Origin, migration and accumulation of petroleum

1.2.1 Origin of petroleum

The great compositional complexity of petroleums (this term includes both oil and gas) reflects the combined effects of all processes involved in the origin of petroleum accumulations and their fate during long periods of geological time. Since relevant geological and geochemical conditions under which these processes proceed can vary from place to place, the composition of petroleums are subject to great variations. The composition of petroleum contains molecular signals which allow to unravel their origin and geological history. As a general rule, the origin of petroleum is never in the reservoir accumulation from which it is produced. Instead, petroleums have experienced a long series of processes prior to accumulation in the reservoir. Petroleum accumulation forms in sedimentary basins and can be discovered by exploration, if the following geological conditions are met (Fig. 1):

- Occurrence of source rocks which generate petroleums under proper subsurface temperature conditions.
- Sediment compaction leading to expulsion of petroleum from the source and into the reservoir rocks (primary migration).
- Occurrence of reservoir rocks of sufficient porosity and permeability allowing flow of petroleum through the pore system (secondary migration).
- Structural configurations of sedimentary strata whereby the reservoir rocks form traps, i.e. closed containers in the subsurface for the accumulation of petroleum.
- Traps are sealed above by impermeable sediment layers (cap rocks) in order to keep petroleum accumulations in place.
- Correct timing with respect to the sequence by which the processes of petroleum generation/migration and trap formation have occurred during the history of a sedimentary basin.
- Favourable conditions for the preservation of petroleum accumulation during extended periods of geologic time, i.e. absence of destructive, such as the fracturing of cap rocks leading to dissipation of petroleum accumulations, or severe heating resulting in the cracking of oil into gas.

The question of the origin of petroleum has been hotly debated for a long time. A great many theories, hypotheses and speculations have been proposed. Decades ago, various ideas on a possible inorganic origin of petroleum were brought forward, e.g. that it results from the reaction of iron carbide with water deep in the Earth’s crust. The main evidence supporting these theories was the occasional occurrence of hydrocarbon fluid inclusions and solid...
bitumens in igneous rocks as well as a few cases of oil and gas fields hosted in fractured basement rocks (e.g. granites, basalts, and metamorphic rocks). However, in most of these cases it could be demonstrated that the petroleum materials were ultimately generated in sedimentary rocks and had been transported, e.g. by convective flow of mineralising aqueous fluids, into the granites, or that they had migrated from sedimentary strata over long distances to accumulate in fractured basement rocks. These cases of petroleums occurring in basement rocks are extremely rare and not commercially important when compared to the vast majority of hydrocarbon reserves in sedimentary basins (Selley, 1998). Today, the evidence in favour of an organic origin of petroleum is overwhelming. One of the main arguments concerns the ubiquitous occurrence of biological marker molecules in petroleums, such as porphyrines, steranes and hopanes. The highly specific carbon structures of these molecules could not be synthesized by inorganic reactions. They are clearly and uniquely derived from molecular structures synthesized by living organisms.

**Petroleum source rocks**

Petroleum source beds are fine grained, clay-rich siliclastic rocks (mudstones, shales) or dark coloured carbonate rocks (limestones, marlstones), which have generated and effectively expelled hydrocarbons. A petroleum source is characterised by three essential conditions: it must have a sufficient content of finely dispersed organic matter of biological origin; this organic matter must be of a specific composition, i.e. hydrogen-rich; and the source rock must be buried at certain depths and subjected to proper subsurface temperatures in order to initiate the process of petroleum generation by the thermal degradation of kerogen. Based on empirical evidence, minimum concentration levels of 1.5% and 0.5% total organic carbon (TOC) in source rocks of siliclastic and carbonate lithologies respectively have been established (Hunt, 1996). The organic carbon concentration is an approximate measure of the organic matter content of a rock. Organic matter is predominantly composed of organic carbon, but also contains minor amounts of hetero-elements (N, S, and O). This minimum concentration of organic carbon in source rocks is controlled by the relationship between the quantity of petroleum generated and the internal storage capacity of the rocks in terms of their porosity. If too little organic matter is present, the small quantities of petroleum generated will not exceed the storage capacity of the rock, i.e. no petroleum expulsion will take place.

Most source rocks which have effectively generated and expelled commercial quantities of petroleum have TOC concentrations in the order of 2-10%. An example of a prolific source rock of siliclastic lithology is the Upper Jurassic Kimmeridge Clay Formation in the North Sea Basin which has generated most of the oil accumulated in many large fields in that area. It has TOC contents ranging mostly between 5 and 12% (Bordenave et al., 1993). A good-quality petroleum source rock of carbonate lithology is exemplified by the Triassic-age Meride Limestone, which is the source of the oil present in several fields in the Po valley area of northern Italy. Its TOC content varies mostly between 0.5 and 1.5% (Leythaeuser et al., 1995). The reason why petroleum source rocks of carbonate lithologies tend to have significantly lower TOC concentrations has to do with the quality and composition of the organic matter present. In carbonate source rocks, the organic matter tends to be richer in hydrogen.

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**Fig. 2.** Petroleum source rocks of siliclastic lithologies often display a well expressed fine stratification and lamination:
A, seen in an outcrop view (note pocket knife for scale, photo by D. Leythaeuser);
B, seen in a thin section under a microscope (width of image is 2 cm, photo by R. Littke).
Most petroleum source rocks display dark brown to black colours. This is due to the presence of finely disseminated organic matter as well as finely dispersed pyrite crystals (FeS₂). A typical feature of many siliclastic petroleum source rocks is a distinctive lamination (Fig. 2 shows fine stratification on mm or sub-mm scale). When exposed to the surface and subjected to weathering these laminae tend to separate so that the outcrop looks like a pile of loose papers (known as *papershale*). The lamination is due to the specific conditions which prevailed during the deposition of the organic matter-rich mud which lithified during burial to become the source rock. In most petroleum source rocks of carbonate lithologies organic matter tends to be distributed in a heterogeneous way. It is often concentrated in narrow bands floating in an organic matter-lean groundmass. These were formed in the subsurface by a process called pressure solution which involves the re-distribution of carbonate minerals and their re-crystallisation away from the organic matter particles.

**Deposition of source rock-type sediments**

The formation of sediments rich in organic matter is restricted to certain conditions of the depositional environment. These sediments are deposited in aqueous environments which receive a certain contribution of organic matter, i.e. residues of dead organisms, along with the sediment particles. In subaerial environments organic matter is readily destroyed by chemical and microbial oxidation shortly after deposition. Good quality petroleum source rocks can be deposited in marine or lake environments as organic-matter-rich muds providing that bottom waters are oxygen-deficient, i.e. that reducing conditions prevail. If the concentration of oxygen dissolved in these waters is less than 0.1 ml/l the environment is referred to as anaerobic, if it is in the range of 0.1-1.0 ml/l the environment is referred to as dysaerobic and if higher oxygen concentrations prevail, the environment is known as oxic. Anaerobic or dysaerobic environments require stagnant water conditions, because turbulent water circulation results in the replenishment of oxygen contents. Recent examples of anaerobic or dysaerobic depositional environments prevail over vast parts of the Black Sea, Gulf of Maracaibo, in deep shelf areas offshore Namibia, offshore Peru and offshore the Arabian Peninsula as well as in the deepest parts of the East African lakes (Hunt, 1996). Sediments deposited in these areas contain more than 4% TOC. Stagnant water conditions imply near-zero transport energy of the water for mineral particles. Only very fine-grained particles, especially clay minerals settle down slowly through the water column along with the residues of dead organisms. No organism other than anaerobic bacteria can live under these conditions. Therefore, the commonly occurring population of bottom-dwelling organisms such as worms, snails and shrimps, etc. (benthic fauna) which are constantly burrowing through the topmost decimetres of the sediment in search for food, are not present. By this activity the original horizontal sediment structure is destroyed leaving behind a stirred arrangement of sediment particles (bioturbation). In anaerobic environments the original fine-scale horizontal stratification of sediment layers is preserved in the form of lamination. These types of depositional environments provide favourable conditions for the preservation of organic matter. Apart from the absence of benthic organisms which would digest organic matter, there is no, or extremely little, oxygen available for the chemical oxidation of organic matter. Furthermore, the rate of degradation of organic matter by anaerobic bacteria is much lower as compared to that by aerobic bacteria. Certain species of anaerobic bacteria living in the sediment pores consume parts of the organic matter, reducing the sulphate (SO$_4^{2-}$) of the sea water and producing hydrogen sulphide (H$_2$S), which is toxic. In siliclastic depositional environments, dissolved iron is always available to remove the dissolved hydrogen sulphide by formation of pyrite (FeS$_2$). In fact, the fine structure of the colonies of these bacteria often gets preserved in the form of tiny aggregates of pyrite crystals called frambooidal pyrite. In environments where carbonate muds are deposited there is usually a lack of dissolved iron. The sulphide produced by these sulphate reducing bacteria enters into chemical reactions with the organic matter (vulcanisation), leading ultimately to the origin of sulphur-rich petroleums. Such oils are of lower economic value since sulphur compounds cause problems during the refinery process.

There are three basic depositional scenarios which ensure favourable conditions for the preservation of organic matter (Demaision and Moore, 1980). The depositional system of the so-called stagnation model requires a silled basin, i.e. a marine basin which has highly restricted water circulation with the open ocean (Fig. 3 A). This is the case today, e.g. of the Black Sea which is up to 2,500 m deep but only has a narrow 25 m deep connection to the Mediterranean Sea. Due to the high input of freshwater from rivers, surface waters of the Black Sea have lower salinity levels. These
Surficial water masses flow into the Mediterranean Sea while high salinity and hence higher density water flows return as a bottom current into the Black Sea. This current follows the bottom topography filling the deep parts of the Black Sea. In this way a stratified water column is established with a sharp contact between higher-salinity and hence denser water masses below and lower-salinity waters above. This kind of contact, which in the Black Sea is permanently located in the 80-100 m water depth only, is referred to as halocline. Below the halocline lies a huge, stagnant water mass which provides favourable conditions for the preservation of dead bodies of algae that settle down from the surface interval where there are light and nutrients for their growth (bioproductivity). The second principal depositional system in this context is the so-called productivity model (Fig. 3 B). In certain areas of today’s world oceans, nutrient-rich bottom water currents upwell across the shelf edges from deep parts of the continental slopes. When they reach the near-surface interval penetrated by sun light (photic zone), a massive growth of marine algae occurs (phytoplanktonic blooms). Enormous quantities of algal biomass are produced by this photosynthetic activity. This is the basis of the marine food chain, i.e. algae are eaten by zooplankton which in turn are eaten by fish, etc. After the residues of all of these dead organisms sink down through the water column, degradation and decay is initiated. The vast majority of this biomass is of phytoplanktonic origin. Due to the great quantity of decaying organic matter, oxygen is consumed at such a rate that dysaerobic and anaerobic conditions are established within the water column. Sharp contact between oxygen deficient bottom waters and oxygen-bearing water masses above, is again observed. This is known as the redox-boundary. On the ocean floor the organic matter is partly degraded by micro-organisms. In this process, bacterial biomass is added to the sedimentary organic matter. TOC contents of sediments deposited under this environmental regime are in the order of 2-4%. The third principal scenario leading to deposition of organic matter-rich sediments is controlled by the global deep oceanic circulation system (Fig. 3 C). Currents of water masses of higher density originate in arctic and antarctic oceanic realms and flow along the deep ocean topography towards lower latitudes. Wherever they encounter major topographic elevations they displace nutrient-rich bottom water masses towards the surface of the ocean. In this way, a series of processes and effects are initiated which are similar to those in the upwelling regime leading to the establishment of an open-ocean-oxygen-minimum zone. Wherever this oxygen-minimum zone impinges on a continental shelf, organic matter-rich sediments are deposited. Such conditions can be observed in today’s oceans, e.g. along parts of the deep shelf offshore India and Pakistan. What has been described here in terms of type of organic matter input for marine sediment systems applies in a similar way to great lakes on the continents, e.g. the lakes in the East African Rift Valley. Biomass derived from freshwater algae and bacteria is deposited in dysaerobic or anaerobic bottom waters of deep lakes, the water masses of which never get overturned.

All the depositional environments of marine and freshwater systems can also receive an input of organic matter derived from higher land plants transported by rivers or glaciers, or wind-blown. In contrast to algal or bacterial biomass which is rich in hydrogen, land plant-derived organic matter tends, due to high contributions by cellulose and lignin-derived precursor materials, to be rich in oxygen. Exceptions are spores and cuticles of plant

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**Fig. 3.** Schematic models for deposition of organic matter-rich sediments under oxygen deficient conditions: A, stagnation model; B, productivity model; C, oxygen-minimum zone model (modified according to Demaison and Moore, 1980).
leaves which are hydrogen-rich. In fact, the organic matter of most source rock-type sediments represents mixtures of residues derived from marine organisms as well as from terrestrial vegetation. It is the relative abundance of each of these organic materials which determines whether the resulting source rock will generate predominantly oil or gas upon burial.

The solid organic matter in source rocks which is insoluble in low-boiling organic solvents is called kerogen. Kerogen is partly formed by the accumulation of resistant macromolecular substances of biological origin such as cellular lipids, algae cell walls, membranes, cuticles, spores and pollen, etc. Other parts of kerogen are formed in sediments during a process called diagenesis. This collectively denotes all of the geochemical and mineralogical processes that occur within the topmost interval of a sedimentary column. Organic matter is synthesized by living organisms in the form of biopolymers such as carbohydrates, proteins, lignin, etc. After the death of the organism, these biopolymers degrade readily into their biomonomeric constituents, e.g. carbohydrates into sugars, proteins into amino acids, etc. These biomonomers are not stable in a sedimentary environment. They get re-arranged by a multitude of reactions controlled by bacterial enzymes into poly-condensed polymer-like organic materials, such as humic acids, fulvic acids and humic substances. These get gradually converted into the ‘geopolymer’ kerogen within a few hundred metres of burial (Tissot and Welte, 1984).

Kerogen is, however, not a polymer in a strict chemical sense, rather a complex mixture of high-molecular-weight substances. The main building blocks are polycondensed aromatic ring-systems with attached aliphatic side chains of various lengths which are interconnected by a variety of functional groups, such as ester, ketone and sulphide-bridges. In summary, kerogen consists of a physical mixture of diagenetically restructured biomass as well as preserved biosynthesized compounds (Killops and Killops, 1993). A useful and initial geochemical approach for determining the complex composition of kerogen is by elemental analysis and consideration of the relationship between the atomic hydrogen/carbon-ratio H/C and the atomic oxygen/carbon-ratio O/C (Fig. 4). In this way, the great variety of kerogens occurring in nature can be classified into three broad categories referred to as type I-, type II- and type III-kerogens (Tissot and Welte, 1984). The high H/C-ratio of type I-kerogens, goes back to a high input of algae and bacterial biomass and chemically consists of a high proportion of long aliphatic chains. The elevated H/C-ratio of type II-kerogens is mostly derived from a high contribution of algal biomass and is made up of a mixture of saturated hydrocarbon ring systems (naphtenes) and aliphatic chains, as well as some polycondensed aromatic ring systems. The formation of both kerogen types require sediments deposited in anaerobic environments. A sub-group of these, are kerogens of so-called type II-S, i.e. sulphur-rich kerogens (not shown in Fig. 4). They originate in carbonate depositional environments. Therefore, petroleums generated by carbonate source rocks tend to be sulphur-rich (more than 1.5% S). Kerogens of type III, in contrast, have high O/C- and low H/C-ratios. The elevated oxygen content, which is present mainly in the form of...
carboxyl groups (—COOH), is either due to a high input of residues of higher land plants, which are always rich in cellulose and lignin-derived structures, or to the deposition of any kind of organic matter derived from marine organisms under dysaerobic to oxic environments. Most prolific source rocks for oil have type II-kerogens. Type I-kerogens are rare in terms of worldwide occurrence and mostly restricted to oil shales (rocks which do not contain oil, but high concentrations of kerogen, which yield oil artificially when the rock is heated to 500°C in an inert atmosphere). Source rocks bearing type III-kerogen generate little oil but more gas and condensate upon exposure to proper subsurface temperatures.

A varying portion of the kerogen present in source rocks, is in the form of particles of a size recognisable under a microscope. Most of these particles can be traced back to their biological or diagenetic origin such as bodies of algae, the cuticles of plant leaves, spores or herbaceous tissues (Taylor et al., 1998). These particles can be separated from a rock sample by exhaustive acid treatment (HCl, HF) and are hence collectively called macerals. These macerals are hydrogen-rich, exhibit fluorescence under UV-light and are collectively called liptinites. Another group of macerals termed vitrinites, are derived from woody tissues and have undergone partial or complete gelification during diagenesis. The inertinite group macerals are derived from organic particles which have been highly oxidized chemically or by bacteria in the depositional environment.

**Petroleum generation**

Oil and gas are generated by the thermal degradation of kerogen in the source beds. With increasing burial, the temperature in these rocks rises and, above a certain threshold temperature, the chemically labile portion of the kerogen begins to transform into petroleum compounds (Fig. 5, McKenzie and Quigley, 1988). The main reaction mechanism is the breaking of carbon-carbon bonds (cracking), which requires that the input of thermal energy exceed certain minimum levels (activation energy). Activation energies vary according to the position and type of carbon-carbon bond within the kerogen structure. The bonds between carbon and heteroatoms (N, S, and O) are more labile and hence easier to break. The first products generated by source rocks during burial are, therefore, N, S, and O compounds together with carbon dioxide (CO₂) and water (see again Fig. 4). At higher temperature levels, petroleum compounds are generated by the cracking of carbon-carbon bonds within the kerogen structure in such a way that long aliphatic side chains and saturated ring structures are removed from it. These reactions result in gradual changes in the elemental composition of the kerogen, especially in a decrease of its hydrogen content. These changes are expressed in the van Krevelen diagram for each kerogen type as trend lines, the so-called evolutionary pathways (see again Fig. 4).

The generation of oil and gas in source rocks is a natural consequence of the increase of subsurface temperature during geologic time. The process of kerogen transformation with increasing temperatures is called maturation, which is subdivided into the catagenesis and metagenesis stages (see again Fig. 4, Tissot and Welte, 1984). With respect to the stage to which petroleum generation has advanced, the organic matter is labelled immature prior to the onset of
hydrocarbon generation, mature if hydrocarbon generation is in progress, or overmature when these reactions have been terminated. Heat is the main driving force in maturation and petroleum generation reactions. In this context, the maximum temperatures reached, i.e. the heating rate as well as the exposure time to maximum temperatures, are important. The temperature interval where oil generation is in progress is referred to as the ‘oil window’ or ‘oil window’. It extends over the temperature interval of about 80-150°C. For petroleum exploration, it is essential to determine the precise stage at which hydrocarbon generation reactions have progressed in a particular source rock. This is done by measuring the so-called maturation parameters. These record the temperature/time integral which the organic matter of a source rock has experienced, i.e. they represent indirect measures of paleotemperatures and their exposure duration. The most commonly used maturation parameters are vitrinite reflectance and biomarker maturity ratios. Vitrinite particles are widespread trace components in many source rocks which can be identified under a reflectance microscope. With increasing maturation, the ability of polished vitrinite particles to reflect a beam of white light increases gradually. The percentage of light reflected is measured in relation to a glass standard and expressed as percentage vitrinite reflectance. Based on empirical evidence from many case history studies it has been shown that the liquid window of petroleum source rocks with type II-kerogens extends over a maturity interval of about 0.5 to 1.3% vitrinite reflectance. Above the maturity interval of 1.3 to 2.0% vitrinite reflectance, lower molecular weight hydrocarbons in the form of condensates and wet gases are generated. At maturity levels in excess of 2.0% vitrinite reflectance, only dry gas is generated (see again Fig. 4, Tissot and Welte, 1984). The reason why this gradual change from oil to condensate to gas generation occurs, is that the supply of hydrogen-rich structures in kerogen gets exhausted. The overall net effect of maturation is that an initially hydrogen-rich kerogen is transformed into a mixture of hydrogen-rich structures (oil, gas, and condensate) leaving behind a hydrogen-deficient kerogen (inert kerogen, see again Fig. 5). If strata bearing such inert kerogen are buried deeper and exposed to the pressure and temperature conditions of rock metamorphism, kerogen undergoes major structural changes whereby it is ultimately transformed into the mineral graphite (see again Fig. 5).

Source rocks with type III-kerogens, which have more of a refractory chemical nature (see again Fig. 5), begin to generate little oil and predominantly gas and condensate only after a maturity stage of 0.7% vitrinite reflectance has been reached. Another means to assess the maturity stage is by monitoring changes of specific biomarker ratios. Thermal stress leads to changes in the stereochemistry of individual biomarker molecules. The spatial arrangement of specific methyl groups (—CH₃) or hydrogen atoms as part of the ring system or side chains, changes systematically as a function of increasing temperature (configurational isomerisation). In this way, the original biological form of the molecule with respect to the 3D-arrangement of these particular groups, is gradually changed into a thermally more stable form. These changes can be precisely monitored by measuring the concentrations of starting and reactant products, which are then expressed as ratios (Waples and Machihara, 1991). Measurements are made using a variety of chromatographic techniques, especially by combination of gas chromatography and mass spectrometry (GC/MS). For a great variety of stereochemical reactions in biomarkers, the molecular pathways have been worked out and calibrated versus maturity stages. The great advantage of these biomarker maturity ratios is that they can also be measured for crude oil samples.

The position of the liquid window with respect to the discussed specific values of all maturity parameters is somewhat flexible and subject to variations from one source rock to another. This is due to the fact that the chemical and structural processes controlling the increase in vitrinite reflectance, or the progressive changes in the stereochemistry of biomarker molecules, obey different rules of reaction kinetics from those governing hydrocarbon generation reactions. During petroleum generation a great number of different reactions take place, each controlled by somewhat different reaction kinetics (activation energy, frequency factor, etc.). Therefore, petroleum generation is not restricted to one single temperature threshold, but extends over a range of temperatures. Reaction kinetics have been worked out experimentally for a number of hydrocarbon generation reactions so that these processes can be modelled by numerical simulation (Schenk et al., 1997). For a given source rock, petroleum generation can thus be quantified. A gross approximation of the amount of petroleum generated can also be obtained by measuring the concentration of petroleum compounds, which can be extracted in the laboratory from source rock samples by low-boiling organic
solvents. At places where the source rock has not been buried deep and exposed to adequate temperatures, very low concentrations of extractable compounds are measured. Such extracts consist mainly of a mixture of biological markers and N, S, and O compounds. As soon as the maturity level marking the onset of the liquid window is exceeded, increasingly higher concentrations of extracts are obtained. They are oil-like mixtures consisting predominantly of hydrocarbons with more than 15 carbon atoms per molecule ($C_{15+}$-fraction). Maximum extract concentrations mark the maturity interval of optimum generation conditions. Decreasing extract concentrations beyond this interval indicate that the supply of oil-like structures in the kerogen is getting exhausted. The floor of the liquid window is reached when extract concentrations are reduced to background values. This trend is rarely observed in nature. The reason being that the extract concentration does not just indicate the amount of $C_{15+}$-hydrocarbons generated, but also reflects the net effect of a combination of constructive and destructive processes, such as petroleum generation by thermal degradation of labile kerogen portions, expulsion of major parts of these petroleum hydrocarbons by means of primary migration and at maturity levels beyond the generation optimum, progressive cracking and conversion of long-chain hydrocarbons into gas.

In the case of good quality source rocks, up to 50% of the kerogen is labile and converted into petroleum hydrocarbons with passage through the liquid window. This is reflected by the drastically decreasing hydrogen contents of the kerogen and decreasing TOC contents, as the originally immature source rock matures and finally overmatures. For a maturity sequence of the Lower Jurassic-age Posidonia Shale, which is the main petroleum source rock in central and Western Europe, a decrease of the TOC content by about 50%, and of the hydrogen content of the kerogen by about 90%, was documented in the transition from an immature to a mature and an overmature stage (Rullkötter et al., 1988). Type III-kerogen bearing source rocks have low proportions of chemically labile structures and hence generate little oil. Instead, a high proportion of refractive structures (see again Fig. 5) lead to the generation of gas at higher maturity levels. Type III-kerogen bearing source rocks are, therefore, referred to as gas-prone source rocks, while their counterparts with type II-kerogens are called oil-prone source rocks. The ratio of the quantities expressed in kg of gas to oil (GOR) generated in a source rock depends on the type of its kerogen and its heating history during burial. The GOR varies in nature between end member values of 0.1 (oil field) and 100 (gas field). Generally, the gas to oil ratio increases with the increasing maturity of a source rock. The increasing concentrations of methane in deeply buried source rocks are a consequence of the fact that methane is, thermodynamically, the most stable hydrocarbon species. For this same reason, oil accumulations which get buried deeper and exposed to higher temperatures are ultimately converted into accumulations of dry gas by cracking processes.

The origin of natural gases is more complex. Both their hydrocarbon and their nonhydrocarbon constituents have multiple sources (Hunt, 1996). The principal sources of hydrocarbon gases are: a) methanogenic bacteria; b) kerogens of any type; c) coal; d) cracking of long-chain hydrocarbons in reservoir and source rock oils. Methanogenic bacteria generate methane (so-called biogenic methane) in shallow sediment intervals either by fermentation or by carbon dioxide reduction. Fermentation resulting in the generation of swamp gas follows the reaction scheme $2CH_4 + 2H_2O \rightarrow CH_4 + 2H_2O + CO_2$, while biogenic methane due to carbonate reduction is formed according to $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. These processes are associated with a pronounced carbon isotope fractionation effect. In order to generate methane, these bacteria consume preferentially the lighter $^{12}CO_2$, rather than the heavier $^{13}CO_2$. Therefore, the resultant biogenic methane has a significantly higher abundance of isotopically light carbon compared to methane generated by the cracking of kerogen or coal (thermogenic methane). This difference in the stable isotope composition of carbon is a reliable tool for pinpointing the origin of methane. Also, bacterially generated gas consists almost exclusively of methane, while thermogenic gases often have significant proportions of ethane and higher homologues ($C_{2+}$-fraction). It has been estimated that among worldwide occurrences of natural gas fields, about 20% of them produce methane of bacterial origin. Most of the gas fields in the Po valley area of Italy and the northern Adriatic Sea are filled with biogenic methane, like e.g. the Porto Corsini and the Porto Garibaldi fields (Mattavelli et al., 1983). In view of the temperature threshold needed for methanogenic bacteria to thrive, it is remarkable that the deepest occurrence of biogenic methane worldwide, located in that part of northern Italy, is 4,467 m deep. Thermogenic hydrocarbon gases originate from the cracking of all kinds of kerogens and
bituminous coals. Hydrogen-rich type II-kerogens generate higher proportions of C<sub>2</sub>-hydrocarbons as compared to type III-kerogens. The latter generate, however, much higher proportions of carbon dioxide and nitrogen.

The nonhydrocarbon constituents of natural gases – carbon dioxide, nitrogen and hydrogen sulphide – have an organic as well as an inorganic origin (Hunt, 1996). The organic origin of carbon dioxide is mainly obtained by the removal of carboxyl groups from type III-kerogens (decarboxylation). The main inorganic origin is obtained through the thermal dissociation of carbonates at places in the subsurface where hot igneous melts get in contact with limestones or dolomites. Nitrogen is formed by the oxidation of igneous melts get in contact with limestones or obtained through the thermal dissociation of (decarboxylation). The main inorganic origin is obtained through the thermal dissociation of carbonates at places in the subsurface where hot igneous melts get in contact with limestones or dolomites. Nitrogen is formed by the oxidation of ammonia (NH<sub>3</sub>), which is derived from the maturation of coal. It can also be traced back to atmospheric sources (air trapped in sediment pores) and even gas inclusions in some igneous rocks rich in nitrogen. The most unwanted constituent of natural gases is hydrogen sulphide (H<sub>2</sub>S). It has to be separated prior to pumping natural gases through pipelines and prior to refining, because it is very corrosive to steel pipes. It is also highly toxic. Likewise, hydrogen sulphide can originate from organic as well as inorganic sources. The organic mechanism mainly concerns the cracking of organic sulphur structures present in the kerogens of many of the source beds of carbonate lithologies, which tend to be sulphur-rich. Inorganically, hydrogen sulphide is produced by the reduction of sulphate dissolved in pore waters, which occurs at temperatures in excess of 100°C. This so-called thermochemical sulphate reduction follows the reaction scheme

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\text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 + \text{H}_2\text{S}.
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It requires hydrocarbons to be oxidised. An extreme case is the Lacq gas field near Pau in south-western France with 15% hydrogen sulphide, which is used to produce elemental sulphur. Any natural gases bearing hydrogen sulphide are called sour gases, whereas the hydrogen sulphide-free equivalents are referred to as sweet gases. Exotic trace components of some natural gas fields are noble gases (helium, argon), hydrogen or even mercury. Helium originates from the radioactive decay of uranium or thorium-bearing minerals in basement rocks. Finally, condensates which are composed mostly of gasoline-range hydrocarbons can have a dual origin. One is by the thermal decomposition, i.e. cracking of oil in a reservoir which is subjected to elevated temperatures post-dating accumulation. The other mechanism is by so-called separation-migration (Silverman, 1965). This process occurs if the cap rocks above oil accumulations at great depths and high pressures get fractured by tectonic activities. Due to pressure release, vapourisation occurs and light oil components escape in gas-phase through fractures and faults in order to accumulate at shallower traps as condensates. Condensates formed by this evaporative fractionation are characterised by pronounced compositional fractionation effects (Thompson, 1987).

### 1.2.2 Migration of petroleum

The generation of petroleum by thermal degradation of kerogen is based on chemical processes controlled mainly by temperatures. Migration of petroleum from its place of origin in the source rock to its place of accumulation in the reservoir trap is controlled by the physical and physico-chemical conditions of the sedimentary strata the oil is moving through. Pressure exercises a major influence on this process. Two types of pressures can be differentiated in the subsurface. The hydrostatic pressure is the weight of the fluid column corresponding to the interconnected network of water-filled pores from a given depth up to the sediment surface. Since subsurface pore waters contain dissolved salt, the hydrostatic pressure gradient is not 10.0 MPa/km (pure water), rather 10.4 MPa/km. It applies to all kinds of pore fillings, i.e. water, oil and gas. The lithostatic pressure is the sum of the weight of the rock column, transmitted from the surface to a given depth by grain-to-grain contacts, plus the weight of the pore fluid column. The lithostatic pressure gradient is 24.4 MPa/km (Hunt, 1996). In a sedimentary basin, any deviation from the hydrostatic pressure is called an abnormal pressure. This can be overpressure or underpressure occurring at specific intervals. Overpressure is caused by the inability of pore fluids to escape from porous rocks in proportion with the overburden load. Thus overpressured shale or mudstone intervals are undercompacted. In some sedimentary basins there is a third type of pressure gradient. The hydrodynamic pressure gradient or fluid potential gradient is caused by active pore water flow. It can be observed in those intervals of high porosity and high permeability sandstones where water flow from an area of meteoric water intake, located at high altitudes towards a deeper discharge area, occurs.
Another set of physical and physico-chemical conditions which exercise major control over the ability of petroleum to move through rocks are porosity and permeability. Porosity is the volume of void spaces as percentage of a given total volume of rock. Besides the abundance of pores in a rock volume, the sizes of the pores are also important with respect to the movement of oil. Most rocks exhibit a great variety of pore sizes, which can be measured and expressed as pore-size distribution. According to a standard classification scheme, pore-size categories are broadly differentiated in: macropores, which have pore widths greater than 50 nm, mesopores between 2 and 50 nm, micropores between 0.8 and 2 nm, and finally ultramicropores less than 0.8 nm. There are several types of so-called primary and secondary porosity (inherited from deposition of a sediment, or generated by mineral dissolution reactions in the subsurface respectively), as well as fracture porosities caused mostly by tectonic processes (Selley, 1998).

All rock pores in the subsurface are filled with water, with the exception of those situations where the pore water has been displaced by petroleum. Another essential requirement to allow movement of petroleum through porous rocks is permeability, i.e. the pores must be connected. Permeability characterises the ability of fluids (water, oil, and gas) to pass through porous rocks. It is measured according to Darcy’s law and expressed in Darcy (d)-units equal to 1,000 milli-Darcy units (md). The relationship between porosity and permeability is highly variable and depends mainly on rock type. Finally, the movement of petroleum through porous rocks is influenced by capillary forces. This is due to the interfacial tension between two immiscible phases (oil/water or gas/water). Capillary forces, therefore, always act in pore systems of mixed wettability, i.e. where water, oil or gas co-exist. The capillary pressure of a rock increases with decreasing pore size. The petroleum compounds generated from kerogen have a very limited primary pore volume available for accumulation in fine-grained source rock-type shales and mudstones. They are forcefully transported through capillaries between the clay minerals and narrow pores towards contact with the nearest strata of higher porosity. This process is referred to as primary migration (expulsion) and differentiated from secondary migration through the greater pores in more permeable carrier beds and reservoir rocks (see again Fig. 1).

**Primary migration**

Primary migration of petroleum follows pressure gradients from the centre of mature source rock intervals towards their contacts with reservoir strata. Several processes control the generation of reservoir strata. One of the main driving forces for primary migration is sediment compaction due to overburden load. Compaction is achieved by the reduction of pore spaces due to the expulsion of pore waters. Freshly deposited clay-rich sediments have 60-80% pore water contents. Most of this pore water is expelled due to compaction within the first 2,000 m of burial. However, at that stage petroleum generation by thermal degradation has not been initiated in most basins. With further burial, very little pore water remains for additional expulsion. This is why sediment compaction was long disputed as a major driving force for primary migration. Now it is known, however, that good quality source rocks experience further compaction with the expulsion of petroleum. In order to understand this process, one has to consider the physical conditions of a source rock in terms of volume relationships. Let us assume a good quality petroleum source rock with an organic carbon content of 10%. This weight-percentage is by multiplication with organic matter-density converted into about 25% by volume. This condition implies that the solid organic matter (kerogen), is load-bearing, i.e. the lithostatic pressure is not carried by the contacts between mineral grains, but rather by the kerogen network. If one then knows, as explained above, that about half of this kerogen is chemically labile and with maturity progress is converted into petroleum, it becomes clear that compaction pressures act as a driving force for primary migration.

In good-quality source rocks, oil is transported as a separate phase (England et al., 1987). Any migrating oil phase, in the narrow pores of the originally water-wet fine-grained source rocks, has to overcome capillary pressures. The non-wetting oil phase has to overcome the resistance of very narrow water-wet pore throats when moving through the rock. The effective flow of oil can only be achieved once an interconnected network of oil-saturated pores has been established. It has been estimated that a minimum saturation of 20% of the pores with oil has to be reached prior to initiation of its active flow. An additional mechanism to provide pressure for the expulsion of petroleum is due to some volume expansion with conversion of solid labile kerogen into liquid and gaseous hydrocarbons plus residual inert kerogen. Expulsion of oil is associated with pronounced fractionation effects with respect to the compound class composition. Saturated hydrocarbons are preferentially expelled, while NSO compounds remain preferentially within the pore space of the source rock. This trend is exemplified by...
the comparison of the compound class composition of extracts of mature Kimmeridge Clay Formation source rocks from the North Sea area (24.2% saturated hydrocarbons; 47.9% NSO compounds) with that of oil accumulated in the interbedded reservoir sandstone interval (50.8% saturated hydrocarbons; 18.2% NSO compounds; Leythaeuser et al., 1988). Within saturated and aromatic hydrocarbon compound classes, there are no molecular fractionation effects in the case of good quality source rocks with type II-kerogens. This observation indicates that the transport of petroleum proceeds as a single-phase oil fluid separate from the water phase during primary migration. Compositional fractionation effects are, however, associated with petroleum expulsion from type III-kerogen bearing source rocks (Leythaeuser and Poelchau, 1991). The small quantities of oil generated from these get transported in gaseous solution. Since solubility of petroleum hydrocarbons in gas decreases with increasing molecular-size, there is a compositional difference between the products generated and the mixtures expelled. In some source rock-type shales which are carbonate cemented, the primary porosity and permeability are so low that effective transport of hydrocarbons is impossible. The newly generated hydrocarbons, which have entered these narrow pore spaces, cause the original pore fluid pressure to increase dramatically. If this rising pore fluid pressure (the sum of the original hydrostatic pressure and fluid pressure from the input of hydrocarbons into pore spaces) reaches about 80% of the lithostatic pressure, the strength of the rock is exceeded and it fractures. Microfracture networks open and serve as permeability avenues for the expulsion of oil. The proportion of oil expelled from the source rock expressed as a percentage of the total oil generated, is called the expulsion efficiency. Expulsion efficiencies increase with maturation progress, i.e. the more oil generated in the source rock, the more that can be effectively expelled from it. Good quality petroleum source beds at peak generation stages reach expulsion efficiencies of between 60 and 80% (McKenzie et al., 1987). A proportion of 20-40% of the petroleum generated, remains in the source rocks adsorbed on pore walls or on kerogen particles. If such a source rock gets buried deeper later on and exposed to higher temperatures, these petroleum hydrocarbons get converted into gas (oil-to-gas cracking). In this way, an oil-prone source rock can, at great depths, be converted into an effective gas source rock.

A special case involves the expulsion of petroleum from source rocks of carbonate lithologies. Several very prolific petroleum source rocks, such as the Upper Cretaceous La Luna Formation in Venezuela or the Upper Jurassic source strata in the Middle East fall into this category. As explained above, the organic matter in most source rocks of this kind, is concentrated into narrow bands during diagenesis by pressure solution processes called solution seams when horizontally oriented, and stylolites when arranged in a zigzag pattern. In the Meride Limestone, which is the source rock of oil accumulated in several fields in northern Italy, compacted bodies of algae are concentrated inside solution seams to such an extent that a three-dimensional kerogen network is formed (Leythaeuser et al., 1995). This arrangement represents an ideal prerequisite for effective petroleum generation and expulsion. Since these solution seams are sealed tightly above and below by carbonate cements, petroleum generation leads to drastic overpressuring of the fluids contained within, causing intensive microfracturing of the rock. Microfracture networks provide favourable permeability avenues for the effective transport of oil resulting in high expulsion efficiencies.

The primary migration of natural gas components occurs mostly when they are dissolved in oil. Oils are good solvents for hydrocarbon gases and vice versa, i.e. compressed gas can dissolve increasing amounts of oil with increasing pressure and temperature. At very great depths, the question whether hydrocarbons migrate in an oil or gas phase is irrelevant. At pressures exceeding the critical point in the phase diagram, oil and gas are present as a single-phase. Methane is soluble in water at elevated pressures. By molecular diffusion through the water-saturated pore space which follows concentration gradients, methane can be effectively transported over short distances into the nearest fracture or fault in gas-prone source rocks or coals (Leythaeuser et al., 1982). Carbon dioxide shows high solubility in water and a high reactivity, i.e. it can enter into mineral reactions such as carbonate dissolution. Likewise, hydrogen sulphide exhibits high solubility in water and a high reactivity. It is so reactive that much of it is transformed into elemental sulphur, iron sulphides or organic sulphur compounds in the subsurface.

**Secondary migration**

As soon as the petroleum has crossed the source/reservoir bed contact and entered the reservoir rock, quite different physical conditions prevail. Significantly higher porosities, permeabilities and pore sizes allow for the formation of oil droplets and small continuous oil stringers, i.e. a network of interconnected oil-filled pores. Their movement
occurs as a discrete oil phase controlled by the interplay of driving and counteracting resisting forces (England et al., 1987). The main driving force is buoyancy which is due to the density contrast between petroleum hydrocarbons and water. Oil densities can vary between 0.5 and 1.0 g/cm³; natural gas densities are much less than 0.5 g/cm³ while pore waters have densities varying between 1.00 and 1.20 g/cm³ depending on their salinity. These density contrasts result in oil/water buoyancy gradients varying between 0 and 6.8 kPa/m, while gas/water buoyancy gradients are much higher, i.e. ranging from 4.5 to 11 kPa/m (Hunt, 1996). The greater the volume of interconnected oil-saturated pores, the more the buoyancy forces increase. A second driving mechanism can be hydrodynamic forces. If pore waters are flowing actively, the passage of oil droplets through bottle necks in the pores is facilitated. However, hydrodynamic pore water systems are relatively rare. The resisting force of capillary pressures counters these driving forces. Capillary pressure is the pressure which oil or gas has to overcome in order to displace the water from the pores of the rock it is trying to penetrate. This displacement pressure depends very much on the size of the pore throats. If a rock has very narrow pore throats, capillary displacement pressures get so high that they cannot be exceeded by the buoyancy of the oil stringer or gas bubble, and entrapment occurs.

Migration of petroleum in sandstone reservoir beds is driven by buoyancy and hence directed upwards into inclined carrier rock strata. This movement is referred to as updip migration (see again Fig. 1). The rate of this movement depends on the volume of the oil stringer, and hence its buoyancy, as well as on the pore-size distribution and permeability of the reservoir rock. Controlled by capillary forces, oil droplets have a tendency to move into the largest-size pores available (England et al., 1987). As soon as saturation of a sufficiently dimensioned interconnected network of large-size pores is achieved, breakthrough occurs and the updip movement of the oil stringer begins. Within sandstone reservoir strata, the distribution of pore sizes is very heterogeneous. It is largely determined by sedimentation processes and partly modified during diageneis by mineral reactions in the form of cementation processes. Therefore, the route which the oil follows during secondary migration is usually split up into many narrow channels which are irregularly distributed throughout the carrier rock volume. Consequently, it is impossible to determine a value for the overall minimum oil saturation of the reservoir rock interval needed for secondary migration to occur. Secondary migration of oil is never 100% efficient in a quantitative sense. Once oil has migrated through an interval of a carrier-bed sandstone, there are invariably traces of oil left adsorbed on pore walls visible as impregnations.

Knowledge of the efficiency of secondary petroleum migration, i.e. the loss associated with this process, is very limited and hence subject to much speculation. This is mainly due to a lack of studies on natural migration systems. Drilling of exploration wells is focused on hydrocarbon traps, i.e. reservoir rock locations updip from secondary migration avenues. Therefore, the availability of samples for studies is very biased. Using the following mass balance approach for well-explored sedimentary basins, the loss of oil in the secondary migration avenue has been estimated as: \( O_{f} - O_{w} = O_{et} + O_{j} \), where \( O_{f} \), \( O_{et} \), and \( O_{j} \) are respectively volume of oil generated by, and expelled from the source rocks, volume of oil accumulated in oil fields and volume of oil lost during secondary migration. For two relatively small, well-explored sedimentary basins in Indonesia a loss of 50 to 80% was determined (McKenzie and Quigley, 1988).

Distances and directions of secondary petroleum migration vary depending on the type and configuration of the sedimentary basin and the spatial relationships between interbedded sandstones and shales, as well as the abundance of fractures and faults (Larter et al., 1996). Short migration distances occur in sedimentary sequences with intensive interbedding of source rock-type shales and reservoir sandstones. This is especially the case in geologically young delta systems, such as the Niger delta in Nigeria or the Mississippi delta in the USA. Lateral migration distances of kilometres or tens of kilometres are common, especially in foreland basins. Examples include the Eastern Venezuela Basin, where secondary migration distances of about 275 km have been documented. The longest migration distance known worldwide is in the Western Canada Basin (Larter et al., 1996). The lateral distance between mature source rocks near the basin centre and the belt of heavy oil fields and tar sands there, is more than 1,000 km. While the oil migrates updip laterally, it covers vertical distances at the same time. A statistical study of hundreds of oil fields from locations worldwide has shown that about 60% of them migrated vertically from source to reservoir, while about 40% involved considerable lateral movement (Hunt, 1996). As petroleum migrate updip from great depths to shallower levels they experience pressure release. This causes a number of physico-chemical effects collectively referred to as PVT changes (pressure,
volume and temperature). The most important one concerns the desorption of gas, i.e. a free gas phase is established. These effects exercise dominant controls where petroleum migrates vertically upwards through faults and associated fracture zones (England, 2002).

### 1.2.3 Accumulation of petroleum

The updip migration of petroleum along inclined carrier beds continues as long as it does not encounter structural configurations where the reservoir strata form traps (see again Fig. 1). Traps are containers in the subsurface where petroleum accumulates. At the Earth’s surface, oil is filling a container from the bottom up due to gravity. In the subsurface, the orientation of the container must be reversed in order to fill it with petroleum. This is because petroleum is lighter than water and hence has considerable buoyancy within its environment of water-filled pore spaces. Therefore, the subsurface container is filled from the top downwards. The most common traps are culminations of folds (called anticlines). Petroleum displaces the pore water there, starting from the top of the culmination and expanding into the flanks of the anticline. The contact between the oil-saturated and the water-saturated pore spaces is always sharp and, in most cases, horizontal. This boundary is referred to as the oil/water-contact (Fig. 6). Provided that the incoming petroleum has an adequate gas/oil ratio and favourable pressure conditions, gas desorption will occur and a free gas phase will separate from the oil. Since gas has the highest buoyancy, it accumulates in the apex of the structure as a so-called gas cap. The gas-oil contact is equally sharp and horizontal. Other terms for the characterisation of an anticlinal petroleum trap are explained in Fig. 6. Many other trapping configurations, besides anticlinal traps are known (see Chapter 1.3). In order for a trap to hold petroleum in place, it must be sealed by an impermeable cap rock. Cap rocks of most petroleum fields are fine-grained, clay-rich sediments like shales or mudstones. Due to their low permeabilities and very small-diameter pores, capillary entry pressures are so high that they cannot be overcome by the buoyancy of a high oil or gas column. The most ideal and best sealing cap rocks are, however, evaporite strata like anhydrite or rock salt. Such good-quality cap rocks hold many of the large petroleum accumulations in the Middle East in-place. Contrary to common belief, petroleum is not accumulated in the subsurface in lakes or giant bubbles. From the preceding discussions, it should be clear that petroleum accumulations occupy the pore spaces of sandstone or porous carbonates in analogy to a sponge in the bathroom which has sucked up water. Most petroleum fields consist of an oil zone, the thickness of which is referred to as the oil leg or oil column, overlain by a gas cap as shown in Fig. 6. In these cases, the gas is called associated gas. Non-associated gas denotes an accumulation of gas without an oil leg, i.e. a natural gas field. There are also oil fields without gas caps. In these cases, the solubility of gas in oil under the prevailing pressure regime is not exceeded, i.e. the gas remains dissolved in oil. The process of the filling of reservoir traps and formation of petroleum accumulations often occurs over extended periods of geologic time. There have been cases where the relevant source rock in the drainage area became

![Fig. 6. Diagram showing a folded sandstone layer representing a reservoir trap. At the apex of this anticline, natural gas and oil below has accumulated. In the pore space of the gas cap and the oil zone, the original pore water was displaced by gas and oil respectively, while below the oil/water-contact the sandstone remains water-saturated (Selley, 1998).](image-url)
continuously buried at greater and greater depths, causing the maturity of the organic matter to increase. Consequently, oils of changing compositions, especially progressively lighter oils, were expelled from these source rocks and migrated towards the trap. In-reservoir mixing of petroleum fluids is often restricted resulting in compositional heterogeneities within the oil column (Leythaeuser and Rückheim, 1989). A similar situation arises when oils from several different source rocks have accumulated in a common reservoir trap.

In most petroliferous basins, there are several source rocks of different geological ages which have generated and expelled petroleums of somewhat different compositions. These oils have accumulated in many reservoir traps, which are often located far away from the areas of mature source beds (so-called ‘oil kitchens’). In some oil fields, several reservoirs are arranged in a vertical sequence (‘stacked reservoirs’). Also, some accumulations contain petroleums of mixed origin, i.e. derived from several source rocks. In all of these cases, the petroleum geologist needs to know the precise origin of each oil discovery as well as the genetic relationships among the many oil occurrences. These problems are solved by detailed geochemical analyses which allow for so-called oil-source rock and oil-oil-correlations.

Among the multitude of techniques developed for this purpose, two approaches are commonly applied. One is based on detailed comparisons of the distribution patterns of homologous series or isomers of biological marker molecules such as, e.g. steranes or triterpanes. As explained above, each source rock was deposited under specific environmental conditions and has received a specific mixture of residues of biological organisms. Therefore, the petroleum generated by each source rock carries, in analogy to a fingerprint, a genetic imprint in the form of a molecular signature. These signatures are often so specific that the geochemist can group the multitude of oils in a sedimentary basin into genetic families, or he can trace individual oils back to their source rocks (Connan, 1993). The other often applied approach, is based on the recognition of similarities with respect to the composition of stable carbon isotopes ($^{13}C/^{12}C$ ratio) of whole-oil samples, or compound classes or even individual molecules separated chromatographically therefrom.

Very special cases of gas accumulations occur in the form of so-called gas hydrates. These are solid, ice-like compounds whereby water molecules are arranged in crystal lattices forming cages (called clathrate compounds). Methane molecules are arranged inside these cages. Per unit volume of reservoir pore space, more methane can be stored in hydrate condition as compared to free gas. One cubic metre of gas hydrate contains 164 m$^3$ of methane. Gas hydrates are formed under high pressures and/or low temperatures (Kvenvolden and Lorenson, 2001). Such conditions are met on Earth in two different regional settings: deep ocean and permafrost. Pressures required for the crystallisation of gas hydrates prevail below the ocean floor at water depths in excess of about 500 m. Over certain areas of the world’s deep oceans, there is enough methane available (produced by methanogenic bacteria) for the formation of gas hydrates. The other situation where the stability conditions of gas hydrates are met concerns arctic land areas which are underlain by so-called permafrost. Subsurface temperatures are below 0°C to depths of several hundred metres so that all pore water is permanently frozen. Below this permafrost zone, gas hydrates are very likely present. Natural gas hydrate occurrences have not been known about for a long time. Active research programs are currently under way in several countries. One of their objectives is to explore gas hydrates as a potential energy resource for the future (Sloan, 2003). So far there is no commercial gas production from methane hydrates. Development of production technologies and corresponding tests are under way in the Messoyakha field in Siberia as well as in the Mallik field in northern Canada. Predictions are that gas hydrates will indeed become an important energy resource in the future when conventional oil and gas resources have much declined. This assumption is based on estimates of enormous quantities of gas hydrates hidden under the deep ocean floors and in arctic permafrost regions. It is estimated that more energy resources are present on Earth in the form of methane hydrates, than exist from the sum of all of the presently known fossil fuel resources (oil, gas, and coal). Optimistic estimates claim that there is twice as much methane available from gas hydrates. However, due to the heterogeneous distribution of gas hydrates as lenses and nodules in marine sediments, and due to the great water depths involved, oceanic hydrate resources may not gain economic interest. Gas hydrate occurrences in permafrost regions which can be present in the form of ‘frozen gas fields’ have a more realistic chance for future economic usage.

A hotly debated issue among petroleum geologists concerns the problem of the accumulation efficiency in petroliferous sedimentary basins. This is the question which concerns what proportion of the total petroleum generated in the source rocks is accumulated in reservoir traps and can be discovered by the explorationist. There is no universal answer to this question. Proportions vary greatly from basin to
basin and percentage numbers quoted on the basis of mass balance approaches represent semi-quantitative estimates at best. In Fig. 7, the quantitative effects of all processes of petroleum generation, migration, dispersion and loss which control the occurrences of petroleum in a petroliferous basin, are illustrated. This scheme also provides an overview of principal geological elements and conditions which the petroleum geologist has to evaluate in order to predict the likelihood of petroleum occurrences. Based on a synthesis of the results obtained by sedimentologists, structural geologists, geochemists and geophysicist teams, etc. the petroleum geologist has to assess the effects and likelihood of an entire system of processes which have occurred over extended periods of geologic time. Fig. 7 is, therefore, also a schematic illustration of the so-called ‘petroleum system’ concept (Hunt, 1996). At the same time, it also represents a summary and extension of the previous discussions in this chapter. Of the total amount of petroleum generated in the source rocks at great depths in this hypothetical sedimentary basin, 75% is expelled in the course of primary migration into nearby high-porosity/permeability carrier beds. During secondary migration, about 50% of the petroleum which has entered the carrier beds remains in the form of impregnations adsorbed on mineral surfaces. About 40% has, at an earlier stage in the history of this sedimentary basin, accumulated in reservoir traps, while the remaining 10% is on its secondary migration route bypassing all traps and eventually leaking out at the Earth’s surface. This process is called petroleum seepage. About 25% of the original petroleum accumulated gets lost by cap rock leakage occurring at a slow rate over long periods of geologic time. Of the remaining petroleum, another 25% gets lost in the course of chemical, physico-chemical and bacterial processes (discussed above). In summary, only about 10% of the petroleum generated in the source rocks of this hypothetical basin can be discovered by exploration and produced for economic usage. This estimate is very much on the optimistic side when considering the known petroliferous basins in the world. In fact, there are only a few reported cases that fall into this category. These include the La Luna-Misso petroleum system of Venezuela and the Arabian/Iranian Basin in the Middle East. More common cases are in the order of 2-5%, such as several petroliferous basins in the USA and Australia (Hunt, 1996).

The leakage of oil and gas from subsurface strata to the surface of the Earth occurs and has occurred continuously at many places both on land and on the ocean floor. Petroleum seepages can be microseeps, which are invisible and can only be recognised by special techniques, or they can be associated with visible effects. Oil seeps include springs with oil-bearing waters, tar pits and asphalt lakes. The asphalt lake in Trinidad is a large-size oil seep. Another one

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**Fig. 7.** Scheme to show the re-distribution of petroleum in a sedimentary basin during its geological history. Sizes of all compartment boxes are dimensioned as relative proportions of the total volume of petroleum generated by the source rocks at depth. These proportions shown here as semi-quantitative estimates vary from basin to basin.
is the La Brea Tar Pits on the outskirts of Los Angeles, USA. It became famous as a treasure chest of vertebrate palaeontology. During Plio-/Pleistocene times, many animals like buffaloes, rhinos or elephant ancestors were deceived while attempting to drink from the shallow water which might have accumulated on top of this asphalt lake, and sunk into the sticky mud. Their bodies, preserved from decay by the asphalt, are still being excavated and studied by palaeontologists and displayed at a nearby museum.

Petroleum seeps occur where permeable pathways in the form of fractures or faults lead to the surface of the Earth either from mature source rocks or from leaking accumulations. They are common in geologically young and tectonically active basins such as the foreland basin of the Zagros Mountains in Iran, the Mesopotamian geosyncline in Iraq or in intramontane basins in Indonesia and Colombia (Hunt, 1996). During pre-industrial times, seeps were exploited as a source of oil and asphalt for various uses. The oldest documented cases include traces of asphalt on arrow heads excavated in Mesopotamia. Stone-age men used asphalt to glue their arrow heads into wooden shafts. The Bible contains many references to the use of asphaltic materials, such as Noah who used asphalt to make his boat watertight. Asphalt was used as a mortar in brick-laying for the tower of Babylon. Egyptian mummies were prepared using asphalt collected at seeps. Asphalt and pitch were also used in those days for warfare and in artwork. The earliest documented speculations of the North Sea basin as Europe’s most important petroleum province (discovered only in the late Sixties of the last century), date back to the year 1752. Erich Pontoppidan, then bishop of Bergen in Norway and a hobby-naturalist, published a big book entitled Norges Naturlige Historie. It contains the following translated statements: “The North Sea’s fattiness is, after its saltiness, a peculiar property […] It can be assumed that in the ocean and on land there exist, here and there, seepages of running oily liquids or streams of petroleum, naphta, sulphur, coal-oils and other bituminous liquids”. In all likelihood, the bishop had found tar balls on his extended walks along the shores, originating from submarine oil seeps and washed onto the beach by waves. This observation illustrates the fact that oceans get polluted locally by petroleum not only through anthropogenic activities, but by natural processes as well. Offshore oil seeps are known in many parts of the world, e.g. in the Gulf of Mexico, the Gulf of Suez, the Red Sea, offshore northern Alaska and Canada, in the South China Sea and in the North Sea. It was estimated that approximately 1.5 million barrels of oil a year are being leaked into the world’s oceans by natural seepage and another 0.5 million barrels come to the Earth’s surface on land (Hunt, 1996). In order to reassure the concerns of environmentalists, it should be emphasised that nature has provided means to cope with this problem of pollution by active seepage. A number of chemical and bacterial weathering processes, which are outlined above, are able to degrade and remove most of the mass of the spilled oil.

Like oil, gas is seeping out at many places on the Earth’s surface. Onshore gas seepages are often expressed at the surface in the form of so-called mud volcanoes. Gas from a leaking accumulation rising upwards through fractures is temporarily trapped in shallow depths below groundwater-filled fractures. As soon as the gas pressure exceeds the pressure exercised by the weight of the water column above, eruption occurs. Since the water in near-surface fracture zones is very muddy, the eruption is associated with an outflow of mud. This process of intermediate accumulation of gas bubbles below groundwater-filled fractures and eruptive outflow of gas and mud, is repeated over and over again. The resulting morphological feature is a cone-shaped mud volcano. In the region of Azerbaijan, north of the Caspian Sea, many mud volcanoes up to several hundred metres in height occur. Some of the eruptions are associated with violent flames of burning methane and massive mud outflows. In the foothills of the Zagros mountains in Iran, there are places where gas is blowing out from solid rock fractures and has caught fire. Since antiquity such sites of ‘eternal fire’ were venerated and may have lead to the origin of the Zoroastrian religion. Gas seeps on the sea floor are expressed morphologically in another way. With each swarm of gas bubbles that erupts, mud from clay-rich unconsolidated sediment is stirred up. After eruption, the sediment particles do not settle down vertically but drift away laterally by slow bottom water currents. Repeated eruptions eventually lead to a circular depression like a negative cone on the seafloor called a pockmark. These are widespread features in many shelf seas, e.g. major areas of the continental shelf of Norway are dotted with pockmarks. Their distribution and abundance has to be known since pockmarks represent hazards for oil industry activities, such as the laying of pipelines (Hovland and Gudmestad, 2001).

**Basin modeling**

The physical and chemical processes involved in the generation, migration and accumulation of petroleum are understood today to such an extent that
their effects can be quantified as a function of the geological history of a sedimentary basin. So-called basin modeling by numerical simulations has become a routine tool for petroleum exploration. Sophisticated software packages have been developed for deterministic forward models which allow the temporal reconstruction of the history of a sedimentary basin and the concomitant evolution of most processes relevant to the formation of petroleum accumulations (Welte et al., 1997). To conduct a basin modeling study, a great deal of input parameters have to be obtained from well data. Invariably, for certain parameters, assumptions based on geological reasoning must be made. Examples of required input parameters (Poelchau et al., 1997) include:

- Rate of subsidence, uplift and deformation of sedimentary basin fill.
- Depositional conditions and types of sediments (sedimentation rates, environments, organic matter accumulation etc.).
- Age and thickness of all sedimentary strata.
- Rock properties such as porosity, permeability, density, thermal conductivity, heat capacity, and compressibility.
- Fluid properties (in water, oil, and gas) such as composition, density, viscosity, etc.
- Thermal history of the basin, i.e. heat input from basement and conditions for conductive and convective heat transport, etc.
- Kinetics of organic matter transformation in source rocks.
- Hydrodynamics and conditions for fluid redistribution.
- Trap formation, e.g. by tectonic processes and their timing.

Basin modeling can be performed in one dimension (for a single well), in two dimensions (for a geologic profile combining several wells), or even in three dimensions. The main advantages of basin modeling if integrated with seismic information are twofold, i.e. quantitative predictions as to where petroleum accumulations can be expected in a sedimentary basin. Most importantly, however, the temporal evolution of all relevant processes and their effects can be reconstructed. For example, maps for individual geological time periods can be obtained which show regional variations in the maturity of the source rocks (areas where they are immature, mature or overmature). Superposition of such maps, which show different aspects of structural evolution for the same time period (type, size and distribution of potential traps), allow to rank petroleum prospects.

1.2.4 Alteration of petroleum

Those petroleum accumulations which are discovered and produced by the oil industry have survived extended periods of geologic time. During these periods, the physical and chemical conditions of the accumulation in the reservoir can have changed. Since petroleum is thermodynamically metastable under geological conditions, it responds to these changing conditions by adjusting its composition, i.e. the original composition is altered (Blanc and Connan, 1993). Geological processes which lead to compositional alteration, and their effects on oil density, expressed in degrees according to the rule formulated by the API (American Petroleum Institute), are schematically illustrated in Fig. 8.

Changes in petroleum composition due to biodegradation

In areas where there are high hydraulic head conditions (groundwater recharge areas at high

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**Fig. 8.** Scheme to show the effects on the API-gravity of a typical oil (central box) by differences in source rock-types and by alteration processes which have post-dated the accumulation (Tissot and Welte, 1984).
altitudes), meteoric waters penetrate along high porosity/high permeability strata deeply into sedimentary basins. They are oxygenated and carry bacteria. Wherever these waters flow past petroleum accumulations, they cause biodegradation and water washing effects (see again Fig. 8). Compounds which have higher solubilities in water, such as benzene and toluene, are preferentially removed. Several species of bacteria degrade and consume petroleum hydrocarbons in a very specific way (Head et al., 2003). Depending on favourable microbial growth conditions, the molecular composition of reservoir petroleums is altered to an increasing extent. The first compounds consumed by the bacteria are the n-alkanes, whereby a systematic chain-length preference starting with the light homologues is shown. Geochemists have designed a molecular scale from 1 to 10 for characterising the degree to which petroleum is biodegraded (Table 1). These molecular criteria are associated with changes of the gross properties of biodegraded petroleums like lowering of the API gravity, which influence their commercial value significantly. With increasing degrees of biodegradation, the following effects are observed (Hunt, 1996):

- Decreasing concentrations of wet gas and gasoline in favour of kerosene-range components (C₂⁻C₆ and C₆⁻C₁₅ respectively).
- Decreasing wax contents due to removal of long-chain n-alkanes.
- Decreasing gas/oil-ratios (GOR).
- Decreasing API gravities (increasing densities).
- Increasing concentrations of asphaltene.
- Increasing contents of sulphur and nitrogen.
- Increasing viscosities.

Bacteria are sensitive to higher temperatures. Based on empirical evidence, a maximum temperature of 88°C has been recognized as the limit for this kind of bacterial activity. For a long time it was believed that biodegradation of petroleums was achieved only by aerobic bacteria. Recently, however, biodegradation was documented as also occurring under anaerobic conditions. Extensive biodegradation and water washing leads to the formation of heavy and extra-heavy oils and tar sands. Heavy oil accumulations, such as those occurring in the province of Alberta in Canada, have specific gravities ranging from 0.93 to 1.00 g/cm³ (10°-20° API) and viscosities varying between 100 and 10,000 centipoises at reservoir conditions. They are still mobile under reservoir conditions, but cannot be pumped at reasonably high production rates. Tar sands are sands in near-surface intervals which are impregnated with extra-heavy oils (specific gravities in excess of 1.00 g/cm³, API° below 10; viscosities higher than 10,000 centipoises). Very large deposits of tar sands occur in northern Canada (Athabasca tar sands) and eastern Venezuela. The total in-place reserves of heavy oils and tar sands of worldwide occurrence is in the same order as the total in-place reserves of conventional crude oils.

**Changes in petroleum composition due to thermal alteration**

Petroleums like kerogen react sensitively to increasing thermal conditions. Reservoired oils which get buried deeper and exposed to higher temperatures react sensitively to increasing thermal conditions. Reservoired oils which get buried deeper and exposed to higher temperatures

<table>
<thead>
<tr>
<th>LEVEL OR EXTENT OF</th>
<th>COMPOSITIONAL CHANGES</th>
<th>BIODERADATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-alkanes C₃ to C₁₅ depleted</td>
<td>Minor</td>
</tr>
<tr>
<td>2</td>
<td>Over 90% C₁⁻to-C₃₅ n-alkanes gone</td>
<td>Light</td>
</tr>
<tr>
<td>3</td>
<td>Isoalkanes, including isoprenoids, attacked; alkylcyclohexanes and alkylbenzenes removed</td>
<td>Moderate</td>
</tr>
<tr>
<td>4</td>
<td>Isoprenoid alkanes and methylnaphthalenes removed</td>
<td>Moderate</td>
</tr>
<tr>
<td>5</td>
<td>C₁₄-C₁₅ bicyclic alkanes removed</td>
<td>Extensive</td>
</tr>
<tr>
<td>6</td>
<td>25-norhopanes may be formed; steranes attacked, with smaller molecules first</td>
<td>Heavy</td>
</tr>
<tr>
<td>7</td>
<td>Steranes gone; diasteranes unaffected</td>
<td>Heavy</td>
</tr>
<tr>
<td>8</td>
<td>Hopanes attacked</td>
<td>Very heavy</td>
</tr>
<tr>
<td>9</td>
<td>Hopanes gone; diasteranes attacked</td>
<td>Severe</td>
</tr>
<tr>
<td>10</td>
<td>Oleanane, tricyclic terpanes, and aromatic steroids survive</td>
<td>Extreme</td>
</tr>
<tr>
<td></td>
<td>Diasteranes and tricyclic terpanes destroyed; aromatic steroids attacked; vanadyl porphyrins survive</td>
<td></td>
</tr>
</tbody>
</table>
thermal regimes undergo compositional changes with maturation (see again Fig. 8). The overall trend concerns a progressive increase in the proportion of low molecular weight components at the expense of their heavier counterparts. This compositional evolution with rising subsurface temperatures is mainly achieved by cracking reactions. Medium-gravity oils are converted into light oils and condensates and ultimately into natural gas accumulations. Invariably a black, solid residue (called pyrobitumen) is left over coating sand grains or filling interstitial pore volumes. Increasing degrees of thermal alteration is the reason why oils accumulated in stacked reservoirs often show an increase in API gravities from the shallowest to the deepest reservoir zone.

Other alteration processes leading to compositional changes in petroleum

Some oil accumulations receive an input of natural gas generated by, and migrated from high-maturity source rocks at great depths, much later during their geological history. This causes a precipitation of asphaltenes. The process is called deasphalting (see again Fig. 8). Due to their higher densities, asphaltene molecules and clusters of them tend to sink down within the oil column (so-called gravity segregation). Near the oil/water contact, a layer of NSO-rich heavy oil is building up which is referred to as a tar mat. Several large-size oil accumulations like, e.g. the Prudhoe Bay field on the North Slope of Alaska have tar mats. They are of limited commercial interest, because they are often not producible.

Another process which leads to significant changes in petroleum compositions is based on a release of reservoir pressure. This can occur e.g. by uplift of the strata which contain petroleum accumulations. Such pressure release causes phase changes, i.e. desorption of gas and a drastic increase of the GOR. A given petroleum volume, e.g. under reservoir conditions at 4 km depth (50 MPa pressure, temperature of 155°C) is present as a single-phase fluid. If this accumulation is due to tectonic processes uplifted to 2 km depth the reservoir pressure and temperature is 20 MPa and 85°C respectively. This has lead to the formation of a sizeable gas cap and a volume expansion by about 30%. If uplift has proceeded to a depth of 1 km (10 MPa pressure, 50°C) the original petroleum volume has experienced a six fold expansion due to the desorption of gas. This has probably exceeded the volume capacity of the trap, i.e. the oil leg was pushed out via the spill point and a natural gas field was left. An area where uplift was associated with such effects concerns parts of the Barent Sea shelf of northern Norway. Faulting and fracturing of the cap rocks of petroleum accumulations at great depths, and vertical migration of escaping petroleum fluids into shallower reservoir traps leads to similar phase changes. The effects of this process, also known as separation-migration (Silverman, 1965), are especially observed in geologically young actively subsiding basins such as in the area of the Mississippi and the Niger deltas.

Finally, natural gas pools which have accumulated tens and hundreds of millions of years ago, have experienced gas loss by diffusion through the shale cap rocks. This has lead to shrinking reserves, or in extreme cases to total dissipation and destruction of the original accumulations. The quantification of this destructive process is a matter of debate. But it appears logical to assume that most known natural gas fields have young accumulation ages. Others may represent, in terms of geological time scales, dynamic systems whereby this diffusive gas loss is continuously replenished by gas migrating in from deeply buried source rocks (Leythaeuser et al., 1982).

References


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