The Origin of Petroleum

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Chapter 2

THE ORIGIN OF PETROLEUM

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1.   HISTORIC OVERVIEW

Man has used petroleum since Biblical times, yet the origin of this natural resource remained a mystery for much of man's history. Classical literature is noticeably devoid of insight and even Roger Bacon laments in his 1268 treatise *Opus Tertium* on the lack of discussion on the origins of oils and bitumen by Aristotle and other natural philosophers.[1]   Two theories on petroleum emerged during the Renaissance. In his 1546 text *De Natura eorum quae Effluunt ex Terra,* Georgius Agricola, a German physician, expanded on the Aristotilian concept of exhalations from deep within the Earth[2] and proposed that bitumen, like other minerals, condensed from sulfur. Andreas Libavius, another German physician, theorized in his 1597 text *Alchemia* that bitumen formed from the resins of ancient trees. These early discussions mark the beginnings of one of the longest running scientific debates: whether petroleum is formed by abiogenic processes that occur deep within the Earth, or from sedimentary organic matter that was once living organisms.

 As fossil evidence emerged during the 18th century that coals were derived from plant remains, many scientists proposed similar origins to explain petroleum. The historic record is somewhat questionable, but Mikhailo Lomonosov is credited by some to have proposed the theory that liquid oil and solid bitumen originate from coal through underground heat and pressure as early as 1757[3] and certainly by 1763[4]. Various biogenic theories emerged during the early 19th century suggesting that petroleum was derived directly from biological remains or through a distillation process[5].

 Modern theories that petroleum originated from ancient sedimentary, organic-rich rocks emerged during the 19th century. T.S. Hunt of the Canadian Geological Survey concluded in 1863 that the organic matter in

some North American Paleozoic rocks must be derived from marine vegetation or marine animals, and that the transformation of this organic matter to bitumen must be similar to the processes involved in coal formation[6]. Leo Lesquereux, the American father of paleobotany, reached similar conclusions after studying Devonian shales in Pennsylvania[7], as did Newberry in his study of Devonian shales in Ohio.[8] Early 20th century field[9] and chemical[10] studies of the Monterey Formation by the U.S. Geologic Survey provided convincing evidence that the oil was derived from diatoms in the organic-rich shales. Similar studies of organic-rich shales conducted in Europe during this time arrived at the same conclusion.[11,12]

Full ascendancy of the biogenic hypothesis began in the mid-20th century with a convergence of scientific advances in paleontology, geology, and chemistry. In 1936, Alfred Treibs established a link between chlorophyll in living organisms and porphyrins in petroleum.[13] Additional geochemical evidence followed with the discoveries that low to moderate maturity oils still retained hydrocarbon fractions with optical activity[14], that the stable isotopes of carbon of petroleum bear a biological fractionation[15], and that oils contain in addition to porphyrins, a host of hydrocarbons that can be traced back to specific biological precursors[16]. Concurrent with these findings were field studies recognizing that organic-rich strata occur in all petroliferous sedimentary basins, that this sedimentary organic matter (kerogen) is derived from biota, that it has been chemically altered from its initial state[17,18] and, that oil and gas is produced from this kerogen as the sediments are buried and heated.[19]

Although there is overwhelming evidence for a biogenic origin, some still advocate abiotic theories. The development of the modern abiogenic concept is rooted in the mid-19th century. The prolific French chemist Marcelin-Pierre Berthelot described in 1860 experiments where *n*-alkanes formed during the acid dissolution of steels.[20] Dmitri Mendeleev reasoned in 1877 that surface waters could percolate deep within the Earth, react with metallic carbides forming acetylene, which could then condense further into larger hydrocarbons.[21] Mendeleev's abiotic theory, further refined in 1902[22], was viewed initially as particularly attractive as it offered an explanation for the growing awareness of the widespread occurrence of petroleum deposits that suggested some sort of deep, global process.

Advocates of abiotic origin theories dwindled under the mounting evidence for a biogenic origin of petroleum. By the 1960's, there was little support for an abiotic origin, except among a small group within in the Former Soviet Union. First proposed in 1951 by Nikolai Kudryavtsev[23] and advanced over the years in numerous Soviet publications,[3] a modernized verison of Mendeleev's hypothesis emerged. This theory relies on a thermodynamic argument, which states that hydrocarbons greater than methane cannot form spontaneously except at the high temperatures and

pressures of the lowest most crustal depths. The theory ignores the fact all of life relies on being in thermodynamic disequilibrium with its environment.

In the West, astronomers have been the most vocal advocates for abiotic petroleum. Carbonaceous chondrites and other planetary bodies, such as asteroids, comets, and the moons and atmospheres of the Jovian planets, certainly contain hydrocarbons and other organic compounds that were generated by abiotic processes.[24] Sir Fredrick Hoyle reasoned in 1955 that as the Earth was formed from similar materials, there should be vast amounts of abiogenic oil.[25] In more recent years, Thomas Gold is the strongest promoter for abiotic petroleum.[26,27] Against the advice of nearly all geochemists and petroleum geologists, Gold convinced the Swedish government to drill two deep wells (Gravberg 1 in 1986-1990 and Stenberg 1 in 1991-1992) into fractured granite under the Siljan ring, the site of an ancient meteorite crater. The wells failed to find economic reserves and evidence for even trace amounts of abiotic hydrocarbons is controversial.[28]

Geochemists do not deny the existence of abiogenic hydrocarbons on Earth. Small amounts of abiotic hydrocarbon gases are known to be generated by rock-water interactions involving serpentinization of ultramafic rocks,[29, 30] the thermal decomposition of siderite in the presence of water,[31] and during magma cooling as a result of Fischer–Tropsch type reactions.[32] However, commercial quantities of abiotic petroleum have never been found and the contribution of abiogenic hydrocarbons to the global crustal carbon budget is inconsequential.[33]

2.   THE PETROLEUM SYSTEM

The accumulation of economic volumes of petroleum (oil and/or gas) in the subsurface requires that several essential geological elements and processes be present at specific time and space.[34,35] *Source rocks* generate and expel petroleum when sufficient thermal energy is imparted to the sedimentary organic matter (kerogen) to break chemical bonds. This heating is induced usually by burial by *overburden rock*. Once expelled, petroleum migrates either along faults and/or highly permeable strata. Accumulations form only when high porosity strata (*reservoir rocks*) are charged with migrating petroleum and the petroleum is prevented from further migration. These petroleum *traps* are formed only when geologic movements result in subsurface topographies (structural and stratigraphic) that block migration and when the reservoir rocks are covered by low permeability strata (*seal rocks*). The mere presence of these geologic elements is insufficient to form petroleum reserves. Traps must be available at the time of oil expulsion and, once charged, their integrity must be preserved until exploited. These elements and processes constitute the *Petroleum System* (Figure 1).
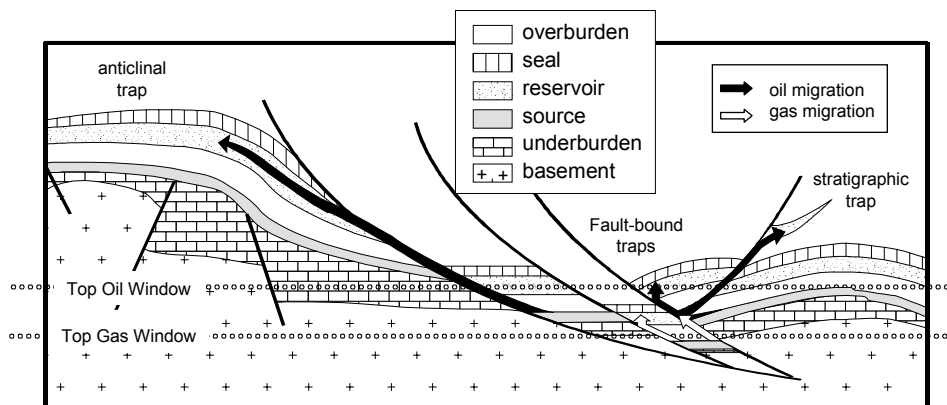
Figure 1. Elements of a Petroleum System. All petroleum systems contain: 1. at least one formation of organic-rich sediments that has been buried to a sufficient depth by overburden rock such that petroleum is generated and expelled, 2. Pathways (permeable strata and faults) that allow the petroleum to migrate, 3. Reservoir rocks with sufficient porosity and permeability to accumulate economically significant quantities of petroleum, and 4. Sealing rock (low permeability) and structures that retain migrated petroleum within the reservoir rock. The top and bottom of the oil window is approximated as a function of burial depth. In actual basins, these depths are not uniform and vary as a function of organic matter type, regional heat flow from basement, in thermal conductivity of the different lithologies, and burial history (e.g., deposition rates, uplift, erosion, and hiatus events).

A rigorous discussion of the origin of petroleum should encompass all of the interrelated elements of the petroleum system. Such a discourse is beyond the scope of this review, which will focus only on the deposition of organic-rich strata and the generation of petroleum from these sources. The reader is referred to *Exploring for Oil and Gas Traps,* a publication of the American Association of Petroleum Geologists, for a complete discussion of all aspects involved with defining the petroleum system for effective exploration.[36] Books by Tissot and Welte[37] and Hunt[38] provide detailed discussions of the principles of petroleum geochemistry, and a recent paper by Peters and Fowler[39] is an excellent review of the application of modern geochemical techniques to exploration and production practices.

3.   DEPOSITION OF ORGANIC-RICH SEDIMENTARY ROCKS

Petroleum *source rocks* are water-deposited sedimentary rocks that contain sufficient amounts of organic matter to generate and expel commercial quantities of oil and/or gas when heated. Such organic-rich strata were deposited throughout Earth's history, in nearly all geologic environments, and in most sedimentary basins. Source rocks, however,

typically represent only a minor amount of basinal strata and are formed only when specific conditions exist.

Three general factors control the deposition of organic-rich sediments: productivity, dilution, and preservation (Figure 2).[40,41,42] Biological productivity determines the amount of organic matter that is contributed to sediments. Dilution refers to the amount of inorganic minerals that mixes with the organic matter. Once deposited, the organic matter must be preserved in a form that may later generated petroleum. There was once an active debate as to which factor was the most important in forming organic-rich sediments.[43] It is now recognized that these three factors are inherently interrelated in a highly complex, and variable manner.
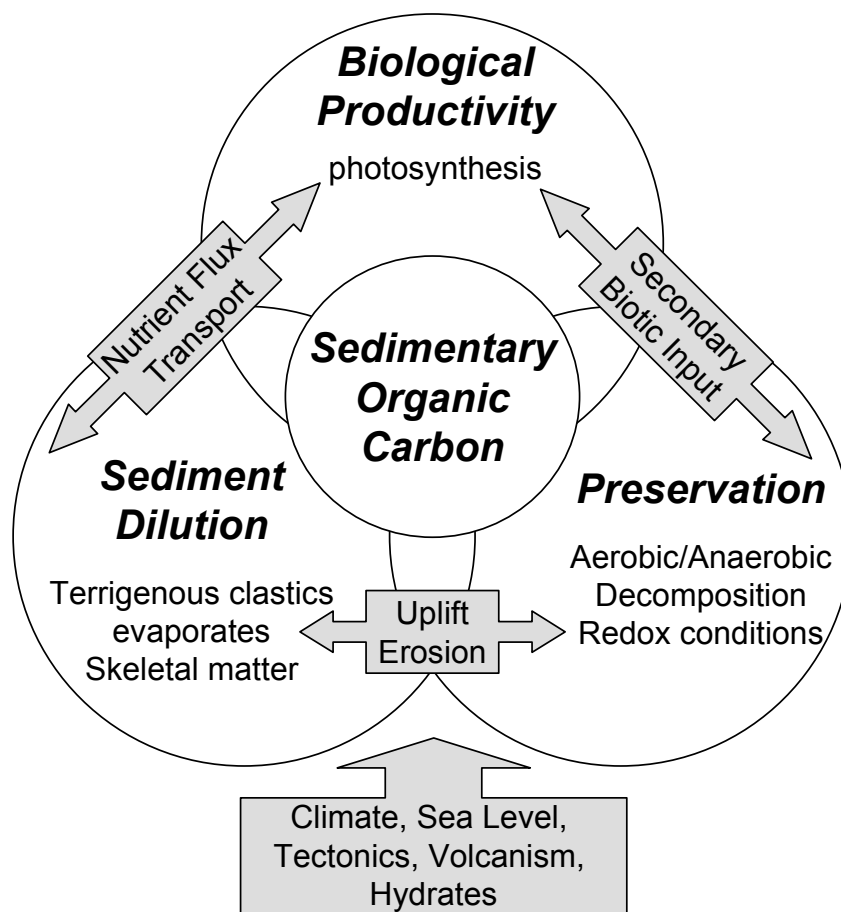

Figure 2. Three major factors, primary productivity, preservation, and dilution, determine whether organic-rich source rocks are deposited. These factors are interrelated and influenced by a number of geologic conditions.

Photosynthetic organisms, which include aerobic cyanobacteria, algae, phytoplankton, land-plants, and some anaerobic bacteria, provide most of the initial organic matter by fixing CO_2 into biomass. The contribution of organic matter by non-photosynthetic chemotrophs is minor, except in some unusual environments, such as the deep-sea hydrothermal vents. Most of the non-photosynthetic biosystems, such as methanotropic communities[44], rely on recycled carbon that was fixed originally by photosynthetic organisms. Many factors moderate the biota and the primary productivity (e.g., such as nutrient input from rivers and coastal upwellings, pCO_2, temperature, and turbidity) that are influenced by global climatic and tectonic conditions.
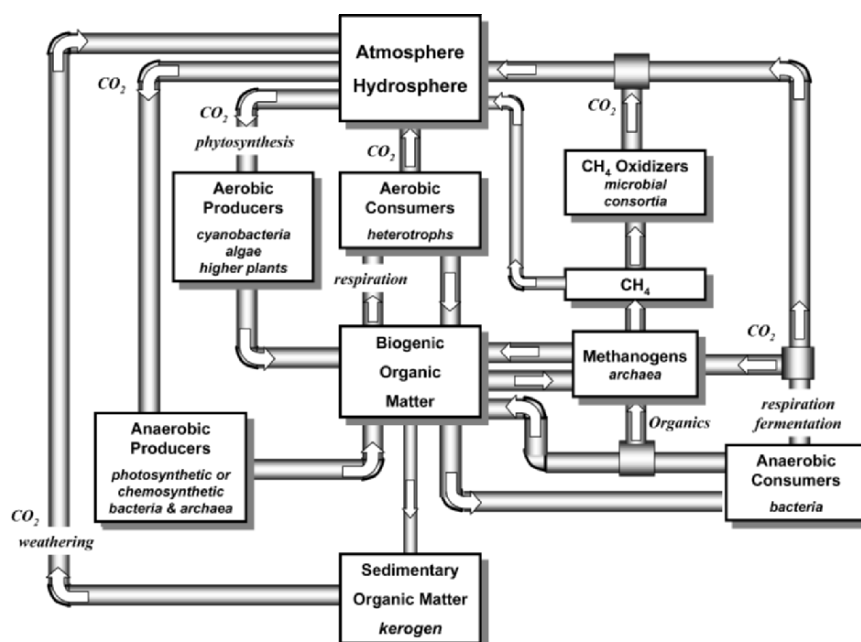
Figure 3. Generalized redox cycle for organic carbon. Production of new organic matter by the photosynthetic fixation of CO_2 (primary productivity) can occur with (aerobic) or without oxygen (anaerobic) as a byproduct. Respiration and other processes result in the nearly complete oxidation of this organic matter back to CO_2. A small amount of the organic matter in sediments escapes biological recycling and is preserved in rocks. Eventually, this carbon is recycled to the surface as CO_2 by geologic processes, such as subduction and venting, erosion and weathering – or more recently, by the combustion of fossil fuels.

Much of the primary organic matter created by photosynthetic or chemosynthetic autotrophs undergoes degradation by other organisms during the secondary production of organic matter. Heterotrophic organisms in the water column, sediments, and rock continually degrade and rework primary aquatic and terrigenous organic matter (Figure 3). Aerobic respiration is very rapid and efficient and primary organic matter may pass through a chain of

water and mud dwelling animals, protozoa, and bacteria, until fully consumed and returned to the atmosphere/hydrosphere as CO_2. Anaerobic bacteria also degrade organic matter either by fermentation or by respiration using terminal electron acceptors other than O_2 (e.g., nitrate, sulfate, iron). These microbial metabolisms are generally slower and may be curtailed by limited nutrient and electron acceptors within the sediment porewaters. Consequently, some of sedimentary organic matter, both from primary and secondary biogenic sources, may escape recycling and become preserved in lithified rock. Hence, anoxic conditions enhance the preservation of oil-prone organic matter and promote the deposition of potential source rocks (Figure 4).
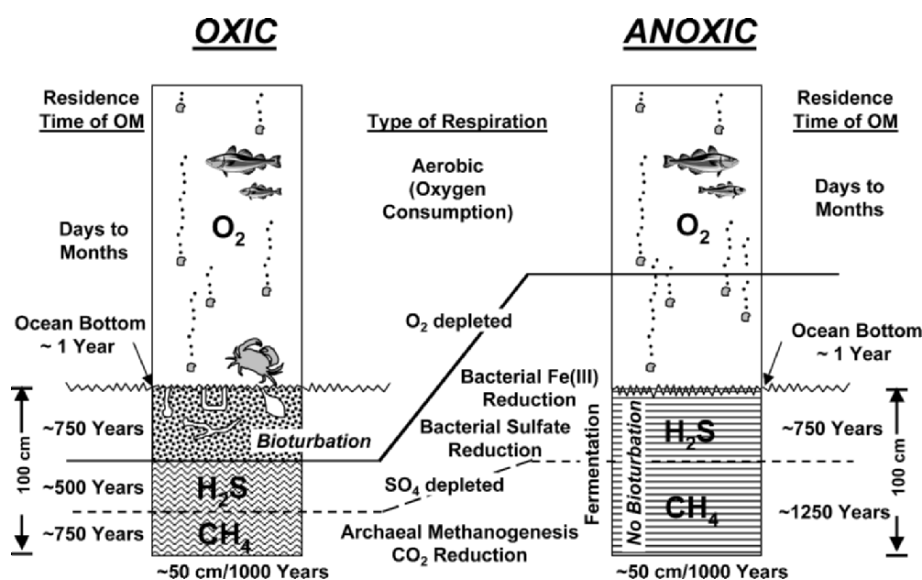

Figure 4. Oxic (left) and anoxic (right) depositional environments generally result in poor and good preservation of deposited organic matter, respectively (after Demaison and Moore, 1980[45]). The solid horizontal line separates oxic (above) from anoxic (below). In oxic settings, bottom dwelling metazoa bioturbate the sediments and oxidize most organic matter. In anoxic settings, especially where the oxic-anoxic boundary occurs in the water column, bottom-dwelling metazoa are absent and sediments are not bioturbated.

The amount of oxygen in bottom waters or sediments is determined by it rate of influx from the photic zone (via circulation and/or diffusion) and its rate of consumption (biological oxygen demand). Topographical barriers, currents, or water stratification due to temperature and salinity gradients may limit water circulation and diffusion. A high supply of primary organic matter raises the biological oxygen demand, rendering pore waters, and even the lower water column, anoxic. This mechanism is seen in terrigenous environments with high input of land-plant material (e.g. swamps, and coastal

plains), and in lake and marine environments with high nutrient influx (e.g, seasonal rains and overturn of water columns, and upwelling zones).

In anoxic marine environments, the most prevalent organisms are bacteria that utilize sulfate and produce H_2S. If not precipitated as pyrite by iron from clays and other clastic minerals, H_2S may react with organic matter, incorporating sulfur. If the production of H_2S is greater than its rate of sequestering, *euxinic* conditions (waters with free H_2S) occur. The transition between oxic and euxinic waters may occur within the sediments or water column. Some strata with excellent source potential were deposited where euxinic conditions extended into the photic zone.[46] Biological activity may also be restricted by hypersaline conditions that occur in playa lakes, lagoons, and restricted marine settings.

Sedimentation rate influences both the preservation and concentration of organic matter. The inorganic materials may be clastic (eroded clays and sands), chemical precipitates (carbonates, salts), or biogenic (siliceous and carbonate shells). Organic matter may be removed from biological recycling by rapid burial, such as in deltaic settings. However, preservation is offset by dilution and the resulting rocks may be relatively low in organic carbon. Similarly, sediments resulting from high primary productivity, such as diatomaceous cherts, may be have an upper limit in organic carbon because of high autodilution. In general, sedimentary rocks with the highest concentrations of organic matter are deposited under conditions of moderate to high influx of primary organic matter, anoxic (possibly euxinic) bottom waters, and low sedimentation rates.

4.   KEROGEN FORMATION AND THE GENERATIVE POTENTIAL OF SOURCE ROCKS

Although derived from biochemicals, the sedimentary organic matter in source rocks, is markedly different in structure and chemical composition. Living organisms are composed mostly of proteins, nucleic acids, and lipids. Structural materials, such as lignin and cellulose, and various resins are fairly well-defined biopolymers composed of a limited number of monomers. With the exception of some halophilic green algae and a few bacteria[47], only trace amounts of hydrocarbons are produced directly as biomass by most living organisms. In contrast, immature sedimentary rocks contain only low concentrations of the functionalized biochemicals. Most of the organic carbon is bound in a condensed, insoluble macromolecular material, termed kerogen, which has comparatively few functional groups. Kerogen has been called a "geopolymer" but this is a misnomer, as the term implies that there is a repetition of distinct monomers and some structural order. Kerogen has no unique molecular structure and can only be defined in terms of bulk elemental composition and average molecular distributions.
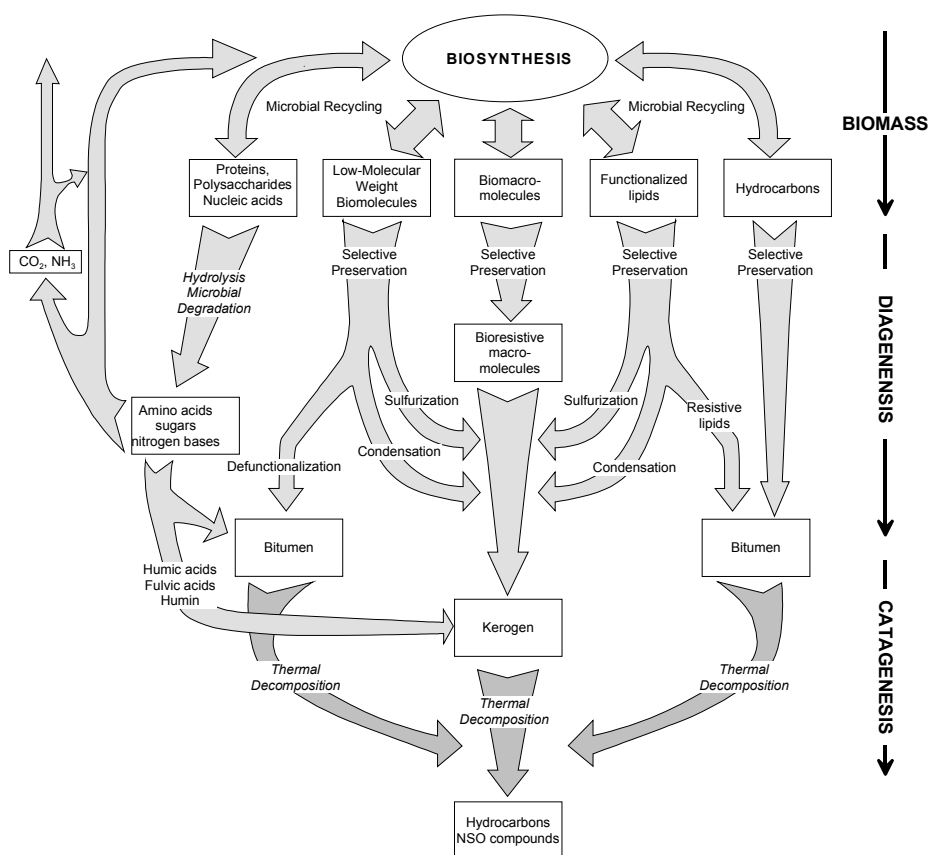
Figure 5. Kerogen is formed during diagenesis by the selective preservation of bio-resistive macromolecules and from the incorporation of lower-molecular weight species. Modified from Tegelaar et al. (1989)[49].

Optically, kerogen is often described as mixtures of amorphous organic matter and *macerals*, morphologically distinct particles that are mostly derived from land-plants. The amorphous matter was once thought to be derived from the complete breakdown of biological macromolecules that then re-assembled in a random fashion with low molecular-weight biochemicals (e.g., lipids).[48] We now realize that there are biological macromolecules that are alkyl-rich and resist microbial recycling.[49] These bio-macromolecules (e.g., cutan, sporopollenin, tannins, and algaenan) may constitute only a small fraction of the initial biomass, but are selectively preserved and enriched during early diagenesis (Figure 5). They provide a core for the incorporation of functionalized low molecular-weight biochemicals, such as membrane lipids and the breakdown products of less resistant bio-macromolecules. A small fraction of this material may remain soluble, which along with biogenic

hydrocarbons and lipids that resist incorporation, becomes the bitumen that can be extracted from immature source rocks using organic solvents.

Kerogen formation begins at the point when living cells die and their biochemicals are exposed to the geologic environment. Microbial processes are mostly responsible for the breakdown of biological macromolecules and the recycling of lower molecular-weight biochemicals, resulting in the selective preservation of the more bio-resistive compounds. Low temperature chemical reactions further alter kerogen through the loss of functional groups (e.g., $-NH_3$, $-COOH$), sulfur incorporation, condensation, cross-linking, and aromatization. The processes and thermal regime under which kerogen forms, termed *diagenesis*, occurs under mild thermal conditions (<80°C).
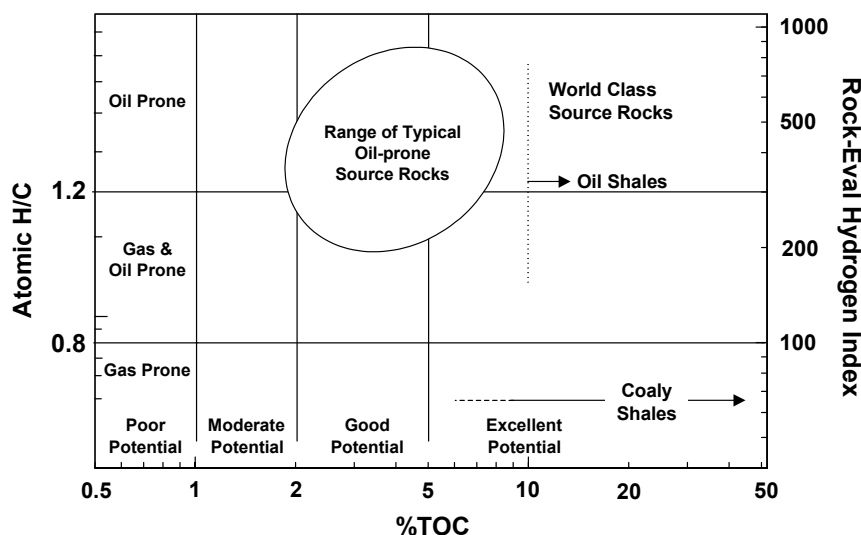

Figure 6. The quantity and quality of kerogen determines the generative potential of a source rock. Boundaries for the classifications of generative potential are approximate. Typical marine source rocks from productive basins contain ~2 to 6% TOC. Basins with world class reservoirs may contain source units with appreciably higher amounts of carbon. Expulsion of oil may be difficult from rocks with <1-2% TOC. The hydrogen content of the organic carbon determines the quality of the expelled hydrocarbons (during metagenesis). Kerogens with high H/C ratios tends to generate oil, while those with low H/C ratios tend to generate gas. The Hydrogen Index is based on the Rock-Eval instrumentation. This pyrolysis method, commonly used by petroleum geochemists to rapidly screen rocks for their generative potential, heats a ground sample and measures the pyrolyzate response on a flame ionization detector and a CO_2 response by an infrared detector. These responses can be calibrated to a rough approximation of the kerogen H/C and O/C atomic ratios.

The quantity and quality of organic matter preserved during diagenesis of sediment determines the generative potential of the source rock and whether it will be prone to expel oil or gas. Quantity is determined by amount of organic input, the degree to which it is preserved (either as primary or

secondary biogenic matter), and by its dilution with inorganic mineral matter. Typical oil-prone, marine source rocks contain 2-5 wt.% total organic carbon (TOC), but strata in the range of 10-20% are known to occur in high yield petroleum systems (Figure 6). Oil shales, many of which are lake deposits, contain over 10% TOC. Coals are >80% TOC, and may be dilute with varying amounts of clastic minerals to yield coaly shales with a wide range of carbon content.

Kerogen quality is mainly a function of hydrogen content – kerogens with high H/C ratios (> 1.2) are oil-prone, while those with lower H/C ratios (0.5 to 0.8) tend to generate mostly gas. Biogenic input of organic matter and the manner of its preservation determine the hydrogen content of kerogen. Some algae and bacteria are extremely rich in membrane lipids and aliphatic biopolymers, such as algaenan. Sediments that receive this input have the potential to be hydrogen-rich (kerogen H/C >1.5). Conversely, land-plant lignins have low H/C ratios and sediments that received only this input are hydrogen-poor (kerogen H/C ratios < 1.0). The hydrogen, sulfur, and oxygen content of kerogen can be modified greatly during deposition and diagenesis. Oxic conditions favor rapid and fairly complete heterotophic consumption of primary organic matter. The organic matter remaining in the sediments tends to be oxidized or inert. Anoxic conditions conserve, or even enhance, the initial H/C ratio of the primary organic matter via selective preservation and/or contributions from secondary biota. Euxinic conditions promote the incorporation of sulfur, resulting in high S/C ratios.

There are many schemes that attempt to classify kerogen types by their morphology, maceral and palynological assemblages, and/or bulk chemical composition. The most widely used is a modification of a method developed for coals[50], whereby the H/C and O/C ratios are plotted (Figure 7). Kerogens are assigned designations as being Type I, II, III, or IV depending where they fall on the plot. Type I and II are oil-prone, Type III is gas-prone, and Type IV is inert carbon.

This classification scheme can be sub-divided further by considering the variation in sulfur content (Table 1). Since the incorporation of sulfur into sedimentary organic matter involves the generated of H_2S by sulfate reducing bacteria, kerogens with high S/C ratios (0.04 to > 0.10) are found mostly in marine (non-clastic) rocks where euxinic conditions may prevail. Type I kerogens are deposited typically in continental lakes, which have no contact with marine waters and lack a ready supply of sulfate. Consequently, sulfur-rich Type IS kerogens arise only in unusual geologic settings where older evaporite beds (e.g., gysum or anhydrite) are exposed and dissolved into normally fresh lake water.[51]
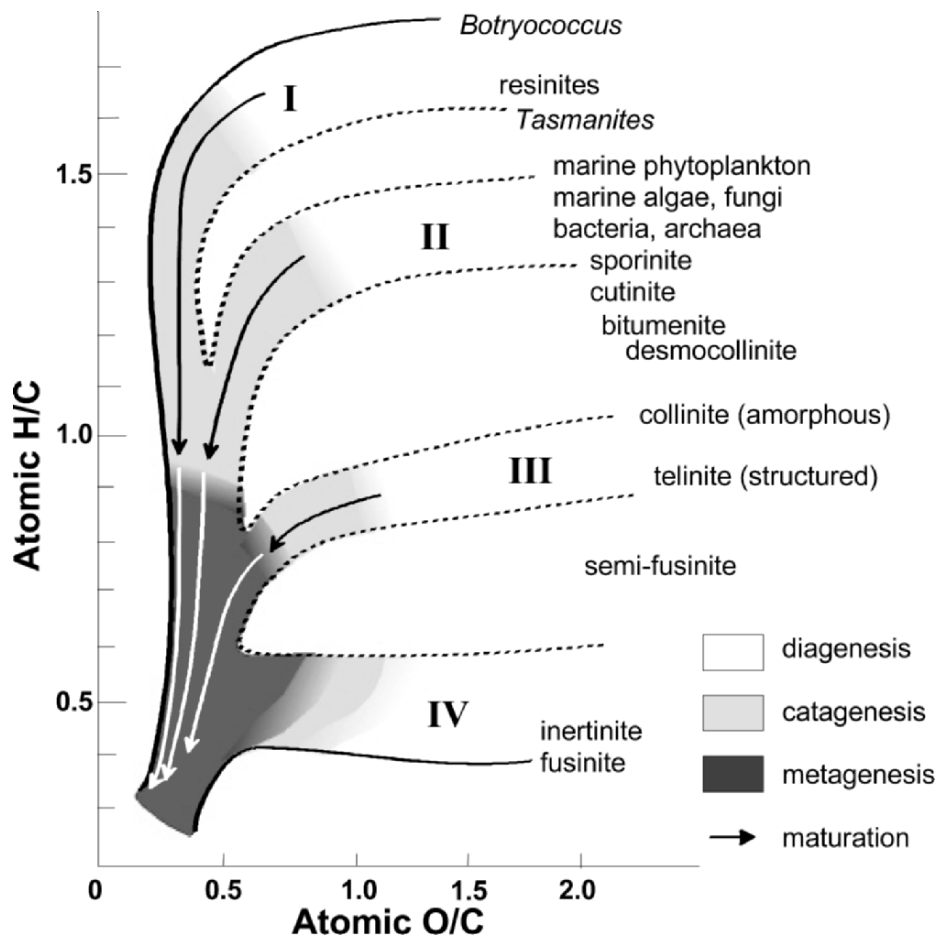
Figure 7. van Krevelen type diagram showing the distribution of kerogen types and some of their precursor macerals in relationship to their H/C and O/C atomic ratios. A substantial portion of their oxygen content is lost during diagenesis. Oil generation occurs during catagenesis, whereby the H/C ratio of the residual kerogens decrease. When the H/C ratio is < 0.5, the residual kerogens are capable of generating only methane.

Type II kerogens are deposited primarily in marine settings dominated by photosynthetic organisms. During early diagenesis, this organic matter may react with H_2S produced by sulfate-reducing bacteria that thrive in marine, anoxic waters and sediments. H_2S also reacts with iron and other metals, forming inorganic sulfides. Consequently, marine Type II kerogens may have varying sulfur content. Marine shales and mudstones, which contain iron oxides and iron-rich clays, yield low-sulfur Type II kerogens and pyrite. Carbonate, evaporite, and chert deposits, which are iron-poor, yield high-sulfur Type IIS kerogens.

Type III kerogens form in swamps and coastal plains. As these depositional environments may or may not have marine influence, the sulfur content of coals can vary, but is generally low. Type III kerogens are frequently allochthonous; that is, they are transported by fluvial systems into delta and nearshore marine sediments where they may mix with locally produced (autochthonous) Type II kerogens. Most Type III kerogens are dominated by vitrinite, a land-plant maceral that has a low H/C ratio and is gas-prone. Some coals, however, contain oil-prone material (Type IIIC) that are derived from associated algae or from the selective preservation of cutinous macromolecules. Many oils from Southeast Asia are generated from Tertiary coaly shales that contain this type of kerogen.

Table 1. Kerogen types, their occurrence and bulk chemistry (at end of diagenesis)

Type	Depositional Setting	Primary Biotic Input	H/C	O/C	S/C
I	Lakes, restricted lagoons	green algae cyanobacteria dinoflagellates	> 1.4	< 0.1	< 0.02
IS	Lakes with a source of sulfate (rare)	green algae cyanobacteria	>1.4	< 0.1	> 0.04
II	Marine shales	marine algae, phytoplankton	1.2 - 1.4	~ 0.1	0.02 - 0.04
IIS	Marine carbonates, evaporites, silicates	marine algae, phytoplankton	1.2 - 1.4	~ 0.1	> 0.04
III	Coals, coaly shales, deltas	vascular land-plants	0.7 - 1.0	> 0.1	< 0.02[1]
IIIC	Coastal plains (oil-prone coals)	vascular land-plants, algae	1.0 to 1.2	> 0.1	< 0.02[1]
IV	Inert carbon due to oxidation or advanced maturity	All possible	< 0.5	< 0.15	< 0.02[2]

[1] Coals generally are low in sulfur. Depositional settings with marine influence may result in coals with S/C > 0.02.
[2] Some inert pyrobitumens may have higher S/C ratios as a result of secondary sulfur incorporation.

5.   GENERATION AND EXPULSION OF OIL AND GAS

During *catagensis*, kerogen thermally cracks and produces bitumen. Weak C—S and C—O bonds break preferentially during the early stages of catagenesis producing bitumen that is highly enriched in polar (NSO) compounds. With additional heating (~90-140°C), C—C bonds break within the evolved polar compounds and from residual kerogen, yielding a hydrocarbon-rich fluid that is then expelled from the source rock's mineral matrix. With additional thermal stress, kerogen yields primarily condensate and then wet gas (C_1-C_6). Catagenesis is complete when the kerogen has expended its capacity to generate C_{2+} hydrocarbons (~150-175°C). *Metagenesis* may then take place under still more severe thermal alteration,

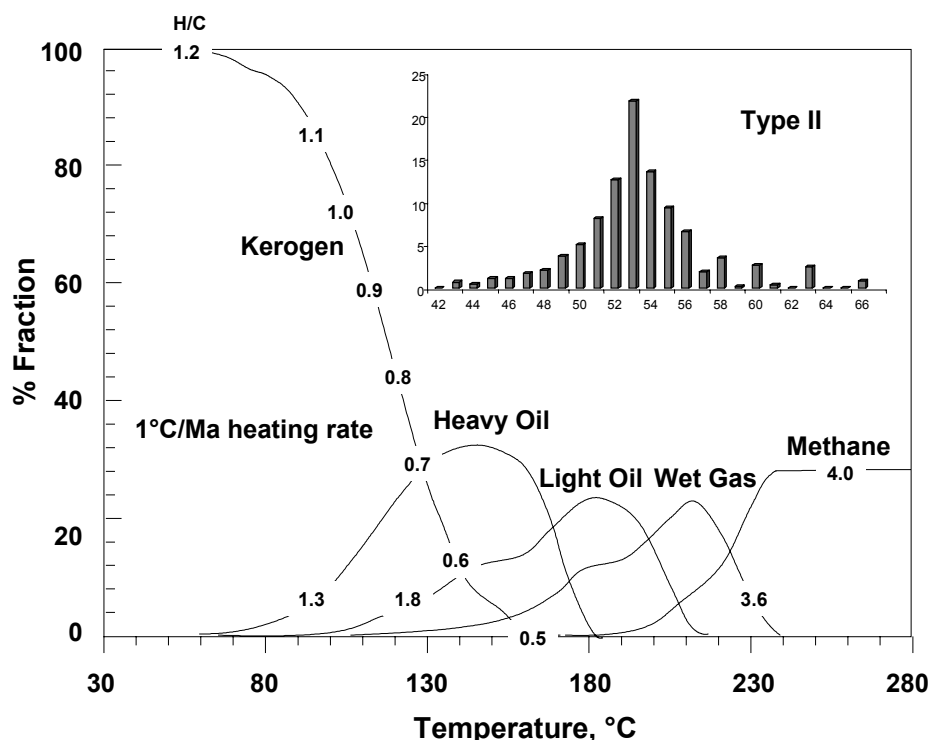where only methane is produced as methyl-groups are cleavage from highly condensed, aromatic structures.

Figure 8. Example of a kerogen decomposition kinetic model with predictions of expelled fluid composition. The rate of kerogen conversion is assumed to follow a series of parallel first order kinetic reactions defined by the Arrhenius equation, $k = Ae^{-(E/RT)}$, where k is the rate coefficient, A is a constant termed the frequency factor, E is the activation energy, R is the universal gas constant, and T is the temperature. The kerogen model was derived by fitting the yield curves of pyrolyzates that evolved from a marine shale source rock containing Type II kerogen heated at several different heating rates under anhydrous conditions. In this case, the model was fitted using a fixed frequency factor, $A = 1 \times 10^{14}$ sec^{-1}. The evolved products are predicted from a more advanced model that accounts for expulsion and secondary cracking of retained bitumen and residual kerogen.

Oil generation is a kinetic process – both time and temperature are critical[52]. The kinetic parameters of kerogen decomposition can be determined by artificially heating immature source rocks using relatively fast heating rates (~300 to 550°C at ~ 1 to 50 °C/min) or lower isothermal temperatures (275-350°C for several days) and measuring either product yield or the residual generative potential. Data are fitted to kinetic models defined by a series of first order parallel reactions, usually at a single frequency factor. When geologic heating rates are applied (~1 to 10°C/Ma), the derived kinetic models yield kerogen maturation results comparable to what is observed in

petroliferous basins.[53,54] More advanced models describe the fluid composition of the expelled products and include secondary cracking reactions (Figure 8).

Although simple thermogensis adequately describes petroleum generation, geocatalysis involving reactive mineral surfaces, clays, trace metals, or organic species have been proposed.[55,56] Such processes are highly speculative, and it is difficult to image how inorganic agents would remain activated under subsurface conditions or how mass transport limitations inherent in solid-solid interactions could be circumvented[57].

Once generated from the kerogen, petroleum is expelled into mineral pore spaces (primary migration) and then through permeable rock and faults to the trap (secondary migration). Oil expelled from a source rock is enriched in saturated and aromatic hydrocarbons relative to the bitumen that remains (Figure 9). The factors that control primary expulsion and bitumen fractionation are largely unknown; and, although there is generally a lack of experimental or observational evidence for the underlying mechanisms, there is no shortage of hypotheses. Expulsion models that attempt to account for these chemical differences generally assume rate-limiting processes occur in the release of generated hydrocarbons from the kerogen or in the movement of hydrocarbons within the mineral matrix.

 Hypotheses based on kerogen-oil interaction postulate that the expulsion of oil is controlled by absorption or adsorption of the products onto the surface of the kerogen,[58,59,60] diffusion of the hydrocarbons through the kerogen[61,62,63,64] and/or relative solubility.[65] These hypotheses attribute little importance to movement of petroleum within the source rock mineral matrix and the efficiency of the release of oil is controlled primarily by the amount of organic carbon and its composition (see, Pepper & Corvi, 1995; and references therein[53]). Expulsion models based on the interactions of generated products with the source kerogen have gained favor in recent years as they have the potential to account for compositional differences between bitumens and expelled oil and for expulsion efficiencies that depend on kerogen type and richness. This thinking can be traced to observations made on source rocks[66] and to recognition of the absorptive capacity of solid organic matter as revealed by solvent swelling experiments.[67,68,69,70] It is now clear that Type I and II kerogens and Type III and IIIC coals have sufficient sorptive properties to explain residual oil concentrations in mature source rocks.
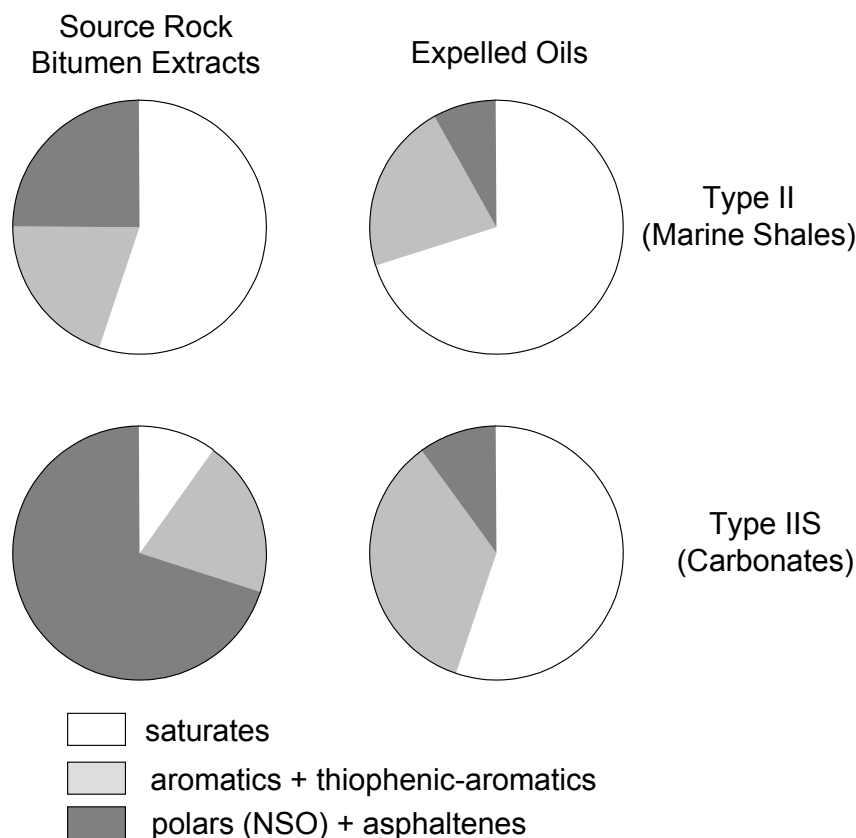
Source Rock
Bitumen Extracts   Expelled Oils

Type II
(Marine Shales)

Type IIS
(Carbonates)

□ saturates
▨ aromatics + thiophenic-aromatics
▤ polars (NSO) + asphaltenes

Figure 9. Comparison of C_{15+} chemical group type distributions of expelled oil and retained bitumens for typical Type II (marine shale) and Type IIS (carbonate) source rocks (middle of the the oil window).

There are many expulsion models that target chemical or physical processes of oil moving within the source rock mineral matrix as the rate determining step. Different aspects have been considered to be important in this movement. Some consider the amount and type of organic matter as being critical to generating sufficient bitumen to exceed a pore saturation threshold.[71,72,73] Others postulate that the establishment of effective and continuous migration pathways within the source rocks is critical.[74,75,76]

Other factors suggested to be key elements in expulsion are: pressure build-up from generation and compaction and the failure of the rock fabric resulting in micro-fracturing,[77] gas availability and movement of oil in a gas or supercritical phase,[78,79] or movement of oil in an aqueous phase.[80,81] For the most part, the conditions that determine these elements are controlled by the primary sedimentological conditions in the depositional environment of the source rock and secondary diagenetic processes. Consequently, the

mechanisms that define oil movement differ according to the lithofacies of the source rock.

6. COMPOSITION OF PRODUCED PETROLEUM

The molecular and isotopic composition of produced petroleum is determined by complex chemical, physical, and biological processes. Generation and expulsion from the source rocks, phase behavior as the petroleum moves from source to reservoir, reservoir fill history, and secondary alteration processes all influence oil and gas compositions.

Each source facies generates oil with distinct chemical composition that reflects biotic input, depositional setting, and thermal history (Figure 10). For example, lacustrine and coaly source rocks generate waxy, low-sulfur crudes, while carbonate and evaporite source rocks generate asphaltic, high-sulfur crudes. These compositional differences are most apparent during the initial stages of oil expulsion and become less distinct as the source proceeds through catagenesis where secondary cracking reactions become prevalent. Although petroleum is derived from biological organic matter, most of the individual compounds cannot be assigned to a specific biochemical precursor. Some petroleum hydrocarbons, termed *biomarkers*, retain enough of their original carbon structure that a likely biochemical precursor can be assigned.[82] The abundance and distribution of biomarkers allow geochemists to infer the origin and thermal history of oils.

Once generated and expelled from the source rock, petroleum composition can be further modified during migration and entrapment within the reservoir. In most petroleum systems, the source formation is at greater temperature and pressure than the reservoir and migrating petroleum fluid may separate into gas and liquid phases that can then migrate independently.[83,84,85] Petroleum also interacts with water and the more soluble hydrocarbons may selectively partition into the aqueous phase.[86]

Once in the reservoir, secondary processes can alter oil composition. Biodegradation, the consumption of hydrocarbons by microorganisms, is likely to occur in shallow, cool reservoirs ($<80°C$).[87,88] This process selectively removes saturated hydrocarbons, enriching the residual crude oil in polar and asphaltic material. Biodegradation forms acids and biogenic CH_4, CO_2, and H_2S. Microbial alteration of crude oils is a relatively fast process and may occur naturally or result from poor production practices. Thermochemical sulfate reduction (TSR) is another reservoir alteration process that can affect oil quality and quantity. It is a chemical redox process that occurs at relatively high temperatures ($>120°C$), where hydrocarbons are oxidized to CO_2 and sulfate is reduced to H_2S.[89,90] The residual oil is depleted in saturated hydrocarbons and enriched in sulfur-aromatic species. Reservoir charging and fill history also can alter oil composition. For example, mixing

of gaseous hydrocarbons with a heavy oil can cause asphaltenes to precipitate, forming a tar mat.[91]
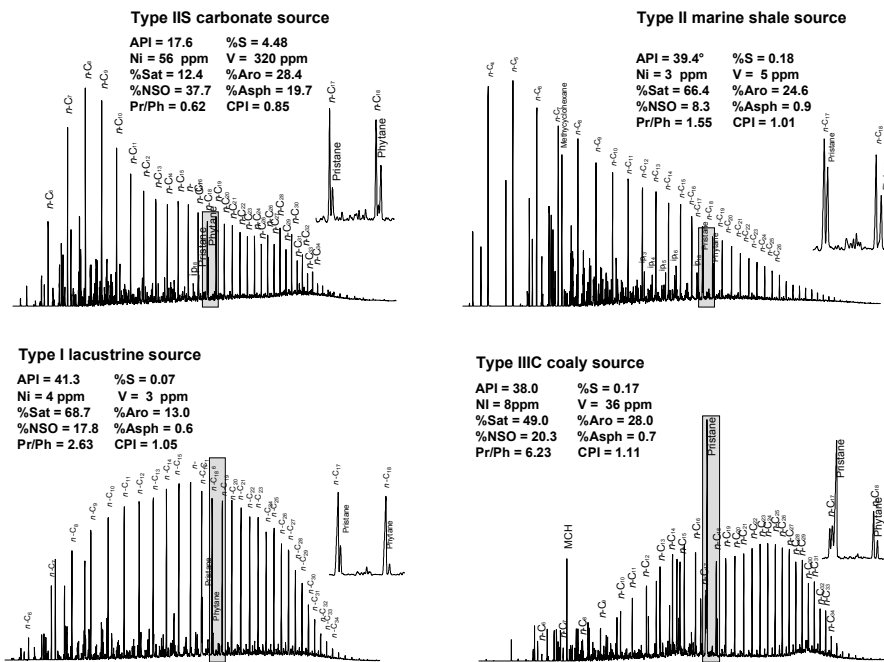

Figure 10. Whole-oil gas chromatograms showing examples of oils from different source kerogens. The grayed area, showing the elution of n-C_{17}, pristane (Pr), n-C_{18}, and phytane (Ph), is enlarged. Pr/Ph is the pristane/phytane ratio, which is used to infer the depositional environment (anoxic, hypersaline Pr/Ph<1, oxic water column/anoxic sediments Pr/Ph 1~2, oxic deposition Pr/Ph>2). CPI is the carbon preference, which is used to infer carbonate/evaporite source facies <1, and higher land-plant input CPI > 1. API gravity, the concentrations of sulfur (S), nitrogen (N), nickel (Ni) and vanadium (V) and the C_{15+} chemical group-type compositions are influenced by of the organic matter, depositional environment, and thermal history of their source rocks and by reservoir alteration processes.

The composition of crude oil that arrives at a refinery is not identical to reservoir fluids. Gas and water is separated at the well head and emulsions are broken. Consequently, oils lose some light hydrocarbons (<C_6) by evaporation during production and transport. Pipeline and tanker oils are frequently blends of oils from multiple fields and reservoirs, which individually may be of varying composition and quality. For these reasons, testing of subsurface fluids from individual reservoirs is necessary to determine field economics and design reservoir management practices.

7.   SUMMARY

The theory that petroleum originates from sedimentary organic matter that was once living organisms is consistent will all natural observations, laboratory analyses and experiments, theoretical considerations, and basin simulations. The accumulation of economic quantities of petroleum (oil and gas) requires that a series of processes occur within sedimentary basins. Organic-rich sediments are deposited only under specific conditions that promote the production of biota and/or transport of biogenic organic compounds and the selective preservation of this material. The sedimentary organic matter converts to kerogen, an insoluble macromolecule with a composition that reflects the biotic input and chemical alterations (sulfurization, condensation, defunctionalization, and aromatization) that occur during diagenesis. Once lithofied, these organic-rich strata have the potential to generate oil and gas when buried and heated to promote thermal cracking. Expelled petroleum migrates from the source through fractures and permeable strata. Economic reserves occur when geological conditions allow for the accumulation, retention, and preservation of significant volumes of migrated petroluem. Collectively, these processes describe a petroleum system.

8.   REFERENCES

[1] Bacon, Roger. *Fr. Rogeri Bacon Opera quaedam hactenus ineditia. I. I. Opus tertium. II. Opus minus. III. compendium philosophiae*. J. S. Brewer (Ed.). London, 1859.

[2] Aristotle,*Meteorology* in *The Complete Works of Aristotle*, Jonathan Barnes (Eds) Princeton Univ. Press, 1995; pp. 555-625.

[3] Kenney, J.F. Considerations about recent predictions of impending shortages of petroleum evaluated from the perspective of modern petroleum science, *Energy World* **1996**, *240*, 16-18.

[4] Wellings, F.E. Geological aspects the origin of oil. *Inst. Petrol. J.* **1966**, *52*, 124-130.

[5] Dott, R.H. Hypotheses for an organic origin. In *Sourcebook for Petroleum Geology, Part 1. Genesis of Petroleum.* R.H. Dott and M.J. Reynolds (Eds). AAPG Memoir 5, Tulsa, 1969; pp. 1-244.

[6] Hunt, T.S. Report on the geology of Canada. Canadian Geological Survey Report: Progress to 1863. Canadian Geological Survey, 1863.

[7] Lesquereux,, L. Report on the fossil plants of Illinois: Ill. Geol. Survey, **1866**, *2*, 425-470.

[8] Newberry, J.S. The general geological relations and structure of Ohio: *Ohio Geological Survey Report 1*, **1873**, pt. 1, 222 p.

[9] Arnold, R. & Anderson, R. Geology and oil resources of the Santa Maria Oil District, Santa Barbara County, California. *USGS Bulletin* **1907**, *No. 322.*

[10] Clarke, F.W. Data of geochemistry. *USGS Bulletin* **1916**, *No. 616.*

[11] Pompeckj, J.F. Die Juraablagerungen zwischen Regensburg und Regenstauf. *Geologisches Jahrbuch*, **1901**, 14, 139–220.

[12] Schuchert, C. The conditions of black shale deposition as illustrated by Kuperschiefer and Lias of Germany. *Proc. Am. Philos. Soc.* **1915**, 54, 259-269.

[13] Treibs, A. Chlorophyll and hemin derivatives in organic mineral substances. *Angewandte Chemie* **1936**, 49, 682-686.

[14] Oakwood, T.S.; Shriver, D.S.; Fall, H.H.; Mcaleer, W.J.; Wunz, P.R. Optical activity of petroleum. *Ind. Eng. Chem.* **1952**, 44, 2568-2570.

[15] Craig, H. The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta* **1953**, *3*, 53-92.

[16] Eglinton, G.; Calvin, M. Chemical fossils. *Sci. Amer.* **1967**, *216*, 32-43.

[17] Forsman, J.P.; Hunt, J.M. Insoluble organic matter (kerogen) in sedimentary rocks of marine origin. In: Weeks, L.G. (Ed.), *Habitat of Oil: A Symposium.* American Association of Petroleum Geologists, Tulsa, Oklahoma, 1958; pp. 747-778.

[18] Abelson, P.H. Organic geochemistry and the formation of petroleum. *6th World Petroleum Congress Proc.*, **1963**, Sec 1, 397-407.

[19] Tissot, B. Premières donnés sur les méchanismes et ala cinétique de la formation du pétrole dans les sédiments. Simulation d'un schéma réactionnel sur ordinateu. *Rev. Inst. Fran. Pét.* **1969**, *24*, 470-501.

[20] Berthelot, M.-P. *Chimie organique fondée sur la synthèse,* 1860

[21] Mendeleev, D. L'origine du petrole. *Revue Scientifique*, **1877**, 2e Ser., VIII, 409-416.

[22] Mendeleev, D. *The Principles of Chemistry*, vol. 1. Second English edition translated from the sixth Russian edition. Collier: New York, 1902; 552 pp.

[23] Kudryavtsev, N.A. Against the organic hypothesis of the origin of petroleum *Petroleum Economy* [*Neftianoye Khozyaistvo*], **1951**, *9*, 17-29.

[24] Cronin J.; Pizzarello S.; Cruikshank D.P. Organic matter in carbonaceous chondrites, planetary satellites, asteroids, and comets. In *Meteorites and the Early Solar System,* Kerridge, J.F.; Mathews, M.S. (Eds), University of Arizona Press, 1988; pp. 819–857

[25] Hoyle, F. *Frontiers of Astronomy,* Heineman: London, 1955; 360 pp.

[26] Gold T. The origin of natural gas and petroleum and the prognosis for future supplies. *Annual Review of Energy,* **1985**, *10*, 53-77.

[27] Gold T. *The Deep Hot Biosphere,* Copernicus: New York, 1999; 235 p.

[28] Kerr, RA. When a radical experiment goes bust, *Science* **1990**, *247*, 1177.

[29] Sherwood Lollar B.S.; Frape, S.K.; Weise, S.M.; Fritz, P.; Macko, S.A.; Whelan, J.A. Abiogenic methanogenesis in crystalline rocks. *Geochim. Cosmochim. Acta* **1993**, *57*, 5087-5097.

[30] McCollom, T.M.; Seewald, J.S. A reassessment of the potential for reduction of dissolved CO_2 to hydrocarbons during serpentinization of olivine. *Geochim. Cosmochim. Acta* **2001**, *65(21)*, 3769-3778.

[31] McCollom, T.M. Formation of meteorite hydrocarbons from thermal decomposition of siderite ($FeCO_3$). *Geochim. Cosmochim. Acta* **2003**, *67(2)*, 311-317.

[32] Potter J.; Rankin, A.H.; Treloar, P.J. The nature and origin of abiogenic hydrocarbons in the alkaline igneous intrusions, Khibina and Lovozero in the Kola Peninsula, N.W. Geological Society London Hydrocarbons in Crystalline Rocks Joint Meeting, London, England, 13-14 February, 2001.

[33] Sherwood, Lollar B.; Westgate, T.D.; Ward, J.A.; Slater, G.F.; Lacrampe-Couloume, G. Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs, *Nature* **2002,** *416*, 522-524.

[34] *The Petroleum System—From Source to Trap,* Vol. AAPG Memoir No. 60, Magoon, L.B.; Dow, W.G. (Eds.) American Association of Petroleum Geologists, Tulsa, 1994; pp. 655..

[35] Magoon, L.B.; Beaumont, E.A. Petroleum Systems. In: *Handbook of Petroleum Geology: Exploring for Oil and Gas Traps*, Beaumont, E.A.; Foster, H.N. (Eds), American Association of Petroleum Geologists, Tulsa, 1999; pp. 3-1 to 3-34..

[36] Beaumont, A.; Foster N.H. *Treatise of Petroleum Geology/Handbook of Petroleum Geology: Exploring for Oil and Gas Traps*, The American Association of Petroleum Geologists, Tulsa, 1999.

[37] Tissot, B.P.; Welte, D.H. *Petroleum Formation and Occurrence*, Springer-Verlag: New York, 1984; 699 p.

[38] Hunt, J.M. *Petroleum Geochemistry and Geology.* W. H. Freeman: New York, 1996; 743 p.

[39] Peters K.E.; Fowler, M.G. Applications of petroleum geochemistry to exploration and reservoir management, *Org. Geochem.* **2002**, *33*, 5-36.

[40] Arthur, M.A.; Sageman, B.B. Marine black shales: a review of depositional mechanisms and significance of ancient deposits. *Annual Review of Earth & Planetary Science* **22**, 499-551.

[41] Canfield, D.E. (1994) Factors influencing organic carbon preservation in marine sediments. *Chemical Geology*, **1994**, *114*, 315-329.

[42] Tyson, R.V. *Sedimentary Organic Matter: Organic Facies and Palynofacies*. Chapman and Hall: London, 1995; 615 pp.

[43] Pedersen, T.F.; Calvert, S.E. Anoxia vs. productivity: what controls the formation of organic-carbon-rich sediments and sedimentary rocks? *AAPG Bulletin* **1990**, *74*, 454-466.

[44] Michaelis, W.; Seifert, R.; Nauhaus, K.; Treude, T.; Thiel, V.; Blumenberg, M.; Knittel, K.; Gieseke, A.; Peterknecht, K.; Pape, T.; Boetius, A.; Amann, R.; Jørgensen, B.B.; Widdel, F.; Peckmann, J.; Pimenov, N.V.; Gulin, M.B. Microbial reefs in the Black Sea fueled by anaerobic oxidation of methane. *Science* **2002**, *297*, 1013-1015.

[45] Demaison, G.L.; Moore, G.T. Anoxic environments and oil source bed genesis. *AAPG Bulletin* **1980**, *64*, 1179-1209.

[46] Koopmans, M.P.; Schouten, S.; Kohnen, M.E.L.,; Sinninghe Damsté, J.S. Restricted utility of aryl isoprenoids as indicators for photic zone anoxia. *Geochim. Cosmochim. Acta* **1996**, *60*, 4467-4496.

[47] Metzger, P.; Largeau, C.; Casadevall, E. Lipids and Macromolecular Lipids of the hydrocarbon-rich Microalga Botryococcus Braunii. *Progress in the Chemistry of Organic Natural Products*, **1991**, *57*, 1-70.

[48] *Kerogen. Insoluble Organic Matter From Sedimentary Rocks*, Durand, B. (Ed.) Éditions Technip: Paris, 1980; 519 p.

[49] Tegelaar E.W.; De Leeuw, J.W.; Derenne, S.; Largeau, C. A reappraisal of kerogen formation. *Geochim. Cosmochim. Acta* **1989**, *53*, 3103-3106.

[50] van Krevelen D.W. *Coal*, Elsevier: New York, 1961; 514 pp.

[51] Sinninghe Damsté, J.S.; de las Heras, F.X.C.; van Bergen, P.F.; de Leeuw, J.W. Characterization of Tertiary Catalan lacustrine oil shales; discovery of extremely organic sulphur-rich Type I kerogens. *Geochim. Cosmochim. Acta* **1993**, *57*, 389-415.

[52] Connan, J. Time-temperature relation in oil genesis. *AAPG Bulletin* **1974**, *58*, 2516-2521.

[53] Tissot, B.P.; Pelet, R.; Ungerer, P. Thermal history of sedimentary basins and kinetics of oil and gas generation. *AAPG Bulletin* **1986**, *70*, 656.

[54] Ungerer, P.; Bessis, F.; Chenet, P.Y.; Durand, B.; Nogaret, E.; Chiarelli, A.; Oudin, J.L.; Perrin, J.F. Geological and geochemical models in oil exploration; principles and practical examples. In: *Petroleum geochemistry and basin evaluation* Demaison, G.; Murris, R. J. (Ed.), American Association of Petroleum Geologists, Tulsa, OK, 1984; pp. 53-77.

[55] Mango, F.D. Transition metal catalysis in the generation of petroleum and natural gas. *Geochim. Cosmochim. Acta* **1992**, *56*, 553-555.

[56] Sabate, R.W.; Baker, C.C. Synergetic catalysis in hydrocarbon generation. In *Gulf Coast Association of Geological Societies Transactions*, 1994; pp. 657-661.

[57] Schoonen, M.A.A.; Xu, Y.; Strongin, D.R. An introduction to geocatalysis. *J. Geochem. Expl.* **1998**, *62*, 201-215.

[58] McAuliffe, C.D. Oil and gas migration: chemical and physical constraints. In *Problems of Petroleum Migration*, Roberts, W. H.; Cordell, R. J. (Eds.) AAPG Geological Studies 10, 1980; p. 89-107.

[59] Sandvik, E.I.; Young, W.A.; Curry, D.J. Expulsion from hydrocarbon sources; the role of organic absorption. *Org. Geochem.* **1992**, *19*, 77-87

[60] Pepper, A.S.; Corvi, P.J. Simple kinetic models of petroleum formation; Part III, Modelling an open system. *Marine Petrol. Geol.* **1995**, *12*, 417-452.

[61] Thomas, M.M.; Clouse, J.A. Primary migration by diffusion through kerogen; I, Model experiments with organic-coated rocks, *Geochim. Cosmochim. Acta* **1990**, *54*, 2775-2779.

[62] Thomas, M.M.; Clouse, J. A. Primary migration by diffusion through kerogen; II, Hydrocarbon diffusivities in kerogen. *Geochim. Cosmochim. Acta* **1990***, 54*, 2781-2792.

[63] Thomas, M. M.; Clouse, J. A. Primary migration by diffusion through kerogen; III, Calculation of geologic fluxes. *Geochimi. Cosmochim. Acta* **1990**, *54*, 2793-2797.

[64] Stainforth, J.G.; Reinders, J.E.A. Primary migration of hydrocarbons by diffusion through organic matter networks, and its effect on oil and gas generation. *Org. Geochem.* **1990**, *16*, 61-74.

[65] Ritter, U. Solubility of petroleum compounds in kerogen: implications for petroleum expulsion *Org. Geochem.* **2003**, *34*, 319-326

[66] Pepper, A. S. Estimating the petroleum expulsion behaviour of source rocks; a novel quantitative approach. In *Petroleum Migration*, England, W. A.; Fleet, A. J. (Eds.) Geological Society of London Special Publication 59, 1991; pp. 9-31.

[67] Shadle, L.J.; Khan, M.R.; Zhang, G.Q.; Bajura, R.A. Investigation of oil shale and coal structures by swelling in various solvents, *Prep. Div. Petr. Chem.* **1989**, *34(1)*, 55-61.

[68] Larsen, J.W.; Li, Shang, Changes in the macromolecular structure of a Type I kerogen during maturation," *Energy Fuels* **1987**, *11*, 897-901.

[69] Larsen, J.W.; Li, Shang, An initial comparison of the interactions of type I and III kerogens with organic liquids, *Org. Geochem.* **1987**, *26*, 305-309.

[70] Larsen, J.W.; Li, Shang, Solvent swelling studies of Green River Kerogen, *Energy Fuels* **1994**, *8*, 932-936.

[71] Tissot, B. Migration of hydrocarbons in sedimentary basins; a geological, geochemical and historical perspective. *Migration of hydrocarbons in sedimentary basins*, 1987; 1-19.

[72] Ungerer, P. State of the art of research in kinetic modelling of oil formation and expulsion. *Org. Geochem.* **1990**, 16, 1-25.

[73] Burnham, A.K.; Braun, R.L. Development of a detailed model of petroleum formation, destruction, and expulsion from lacustrine and marine source rocks. *Org. Geochem.* **1990**, *16*, 27-39.

[74] Dickey, P.A. Possible migration of oil from source rock in oil phase. *AAPG Bulletin* **1975**, *72*, 337-345.

[75] Palciauskas, V.V.; Domenico, P.A. Microfracture development in compacting sediments: relation to hydrocarbon-maturation kinetics. *AAPG Bulletin* **1980**, *64*, 927-937.

[76] Mann, U. Sedimentological and petrophysical aspects of primary migration pathways. In *Sediments and Environmental Geochemistry*, Heling, D.; Rothe, P.; Förstner, U.; Stoffers, P. (Eds.), Springer: New York, 1990; pp. 152-178.

[77] Düppenbecker, S. J.; Welte, D. H. Petroleum expulsion from source rocks; insights from geology, geochemistry and computerized numerical modelling. *Thirteenth World Petroleum Congress*, **1992**; 165-177.

[78] Price, L.C. Primary petroleum migration from shales with oxygen-rich organic matter. *J. Petrol. Geol.,* **1989**, *12*, 289-324.

[79] Leythaeuser, D.; Poelchau, H.S. Expulsion of petroleum from type III kerogen source rocks in gaseous solution; modeling of solubility fractionation. In *Petroleum migration*, Vol. 59, England, W. A.; Fleet, A. J. (Eds.), Geological Society of London: London, 1991; pp. 33-46.

[80] Barker, C. Aquathermal pressuring: role of temperature in development of abnormal pressure zones. *AAPG Bulletin* **1972**, *56*, 2068-2071.

[81] Magara, K. Agents for primary hydrocarbon migration; a review. In *Problems of petroleum migration,* Roberts, III W. H.; Cordell, R. J. (Eds.), American Association of Petroleum Geologists, Tulsa, OK, 1980; pp. 33-45..

[82] Peters, K.E.; Moldowan, J.M. *The Biomarker Guide; Interpreting Molecular Fossils in Petroleum and Ancient Sediments.* Prentice Hall: Englewood Cliffs, NJ, 1993; 363 pp.

[83] Werner, A.; Behar, F.; de Hemptinne, J.C.; Behar, E. Thermodynamic properties of petroleum fluids during expulsion and migration from source rocks. *Org. Geochem.* **1996**, *24*, 1079-1095.

[84] Kuo, L.C. Gas exsolution during fluid migration and its relation to overpressure and petroleum accumulation. *Marine Petrol. Geol.* **1997**, *14*, 221-229.

[85] Di Primio, R.; Dieckmann, V.; Mills, N. PVT and phase behaviour analysis in petroleum exploration. *Org. Geochem.* **1998**, *29*, 207-222.

[86] Palmer, S.E. Effect of water washing on C_{15}+ hydrocarbon fraction of crude oils from northwest Palawan, Phillipines. *AAPG Bulletin*, **1984**, *68*, 137-149.

[87] Connan, J. Biodegradation of crude oils in reservoirs. In *Advances in Petroleum Geochemistry*, *1,* Brooks, J.; Welte, D.H. (Eds.), . Academic Press: London, 1984; pp. 299-335.

[88] Seifert, W.K.; Moldowan, J.M.; Demaison G. J. Source correlation of biodegraded oils: *Org. Geochem.* **1984**, *6*, 633-643.

[89] Orr, W.L. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-Study of Big Horn Paleozoic oils. *AAPG Bulletin*, **1974**, *58*, 2295-2318.

[90] Machel, H.G. Bacterial and thermochemical sulfate reduction in diagenetic settings - old and new insights. *Sedimentary Geology* **2001**, *140*, 143-175.

[91] Wilhelms, A.; Larter, S.R. Origin of tar mats in petroleum reservoirs: part II: formation mechanisms for tar mats. *Marine Petrol. Geol.* **1994**, *11*, 442-456.