

intriguing part is that if you replace the element names with their atomic numbers, those add up as well (Michael Keith)

7. Finally, no overview of the periodic table is complete without the Elements Song, written in 1959 by Tom Lehrer, who also performs it in the video: <https://www.youtube.com/watch?v=DYW50F42ss8>

Cross-References

- ▶ Alkali and Alkaline Earth Metals
- ▶ Atmophile Elements
- ▶ Atomic Number, Mass Number, and Isotopes
- ▶ Chalcophile Elements
- ▶ Earth's Continental crust
- ▶ Earth's Core
- ▶ Earth's Oceanic Crust
- ▶ Electronegativity
- ▶ Elements: Metalloids
- ▶ Formation and Evolution of the Earth
- ▶ Geochemical Classification of Elements
- ▶ High Field Strength Elements
- ▶ Ionic Radii
- ▶ Lanthanide Rare Earths
- ▶ Large-Ion Lithophile Elements
- ▶ Lithophile Elements
- ▶ Mantle Geochemistry
- ▶ Nucleosynthesis
- ▶ Platinum Group Elements
- ▶ Quantum Numbers
- ▶ Siderophile Elements
- ▶ Trace Elements
- ▶ Transition Elements
- ▶ Unified Atomic Mass Unit, Avogadro Constant, and Mole

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Petroleum

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Definition

Petroleum, from greek *petra* (rock) and latin *oleum* (oil), is a mixture of natural origin, made of numerous organic molecules, mostly hydrocarbons, from 1 to 80 carbon atoms. Petroleum is found as a liquid phase (oil), a gaseous phase (▶ *Natural Gas*), or a solid-like phase (bitumen) in the porosity and cracks of reservoir rocks where it has accumulated. These different forms result from a common origin, as petroleum is the product of the thermal or bacterial degradation of sedimentary organic matter in deep strata of sedimentary basins. The range of conditions produces a continuum of compositions between natural gas, oil, and bitumen.

History

Natural ▶ *Oil-seeps* have been used as sealing agent, adhesive, cosmetics, and fuel in oil lamps, from three millennia before BC in Ancient Egypt and the Middle East. *Biomarker*

analysis has allowed to trace back the origin of these bitumen (Connan 1999). In Asia, hand-dug wells were used to produce petroleum from 900 BC (Hunt 1995; Thornton 2015). In Europe, petroleum was also mined locally (e.g., in Pechelbronn, France) in the seventeenth century. The industrial production of oil by drilling wells – instead of mining – and processing oil in refineries appeared in 1857 in Ploiesti (Romania) and in 1859 in Titusville (Pennsylvania, USA). The increase of oil and gas production during the twentieth century was made possible by the discovery of new accumulations, particularly in the Middle East where the largest fields of oil (Ghawar, Saudi Arabia) and of natural gas (North Dome – South Pars, Qatar, and Iran) of the world were discovered in the 1948 and 1971, respectively. In the second half of the twentieth century, exploration was also successful in offshore continental margins (North Sea, Gulf of Mexico, Alaska, among others). Since 2000, exploration has extended to offshore areas with water depths of 1–3 km (e.g., S. Atlantic, W. Mediterranean sea) and arctic regions. According to Campbell and Laherrère (1998), the rate of new discoveries should not compensate for the production from conventional reservoirs (i.e., allowing economic production rates with the original reservoir permeability). The oil and gas industry is indeed producing an increasing volume of unconventional resources which need specific technologies to increase production rates. These are mainly extraheavy oils and bitumen (e.g., W. Canada), shale gas (e.g., Barnett formation, USA), and shale oil (e.g., Bakken formation, USA).

Distribution of Petroleum Reserves

A summary of oil and gas reserves and distribution is given in Table 1. Estimates of reserves are subject to significant uncertainties (10–20%) and their precise definition may change according to the data source. The percentage of oil in place that can be produced economically with current technology

(i.e., the recovery factor) is approximately 35% (world average) for conventional oil reservoirs and approach 80% for natural gas (IFPEN 2017). There are important variations depending on reservoir characteristics. The resources of extraheavy oils and bitumen have been shown separately in Table 1 because they involve important volumes of oil in place (747 Gt) and low recovery factors (<10%) in current estimates. The possible resources of shale oil (US DOE-EIA 2013) are not shown in Table 1, as it is uncertain whether their production will be economic on a significant basis. Until 2016, the cumulated amount of oil and natural gas liquids produced worldwide is estimated to 200 Gt (IFPEN 2017). This is larger than the remaining reserves of conventional oil (178 Gt in Table 1).

Petroleum Composition

Petroleum composition is highly variable, as it results from a series of complex transformations involving chemical reactions and basin-scale migration (see below section on “Origin” and “Petroleum Migration”). In addition to its variability, petroleum composition is delicate to understand because it cannot be preserved in its original phase state when brought in surface conditions. For instance, the low molecular weight components e.g., (methane, C₂–C₄ alkanes, CO₂, H₂S) are gaseous in surface conditions and they may be dissolved in a liquid phase due to the high pressure prevailing in reservoir conditions. As another example, a methane-rich natural gas often contains significant concentrations of gasoline-range and gas-oil range hydrocarbons, which are dissolved in the gas phase in reservoir conditions, and liquid in surface conditions (Pedersen et al. 2014).

Finally, petroleum contains dissolved organic compounds of high molecular weight (asphaltenes, waxes). The abundance of these compounds in bitumen or in high wax oils explains their solid-like behavior, and their presence in

Petroleum, Table 1 Distribution of proven reserves, original oil in place (OOIP), and natural gas reserves on a global basis. Conventional oil reserves include natural gas liquids, i.e., hydrocarbons of natural gas collected in a liquid state by processing in surface conditions. Extra-heavy oils reserves (including “bitumen” and “tar sands”) are taken from

the same source as a conventional oil (BP 2017) and the corresponding OOIP are taken from Total (2006). Oil reserves are expressed in billion tons (Gt) assuming average densities of 1000 kg/m³ for extraheavy oils for volume/mass conversions. Natural gas reserves (source: BP 2017) are expressed in Tm³ (10¹²) in standard surface conditions

Region	Conventional (crude oil and Natural gas liquids)	Extraheavy oils		Natural gas (Tm ³)
	Proven reserves (2016), Gt	Estimated reserves (2016), Gt	Estimated OOIP, Gt	Proven reserves (2016)
North America	7.6	26.9	318	11.1
South America	15.1	35.7	207	7.6
Europe-Eurasia	21.8	–	222	56.7
Middle-east	110.1	–	747	79.4
Africa	16.9	–		14.3
Asia-Pacific	6.4	–		17.5
Total world	178	62.6	747	186.6

Petroleum, Table 2 Main petroleum fractions ranked by normal boiling temperature (Tb) and economic use. Direct use refers to fractions or compounds obtained by distillation or more specific separations, and

conversion refers to chemical transformations by specific processes (thermal or catalytic) in refineries

Fraction	Tb, °C	Standard state at 25 °C, 1 atm	Carbon number range	Main direct use (products obtained by distillation or separations)	Main conversion products (obtained by chemical transformation)
Methane	−162	Gas	1	Distribution gas	Methanol, H ₂
Other gases (C ₂ –C ₄ alkanes, CO ₂ , H ₂ S)	−89 to 0	Gas	0–4	LPG fuel	Light olefins (ethylene, propylene), ethers
Gasoline (alkanes, cycloalkanes, aromatics)	0–204	Liquid	4–11	Fuel, chemicals	Light aromatics and olefins (e.g., paraxylene, ethylene)
Gas oil	204–315	Liquid	11–18	Diesel fuel, jet fuel	
Atmospheric and vacuum gas oil (AGO- VGO)	315–538	Liquid	14–40	Fuel oil, lubricant bases, waxes	Gasoline and diesel fuel
Vacuum residue (mostly polyaromatics)	>538	Amorphous solid	22–100 ^a	Road asphalt, roof sealing	Gasoline and diesel fuel, coke

^aIndicative maximum number of carbons of crude oil asphaltenes.

reservoir oils may also cause solid deposits when brought to surface conditions.

Whether petroleum is a natural gas, a reservoir oil, or a bitumen, its composition is first described by its main boiling point fractions (Table 2). It is worth noting that some families are systematically absent from natural petroleum: this is particularly the case of alkenes (also named olefins) of linear, branched, or cyclic structure. Similarly, three- and four-membered saturated cycles are marginal building units in petroleum hydrocarbons, their absence being explained by the lower stability of these small cycles compared with five- and six-membered cycles. A common characteristic of all petroleum fractions is the absence of the radioactive ¹⁴C isotope of carbon, as a consequence of residence time of organic matter and petroleum >10⁶ years in the subsurface. Petroleum fractions are also displaying a lighter ¹³C composition than standard ($\delta^{13}\text{C} = -25$ to -100‰ for methane, usually -25‰ to -35‰ for other fractions) which is caused by the isotopically lighter carbon of living organisms and hence of sedimentary organic matter. Deuterium is also displaying lighter than average concentrations (Schoell 1980).

Light hydrocarbons (1–4 carbon atoms) are the major compounds of natural gas, and they are also found dissolved in reservoir oils. Methane represents generally 60–95% of natural gas and 0–50% of reservoir oil on a molar basis.

Nonhydrocarbon compounds of low molecular weight (CO₂, H₂S, N₂) show variable concentrations: 70% of natural gas reserves are reported to contain molar fractions of CO₂ lower than 2% vol and H₂S contents lower than 1% vol (Rojey et al. 1997). Occasional CO₂ contents of 10% and higher have been reported, possibly linked with magmatic contribution (e.g., 8–18% in Lula field offshore Brazil). H₂S concentrations in excess of 10% are also found in some deep reservoirs (e.g., 15.3% H₂S in Lacq field, France). Nitrogen content is

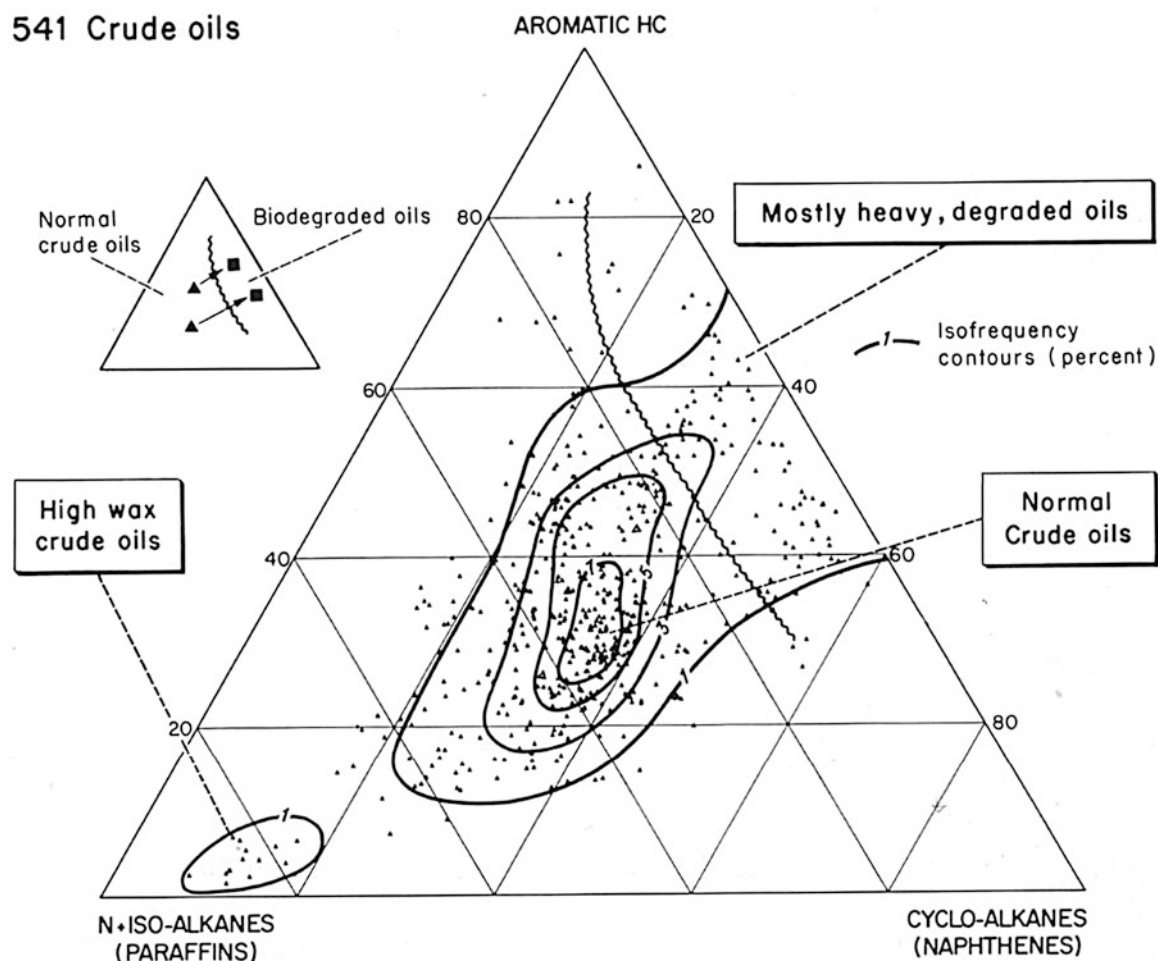
generally low in natural gas and associated gas (0–3%) but may be higher in deep gas reservoirs (e.g., 14% in Groningen field, Netherlands).

The gasoline fraction usually contains linear and branched alkanes, monocyclic alkanes (alkylcyclopentanes, alkylcyclohexanes), and light aromatics (benzene, toluene, xylene isomers, and other alkylbenzenes). Among cyclic hydrocarbons, the unsubstituted end-members (cyclopentane, cyclohexane, benzene) are generally less abundant than the methyl-, dimethyl-, or ethyl- bearing compounds of the same families. Compared with heavier fractions, the composition of gasoline-range hydrocarbons is more delicate to sample because of possible evaporation of volatile compounds. It is also less specific of petroleum origin. It provides, however, useful indications of possible compositional variations revealing different blocks in a given reservoir.

The gasoil and intermediate distillate fractions contain linear and branched alkanes, naphthenes (i.e., cyclic alkanes), and aromatic hydrocarbons (Fig. 1). On average, these fractions display comparable mass fractions. The distribution of linear alkanes generally displays a broad distribution providing some insight in petroleum origin: a distribution showing a clear maximum above C₂₀ and significant odd/even preference is an indication of a low degree of secondary reactions and an exponentially decreasing tail is an indication of more transformations. The absence of n-alkanes is an indication of oil biodegradation.

With the exception of isoprenoids, branched alkanes (alkanes bearing a branched methyl group every fourth carbon) are more difficult to identify because of the very large number of isomers. Among isoprenoids, pristane and phytane display comparable abundance to linear alkanes of similar molecular weight (Fig. 2).

Cyclic hydrocarbons in the gasoil fraction and vacuum gasoil fraction are either fully saturated (naphthenes with



Petroleum, Fig. 1 Distribution of the oil fraction boiling above 210 °C in a ternary diagram (n + iso alkanes, naphthenes, aromatics) (After Tissot and Welte 1984)

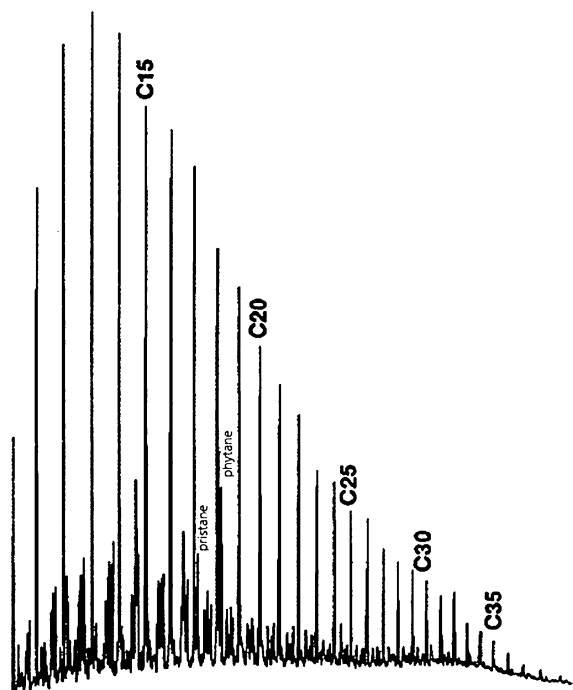
1–5 condensed cycles), aromatic (1–5 cycles), or mixed (naphthenoaromatics). In these fractions, polycyclic naphthenes comprise several families of biomarkers analyzed by ►GC-MS to trace oil origin: steranes (four condensed cycles), hopanes, gammacerane, and oleananes (five condensed cycles), among others. Among polycyclic hydrocarbons, alkyl-substituted molecules (e.g., methylnaphthalenes, dimethylnaphthalenes) are more abundant than the condensed molecule (e.g., naphthalene). In gasoil and vacuum gasoil fractions, the structure of polyaromatic molecules and the decrease of alkyl substituents are often linked with the aromatization of polycyclic naphthenes at advanced stages of thermal degradation.

The heavy molecular weight compounds of crude oils present in vacuum residue are defined as solubility classes: resins are soluble in light alkanes, and asphaltenes are not. The presence of polyaromatic nuclei in asphaltenes (Fig. 3) explains why they can aggregate by stacking and segregate if aggregates are large enough (Mullins et al. 2012). Their

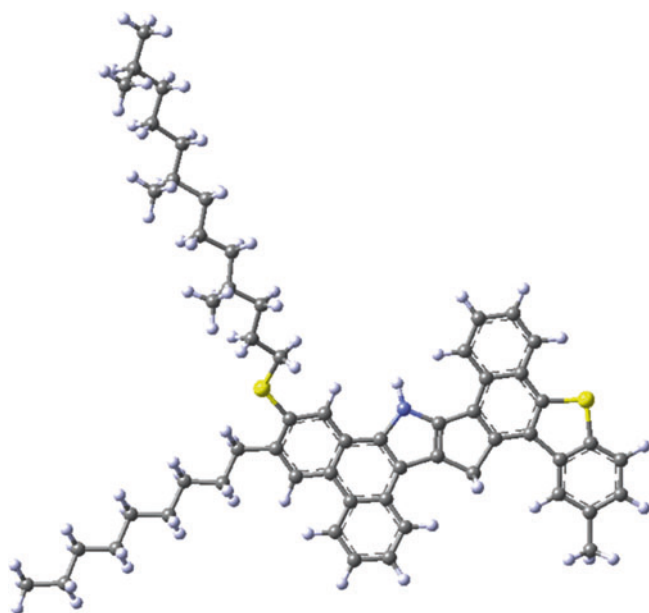
elemental analysis (atomic H/C = 0.9–1.25 according to Rogel et al. 2012, 2013) and their investigation by Atomic force microscopy (Schuler et al. 2015) reveal important variations in structure and molecular weight. Resins and asphaltenes commonly display significant contents in sulfur, nitrogen, and oxygen.

Although dominated by hydrocarbons, petroleum contains also organic compounds including sulfur, oxygen, or nitrogen in functional groups or embedded in chains and cycles. These are mostly sulfur-bearing (thiols R-SH, alkylsulfides, thiophene derivatives), nitrogen-bearing (e.g., amines, pyrrole derivatives), oxygen-containing compounds (e.g., alkanols, carboxylic acids), and organometallic compounds (Filby and Branthaver 1987). Ni- and VO-►Porphyrins are typical examples. As a general rule, the percentage of non-hydrocarbon compounds is small for light fractions and increases with molecular weight. Crude oils may contain up to 7% wt sulfur (average < 1%), up to 200 ppm of Nickel and up to 1500 ppm of Vanadium.

Ghawar Arab-Reservoired Oil



Petroleum, Fig. 2 C15+ chromatogram of a representative sample of Ghawar reservoir oil (After Carrigan et al. 1995)



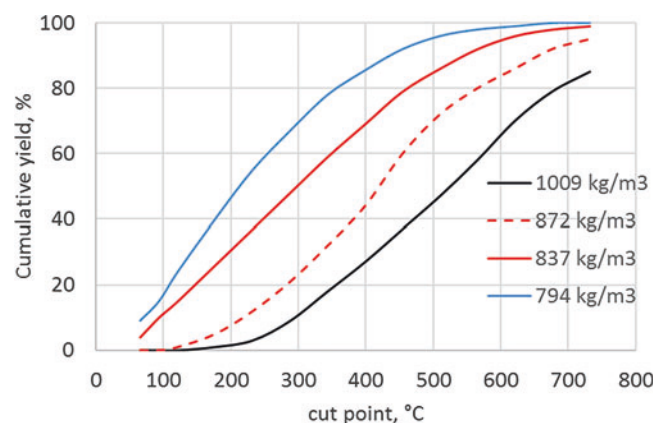
Petroleum, Fig. 3 Example of molecular structure of asphaltene ($C_{59}H_{71}NS_2$) in which the polyaromatic nucleus is derived from Atomic force microscopy data (Schuler 2015). Alkyl chains and functional groups containing nitrogen (blue) and sulfur (yellow) are included to approach the average composition of asphaltenes from heavy oils. This is just one out of many possible structures of asphaltenes

Among the average properties that serve to characterize the composition of petroleum, gas-oil ratio, and oil density are of particular importance. Both properties are measured after liquid-vapor separation in standard surface conditions. The gas-oil ratio (or GOR) is the volume ratio of vapor to liquid, expressed in std. m^3 of gas per m^3 of oil. Oil density defines the main categories of reported petroleum resources: light oils (less than 870 kg/m^3), medium and heavy oils ($870\text{--}1000 \text{ kg/m}^3$), and extraheavy oils ($>1000 \text{ kg/m}^3$). High density is generally associated with a high content of high boiling point fractions, as illustrated in Fig. 4.

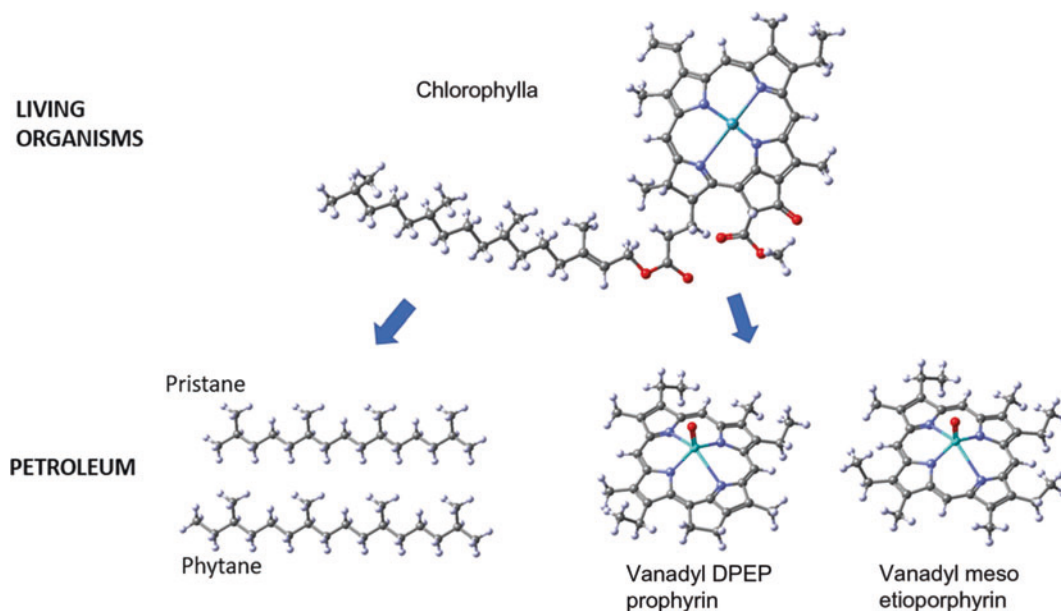
Origin

Petroleum is the byproduct of the thermal evolution of **Kerogen**, the organic matter contained in fine-grained sediments, called source rocks. In 1934, Treibs attributed the origin of petroleum **Porphyryns** (Treibs 1934) to parent molecules of living organisms like chlorophyll (Fig. 5). Now there is no doubt that petroleum is dominantly issued from the transformation of biogenic material. The investigation of petroleum *biomarkers* and their origin in living microbial, vegetal, or animal organisms has become an important branch of **Organic Geochemistry**, based on **Gas Chromatography-mass Spectrometry (GC-MS)** among other techniques. The biogenic origin of petroleum is also supported by its negative $\delta^{13}C$, because carbon produced by photosynthesis is isotopically lighter than the atmospheric CO_2 source (see **“Carbon Isotopes”**).

The deposition of organic-rich source rocks occurs in specific sedimentary environments in which a fair organic productivity and good preservation conditions prevail (see **“Organic Matter Degradation and Preservation”**). Preservation requires anoxic conditions (i.e., a very low **Fugacity** of oxygen). The Black Sea and Great African lakes are contemporary examples. Analyzing preservation



Petroleum, Fig. 4 Boiling point distribution of two light oils (std density 794 and 837 kg/m^3), an intermediate oil (872 kg/m^3), and an extraheavy oil (1009 kg/m^3) (Redrawn from Boduszynski et al. 1998)



Petroleum, Fig. 5 Example of common petroleum *biomarkers* (vanadyl ► *Porphyryns*, pristane, phytane) and typical precursor (chlorophyll *a*). Chlorophyll *a* is a universal Mg-porphyrin involved in photosynthesis in living plants (color code as Fig. 3 for C, H, N, and

oxygen in red). Arrows summarize a multistage diagenetic process involving the rupture of the alkyl chain and the exchange (► *Chelation*) of Mg^{2+} ion (emerald blue) by the vanadyl group $(VO)^{2+}$

conditions in the context of plate tectonics, as initiated by Tissot and Welte (1984), helps understanding the occurrence of organic-rich sediments. For instance, good source rocks deposited in the early phases of opening of the Atlantic ocean during Lower Cretaceous: the Bucomazi formation, Congo coastal basin (Burwood et al. 1995), the La Luna and Querequal formations in Venezuela (Talwani 2002), and the Lagoa Feia formation in Campos basin, offshore Brazil (Trindade et al. 1995). This helped exploration to find large accumulations in the Southern Atlantic presalt units.

Building upon the findings of ► *Coal* science (van Krevelen 1993), it has been recognized in the 1970s that different types of kerogen could be identified and that their composition followed systematic paths with increasing depth in a given basin (Tissot et al. 1974). The van Krevelen diagram (H/C vs O/C) allows to identify three main types, corresponding to different types of sedimentary environment (Fig. 6): type I kerogen, deposited in confined anoxic lakes such as the Green River Shales (Uinta basin, USA) is characterized by high H/C (1.35–1.55) at low depths of burial; type II kerogen, deposited in anoxic marine environments such as the Lower Torcian shales (Paris Basin, France) or the Upper Jurassic Kimmeridge Clay (North Sea) is displaying slightly lower H/C (1.2–1.3) at low depth; it is the most common form of organic matter in prolific source rocks; type III kerogen, originated from higher plants, is found in organic-rich shales or coals in deltaic environments like the Mahakam Delta (Indonesia). It displays a higher initial oxygen

content ($O/C = 0.1\text{--}0.3$) and lower hydrogen content ($H/C = 0.8\text{--}1.0$).

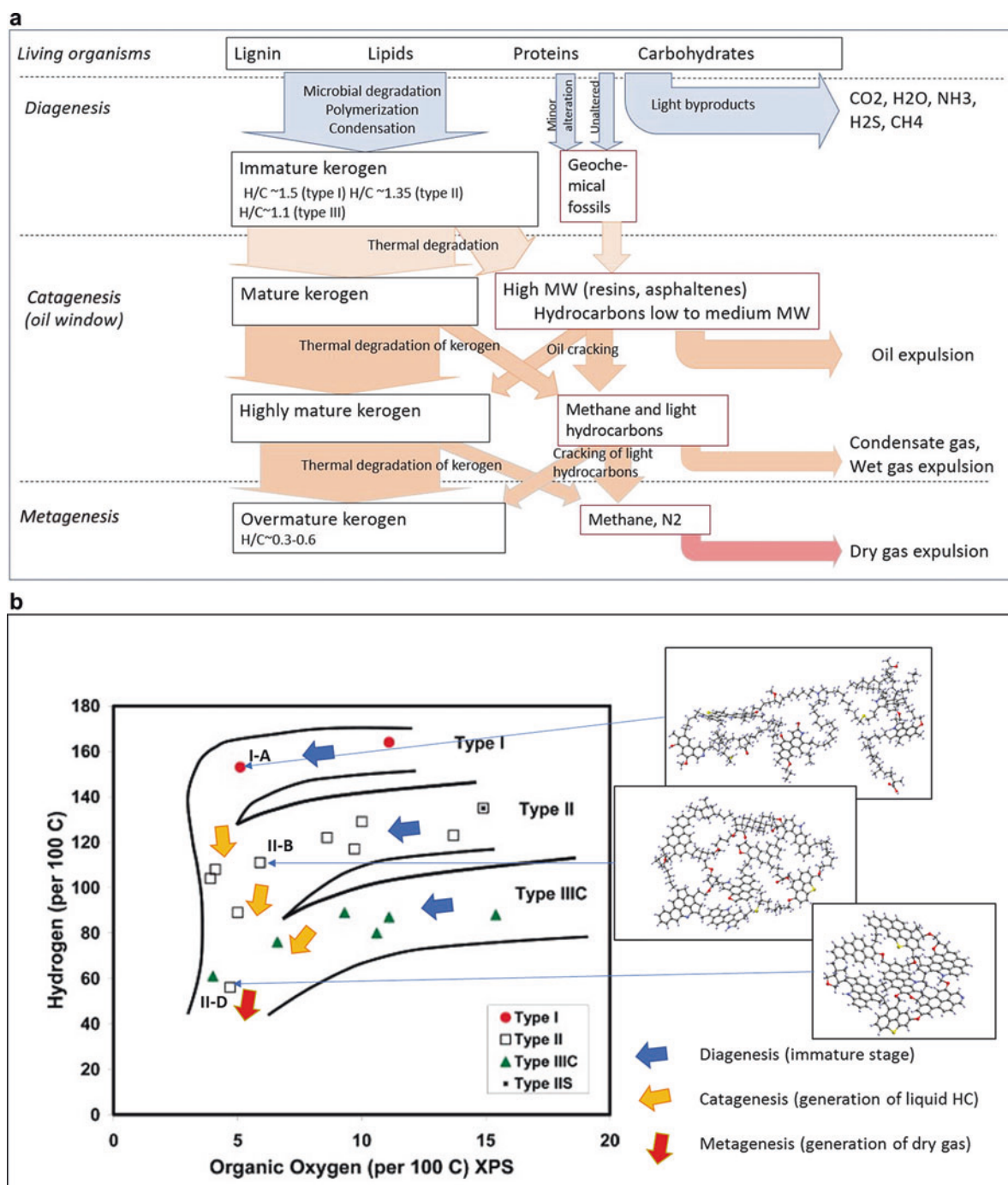
In a given area with continuous sedimentation, three successive stages are observed with increasing depth (Fig. 6).

During the immature stage (organic diagenesis), petroleum formation has not significantly started and only small quantities of biomarkers are present. This stage is characterized by the degradation of labile functional groups of kerogen, such as amines, carboxylic acid, carbonyl, and hydroxyl. It results in the loss of CO_2 and H_2O .

The mature stage (also called “catagenesis” or “oil window”), starting below depths of 2–3 km, is characterized by the maximum amount of petroleum amount in organic-rich rocks. High molecular weight compounds are generated first, then augmented with larger amounts of gasoil- and gasoline-range hydrocarbons; these fractions decrease in their turn while light $C_1\text{--}C_4$ hydrocarbons increase, so that the content of liquid-behaving compounds shows a maximum (peak oil generation).

The overmature stage (metagenesis), below 3.5–5 km, is characterized by the final stages of the thermal degradation responsible for the decrease of gasoline-range and heavier fractions. Most C_2+ alkanes are then degraded into methane and polyaromatic solids (pyrobitumen).

The thermal degradation process described above is named *maturation*. There is, however, no universal maturity indicator to quantify maturation. In addition to the position in the van Krevelen diagram (Fig. 6b), the main maturity indicators measured on organic matter samples are the vitrinite



Petroleum, Fig. 6 (a) Schematic diagram indicating the successive stages of petroleum formation in a basin with continuous sedimentation, adapted from a diagram of Tissot and Welte (1984). (b) van Krevelen

diagram illustrating the change of atomic composition and schematic molecular structure of kerogen with organic type and maturity (Adapted from Kelemen et al. 2007 and Ungerer et al. 2015)

reflectance, obtained from optical reflectivity measurements of specific components of kerogen, and the peak temperature T_{max} measured in programmed temperature pyrolysis. Maturity indicators are also defined to estimate the thermal degradation of oils from their composition (Radke and Welte 1981; Mackenzie and McKenzie 1983). These are based on the dilution or degradation of biomarkers (e.g., pristane/n-alkane,

sterane isomerization) or on the dealkylation of polyaromatic structures (e.g., methylphenanthrene index), among other examples.

The isotopic composition carbon is providing indications of petroleum origin: thermogenic gas displays ^{13}C content similar to oil (usually $\delta^{13}\text{C} = -30$ to -40‰), and biogenic methane generated at temperatures lower than 80°C displays

lighter isotopic composition ($\delta^{13}\text{C} = -50$ to -100‰). The presence of C_2+ hydrocarbons in gas is another marker of thermogenic origin, as opposed to biogenic gas in which C_2+ hydrocarbons are absent.

When source rocks are buried under a column of sediments, temperature increases due to the local geothermal gradient (generally 20–30 °C/km, with important variations and extreme values reaching 80 or 90 °C/km). This is the main factor of organic matter thermal degradation and petroleum formation. When maturation progresses, the remaining kerogen is more aromatic and its hydrogen content decreases as a result of the release of hydrocarbons (Tissot et al. 1974).

Thermal degradation is controlled by chemical *kinetics* at moderate temperatures in sedimentary basins (typically 70–150 °C) where source rocks are submitted to long heating times (1–100 Myr, i.e., 3×10^{13} to 3×10^{15} s). Petroleum formation can be simulated by pyrolysis in the laboratory, where higher temperatures (300–500 °C) compensate for shorter heating time ($1\text{--}10^7$ s). This has provided the basis of *Rock-Eval pyrolysis*, a standard thermal analysis under inert gas flow specifically designed to characterize the petroleum generation potential and kerogen maturity of large series of source rock samples (Espitalié et al. 1985/1986). Alternative methods of pyrolysis in high pressure vessels allow investigation of secondary reactions (Lewan 1985; Behar et al. 1997). Being kinetically controlled, thermal degradation explores lower free energy conformations of the kerogen + petroleum system, and it is thus essentially irreversible. The role of liquid water and natural catalysts (clay minerals) does not appear necessary to explain the main aspects of petroleum formation. The main influence of minerals is more likely to adsorb preferentially the polar and aromatic compounds, compared with the alkanes. Reservoir oils are indeed richer in alkanes than source rock extracts (Vandenbroucke 1993).

The *kinetics* of petroleum formation and cracking are generally modelled by first order reactions:

$$\text{dx/dt} = Kx$$

where x is the initial petroleum and generation potential and K is the rate constant (1/s) that changes with temperature according to Arrhenius law:

$$K = A \exp(-E/RT)$$

where A a prefactor, E an apparent activation energy, R universal gas constant (8.3145 J/mol/K), and T absolute temperature (K). In order to address a large range of conditions and kerogen types, several parallel and successive reactions are included, with activation energies in the range 190–250 kJ/mol (Tissot et al. 1987; Burnham et al. 1987; Ungerer 1990; Behar et al. 1997). Based on

► **Paleotemperature** reconstructions, these models allow to understand the timing and spatial distribution of petroleum formation in a given basin. These models account for the differences in petroleum potential between major ► **Kerogen** types: type I kerogen, generates 600–800 mg of *hydrocarbons and NSO compounds* per g of initial total organic carbon (TOC); type II kerogen, generates 400–600 mg/g TOC; and type III kerogen issued from higher plants generates 100–300 mg/g TOC. Type III kerogen generates mostly methane and $\text{C}_2\text{--C}_4$ hydrocarbons, but hydrogen-rich type III containing long alkyl chains are also considered to generate significant gasoline-range hydrocarbons and heavier fractions.

The role of pressure in petroleum formation *kinetics* is modest compared to temperature. Detailed kinetic models, based on free radical mechanisms, explain why natural petroleum does not contain linear alkenes, which are important products in low pressure pyrolysis (Enguehard et al. 1990). Detailed kinetic models are also useful in understanding the role of high pressure conditions (20–120 MPa) and hydrocarbon structure on the rates of thermal degradation (Dominé et al. 1991, 2002; Burklé-Vitzthum et al. 2011).

Petroleum Migration

Petroleum migration is an essential step of petroleum formation and accumulation, involving important changes of composition. The understanding of migration is primarily based on the possible phase state and properties of petroleum in the conditions prevailing in sedimentary basins. The water solubility of hydrocarbons is lower than a few ppm in diesel-range fractions and above (McAuliffe 1966). As a result, petroleum forms a separate phase from pore water. At very high pressure ($P > 35$ MPa), petroleum is most often forming a single phase even when it contains a high percentage of methane (Fig. 7).

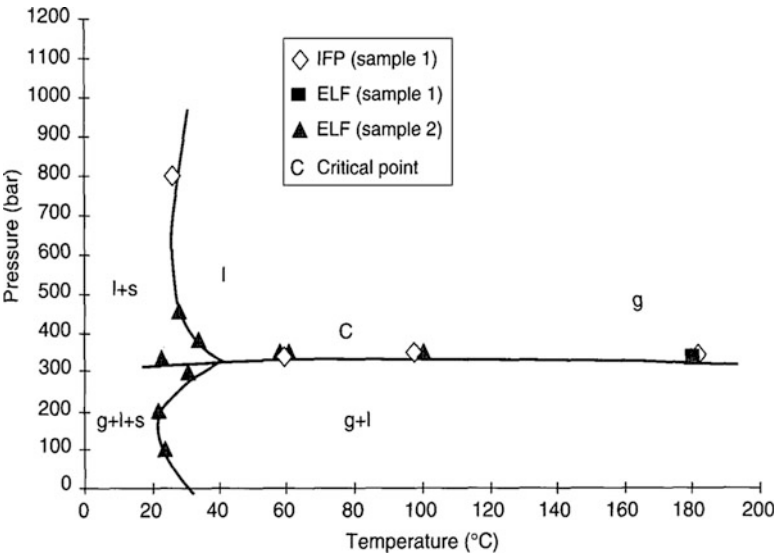
Another important property for petroleum migration is its viscosity (μ_i), which controls flow rates in porous media through the two-phase Darcy's law:

$$u_i = -\frac{K}{\mu_i} k_{r,i} (\nabla P_i - \rho_i g)$$

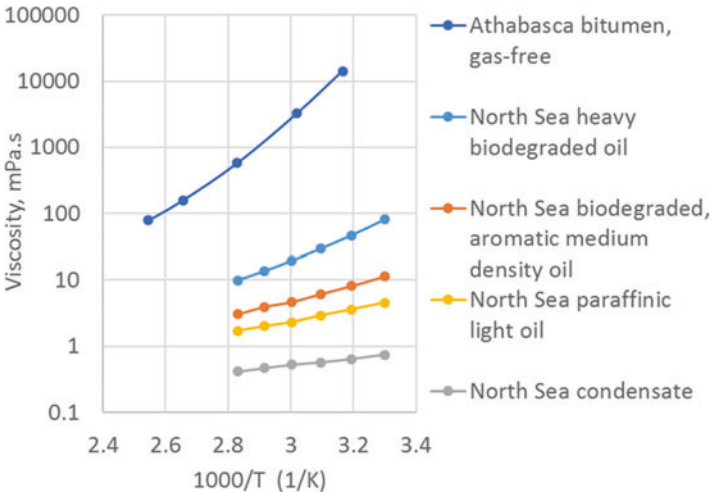
Viscosity changes by several orders of magnitude with petroleum composition and local conditions: it is lower than 0.1 mPa.s for natural gas, 1–100 mPa.s for most oils. It reaches 100 Pa.s for bitumen at low temperature (Fig. 8). This is why bitumen appears solid at human timescale although it is a complex fluid.

Petroleum migration is generally described with the main steps illustrated in Fig. 9.

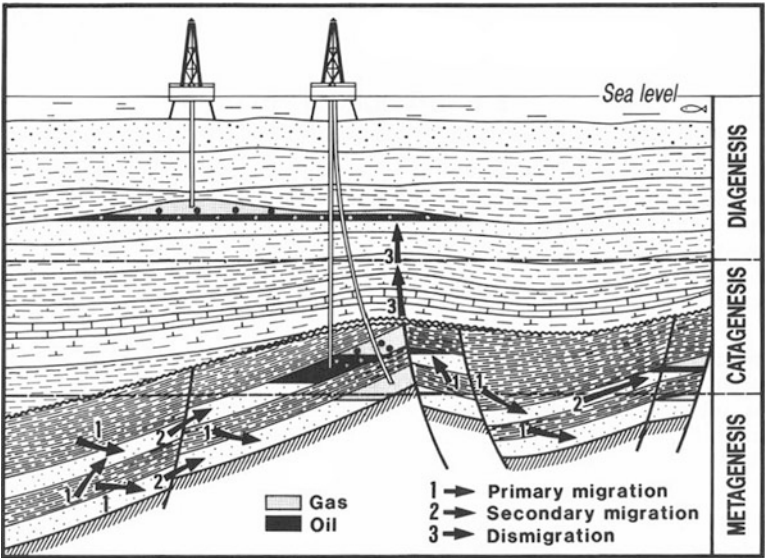
Petroleum, Fig. 7 P, T phase diagram of a methane-rich petroleum fluid (Ungerer et al. 1995) showing gas + liquid (g + l) phase split below 310 bar, and a monophasic region for higher pressure, either vapor (g) above 80 °C or liquid (l) below 80 °C. Wax crystallization below 20–30 °C results in three phases (g + l + s) below 310 bar and two phases (l + s) above 310 bar



Petroleum, Fig. 8 Viscosity of Athabasca bitumen (Data from Mehrotra and Svrcek 1986) and of selected oils from North Sea Viking graben (Data from Roenningsen et al. 1991) as a function of inverse temperature at ambient pressure (P = 1 atm)



Petroleum, Fig. 9 Schematic cross-section illustrating primary migration and secondary migration, inspired by the case studies of the North sea Viking graben (reprinted from Durand 1988, with permission)



Primary migration refers to the expulsion of petroleum from source rocks, i.e., from low porosity shales with permeability (K in Darcy's law) as low as 1 nanodarcy (10^{-21} m^2), toward surrounding carrier beds. This process is considered to be controlled mostly by fluid pressure build-up, molecular scale transport (Collell et al. 2014) and compaction. Expulsion occurs when a sufficient amount of petroleum has been generated, creating a continuous path of saturated pores or microfractures (Vandenbroucke 1993). It is considered to require a total organic carbon content (TOC) of 0.5%wt at least for type II organic matter.

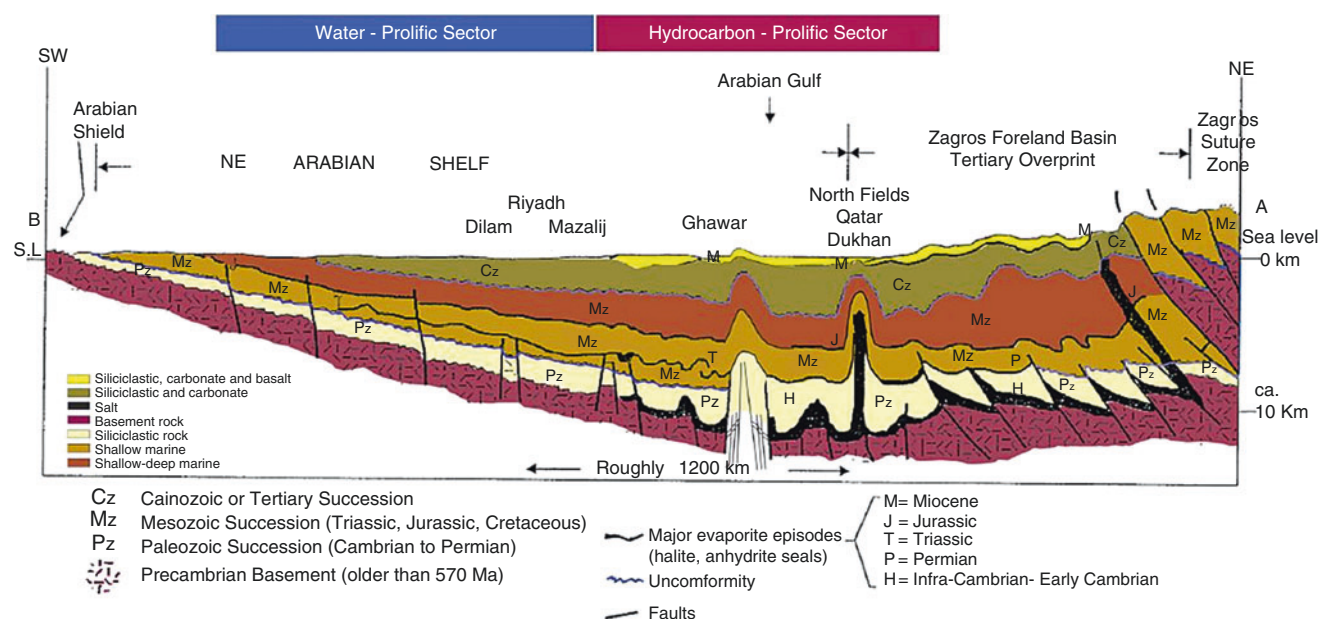
Secondary migration, in which petroleum flows inside more permeable units or faults, is a process dominated by gravity, capillary forces, and phase behavior. In this process, low permeability strata (called caprocks) plays an essential role in favoring horizontal migration. Caprocks may be ► *Evaporites* (halite, anhydrite) or shales. Migration follows the top of permeable units until it faces other obstacles (anticline, fault, pinch-out) where petroleum may eventually get trapped. Secondary migration is often associated with a liquid-gas phase split in the reservoir, as a result of pressure decrease along migration path. The consequences of phase split with decreasing reservoir pressure are the following: accelerated migration of the gas phase due to its lower viscosity and lower density; decreasing GOR of reservoir oil; decreasing condensate content of the gas and molecular fractionation (Carpentier et al. 1996). When a deep gas migrates

into a shallower reservoir, the liquid dropout may generate light oil accumulations (oil rim) below the gas accumulation.

The distances covered during secondary migration are commonly a few hundred meters to a few km vertically, a few km to several hundreds of km horizontally. Together with prolific source rock deposition and maturation conditions, favorable structure to long-distance migration explains the size of the Middle East accumulations, as illustrated in Fig. 10.

The composition of the oil in a given trap results from the mixing of areas with different maturity, the less mature providing more heavy compounds (resins, asphaltenes) and the more mature providing lighter ► *Hydrocarbons* and gas. It is generally considered that diffusivity and thermally driven natural convection in the reservoir are sufficient to equilibrate petroleum composition vertically. Significant differences in composition persist horizontally when permeability barriers or large horizontal distances prevent petroleum from homogenizing. The mixing of light oil or gas with a heavy oil may cause the segregation of highly viscous oil (tar mats) near the oil-water contact.

A third stage of migration may be defined to address the leakage of accumulations (Fig. 9). On a geological timescale, an accumulation of petroleum may lose ► *Hydrocarbons* in various ways: erosion of caprock; differential subsidence reducing trap volume; growth of gas cap causing spill-over of oil; leakage through fractures; aerobic and anaerobic



Petroleum, Fig. 10 SW-NE cross-section across Saudi Arabia, Qatar, and Iran showing the geological context of major Middle East petroleum accumulations (reprinted from Jagu et al. 2016, with permission). Prolific source rocks are Upper Jurassic Tuwaiq mountain and Hanifa formations (Carrigan et al. 1995), which have sourced the Jurassic reservoirs; paleozoic Silurian intervals that have sourced Permian and

Ordovician accumulations (Konert et al. 2001). Several basin-wide evaporitic episodes have provided efficient caprocks allowing long-distance horizontal migration and preservation of major oil fields (e.g., Ghawar) and *natural gas* fields (South Pars, North Dome) on the Arabian platform as well as large accumulations in the Zagros thrustbelt and its foreland

biodegradation of petroleum, which may occur up to 80 °C (Connan et al. 1997; Aitken et al. 2004); and thermal cracking of gasoline-range and heavier fractions of oil into lighter alkanes (mostly methane) and pyrobitumen in high temperature reservoirs. Thermal cracking of oil into gas occurs mainly at temperatures above 150 °C, and some deep reservoir fluids are still containing significant concentrations of gasoline-range and gasoil-range hydrocarbons although the reservoir temperature is 190 °C (Ungerer et al. 1995). Biodegradation is specific as light linear alkanes and saturated ► *Hydrocarbons* are preferentially degraded. It results in a significant increase in density and viscosity, and also higher concentrations in sulfur and metals (Huc 2010). Biodegradation in shallow reservoirs explains the origin of extraheavy oils and bitumen in Western Canada (Fig. 11) and Venezuela (Eschard and Huc 2008; Talwani 2002).

Interactions with Mineral Diagenesis

In an oil-saturated reservoir rock, mineral ► *Diagenesis* is considerably slowed down as it requires a continuous ► *Water* phase. Pore filling with oil or gas interrupts the growth of diagenetic minerals (e.g., clay minerals) and also the porosity reduction by pressure solution, which is the dominant mode of compaction (Gratier et al. 2013). In the example of the Ekofisk field (Norwegian North Sea), a high porosity (up to 35%) is preserved in the oil-saturated zone while porosity is reduced to a few % in the water-saturated zone of the same chalk reservoir (Van den Bark and Thomas 1981). The unconsolidated nature of oil sands in W. Canada and in Venezuela is probably also caused by an early

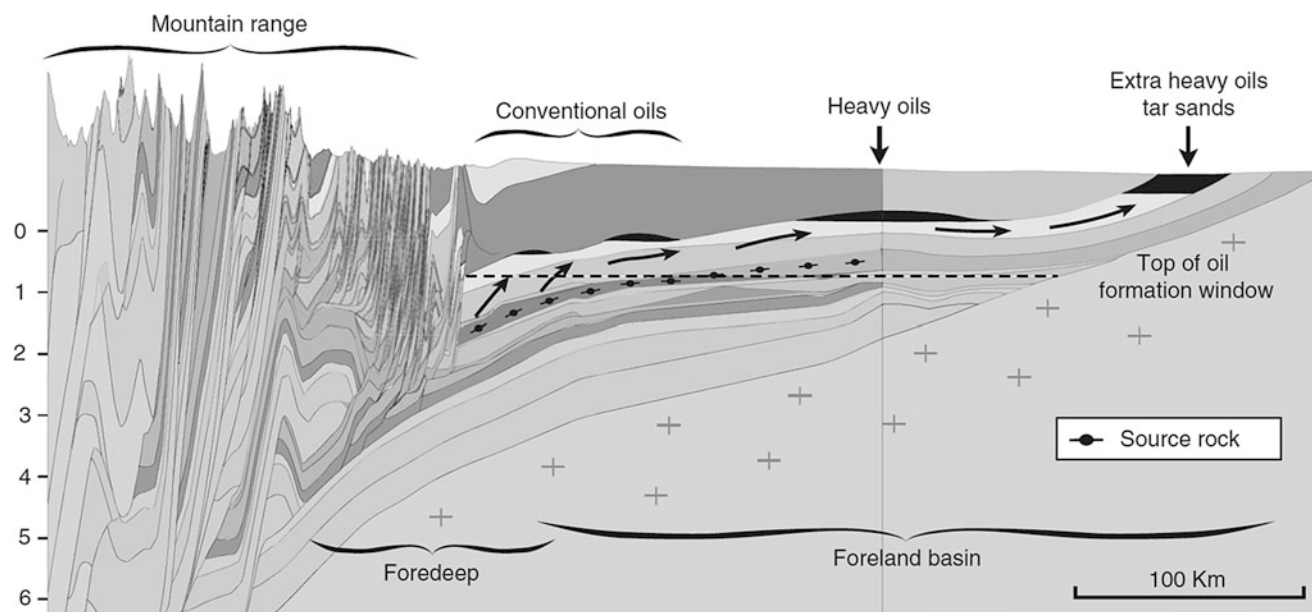
migration of oil in the reservoir. This may have important effects on oil production such as producing loose sand together with extraheavy oils (Tremblay et al. 1997). It may also cause significant surface subsidence when petroleum is replaced by injected water (Doornhof et al. 2006).

In evaporitic series, thermal sulfate reduction (TSR) of calcium sulfate (e.g., anhydrite) by *hydrocarbons* may generate important amounts of H₂S and other reduced form of sulfur, together with CO₂, at temperatures in the range 100–140 °C mainly (Machel 2001). These reactions are responsible for high H₂S contents in ► *Natural Gas* and associated gases in SW France, Western Canada, and the Middle East, among other regions (see ► “Sulfur Cycle”).

Petroleum in the Global Carbon Cycle

According to BP statistical review (2017), the global production of oil was 4.6 Gt/yr. (i.e., ~4 Gt of carbon) and the production of natural gas was 3.55 Tm³/yr. (i.e., ~2 Gt of carbon) in 2016. The total flux (6 Gt of carbon/yr) represents 10% and 5% of the yearly fluxes of carbon between ocean/atmosphere and atmosphere/continent, which are estimated to ~60 GtC per year and 120 GtC/yr., respectively (IPCC 2013).

Based on reserve estimates of Table 1, average recovery factors, and other sources (e.g., shale oil estimates from US DOE-EIA 2013), the overall amount of petroleum in the subsurface may be roughly estimated to 2720 Gt (~900 Gt in conventional reservoirs, 750 Gt in extraheavy oil and bitumen reservoirs, 900 Gt of shale oil, and 175 Gt in natural



Petroleum, Fig. 11 Schematic geological cross-section of foreland basin showing the location of conventional oils, heavy oils, and extra-heavy oils as a result of petroleum generation in deep source rocks,

migration along carrier beds, and biodegradation in shallow reservoirs (reprinted from Eschard and Huc 2008 with permission)

gas accumulations, excluding natural gas hydrates). A small fraction of this amount (<10%) appears as technically recoverable.

Summary

Petroleum composition is highly variable and complex, as a consequence of the large range of conditions during its formation and accumulation along geologic time. The origin of petroleum by thermal degradation of the sedimentary organic matter is the dominant process, bacterial degradation playing a significant role in methane generation and oil biodegradation. The influence of phase equilibria and petroleum migration on the distribution and composition of petroleum accumulations is also reasonably understood.

This knowledge has contributed to the success of oil and gas exploration. However, the rate of new significant discoveries slows down because fewer regions are still unexplored. Conventional petroleum accumulations appear as a finite resource from which more than 50% has been produced. In the long range, petroleum production will rely increasingly on the production of unconventional resources (particularly extraheavy oils and bitumen).

Cross-References

- Biomarkers: Petroleum
- Biomarker: Assessment of Thermal Maturity
- Carbon Cycle
- Carbon Isotopes
- Coal
- Diagenesis
- Evaporites
- Gas Chromatography–Mass Spectrometry (GC–MS)
- Gas Hydrates
- Hydrocarbons
- Hydrogen
- Kerogen
- Kinetics of Geochemical Processes
- Natural Gas
- Oil Seeps and Coastal Bitumen
- Oil Shale
- Oil–Oil and Oil–Source Rock Correlations
- Organic Geochemistry
- Organic Matter Degradation and Preservation
- Paleotemperatures
- Phase Equilibria
- Porphyrins
- Programmed Temperature Pyrolysis
- Sulfur Cycle
- Water

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