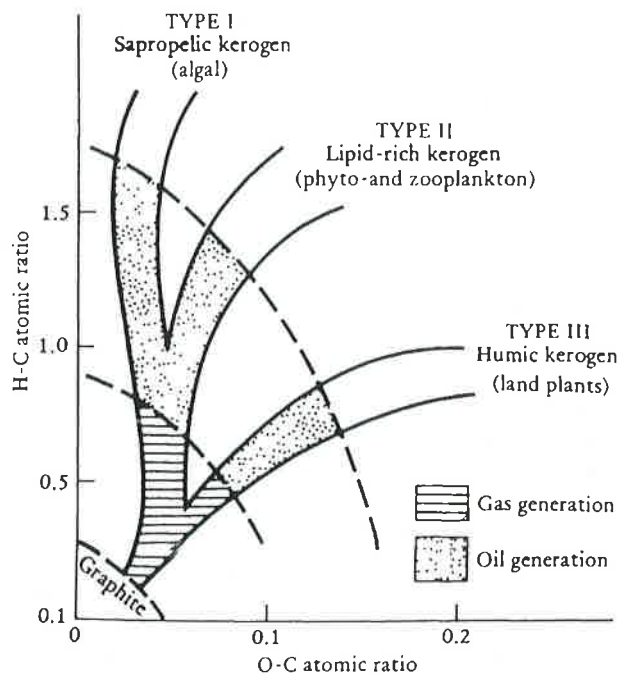
FIGURE 5.15   Graph showing the maturation paths of the three different types of kerogen.
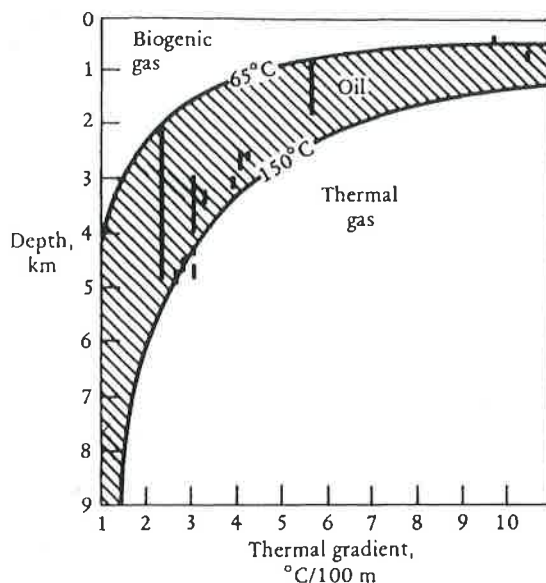

FIGURE 5.16   Graph of depth versus thermal gradient showing how oil occurs in a liquid window of between 65 and 150 °C, which extends from shallow depths with high thermal gradients to deep basins with lower gradients. *After Pusey (1973a).*

A number of workers have documented an empirical correlation between temperature and petroleum generation (Pusey, 1973a,b; Philippi, 1975; Hunt, 1996). Significant oil generation occurs between 60 and 120 °C, and significant gas generation between 120 and 225 °C. Above 225 °C, the kerogen is inert, having expelled all hydrocarbons; only carbon remains as graphite (Fig. 5.16). The temperatures just cited are only approximate boundaries of the oil and gas windows.

5.3.3.1 The Chemical Laws of Kinetics

The chemical laws of kinetics, as expressed in the Arrhenius equation, state that the rate of a chemical reaction is related to temperature and time. Reaction rate generally doubles for each 10 °C increase. Thus, many geologists have considered that kerogen maturity is a function of temperature and time (Fig. 5.17). Petroleum may therefore have been generated from old, cool source rocks as well as from young, hot ones (e.g., Connan, 1974; Erdman, 1975; Cornelius, 1975). Several techniques have been developed that try to quantify the relationship of temperature and time to kerogen maturity. These techniques are generally based on a burial history curve (Van Hinte, 1978), which is a graph on which burial depth is plotted against geological time for a particular region (Fig. 5.18).

Two commonly used maturation indices are the time—temperature index (TTI) and the level of organic maturation (LOM). The TTI was first proposed by Lopatin (1971) and developed by Waples (1980, 1981). The TTI is calculated from a formula that integrates temperature with the time spent in each temperature (in increments of 10 °C) as a source rock is buried. The length of time spent in each temperature increment is established from the burial curve. The LOM was first proposed by Hood et al. (1975) and developed by Royden et al. (1980) and Cohen (1981). The LOM is based on the assumption that reaction rate doubles for each 10 °C increment of temperature. Oil generation occurs between LOM values of 7 and 13, and gas generation occurs between values of 13 and 18.
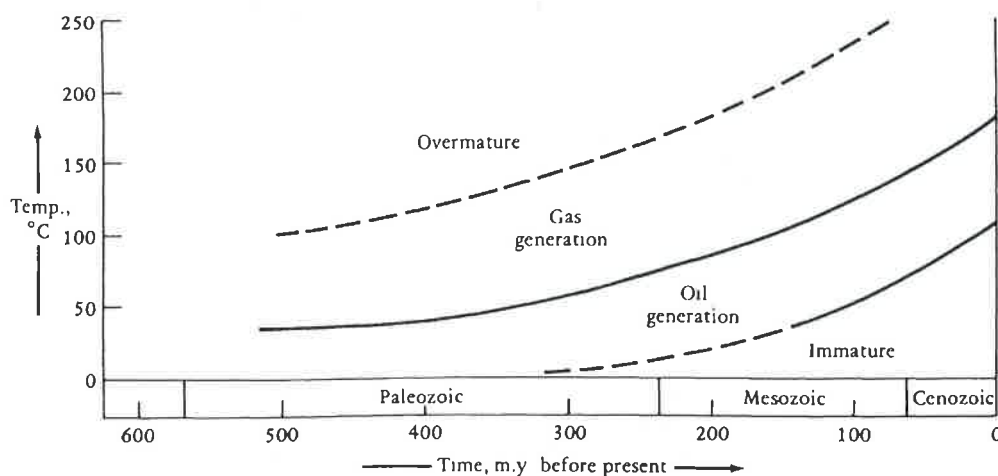

FIGURE 5.17 Graph of temperature against time of oil and gas formation. For the problems of interpreting this figure, see the text. *After Connan (1974), Erdman (1975) and Cornelius (1975).*
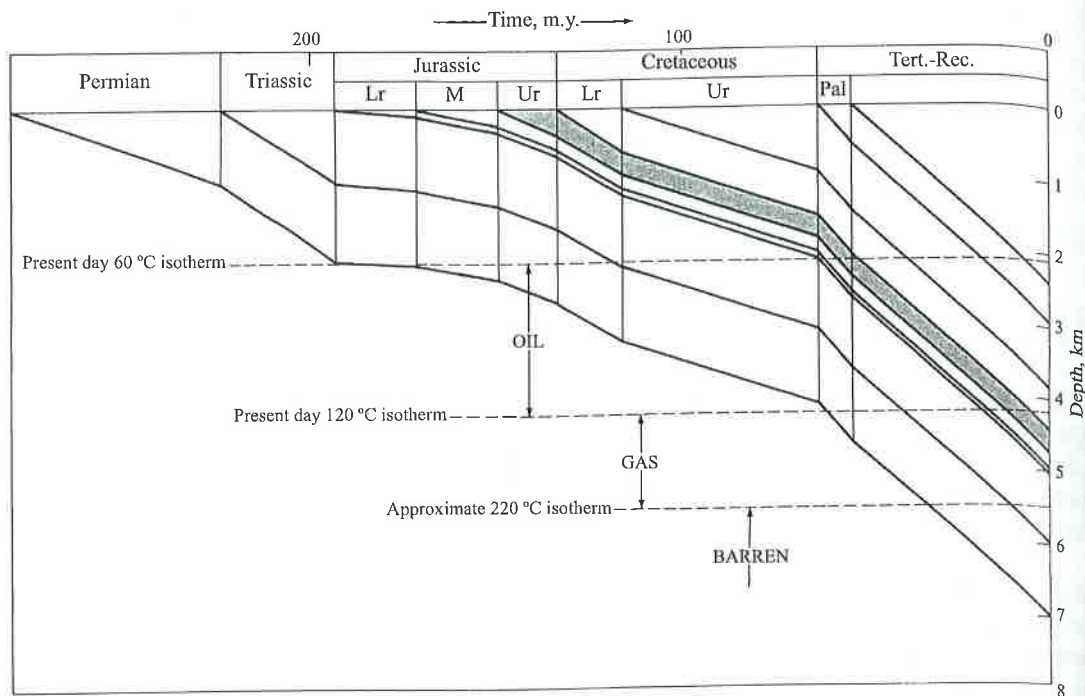
FIGURE 5.18   Burial curve for the Central Graben of the North Sea. Major Kimmeridge clay source rock shown in black. Since present-day isotherms are used, the graph only gives a rough idea of when the source rock entered the oil and gas windows. *After Selley (1980).*

Both the TTI and LOM must be used with caution. They assume that the geothermal gradient has been constant through time, which is seldom likely to be true. Burial curves must also be used carefully, not only considering the present-day depth of the formations but also allowing for compaction, uplift, and for the fact that in few basins do subsidence and sedimentation balance one another. Price (1983) has cast still more doubts on these methods. His careful analysis of his own data and previously published data led him to conclude that only temperature affects organic metamorphism; time is not important.

Whatever may be the case regarding the effects of temperature and time, measuring the maturity of kerogen is obviously necessary. Many techniques are available, some of which are described in the following sections.

5.3.4 Paleothermometers

Because of the important relationship between temperature and petroleum generation, measuring the maturity of the kerogen is important. It is not enough to be able to answer these questions: Are there organic-rich source rocks in the basin? Are they present in large-enough volumes? Are they oil prone or gas prone? It is also necessary to know whether or

not the source rocks have matured sufficiently to generate petroleum or whether they are supermature and barren.

To measure only the bottom hole temperature from boreholes does not answer the question of kerogen maturity. This measurement only indicates the present-day temperature, which may be considerably lower than that of the past. It is necessary to have a paleothermometer, which can measure the maximum temperature to which the source rock was ever subjected. Several such tools are available, each varying in efficiency and each requiring expensive laboratory equipment and a considerable degree of technical expertise. Broadly speaking, two major groups of techniques are used for measuring the maximum paleotemperature to which a rock has been heated (Cooper, 1977):

1. Chemical paleothermometers
   a. Organic
      - Carbon ratio
      - Electron spin resonance (ESR)
      - Pyrolysis
      - Gas chromatography

   b. Inorganic
      - Clay mineral diagenesis
      - Fluid inclusions
2. Biological paleothermometers
   a. Pollen coloration
   b. Vitrinite reflectance

5.3.4.1 *Chemical Paleothermometers*

One of the oldest and most fundamental of maturation indices is the carbon ratio method. Obviously, as organic matter matures, organic carbon is lost; first as carbon dioxide during decarboxylation and later during petroleum generation. The net result of kerogen maturation is thus a gradual decrease in the proportion of movable organic carbon and a relative increase in the proportion of fixed carbon. The carbon ratio method compares the TOC (C_T) in the sample with the residual carbon (C_R) after pyrolysis to 900 °C. The ratio C_rC_I increases with maturation (Gransch and Eisma, 1970). This paleothermometer is not easy to calibrate, however, because of the variations in the original carbon content in the different types of kerogen and the risky assumption that their carbon ratios change at the same rate.

A second chemical thermometer is the ESR technique developed by Conoco (Pusey, 1973b). The ESR method is based on the fact that the atomic fraction of kerogen contains free electrons, whose number and distribution are related to the number and distribution of the benzene rings. These electron characteristics change progressively as the kerogen matures (Marchand et al., 1969). Kerogen can be extracted from the source rock and placed in a magnetic field whose strength can be controlled. If the sample is then exposed to microwaves, the free electrons resonate (hence the term ESR) and, in so doing, alter the frequency of the microwave. With an electrometer, certain properties of the electrons can be measured, including their number, signal width, and the location of the resonance point. As already stated, these parameters have been shown to vary with kerogen maturation.

The ESR technique was originally developed as a paleothermometer in the Gulf Coast of the United States (Pusey, 1973b) and later in the North Sea (Cooper et al., 1975). The method has the advantage of being quick (once a laboratory is established), and it can be used on minute and impure samples of kerogen. As with most paleothermometers, great care must be taken that the shale samples gathered during drilling are not caved; ideally, core or sidewall core material should be used. Again, as with the carbon ratio method, the ESR has certain problems caused by original variations in kerogen composition and the presence of recycled organic detritus (Durand et al., 1970).

Pyrolysis, the heating of kerogen or source rock, was the process developed to produce petroleum from oil shales. In 2014, the pyrolysis of kerogen samples is an important laboratory technique in source rock analysis (Espitalie et al., 1977; Tissot and Welte, 1978; Peters, 1986; Hunt, 1996). Pyrolysis is carried out with a flame ionization detector. Initially, it was necessary to separate the kerogen from the source rock. Nowadays, however, analysis can be carried out on whole rock samples using the Rock–Eval pyroanalyzer designed by the Institut Français du Petrole. The sample is heated in a stream of helium. The temperature is gradually raised at a carefully measured rate, and the expelled hydrocarbon gases recorded with a hydrogen flame ionization detector. At relatively low temperatures (200–300 °C), any free hydrocarbons in the sample are volatilized. These hydrocarbons are referred to as S_1. With increasing temperature, hydrocarbons are expelled from the kerogen itself. These hydrocarbons are termed S_2. With further heating to some 390 °C, carbon dioxide is expelled to generate a third peak, S_3. Pyrolysis generally continues up to 800–900 °C. The temperature at which the S_2 peak occurs is termed T_{max}. The three readings can be used to determine the maturation level of the source rock. Where migration has not occurred, the ratio $S_1/(S_1 + S_2)$ shows the amount of petroleum generated compared with the total amount capable of being generated. This ratio is referred to as the transformation ratio or production index (PI). When plotted against depth, PI will generally show a gradual increase as the source rock matures.

Another important parameter established by pyrolysis is the hydrogen index (HI); this indicates the amount of pyrolyzable organic compounds (hydrocarbons) from the S_2 peak, relative to the TOC (or C_{org}). Similarly, the oxygen index indicates the amount of carbon dioxide generated compared to the TOC. Figure 5.19 illustrates a typical pyrolysis well log. A critique of the pyrolysis method can be found in Snowdon (1995).

Gas chromatography is another method of assessing the maturity of a source rock. This is used to study the distribution of n-alkanes, since Allan and Douglas (1977) have shown that there is a correlation between the shift in the pattern of these when compared with other paleothermometers such as vitrinite reflectance (to be discussed shortly). Gas chromatography shows that n-alkanes evolve with increasing temperature and burial depth. The gas chromatographs of immature source rocks of n-alkanes show a broad "whaleback," with a bimodal distribution of unsolved components. As the temperature increases and the source rock matures, the whaleback submerges and the unsolved components form a single peaky mode (Fig. 5.20). Degraded oils are characterized by a broad low whaleback that is devoid of spikes.

Clay mineral analysis is one of the oldest of the inorganic paleothermometers, having been studied quite independently of kerogen maturation. Newly deposited clay minerals include smectites (montmorillonite), illite, and kaolin. The varying abundance of different mineral
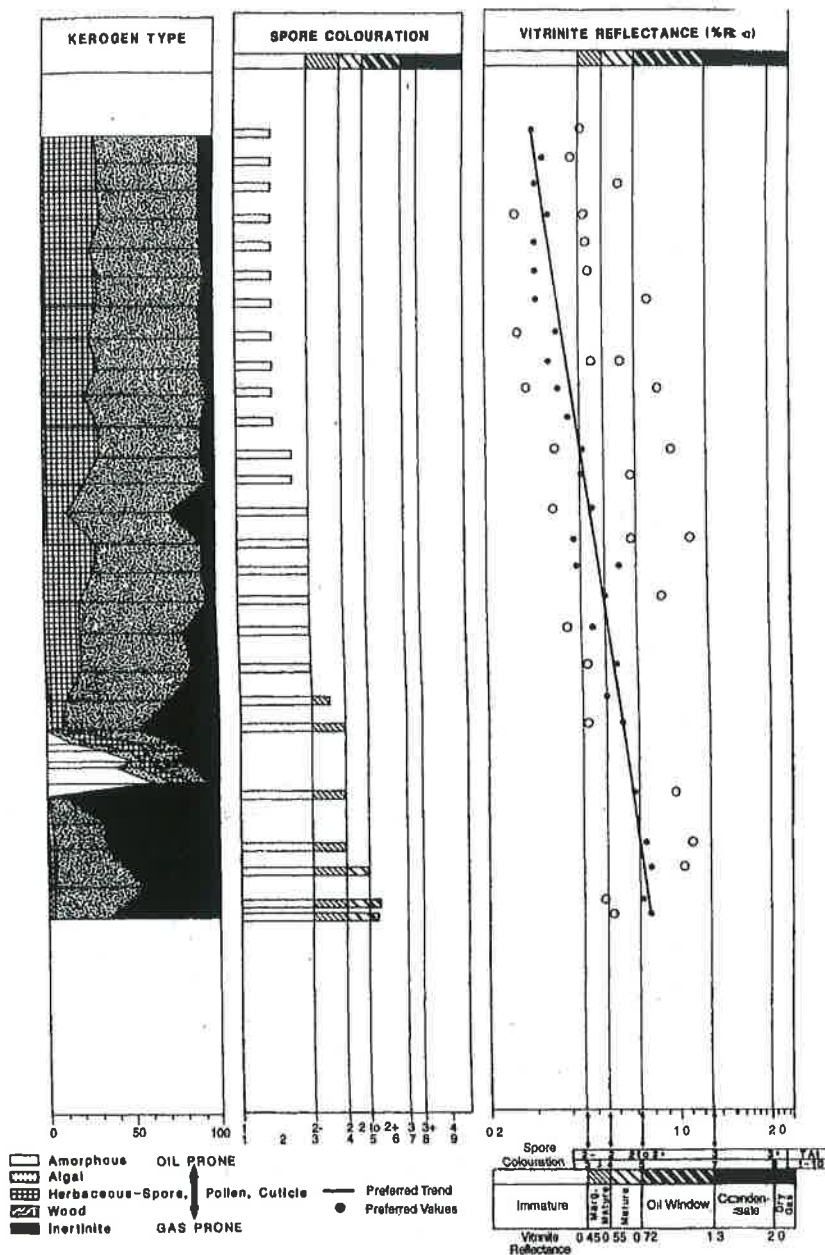
FIGURE 5.19   An example of a geochemical well log compiled to document the quantity, quality, and maturation level of a source rock. *Left*: From left to right, logs illustrate the lithology, TOC content, and Rock–Eval parameters of S2 and HI as explained in the text. *Right* From left to right, logs of kerogen type give an indication of the oil- or gas-prone nature of the source rock and two paleothermometers, spore coloration, and vitrinite reflectance, as discussed in the text. *Courtesy of Geochem, Ltd.*
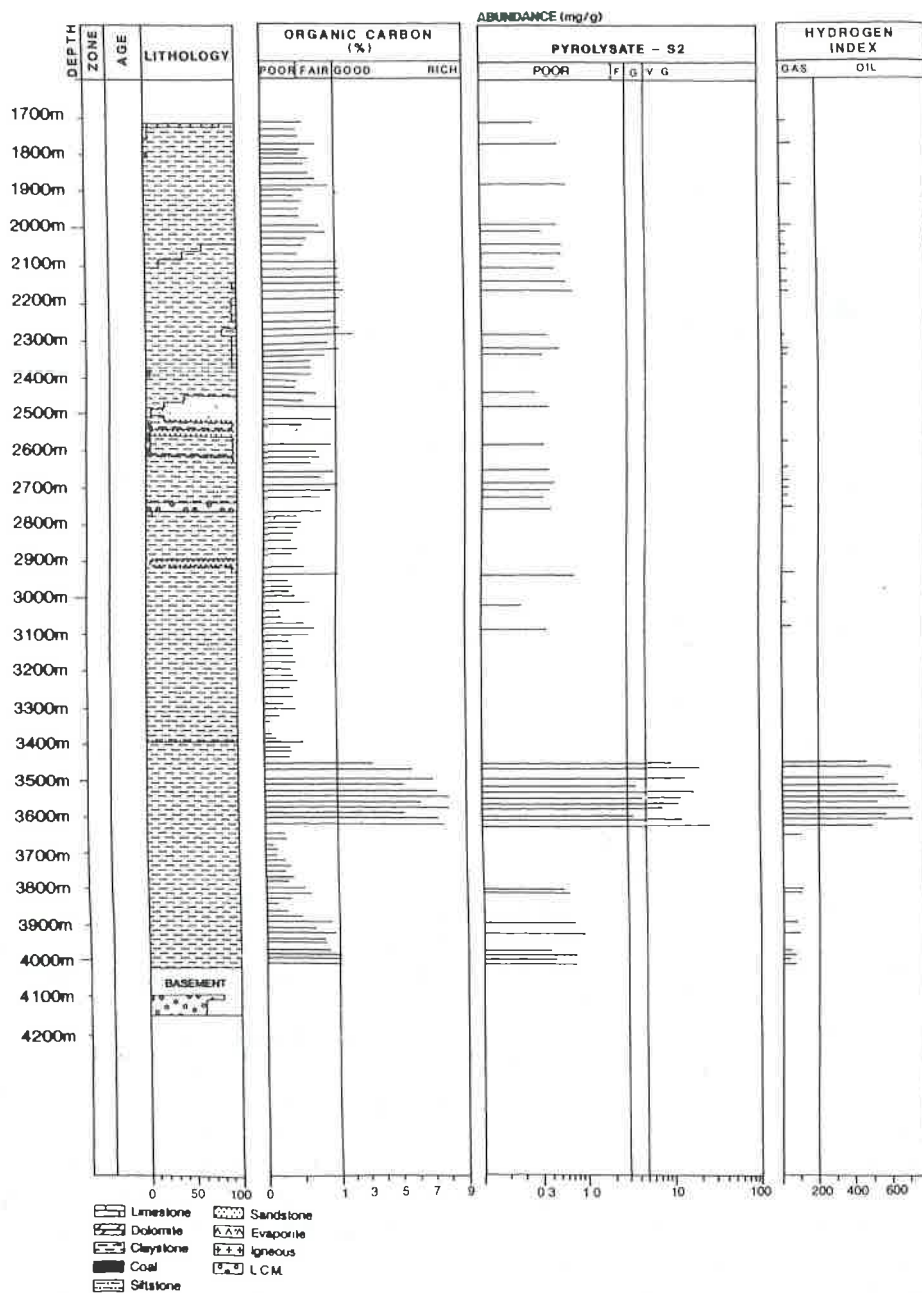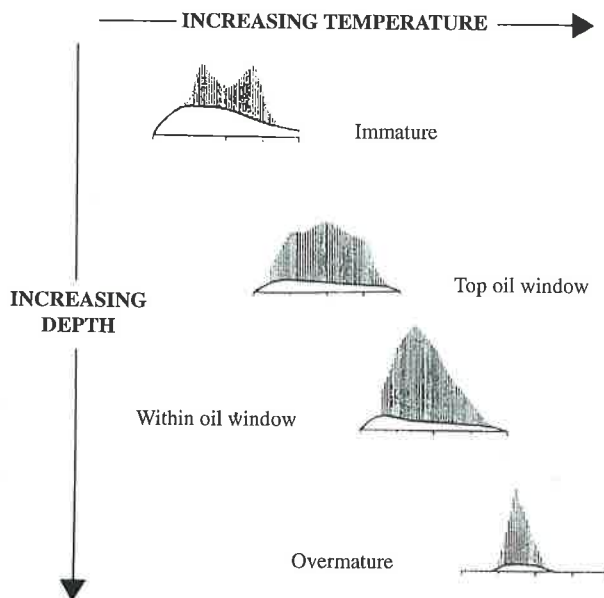
FIGURE 5.19   Cont'd

FIGURE 5.20 Diagram of gas chromatographs that show the evolution of *n*-alkanes with increasing temperature and burial depth. Each specimen is plotted on a carbon number scale of 0–40. Developed from Kinghorn (1982–1983). Immature source rocks show a broad whaleback, with a bimodal distribution of unsolved components. As the temperature increases and the source rock matures, the whaleback submerges and the unsolved components form a single peaky mode. Degraded oils are characterized by a broad low whaleback that is devoid of spikes.

types depends partly on the source area and partly on the depositional environment. As clays are buried, they undergo various diagenetic changes. Illite and kaolin authigenesis is largely related to the pH of the pore fluid. With increasing depth of burial, higher temperatures recrystallize the clays. Of particular interest is the behavior of the smectites, which dewater and change to illite within the optimum temperature for oil generation (80–120 °C). This phenomenon is considerably important to oil migration (Powers, 1967) and is discussed later in this chapter.

As temperatures increase to the upper limits at which oil and gas form, another major change in clay takes place. Kaolin and illite recrystallize into micas, whereas in ferromagnesian-rich environments they form chlorites. A number of studies have documented these changes (e.g., Fuchtbauer, 1967). These calibration points are rather imprecise to pick on the kerogen maturation scale. A greater degree of sophistication was achieved, however, by Gill et al. (1979), who showed how the crystallinity of kaolin and illite could be mapped across the South Wales coal basin and how those variations correlated with coal rank. This technique can undoubtedly be applied to other regions.

Another inorganic paleothermometer is provided by the study of fluid inclusions. This method has been used for many years by hard rock geologists interested in finding the temperature of formation of crystalline minerals (Roedder, 1984). It is now widely used in the oil industry, but principally as an aid to understanding diagenetic processes in petroleum reservoirs (Rankin, 1990). Thus, it is discussed in Chapter 6.

5.3.4.2 *Biological Paleothermometers*

In addition to chemical methods for paleotemperature measurement, several biological paleothermometers are used. One of these techniques measures the color of the organic matter in the source rock. Kerogen has many colors and shades, which are dependent on both maturation and composition. Spores and pollen, however, begin life essentially colorless. As they are gradually heated, they change to yellow, orange, brown (light to dark), and then to black. Palynologists have used this color change pattern for years to differentiate recycled spores and pollen from indigenous ones, since the former will be darker than average for a particular sample.

More recently, it has been realized that these color changes can be related to the degree of maturation of the associated kerogen. Several color codes are used by palynologists; some have been developed by palynologists themselves, others are borrowed from brewers. One popular system is the 10-point Spore Color Index of Barnard et al. (1978); another is the 5-point Thermal Alteration Index of Staplin (1969). Using the simple brewer's color code, the following relationship between pollen color and hydrocarbon generation has been noted: water: immature; lager: oil generation; bitter: condensate generation; Guinness: dry gas. It has been argued that pollen color measurement is a subjective assessment, but with reference standards and adequate operator experience, the results seem to be valid. The technique is relatively fast and economical, since the palynologists will review their samples as a routine check for contamination and recycling anyway.

The last paleothermometer to consider is vitrinite reflectance (Dow, 1977; Dow and O'Connor, 1979; Cooper, 1977), a very well-established technique used by coal petrographers to assess the rank of coal samples. Basically, the shininess of coal increases with rank from peat to anthracite. This shininess, or reflectance, can be measured optically. Vitrain, the coal maceral used for measurement, occurs widely, if sparsely, throughout sedimentary rocks. Kerogen, which includes vitrain, is separated from the sample by solution in hydrofluoric and hydrochloric acids. The residue is mounted on a slide, or in a resin block with a low-temperature epoxy resin and then polished. A reflecting-light microscope is then used to measure the degree of reflectivity, termed R_o. This step requires great care and can only be done by a well-trained operator. The prepared sample may contain not only indigenous kerogen but also caved and recycled material, as well as organic material from drilling mud (lignosulfonate). Reflectivity may also vary from the presence of pyrite or asphalt. A number of reflectivity readings are taken for each sample and plotted on a histogram, reference being made to standard samples of known R_o values. R_o may be measured for a series of samples down a borehole, and a graph of reflectivity versus depth may be plotted.

An empirical relationship has been noted between vitrinite reflectance and hydrocarbon generation. Crude oil generation occurs for R_o values between 0.6 and 1.5. Gas generation takes place between 1.5 and 3.0; at values above 3.0 the rocks are essentially graphitic and devoid of hydrocarbons. These values are only approximate because, as already discussed, the oil- or gas-generating potential of kerogen varies according to its original composition.

Reflectivity is generally assumed to increase with temperature and time. McTavish (1978) and Fang et al. (1995) have shown, however, the retarding effect of overpressure and, as
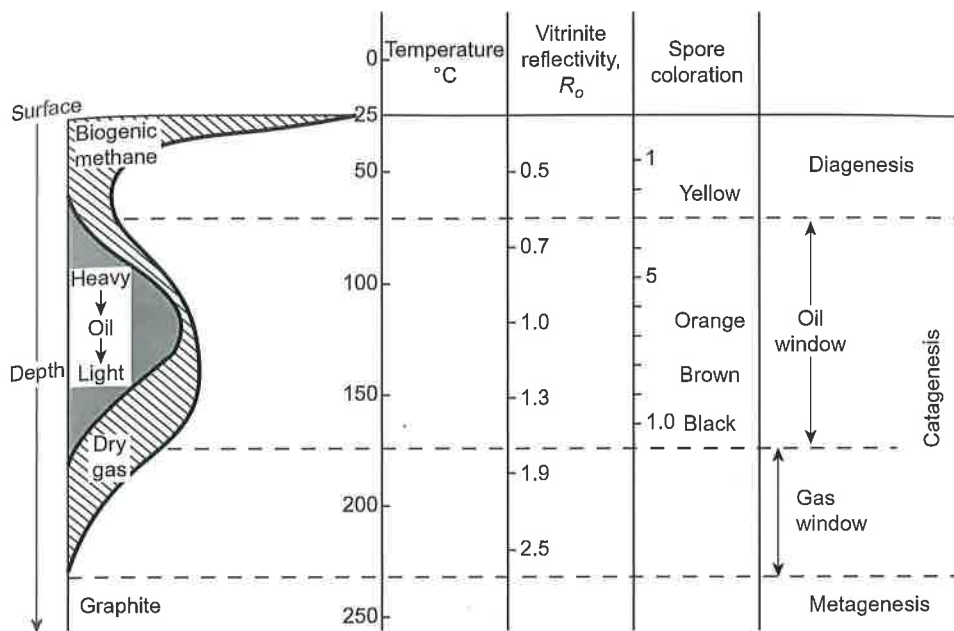
FIGURE 5.21 Correlation between hydrocarbon generation, temperature, and some paleothermometers.

already noted, Price (1983) considers temperature to be the only important variable. The measurement of vitrinite reflectivity is one of the most widely used techniques for establishing the maturity of a potential source rock in an area. Among other uses, borehole logs that plot R_0 against depth indicate the intervals in which oil or gas may have been generated. Abrupt shifts in the value of R_0 with depth may indicate faults or unconformities. An abrupt increase in R_0 with depth followed by a return to the previous gradient may be caused by igneous intrusives.

This review of paleothermometers shows that a wide range of techniques is available. All the methods require elaborate laboratory equipment, carefully trained analytical operators, and skilled interpretation of the resultant data. There are many pitfalls for the inexperienced interpreter. Probably, pollen coloration and vitrinite reflectivity are the most reliable and widely used maturation indices at the present time. Figure 5.21 shows the relation between R_0, spore coloration, and hydrocarbon generation. Figure 5.22 shows a maturation range chart with various types of kerogen.

5.4 PETROLEUM MIGRATION

The preceding sections of this chapter showed that petroleum is of organic origin; discussed the production of organic matter and its preservation in sediments; and traced the diagenesis of organic matter into kerogen and the maturation of kerogen as petroleum is expelled. The object of this section is to discuss how fluid hydrocarbons may emigrate from the source rock to the reservoir.
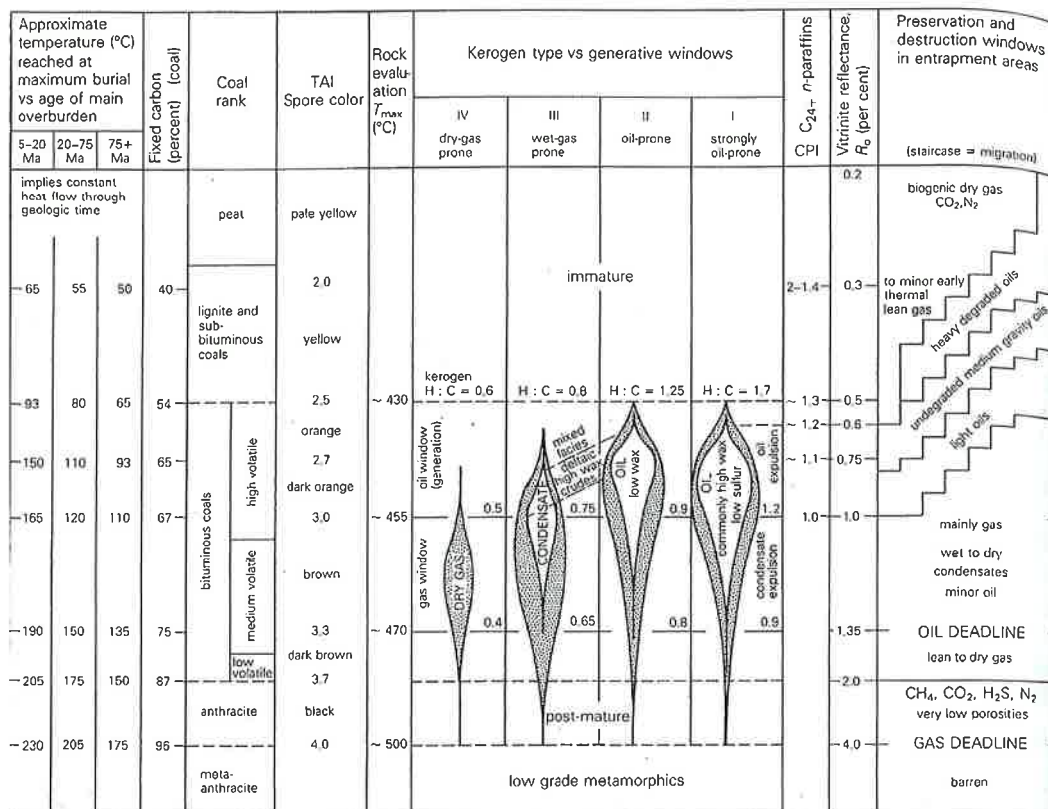
Approximate temperature (°C) reached at maximum burial vs age of main overburden			Fixed carbon (percent) (coal)	Coal rank	TAI Spore color	Rock evaluation T_{max} (°C)	Kerogen type vs generative windows				C_{24+} n-paraffins CPI	Vitrinite reflectance, R_o (per cent)	Preservation and destruction windows in entrapment areas (staircase = migration)
5–20 Ma	20–75 Ma	75+ Ma					IV dry-gas prone	III wet-gas prone	II oil-prone	I strongly oil-prone			
implies constant heat flow through geologic time				peat	pale yellow				immature			0.2	biogenic dry gas CO_2, N_2
65	55	50	40	lignite and sub-bituminous coals	2.0 / yellow						2–1.4	0.3	to minor early thermal lean gas
93	80	65	54		kerogen H:C = 0.6 / 2.5 orange	~430	H:C = 0.6	H:C = 0.8	H:C = 1.25	H:C = 1.7	~1.3	0.5	
150	110	93	65	bituminous coals (high volatile)	2.7 dark orange						~1.2	0.6	light oils
165	120	110	67	(medium volatile)	3.0 brown	~455	0.5 / 0.4	0.75 / 0.65	0.9 / 0.8	1.2 / 0.9	~1.1	0.75	mainly gas; wet to dry condensates minor oil
190	150	135	75	(low volatile)	3.3 dark brown	~470					1.0	1.0	OIL DEADLINE — lean to dry gas
205	175	150	87	anthracite	3.7 black				post-mature			1.35 / 2.0	CH_4, CO_2, H_2S, N_2 very low porosities
230	205	175	96	meta-anthracite	4.0	~500		low grade metamorphics				4.0	GAS DEADLINE — barren

FIGURE 5.22   Maturation range chart. *Modified from Demaison (1980), North (1985).*

A number of lines of observational evidence show that oil and gas do not generally originate in the rock in which they are found, but that they must have migrated into it from elsewhere. This theory is proved by the following observations:

1. As previously discussed, organic matter is easily destroyed by oxidization in porous, permeable sediments at the earth's surface. It must therefore have invaded the reservoir rock after considerable burial and raised temperature.
2. Oil and gas often occur in solution pores and fractures that must have formed after the burial and lithification of the host rock.
3. Oil and gas are trapped in the highest point (structural culmination, or stratigraphic pinchout) of a permeable rock unit, which implies upward and lateral migration.
4. Oil, gas, and water occur in porous, permeable reservoir rock stratified according to their relative densities. This stratification implies that they were, and are, free to migrate vertically and laterally within the reservoir.

These observations all point to the conclusion that hydrocarbons migrate into reservoir rocks at a considerable depth below the surface and some time after burial.

An important distinction is made between primary and secondary migration. Primary migration is understood as the emigration of hydrocarbons from the source rock (clay or shale) into permeable carrier beds (generally sands or limestones). Secondary migration refers to subsequent movement of oil and gas within permeable carrier beds and reservoirs (Showalter, 1979; England, 1994). There is consensus that secondary migration occurs when petroleum is clearly identifiable as crude oil and gas, and, although gas may be dissolved in oil, their solubility in connate water is negligible. Secondary migration occurs by buoyancy due to the different densities of the respective fluids and in response to differential pressures, as discussed in Chapter 4.

Primary migration, the emigration of hydrocarbons from source bed to carrier, is still a matter for debate. The object of this section is to examine the problem of primary hydrocarbon migration, which is to many people the last great mystery of petroleum geology. Seminal works on this topic are by Magara (1977), Momper (1978), Tissot and Welte (1978), McAuliffe (1979), Hunt (1979, 1996), Roberts and Cordell (1980), Lewan (1987), England and Fleet (1991), Verweij (1993), Mann (1994), and Pepper and Corvi (1995a,b,c). The following account draws freely on these works.

A number of basic questions need to be answered before the problem of primary migration can be fully understood. These questions include "When did migration occur?" "What was the physical environment (temperature, pressure, permeability, porosity) of the source bed at that moment?" "What was the chemical composition of the source bed at that moment (clay mineralogy may be one critical factor; water content another)?" "What was the nature of the hydrocarbons?" "Were they in the form of protopetroleum, some nebulous substance transitional between kerogen and crude oil or gas?" "Did oil and gas emigrate in discrete phases, in solution (one in the other), in pore water, or in complex organic compounds in the pore fluid?" These questions are numerous and complex. They require much geological data that are difficult to acquire, and they are hard to attack experimentally because of the time, temperatures, and pressures involved. In addition, a knowledge of physics and chemistry beyond that of the many older geologists is required.

The study of primary migration contains a major paradox. Oil and gas are trapped in porous, permeable reservoirs. The source rocks from which they emigrated can be identified (Welte et al., 1975; Hunt, 1979; Magara, 1979; Flory et al., 1983). Yet these same source rocks are impermeable shales. How then did the fluids emigrate? It would be nice to believe that oil and gas were squeezed from the source clay during early burial before compaction destroyed permeability. This process cannot be so, however, because the temperatures necessary for hydrocarbon generation are not reached until compaction has greatly diminished permeability and water saturation.

At this point, a review of the relationship between clay porosity, permeability, compaction, water loss, and hydrocarbon migration is appropriate. Numerous compaction curves for argillaceous sediments have been published (Fig. 5.23). These curves show that most water expulsion by compaction occurs in the upper 2 km of burial. Pore water expelled by compaction is minimal below this depth. Note that for an average geothermal gradient (25 °C/km), oil generation begins below the depth at which most of the compactional pore water has been expelled. The migration of oil by the straightforward flushing of pore water is not therefore a viable proposition.

FIGURE 5.23   Shale compaction curves from various sources. Note that there is minimal water loss through compaction over the depth range of the oil window.
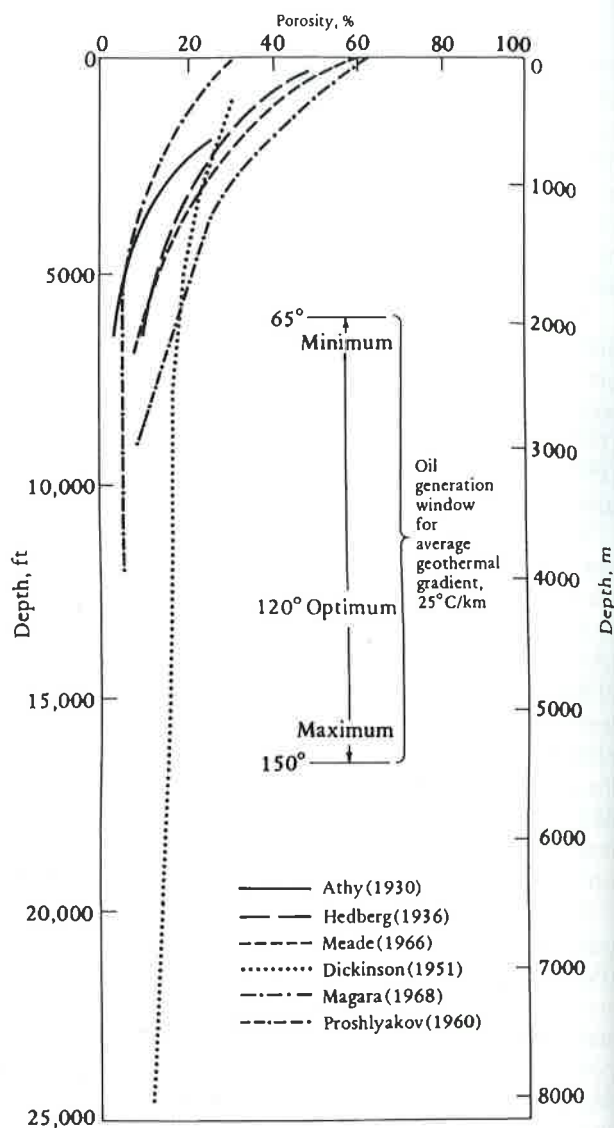
Other factors, however, are relevant to this problem, including consideration of the role of supernormal temperatures and pressures and the diverse kinds of water present in clays. Many major hydrocarbon provinces have been widely noted to be areas of supernormal temperatures and pressures. The Tertiary clastic prism of the Gulf of Mexico in the United States, which has undergone intense detailed studies, is a case in point.

Powers (1967) pointed out that there are two types of water in clays: normal pore water and structured water that is bonded to the layers of montmorillonitic clays (smectites), as
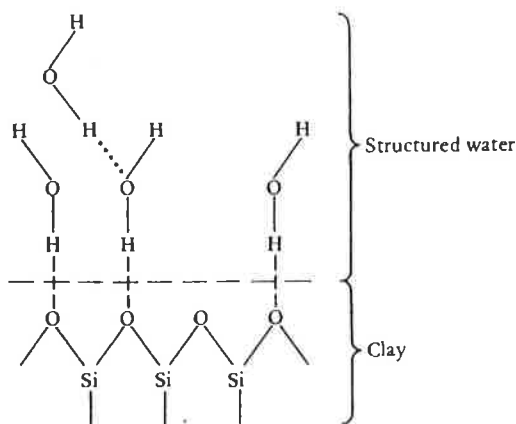
FIGURE 5.24   The relationship of structured water molecules to clay mineral lattice. *Modified from Barker (1978), reprinted by permission of the American Association of Petroleum Geologists.*

shown in Fig. 5.24. When illitic or kaolinitic clays are buried, a single phase of water emission occurs because of compaction in the first 2 km of burial. When montmorillonitic-rich muds are buried, however, two periods of water emission occur: an early phase and a second, quite distinct phase when the structured water is expelled during the collapse of the montmoril-lonite lattice as it changes to illite (Fig. 5.25). Further work by Burst (1969) detailed the trans-formation of montmorillonite to illite and showed that this change occurred at an average temperature of some 100–110 °C, right in the middle of the oil generation window (Fig. 5.26). The actual depth at which this point is reached varies with the geothermal gradient, but Burst (1969) was able to show a normal distribution of productive depth at some 600 m above the clay dehydration level (Fig. 5.27). By integrating geothermal gradient, depth, and the clay change point, it was possible to produce a fluid redistribution model for the Gulf Coast area. Similar studies have been reported from other regions (Foscolos and Powell, 1978).

Barker (1980) has pursued this idea, showing that not only water but also hydrocarbons may be attached to the clay lattice (Fig. 5.28). Obviously, the hydrocarbons will be detached from the clay surface when dehydration occurs. The exact physical and chemical process whereby oil is expelled from the source rock is still not clear, but Fig. 5.24 demonstrates an empirical relationship between clay dehydration and hydrocarbon accumulation. Regional mapping of the surface at which this change occurs is thus a valid exploration tool, although the processes responsible for the relationship may not be fully understood.

Several qualifications must be placed on this technique. These data pertain to the Tertiary Gulf Coast of the United States. In many other hydrocarbon provinces in the world, smectitic clays are largely absent. The dewatering of clay cannot therefore be advocated as the dominant process of emigrating hydrocarbons from source rocks. Overpressure is obviously a factor that may aid pe-troleum generation by maintaining porosity and permeability and inhibiting the formation of a rigid framework to the rock. Several geologists have suggested that fluid emigration from clays is aided by the development of microfractures (e.g., Palciauskus and Domenico, 1980). These
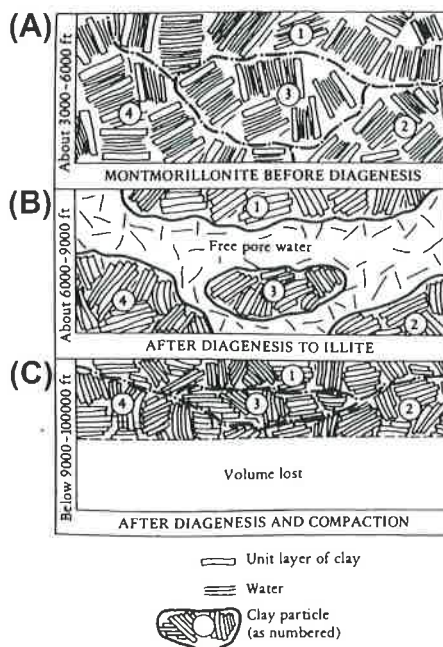
FIGURE 5.25   The two-stage dewatering of montmorillonitic clay. *From Powers (1967), namely Fig. 1, p. 1242.*
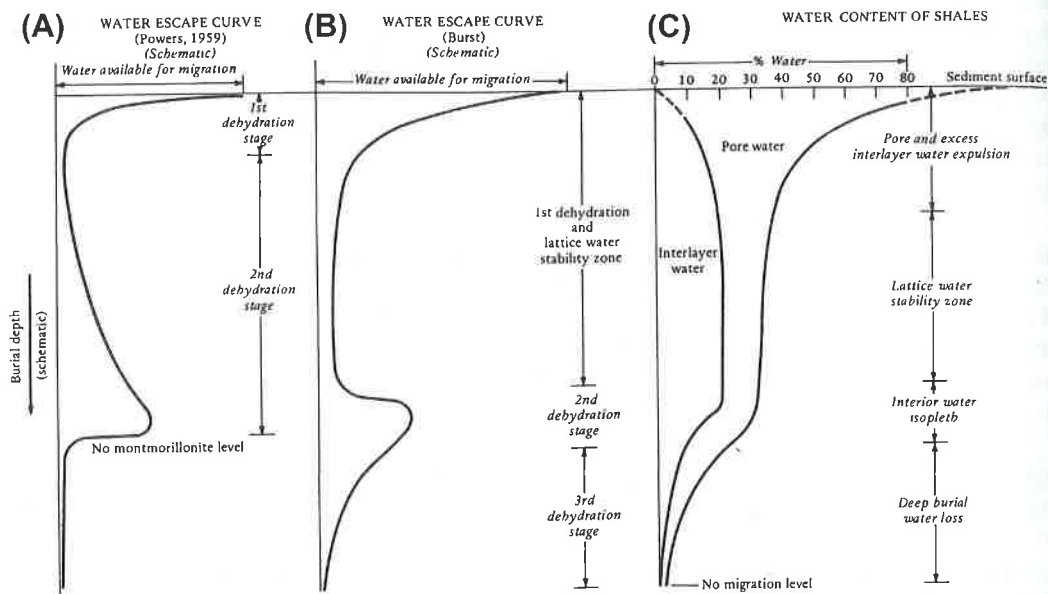

FIGURE 5.26   Dewatering curves for clay burial. *From Burst (1969), namely Fig. 5.9, p. 86.*
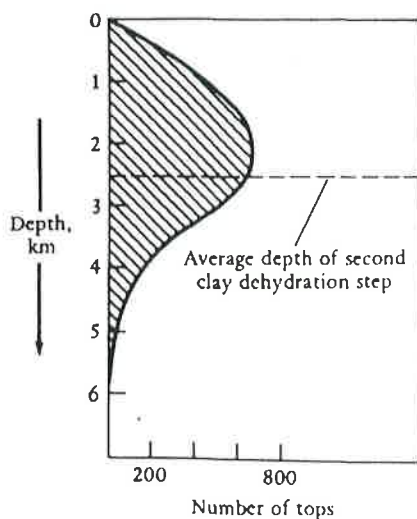
FIGURE 5.27 Depth–frequency curve of the top of 5368 oil reservoirs in the Gulf Coast of the United States. This curve shows that the peak production depth is at about 600 m above the average depth at which the second phase of clay dehydration occurs. *Modified from Burst (1969), reprinted by permission of the American Association of Petroleum Geologists.*

microfractures would cause a marked increase in permeability and thus allow fluid to escape. The microfractures would then close as pore pressure dropped. It has been suggested that petroleum globules could migrate by shouldering aside the unfixed clay grains. This process was introduced in Chapter 4 where evidence was presented that overpressured basins bleed of excess fluid, not in a slow steady discharge, but in episodic hot flushes (Capuano, 1993; Cartwright, 1994; Miller, 1995; Roberts and Nunn, 1995).
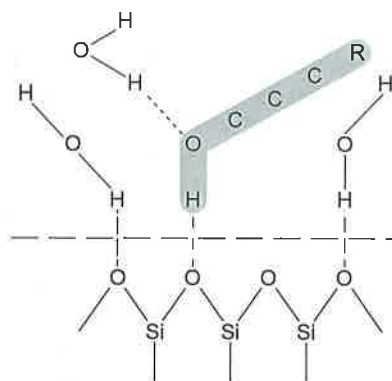

FIGURE 5.28 Sketch showing how hydrocarbon molecules (in this case an R—C—C—COH alcohol) may be attached to a clay mineral lattice together with water molecules. *Modified from Barker (1978), reprinted by permission of the American Association of Petroleum Geologists.*

Clay dehydration is only one of several causes of supernormal pressure. Inhibition of normal compaction due to rapid sedimentation, and the formation of pore-filling cements, can also cause high pore pressures. Furthermore, some major hydrocarbon provinces do not have supernormal pressures. In some presently normally pressurized basins, the presence of fibrous calcite along veins and fractures may be a relict indicator of past overpressures. It is significant that in some instances, such as the Wessex basin of southern England, these calcite veins contain traces of petroleum (Stoneley, 1983).

Nevertheless, the late expulsion of water, of whatever origin, must play an important role in the primary migration of petroleum. The various theories for primary hydrocarbon migration can be grouped as follows:

1. Expulsion as protopetroleum
2. Expulsion as petroleum
    a. In solution
        - Dissolved in water (derived from compaction, expelled from clays, or dissolved from meteoric flushing)
        - Within micelles
        - Solution of oil in gas

    b. Globules of oil in water
    c. Continuous phase

The merits and limitations of these various mechanisms are described and discussed in the following sections.

5.4.1 Expulsion of Hydrocarbons as Protopetroleum

To study hydrocarbons actually in the act of primary migration is, of course, extremely difficult. The evolutionary sequence from kerogen to crude oil and/or gas is very complex. Assessing whether this transformation is completed before, during, or after migration from source rock to carrier bed is very difficult.

One of the major problems in understanding hydrocarbon migration is their low solubility in water. Hunt (1968) suggested that emigration occurs before the hydrocarbons are recognizable crude oil, that is, while they are in the form of ketones, acids, and esters, which are soluble in water. This transitional phase is termed *protopetroleum*.

This mechanism contains several problems (Cordell, 1972). The observed concentrations of ketones, acids, and esters in source rocks are low, and it is difficult to see how they can actually migrate to the carrier bed and, once there, separate from the water. These compounds are likely to be adsorbed on the surface of clay minerals and to resist expulsion from the source rock. If, however, they do emigrate to a carrier bed, it is difficult to envisage how they evolve into immiscible crude oil, since they are soluble in water.

5.4.2 Expulsion of Hydrocarbons in Aqueous Solution

One obvious possibility to consider is that the hydrocarbons emigrate from the source bed fully formed, yet dissolved in water. The solubility of hydrocarbons is negligible at the earth's
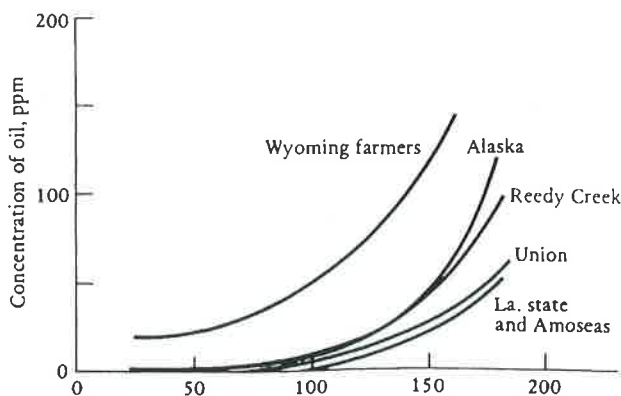
FIGURE 5.29 Graph showing the solubilities of various crude oils plotted against temperature. *From Price (1976), namely, Fig. 5.4, p. 218.*

surface, but may be enhanced by temperature or the presence of micelles. These two mechanisms are examined in the following sections.

5.4.2.1 *The Hot Oil Theory*

Figure 5.29 shows the solubility of various crude oils plotted against temperature. This graph shows that solubilities are negligible below about 150 °C and do not become significant until about 150 °C. It is worth remembering that paleotemperature analysis shows that optimum oil generation occurs at about 120 °C; at this temperature experimental data suggest solubilities of the order of 10–20 ppm.

This information does not seem very helpful. Hydrocarbon solubility is worth looking at in more detail. Figure 5.30 shows the solubility of hydrocarbons plotted according to hydrocarbon numbers. This graph shows that hydrocarbon solubility increases with decreasing carbon number for both the normal alkanes (paraffins) and the aromatic series. Note particularly that solubilities are very high, several hundred to several thousand milligrams per liter, for the paraffin gases (C_1–C_5). Perhaps this information has solved part of the problem of understanding primary migration. It seems quite easy for the gaseous hydrocarbons to emigrate from the source bed dissolved in pore water. Exsolution may then occur when they reach the lower temperatures and pressures of the carrier bed.

Only about 25% of a typical crude oil is composed of the moderately soluble alkanes, and another 25% is composed of the heavy naphthenoaromatics and resins, which are virtually insoluble in water. Nonetheless, there are advocates for primary oil emigration by solution in water (e.g., Price, 1976, 1978, 1980, 1981a,b). Experimental data show that solubilities of as much as 10 wt.% occur for hydrocarbons in pressured salty water. Solubility is enhanced by the presence of gas. Even so, Price advocates temperatures of between 300 and 350 °C for oil generation. As already seen, these temperatures are well above those that paleothermometers indicate as optimal for oil generation.

Further, at these temperatures, diagenesis will probably have destroyed the porosity and permeability of source and carrier beds alike. The stability of hydrocarbons at these temperatures has also been queried (Jones, 1978).

5.4.2.2 *The Micelle Theory*

Another way in which the solubility of hydrocarbons in water may be enhanced is by the presence of micelles (Baker, 1962; Cordell, 1973). Micelles are colloidal organic acid soaps whose molecules have hydrophobic (water-insoluble) and hydrophylic (water-soluble) ends. Their presence may thus enhance the solubility of hydrocarbons in water by acting as a link between OH radicals on their hydrophylic ends and hydrocarbon molecules on their hydrophobic ends. Baker (1962) showed that the particle sizes of micelles in crude oils have a bimodal log-normal distribution. This distribution is related to two basic micelle types—the small ionic and large neutral micelles. The principles by which soaps may be used to enhance the solubility of hydrocarbons are familiar to petroleum production engineers. The process of micellar flooding of a reservoir is frequently used to enhance recovery.

If this micelle theory is correct, then the proportions of different hydrocarbons in a crude oil should be related to their micellar solubility. Experimental data show this to be the case. The naphthenic and aromatic fractions are present in monomodal log-normal frequency distributions. By contrast the paraffins, both normal and branched, show a frequency distribution suggesting that they are solubilized by both ionic and neutral micelles. Hydrocarbons of low atomic weight (C_5 or less) show a normal frequency distribution. As already shown, this distribution is probably related to the fact that they are naturally soluble in water and do not require the assistance of micelles.

Numerous writers have reviewed the micelle theory. Major objections listed by McAuliffe (1979) include the requirement of a very high ratio of micelles to hydrocarbons to provide an effective process. Micelles are commonly only present in traces. In addition, the size of micelle
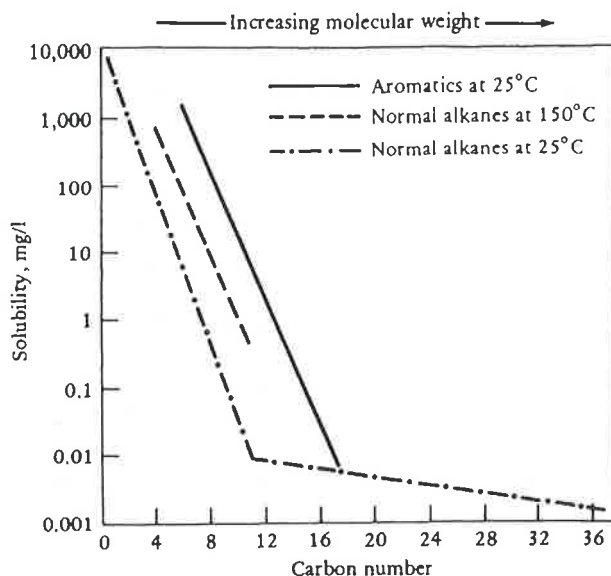

FIGURE 5.30   Solubility of hydrocarbons with different carbon numbers. Solubility decreases with increasing molecular weight. *From McAuliffe (1979), namely Fig. I, p. 762.*

molecules is greater than the diameter of pore throats in clay source beds. The processes whereby the micelles lose their hydrocarbon molecules and presumably break down are not clear.

5.4.3 Expulsion of Oil in Gaseous Solution

Other theories of hydrocarbon migration have considered the role of gases in acting as catalysts or transporting media. Momper (1978), in particular, has discussed the role of carbon dioxide, which is known to be driven off during kerogen maturation. Directly and indirectly, carbon dioxide may have considerable influence on hydrocarbon migration. Indirectly, by combining with calcium ions it precipitates calcite cement, which diminishes pore volume and thus increases pore pressure. The presence of carbon dioxide gas in solution lowers the viscosity of oil, thus increasing its mobility. It causes the precipitation of the N–S–O heavy ends of oil, thus making the residual oil lighter and increasing the gas:oil ratio.

On the debit side, however, the precipitation of calcite cement may diminish permeability. Further, the main phase of decarboxylation of kerogen is known to occur before hydrocarbon generation. Concentrations of carbon dioxide at the time of petroleum generation may thus be too low to assist migration in the ways previously outlined.

Gases may play a direct role in oil migration in another way. Hydrocarbon gases in deep wells are well known to carry oil in gaseous solution. The oil condenses when pressure and temperature drop as the hydrocarbon gases are brought to the surface. Therefore, oil may possibly migrate in this manner from the source bed. This mechanism quite satisfactorily explains the secondary migration of condensates through carrier and reservoir beds. As McAuliffe (1979) points out, however, it does not quite satisfactorily explain the secondary migration of normal crudes, or the primary migration of any oil. The solubility of the heavier naphtheno-aromatics and resins appears to be negligible. The expulsion of a gas bubble through a shale pore throat is as difficult as it is for an oil droplet. As is shown shortly, this presents considerable problems for theories of primary oil phase migration.

5.4.4 Primary Migration of Free Oil

A whole spectrum of theories postulates that oil emigrates from the source bed not in any kind of solution but as a discrete oil phase. There are two major types of such migration: the expulsion of discrete droplets associated with pore water and the expulsion of a three-dimensional continuous phase of oil (Magara, 1981). Hobson and Tiratsoo (1981) have shown mathematically how in water-wet pores it is impossible for a globule of oil to be squeezed through a pore throat in a clay source rock, either by virtue of its own properties (e.g., buoyancy or immiscibility) or by the assistance of flowing water. This mathematical hypothesis is based on the assumption that the diameter of the oil globule is greater than that of the pore throat. Hobson and Tiratsoo (1981) cite pore diameters of the order of 50–100 Å for shales at 2000 m. Individual molecules of asphaltenes and complex ring-structured hydrocarbons have diameters of 50–100 Å and 10–30 Å, respectively (Tissot and Welte, 1978). Figure 5.31 illustrates the interrelationship of various physical parameters (porosity, temperature, fluid pressure, shale pore diameters) with increasing depths of burial for shale-type sediments. Figure 5.32 illustrates the sizes of hydrocarbon molecules and pore throats in shales. Therefore, it is hard to see how discrete oil globules
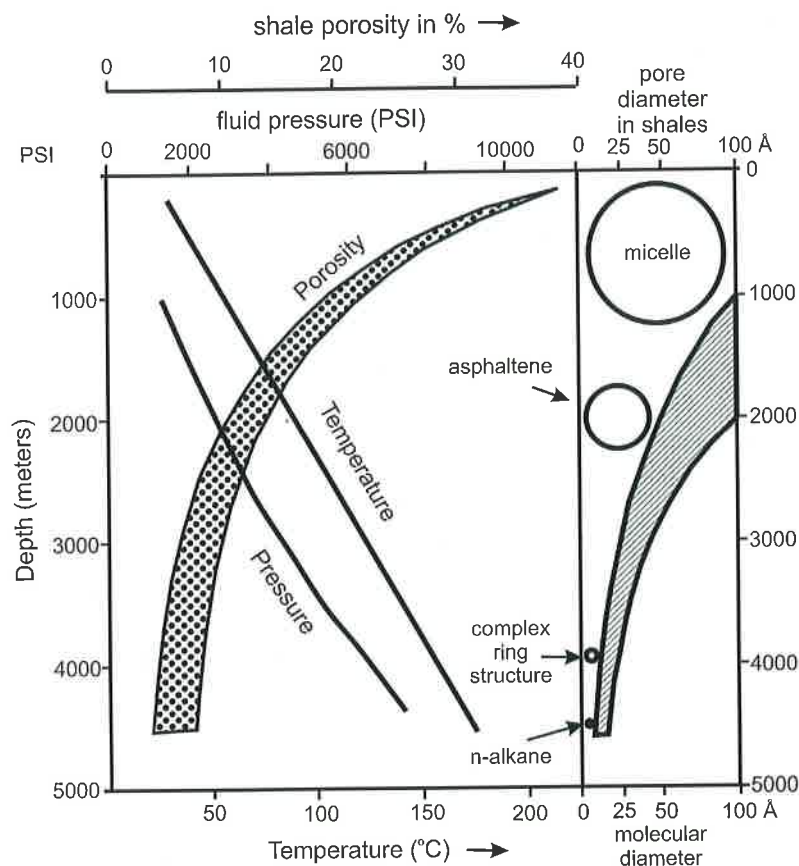
FIGURE 5.31   Interrelationship of various physical parameters (Pressure, Temperature, Porosity, and Shale pore diameters) with increasing depths of burial for shale-type sediments. *Modified from Tissot and Welte (1984).*
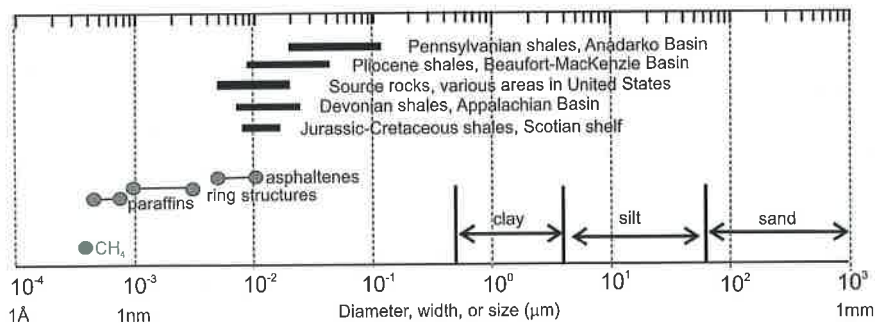

FIGURE 5.32   Sizes of hydrocarbon molecules and pore throats in shales on a logarithmic scale covering several orders of magnitude. *Modified from Nelson (2009).*

could have diameters less than those of pore throats. It is possible, however, that organic-rich source rocks are not water wet, but oil wet. In this situation, petroleum would not migrate as discrete globules of oil in water, but as a continuous three-dimensional phase. This mechanism is the so-called "greasy wick" theory, pointing to the analogy of molten wax moving through the fiber of a candle wick. Such a mechanism may work for rich source rock, but is less likely in leaner source rocks, which are probably water wet.

Hydrous pyrolysis and petrographic thin section work by Lewan (1985) illustrates in a laboratory setting how oil generation and expulsion occurs. These analyses are thought to be similar to actual oil generation. The following was observed by Lewan on samples from the Woodford Shale of Oklahoma. The samples analyzed had amorphous masses of kerogen dispersed in the shale. As thermal stress increased, viscous bitumen generated from the kerogen impregnated the planar bedding fabric of the shale. The bitumen was water soluble and polar-rich. This was followed by a continuous bitumen network forming when the amount and distribution of organic matter were favorable (>2.5 wt.% TOC). Increasing thermal stress resulted in generation of oil from the bitumen. Dissolved water in the bitumen acts as a source of hydrogen for the oil. The oil generated impregnated micropores and microfractures and was expelled. Any oil or bitumen that remained in the shales was carbonized to pyrobitumen.

For most petroleum accumulations, micropressuring is probably a major mechanism for primary migration. The micropressure is created by a net volume increase of organic matter within a confined matrix space (Fig. 5.32). The increase in volume and pressure is caused by thermal expansion of the generated liquid organic phase and overall decrease in the density of the reaction products (Lewan, 1985).

The pressure build-up, microfracturing, subsequent pressure release, expansion of a fluid or gas is an episodic process (Figs 5.33, 5.34, 5.35). Meaningful oil or gas migration requires this process be repeated many times. Fluid or gas escapes after a fracture is opened followed by the fracture closing because of overburden stress. The process then repeats itself. Figure 5.35 illustrates the interrelationship of porosity, pore pressure, and hydrocarbon generation with depth of burial for shale-type sediments (Momper, 1981). Pore pressure created by hydrocarbon generation and aquathermal expansion of any pore water may create pore pressures that exceed the fracture gradient of the shale.

Tissot and Welte (1984) state that the pressure build-up inside a pore network of a shale source rock does not always create microfractures. If a continuous organic phase and/or three-dimensional network of kerogen or if capillary pressures are not too high because pore throats are not too narrow exists, then oil or gas can be driven out of the kerogen without microfracturing.

Thus, pressure-driven hydrocarbon movement with or without microfracturing is an important part of primary migration.

5.4.5 The Importance of Hydrocarbon Adsorption in Source Rocks

Shale oil and gas reservoirs are becoming an important target for the petroleum industry as the switch to unconventional reservoirs. Shale oil and gas account for a large majority of the remaining oil and gas resources in the world.
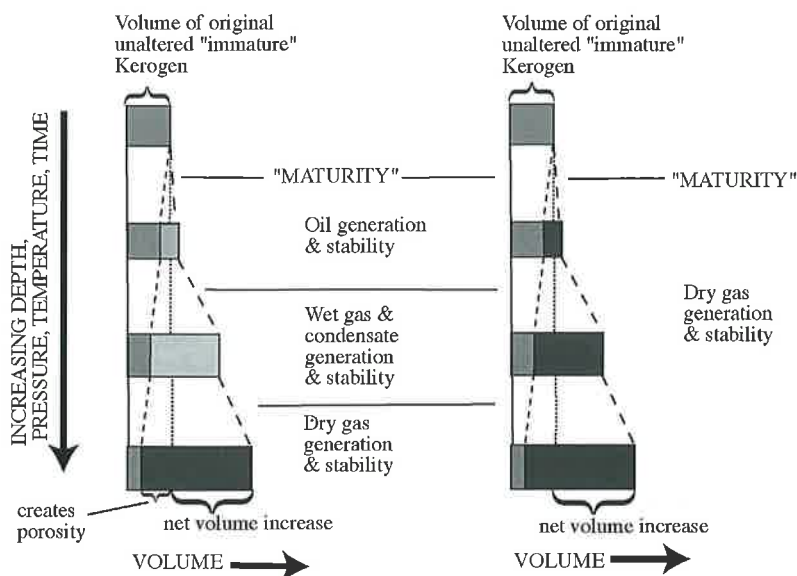
FIGURE 5.33 Illustration of petroleum volume increases associated with both oil-prone (left) and gas-prone (right) kerogens. *From Meissner (1980).*

The geochemistry of the shales is an important aspect to understand. Parameters like thermal maturity and TOC content need to be assessed. TOC is responsible for the volumes of hydrocarbons generated. Thermal maturity of kerogen is a measure of the amount of kerogen that has to be converted to hydrocarbons. Thus, a play is dependent on a combination of thermal maturity and TOC content.

Shales can act as both source rock and reservoir rock. Hydrocarbons are stored in shales in the matrix pore volume, and they are adsorbed onto the surface areas of the pores.
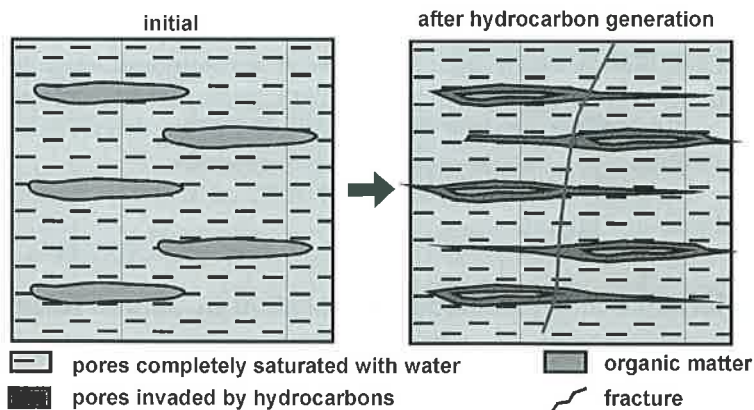

FIGURE 5.34 Microfracturing and hydrocarbon invasion in a source rock during hydrocarbon generation in a kerogen. *Tissot and Welte (1984).*
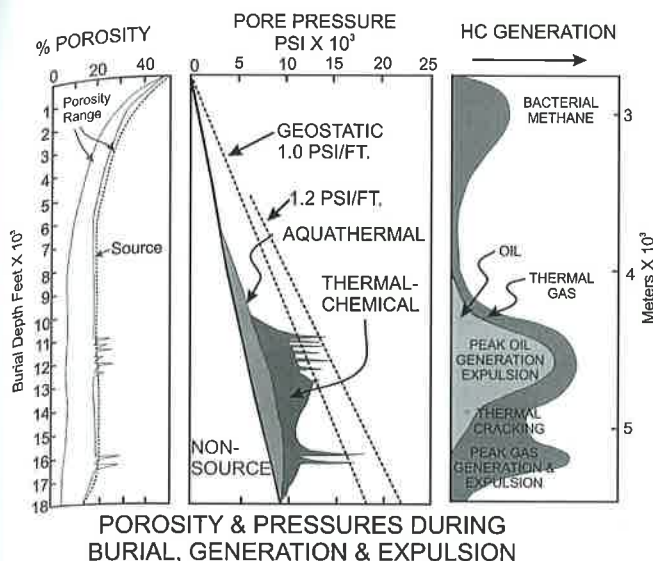
FIGURE 5.35 Interrelationship of porosity, pore pressure, and hydrocarbon generation with depth of burial for shale-type sediments. *Modified from Momper (1981).*

Adsorbed hydrocarbons plus interstitial hydrocarbons (free hydrocarbons) equals total hydrocarbons in place.

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid (adsorbate) to a solid surface (adsorbent). Molecules attach themselves on a surface in two ways: (1) weak van der Walls attraction of the adsorbate to the solid surface; (2) chemisorption where adsorbate sticks to solid surface by formation of chemical bond with surface. This type of bond is much stronger than the van der Walls attraction.

To properly assess a hydrocarbon shale play, the adsorbed and free hydrocarbons must be assessed.

5.5 THE PETROLEUM SYSTEM

Having established that commercial quantities of petroleum are of organic origin, and having discussed the primary migration of petroleum from the source rock into the carrier bed, it is appropriate to conclude this chapter with a discussion of the petroleum system, that is to say, the integration of petroleum migration with the thermal and tectonic evolution of a sedimentary basin. This involves consideration of the distance of secondary migration of petroleum, and the mathematical modeling of the time and amounts of petroleum that may have been generated within a given sedimentary basin.

The petroleum system is defined as a hydrocarbon fluid system that encompasses a pod of active source rock and all related oil and gas accumulations (Magoon and Dow, 2000). It includes the essential elements (source bed, reservoir rock, seal rock, and overburden rock) and processes (generation, migration, accumulation, preservation, and entrapment) needed for oil and gas accumulations to exist. Understanding petroleum systems reduces exploration
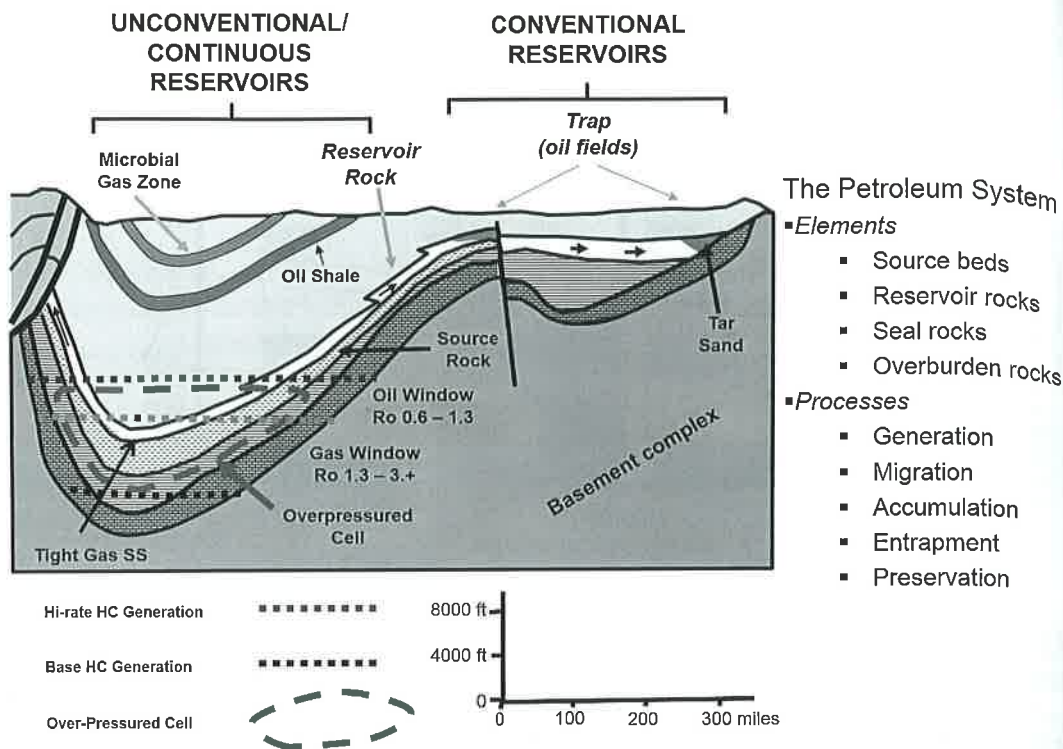
FIGURE 5.36 Cross-section of hypothetical basin illustrating aspects of a petroleum system. *Modified from (Magoon, 1988). See Chapter 9 for a discussion of unconventional reservoirs.*

risk in the search for undiscovered petroleum resources. Figures 5.36 and 5.37 illustrate the petroleum system. Unconventional reservoirs are discussed in Chapter 10.

5.5.1 Measurement of the Distance of Petroleum Migration

The lateral distance to which petroleum can migrate has always been debated. It is a difficult parameter to measure. Traditionally, it is done by physically measuring the distance between the petroleum accumulation and the nearest mature source rock; however, maturity and source rock might be defined. Both two- and three-dimensional studies have been attempted. Where oil is trapped in sand lenses surrounded by shale, the migration distance must have been short. Where oil occurs in traps with no obvious adjacent source rock, extensive lateral migration must have occurred. Correlation between source rock and reservoir oil can be carried out by fingerprinting using gas chromatography (Bruce and Schmidt, 1994).

Table 5.4 cites some documented examples of long-distance lateral petroleum migration. The record for the longest distance of oil migration is held by the West Canadian basin, where
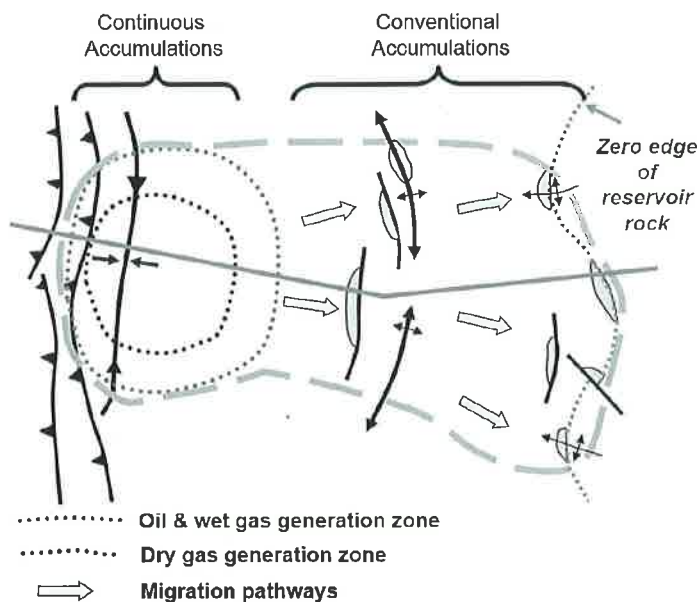
FIGURE 5.37   Map view of a petroleum system. *Magoon (1988).*

a migration distance of more than 1000 km has been calculated (Garven, 1989). A new geochemical method for calculating migration distances has been developed by Larter et al. (1996). This is based on the regional variation of traces of nonalkylated benzocarbazoles. The method is apparently effective, irrespective of the maturity of the oils.

Accurate estimates of the distance from the "devil's kitchen" to the petroleum trap is an essential part of basin modeling discussed in the next section. For a further discussion of this important parameter, see Hunt (1996, pp. 281–286).

TABLE 5.4   Some Published Accounts of Long-Distance Petroleum Migration[a]

Basin	Migration distance (km)	Reference
Athabasca Tar Sands, Canada	100	Tissot and Welte (1978)
Magellan basin, Argentina	100	Zielinski and Bruchhausen (1983)
Pennsylvanian Oklahoma, United States	120	Levorsen (1967)
Gulf Coast, Pleistocene	160	Hunt (1979)
Illinois basin, United States	200	Bethke et al. (1991)
Paris basin	200	Gaullier et al. (1991)
Phosphoria formation, Wyoming and Idaho, United States	400	Claypool et al. (1978)
Alberta basin, Canada	1000	Garven (1989)

[a]*Previously based in geometric analysis, it is now possible to use geochemistry to measure migration distance.*

5.5.2 The Petroleum System and Basin Modeling

It is useful to be able to assess the amount of petroleum that has been generated in a sedimentary basin. Such an assessment is obviously very difficult in a virgin area with no data. In a mature petroleum province where a large quantity of data is available, it is considerably easier. A knowledge of the quantity of reserves yet to be discovered is important for deciding whether continuing exploration is worth the expense if only small reserves remain to be found. The volume of oil generated in an area may be calculated using the geochemical material balance method (White and Gehman, 1979). The basic equation may be expressed as follows:

Volume of oil generated = Basin area × Average total thickness of source rock

× Transformation ratio.

The volume of source rock can be calculated from isopach maps. The average amount of organic matter must be estimated from the geochemical analysis of cores and cuttings, extrapolating from wireline logs where possible. The genetic potential of a formation is the amount of petroleum that the kerogen can generate (Tissot and Welte, 1978). The transformation ratio is the ratio of petroleum actually formed to the genetic potential, and, as described earlier, these values are determined from the pyrolysis of source rock samples.

Estimates of the volumes of petroleum generated in various basins have been published by Hunt and Jamieson (1956), Hunt (1961), Conybeare (1965), Pusey (1973a), Fuller (1975), and Goff (1983). These studies show that the transformation ratio needs to be >0.1 for significant oil generation and is usually in the range of 0.3—0.7 in major petroleum provinces.

The concept of the petroleum system is old, though it has become very fashionable now because it facilitates the modeling of sedimentary basins as a means of finding out how much petroleum they may have generated and where it may be located. The petroleum system integrates the sedimentary and structural history of a basin with its petroleum characteristics, in terms of the richness, volume, and maturity of source rocks. The petroleum system has been variously defined as "a dynamic petroleum generating and concentrating physico-chemical system functioning in a geologic space and time" (Demaison and Huizinga, 1991, 1994), or as the relationship between "a pod of active source rock and the resulting oil and gas accumulations" (Magoon and Dow, 1994). The latter authors see the petroleum system as part of a hierarchy; thus,

——————— Economics of increasing significance ———————▶
Sedimentary Basin   Petroleum System   Play   Prospect
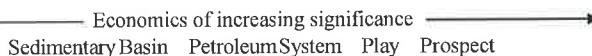
Demaison and Huizinga (1991, 1994) classify petroleum systems according to three parameters: the charge factor, the style of migration (vertical or lateral), and the entrapment style. The charge factor is calculated on the basis of the richness and volume of the source rocks in a basin. This is measured according to the source potential index; thus,

$$\text{SPI} = \frac{h(S_1 + S_2)p}{1000},$$

where

SPI is the maximum quantity of hydrocarbons that can be generated within a column of source rock under 1 m² of surface area

h is the thickness of source rock (meters)

S_1+S_2 is the average genetic potential in kilograms hydrocarbons/metric ton of rock

p is the source rock density in metric tons/cubic meter.

The style of migration drainage is subdivided according to whether migration is principally lateral or vertical, though this can, of course, vary in time and space within the history of one basin. The style of entrapment is dependent on the length and continuity of carrier beds, the distribution and effectiveness of seals, and tectonic style. All these together control the degree of resistance of the basin to the dispersion of the petroleum charge. Thus entrapment style may be categorized as high or low impedance. Table 5.5 documents examples of the different types of petroleum system classified according to these three parameters.

The concept of the petroleum system can be usefully applied to the computer modeling of sedimentary basins. The object of this discipline is to try to discover how much petroleum a sedimentary basin may have generated and where it may be located. Basin modeling may take place in one, two, or three dimensions. Basin modeling is done by a computer. Several software packages are available. New versions and new packages are appearing constantly (Welte and Yukler, 1984; Waples et al., 1992a,b; Waples, 1994).

One-dimensional modeling involves no more than the construction of a burial history curve for a particular point in a basin, such as a well location (refer to Fig. 5.16). This may be used to establish the maturity of a source rock interval, either using a modern geothermal gradient data (if the well has been drilled) or developing a geothermal history based on the tectonic regime of the location.

A two-dimensional model consists of a cross-section. This may be constructed by "backstripping" the geological history, based on a seismic section, calibrated with well data, if available. To do this, we need to estimate the depositional depth and compaction history of the sedimentary sequence. Then, a geohistory scenario can be plugged in. This can then be used to establish the pressure system of the section and the migration and entrapment history of petroleum (Plate 5.5). Examples of 2D modeling using TEMISPACK have been

TABLE 5.5 Examples of the Different Types of Depositional Systems Classified According to the System of Demaison and Huitzinga (1991)

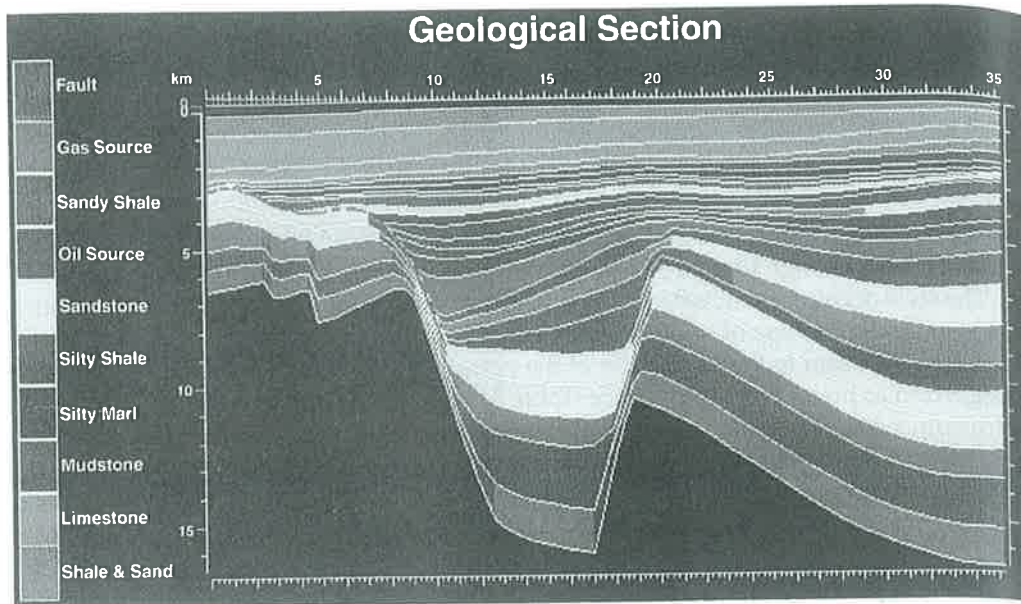| Type of drainage	Charge	Impedance	Example
Lateral	Super	High	North slope of Alaska, United States
	Normal	Low	Williston basin, United States
Lateral	Super	Low	Venezuela foreland basin
Vertical	Super	High	Central Graben, United Kingdom North sea
Vertical	Normal	High	Tertiary Niger Delta
Vertical	Super	High	Los Angeles basin, United States

PLATE 5.5   Three computer-generated cross-sections to illustrate how a sedimentary basin may be modeled to predict the distribution of pressure and petroleum (See the color plate). *Courtesy of A. Vear and British Petroleum.*

published from the eastern offshore Canada and Williston basins by Forbes et al. (1992) and Burrus et al. (1996) respectively.

A three-dimensional model involves the same operations as just described, however, not for a cross-section, but for a volume of rock. An example of 3D modeling in the Gulf of Mexico basin has been published by Anderson et al. (1991).

5.5.3 Hydrocarbon Generation and Migration: Summary

Understanding the primary migration of hydrocarbons is one of the last problems of petroleum geology. Research in this field is currently very active, so any review is bound to date quickly; nonetheless, a summary of this complex topic is appropriate:

1. Commercial quantities of oil and gas form from the metamorphism of organic matter.
2. Kerogen, a solid hydrocarbon disseminated in many shales, is formed from buried organic detritus and is capable of generating oil and gas.
3. Three types of kerogen are identifiable: type I (algal), type II (liptinitic), and type III (humic). Type I tends to generate oil; type III, generates gas.
4. The maturation of kerogen is a function of temperature and, to a lesser extent, time. Oil generation occurs between 60 and 120 °C, and gas generation between 120 and 225 °C.
5. Source rocks generally contain >1500 ppm organic carbon, but yield only a small percentage of their contained hydrocarbon.
6. Several techniques may be used to measure the maturity of a source rock.

Present Day Overpressures
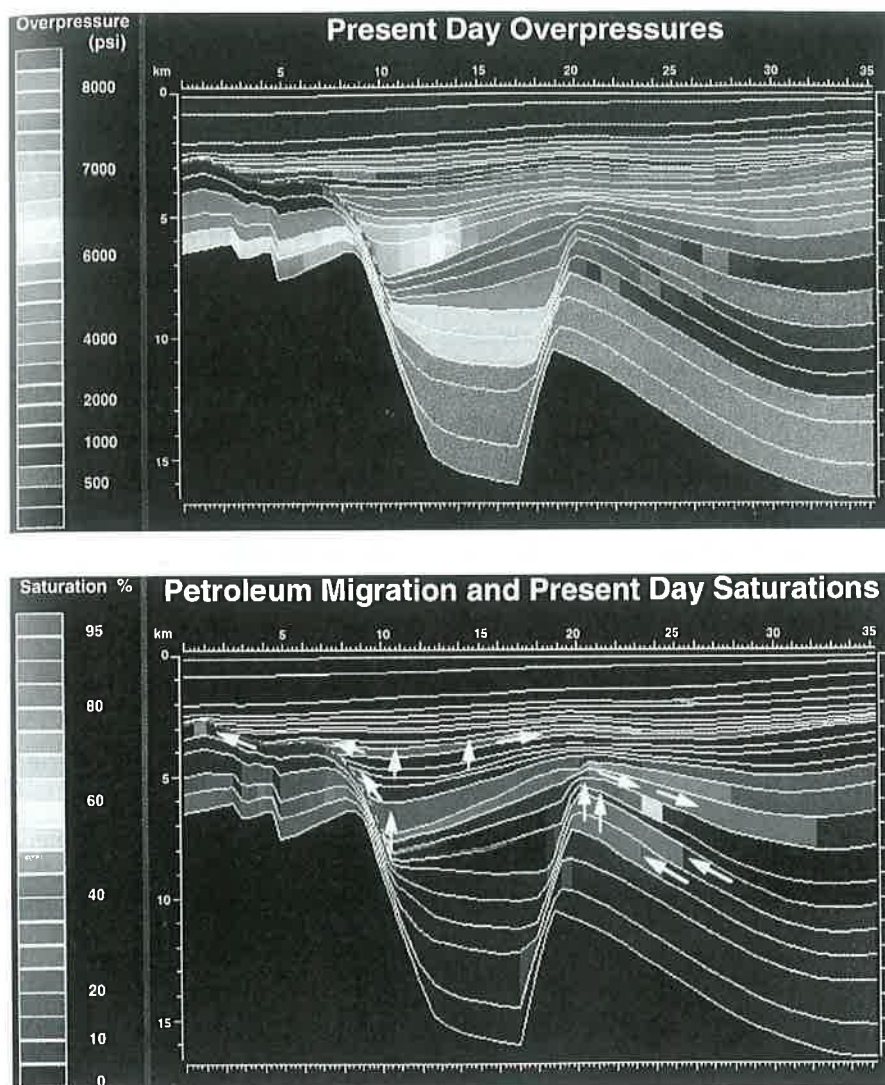

Petroleum Migration and Present Day Saturations

PLATE 5.5 cont'd

7. The exact process of primary migration, whereby oil and gas migrate from source beds, is unclear. Solubility of hydrocarbons in water is low, but, for the lighter hydrocarbons, is enhanced by high temperature and the presence of soapy micelles. An empirical relationship between oil occurrence and clay dehydration suggests that the flushing of water from compacting clays plays an important role in primary migration. There is much evidence to suggest that the episodic fshing of water from overpressured shales by hydraulic fracturing is an important pross in allowing petroleum to emigrate from source rocks.