Basic Petroleum Geochemistry for Source Rock Evaluation

As the search for oil and gas prospects grows increasingly complex, more E&P companies are turning to geochemistry to evaluate a component that is central to the success of each well: the source rock.

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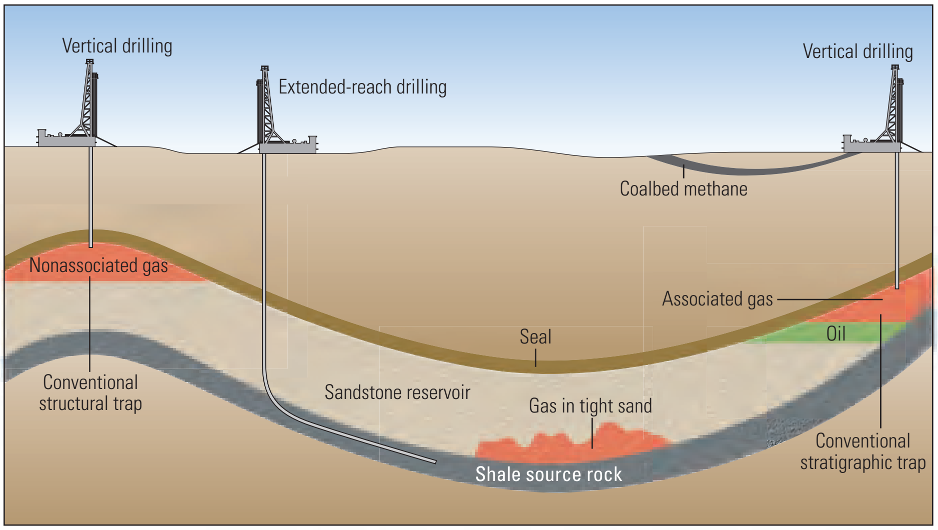
Every oil or gas play originates from source rock. The viability of each play—conventional or unconventional, oil or gas—depends on its source rock. Without this source of petroleum, all other components and processes needed to exploit a play become irrelevant.

A source rock can be broadly defined as any fine-grained, organic-rich rock that is capable of generating petroleum, given sufficient exposure to heat and pressure. Its petroleum-generating potential is directly related to its volume, organic richness and thermal maturity.[1] Although its volume—a function of thickness and areal extent—must not be discounted, this article focuses on the other two characteristics. Organic richness refers to the amount and type of organic matter contained within the rock. Thermal maturity refers to a source rock's exposure to heat over time. Heat increases as the rock is buried deeper beneath successive layers of sediment. It is the thermal transformation of organic matter that causes a source rock to generate petroleum.



^ Petroleum systems. A conventional petroleum system requires four components: source rock, reservoir rock, trap and seal—and two processes: petroleum generation and migration. Timing between petroleum migration and creation of the reservoir, trap and seal is also critical. Unconventional systems require, at a minimum, the deposition of source rock and sufficient overburden to achieve thermal maturity.

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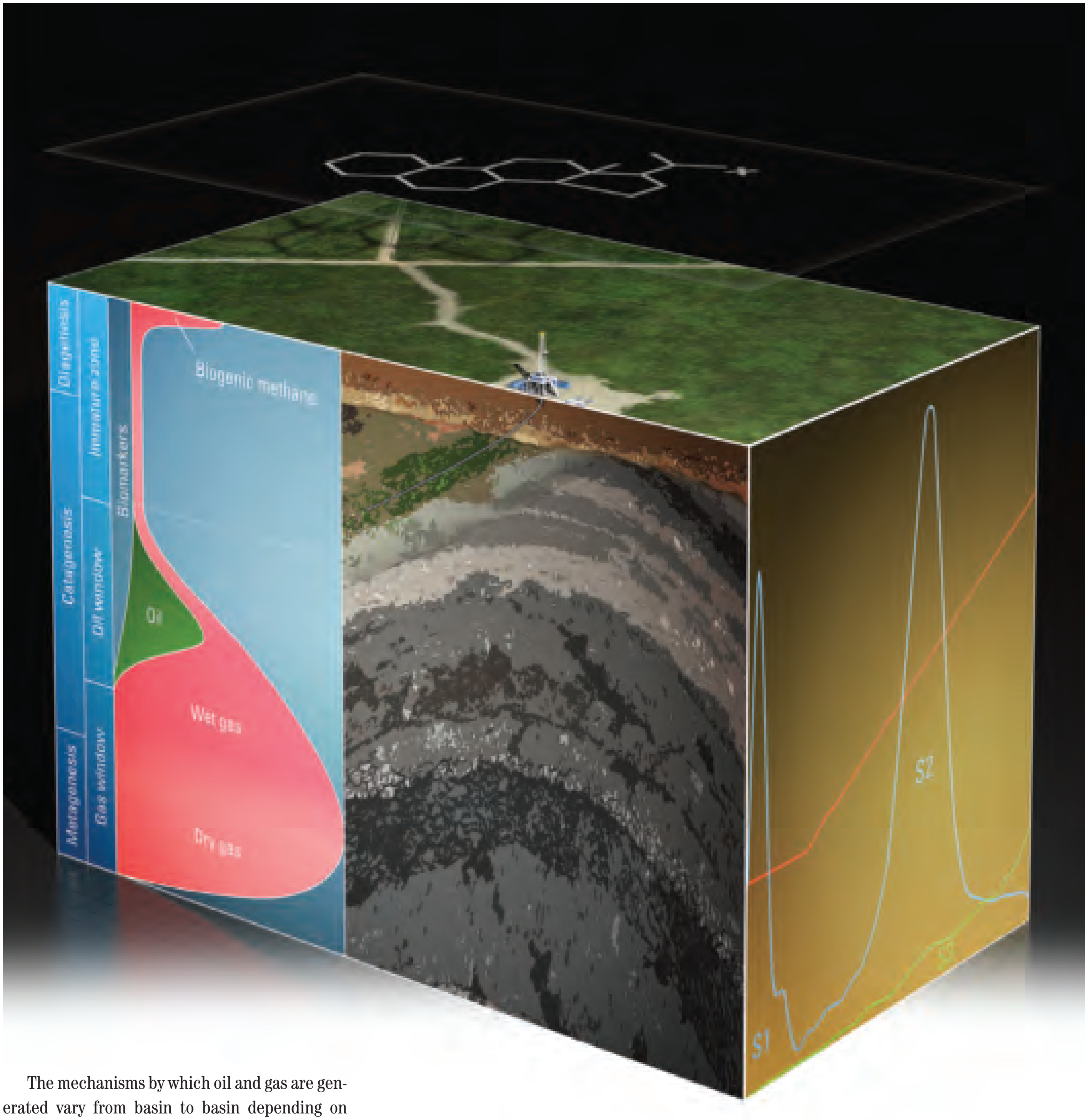
[1] In this article, the term "petroleum" refers not only to crude oil, but also to the fluid in either its liquid or gaseous state. Also, the term "hydrocarbons," which tends to be used casually in the oil industry, will be treated as a loose equivalent to "petroleum."

[2] Kerogen is the particulate organic matter disseminated within sedimentary rocks that is insoluble in common organic solvents. Bitumen is a thermally degraded derivative of kerogen, but is soluble in organic solvents. The exact relationship between kerogen, bitumen and the hydrocarbons that evolve during heating of organic matter is still a subject of investigation. For more on these components: Peters KE, Walters CC and Moldowan JM: *The Biomarker Guide,* 2nd edition. Cambridge, England: Cambridge University Press, 2005.

[3] Magoon LB and Dow WG (eds): *The Petroleum System—From Source to Trap.* Tulsa: The American Association of Petroleum Geologists, AAPG Memoir 60, 1994.

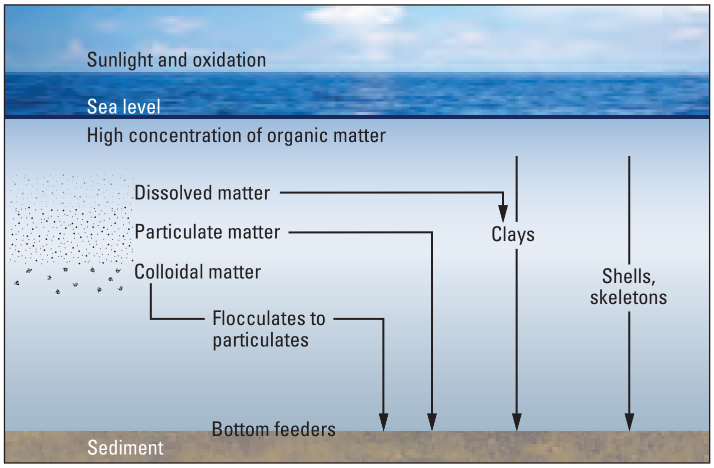


The mechanisms by which oil and gas are generated vary from basin to basin depending on sedimentary facies, burial history, tectonics and other geologic processes; however, the general model is fairly straightforward. Following deposition of organic-rich sediments, microbial processes convert some of the organic matter into biogenic methane gas. Greater depths of burial are accompanied by increases in heat in accordance with the basin's geothermal gradient. This heat causes the organic matter to gradually transform into an insoluble organic matter known as kerogen. The kerogen continues its alteration as heat increases; these changes, in turn, result in an evolution of the petroleum compounds that are subsequently generated. Further heating converts the kerogen, yielding bitumen and petroleum.[2] The kerogen becomes more depleted of hydrogen as it gives off petroleum. Increasing maturity also causes initially complex petroleum compounds to undergo structural simplification—typically starting with oil, then wet gas and ending at dry gas.

This basic model is integral to one of the most fundamental concepts of oil and gas exploration: the petroleum system.[3] This concept accounts for the generation, expulsion, migration and accumulation of oil and gas—and source rock lies at its foundation (previous page). In conventional petroleum systems, overburden rock buries the source rock to depths where petroleum is generated. Petroleum generated by thermally mature source rock is expelled into a porous and permeable carrier bed and then migrates into a reservoir rock, where it becomes structurally or stratigraphically trapped beneath an impermeable seal.[4] However, the requisite processes of petroleum generation, expulsion, migration and trapping are not always carried to completion, as evidenced by the myriad of dry holes drilled into clearly delineated traps.

Ongoing advances in production technology are opening new plays to exploration and development. Resource plays, exemplified by the boom in shale gas production, are founded on unconventional petroleum systems, where source rock also serves as reservoir and seal. Petroleum generated in this self-contained petroleum system does not migrate but remains trapped within the micropores and fractures of the low-permeability source rock.[5] Oil shales are yet another variation on the resource play; operators who exploit these source rocks must apply heat to produce the oil.[6]

The world's remaining oil and gas resources are becoming more challenging to find and develop. As the industry targets these resources, the need to thoroughly understand and characterize all components of prospective petroleum systems becomes more acute. Thus, in addition to assessing the reservoir, trap and seal of their prospects, E&P companies must evaluate the petroleum-generating capacity of the source rock. Petroleum geochemistry is improving the efficiency of exploration and production through characterization of the elements and processes that control the richness and distribution of petroleum source rocks, thus providing valuable input for basin and petroleum system modeling. This article describes basic geochemical principles and techniques used by geoscientists to evaluate source rock quality, quantity and maturity.



^ Organic matter in the water column. Organic matter in solution may be adsorbed onto clay particles that sink slowly through the water. Colloidal organic matter flocculates before it settles. Particulate matter may simply drop to the bottom. (Modified from Barker, reference 8.)

Source Rock Fundamentals

Source rocks result from a convergence of physical, biochemical and geologic processes that culminate in the formation of fine-grained sedimentary rocks containing carbon- and hydrogen-rich organic matter. The amount and type of organic material incorporated into a source rock are controlled, in part, by environmental and depositional conditions. Source rocks form where environmental conditions support biologic activities that produce large quantities of organic matter, where depositional conditions concentrate this matter and where postdepositional conditions permit its preservation.[7]

Organic content is controlled largely by biologic productivity, sediment mineralogy and oxygenation of the water column and sediment. Biologic contributions to organic content range from hydrogen-poor woody fragments to hydrogen-rich algal or bacterial components. From these, a variety of organic compounds may be created.

Within the water column, organic matter may exist in solution, in colloidal form or in particulate form, the highest concentrations of which are found near the water's surface.[8] The route from the water surface to its eventual incorporation into the sediment varies for each form (left). The organic matter is subjected to various chemical and biologic processes as it descends through the water column to the water/sediment interface.

Oxygen in the water column supports biologic productivity of organic matter but also promotes biodegradation and oxidation. The matter can also be altered by physical abrasion or chemical changes in water Eh and pH.[9] Once this matter settles to the bottom, bacteria, worms and other bottom feeders take in what they can metabolize, converting some of it to simple molecules. The net result of biodegradation and oxidation is a reduction in organic richness, leaving only relatively resistant organic materials to be incorporated into the sediment.

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4. For more on petroleum systems: Al-Hajeri MM, Al Saeed M, Derks J, Fuchs T, Hantschel T, Kauerauf A, Neumaier M, Schenk O, Swientek O, Tessen N, Welte D, Wygrala B, Kornpihl D and Peters K: "Basin and Petroleum System Modeling," *Oilfield Review* 21, no. 2 (Summer 2009): 14–29.
5. It is not unusual for source rocks that are exploited for their shale gas to also be effective sources of conventional hydrocarbons in other parts of the basin.
6. For more on oil shales: Allix P, Burnham A, Fowler T, Herron M, Kleinberg R and Symington B: "Coaxing Oil from Shale," *Oilfield Review* 22, no. 4 (Winter 2010/2011): 4–15.
7. Jacobson, SR: "Petroleum Source Rocks and Organic Facies," in Merrill RK (ed): *Source and Migration Processes and Evaluation Techniques*. Tulsa: AAPG (1991): 3–11.
8. Barker C: *Organic Geochemistry in Petroleum Exploration*. Tulsa: American Association of Petroleum Geologists, AAPG Course Note Series no. 10, 1997.
9. Jacobson, reference 7.
   Eh is a measure of the oxidation-reduction state of a solution; pH is a measure of its acidity or alkalinity.
10. Demaison GJ and Moore GT: "Anoxic Environments and Oil Source Bed Genesis," *AAPG Bulletin* 64, no. 8 (August 1980): 1179–1209.
11. Jacobson, reference 7.
12. Palacas JG: "Characteristics of Carbonate Source Rocks of Petroleum," in Magoon LB (ed): *Petroleum Systems of the United States*. US Geological Survey Bulletin 1870. Washington, DC: US Government Printing Office (1988): 20–25.
13. Jones RW: "Comparison of Carbonate and Shale Source Rocks," in Palacas JG (ed): *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*. Tulsa: The American Association of Petroleum Geologists, AAPG Studies in Geology 18 (1984): 163–180.
14. Macerals are microscopically recognizable constituents of organic matter found in coals and kerogen, analogous to mineral constituents in a rock.
15. Tissot B, Durand B, Espitalié J and Combaz A: "Influence of Nature and Diagenesis of Organic Matter in Formation of Petroleum," *AAPG Bulletin* 58, no. 3 (March 1974): 499–506.
16. Klemme HD and Ulmishek GF: "Effective Petroleum Source Rocks of the World: Stratigraphic Distribution and Controlling Depositional Factors," *AAPG Bulletin* 75, no. 12 (December 1991): 1809–1851.
17. Vandenbroucke M: "Kerogen: From Types to Models of Chemical Structure," *Oil & Gas Science and Technology—Revue de l'Institut Français du Pétrole* 58, no. 2 (2003): 243–269.
18. Tissot et al, reference 15.

^ Undisturbed sediments. Fine laminations, or varves, in this core sample denote successive deposits in quiet waters with no disturbance from bottom dwellers.

Kerogen type	Source material	General environment of deposition
I	Mainly algae	Lacustrine setting
II	Mainly plankton, some contribution from algae	Marine setting
III	Mainly higher plants	Terrestrial setting
IV	Reworked, oxidized material	Varied settings

^ Kerogen types. Kerogen can be classified by its source material.

Within this depositional setting, oxygen and energy levels are perhaps the most critical aspects controlling the concentration and preservation of organic matter in the sediment. Oxygen-depleted, or anoxic, sediments provide the best media for preserving organic matter. Low oxygen levels create a reducing environment that shelters organic material from oxidation while also restricting the activity of bottom feeders. Anoxic conditions are evidenced by source rocks that have minute laminations, or varves (above). These features are indicative of persistent, stagnant anoxic water above the sediment, as well as an absence of bioturbation, thus implying a hostile environment for sediment-churning bottom feeders that graze on organic matter.[10] These conditions are also closely linked with low-energy depositional environments.

Because quiet waters reduce the exchange of oxygen and organic matter, they create an environment in which anoxic conditions can exist. These low-energy environments permit the deposition of finer-grained sediments as well. Thus, there is a relationship between grain size and organic content in source rocks. Source rocks do not form in high-energy environments—such as beaches or sand bars—where sands are typically deposited.[11] Wave action oxygenates the deposit and flushes clay-sized materials and small particles of organic material away from the sands then deposits them together in quieter waters. Sands, therefore, generally contain only small amounts of organic matter relative to shales.

Mineralogy also plays an integral role in source rock development. Minerals, transported and precipitated in the sediment, can react with organic compounds and ultimately dilute the relative concentration of organic matter within the sediment. This dilution may affect a source rock's capacity to generate and expel petroleum. Although many organic-rich source rocks are argillaceous, carbonates (typically marls) can also make excellent source rocks and reservoirs. Some carbonates may contain as much as 10% to 30% total organic carbon (TOC), unlike shales, which may contain less than 5%.[12]

In general, quality source rocks—whether carbonate or shale—share a number of common characteristics. They form in anoxic, or highly reducing, environments, are generally laminated, have moderate to high TOC and contain organic matter exemplified by atomic hydrogen/carbon ratios exceeding 1.2.[13]

Although deposited under anoxic conditions, these fine-grained, organic-rich sediments are still missing a critical component: thermally mature kerogen. The formation of mature kerogen requires heat.

Thermal Transformations

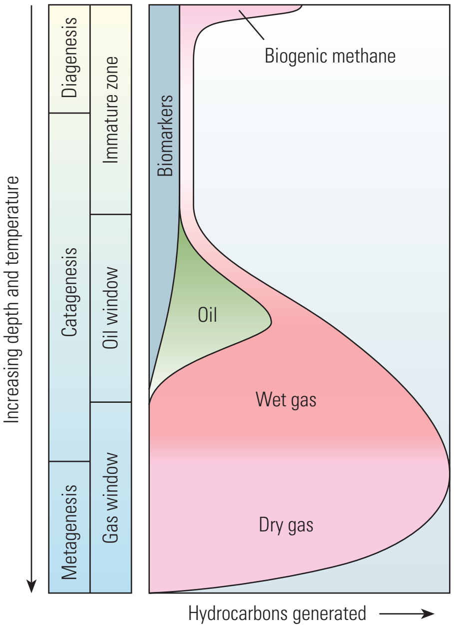
Sediment slowly cooks as pressure and temperature increase with burial depth. Given sufficient heat, pressure and time, the sediment lithifies and the organic matter contained within transforms into kerogen. Kerogen can be classified into four types, based on provenance, as indicated by specific macerals (above right).[14] It can also be classified on the basis of hydrogen, carbon and oxygen content. Each type has a distinct bearing on what kind of petroleum, if any, will be produced.[15]

Type I kerogen is generated predominantly from lacustrine environments and, in some cases, marine environments. It is derived from algae, plankton or other matter that has been strongly reworked by bacteria and microorganisms living in the sediment. Rich in hydrogen and low in oxygen, it is oil prone but, depending on its stage of thermal evolution, can also produce gas. Responsible for less than 3% of the world's oil and gas reserves, Type I kerogens are not common.[16] An example of Type I kerogen is found in the Green River Formation of the western USA.

Type II kerogen is typically generated in reducing environments found in moderately deep marine settings. It is derived primarily from the remains of plankton that have been reworked by bacteria. Rich in hydrogen and low in carbon, this kerogen can generate oil or gas with progressive heating and maturation.[17] Renowned examples of Type II kerogen include the Kimmeridge Clay of the North Sea and the Bazhenov Formation of Siberia. Certain depositional environments promote increased incorporation of sulfur compounds, resulting in a variation known as Type II-S kerogen. This variation is seen in the Monterey Formation of California, or the La Luna Formation of Venezuela. The significance of this type is that generation of oil starts much earlier, thought to be caused by kinetic reactions involving sulfur-bearing compounds.

Type III kerogen is derived primarily from terrigenous plant debris, which has been deposited in shallow to deep marine or nonmarine environments. Type III kerogen has lower hydrogen and higher oxygen content than Types I or II; consequently, it tends to generate dry gas. Most coals contain Type III kerogens.

Type IV kerogen is derived from residual organic matter found in older sediments that have been reworked after erosion. Prior to final deposition, this kerogen may have been altered by subaerial weathering, combustion or biologic oxidation in swamps or soils. This type of kerogen has high carbon content and is hydrogen poor. Considered a form of dead carbon, Type IV kerogen has almost no potential for generating oil or gas.[18]



^ Thermal transformation of kerogen. The generation of hydrocarbons in source rocks is controlled primarily by temperature as the kerogen content evolves from reactive carbon to dead carbon. Gas is given off during early diagenesis, primarily through biologic activity. Catagenesis takes place with further burial, during which oil and gas are given off. With increasing depth and temperature, any remaining oil is cracked during metagenesis, initially giving off gas, followed by simpler forms of dry gas. The process varies somewhat from one kerogen type to another. (Modified from Tissot et al, reference 15.)

In general, hydrogen-rich kerogens are responsible for generating both oil and hydrocarbon gas; those with lesser amounts of hydrogen will generate mainly hydrocarbon gas. After hydrogen is depleted from the kerogen, generation of hydrocarbons will cease, regardless of the amount of available carbon.[19]

As temperature and pressure increase during burial, organic materials emit oil and gas. Overall, this thermal maturation process produces a series of progressively smaller hydrocarbon molecules of increasing volatility and hydrogen content, culminating with methane gas. And, as the kerogen evolves through thermal maturity, its chemical composition progressively changes, transforming it into a carbonaceous residue of decreasing hydrogen content.[20]

The thermal maturation process can be divided into three stages (above).

- Initially, the sediment is subjected to diagenesis. In its broadest sense, this term encompasses all natural changes in sediments occurring from the moment of deposition until just before the onset of significant thermal alteration processes.[21] For source rocks, however, this stage is characterized by alteration of organic matter, typically at temperatures below about 50°C [122°F].[22] During diagenesis, oxidation and other chemical processes begin to break down the material. If deposited under anoxic conditions, this material may be converted by methanogenic bacteria into dry gas.[23] With increasing temperatures and changes in pH, the organic matter is gradually converted to kerogen and, in lesser amounts, bitumen.
- The source rock matures with increasing heat, and it undergoes catagenesis. During this stage, petroleum is generated as temperature increases to between 50°C and 150°C [122°F and 302°F], causing chemical bonds to break down within the kerogen.[24] Within this oil window, Type I and II kerogens produce both oil and gas, while Type III kerogens produce mainly hydrocarbon gas. Further increases in burial depth, temperature and pressure force the source rock into the upper part of the gas window, where secondary cracking of the oil molecules produces wet gas containing methane, ethane, propane and heavier hydrocarbons.[25]
- Metagenesis marks the final stage, in which additional heat and chemical changes convert much of the kerogen into methane and a carbon residue. As the source rock moves farther into the gas window, late methane, or dry gas, is evolved, along with nonhydrocarbon gases such as carbon dioxide [CO_2], nitrogen [N_2] and hydrogen sulfide [H_2S]. These changes take place at temperatures ranging from about 150°C to 200°C [302°F to 392°F].[26]

These stages have a direct bearing on source rock maturity. Thermally immature, or potential, source rocks have been altered by diagenesis but have yet to be exposed to sufficient heat for thermally generated petroleum. Thermally mature, or effective, source rocks that are (or were) in the oil window, have been subjected to thermal processes necessary to produce petroleum and are actively generating petroleum. Thermally postmature, or spent, source rocks have entered the gas window and have already generated petroleum; in so doing they have exhausted all hydrogen necessary for further oil or gas generation.[27]

Although maturation is largely related to increasing burial depths caused by continual sedimentation within a basin, it can also be locally or regionally influenced by heat flow arising from crustal tectonics, proximity to igneous bodies and natural radioactive decay within the crust. The geologic processes that control subsidence and uplift also affect maturation within a basin. Maturation can be interrupted if the basin is subjected to uplift, only to continue when subsidence resumes.

At the depths drilled by E&P companies, the petroleum-generation process is often incomplete, leaving the source rock with a degree of generating potential.[28] Thus, rock samples obtained from the subsurface may contain generated hydrocarbons along with organic matter that is reacted incompletely. Some of these reactions can be observed and measured in the laboratory, where pyrolysis of organic matter parallels changes in the subsurface and provides a useful technique to characterize organic matter.

Basic Source Rock Analysis

Some petroleum compounds within source rock are released at temperatures lower than those needed to break down the kerogen. By monitoring the compounds released during a steady increase in temperature, geochemists can determine the amount of generated petroleum relative to a rock's total potential. In addition, the temperature corresponding to the maximum evolution of gas gives an indication of source rock maturity.

Geoscientists employ a variety of techniques to evaluate the hydrocarbon-generating capacity of source rocks. Geochemical testing of outcrop samples, formation cuttings, sidewall cores and conventional cores can help determine the amount, type and thermal maturity of organic matter present in the rock.[29] The results help geoscientists ascertain whether, how much, when and what kind of petroleum might have been generated as well as determine what secondary processes may have occurred following the expulsion of hydrocarbons from the source rock.

Carbon is an essential element of any organic compound, and one way to assess the organic richness of a rock is to measure its carbon content.[30] Because the oil or gas potential of a formation is related to its carbon content, the TOC measurement is a priority in source rock assessment. This initial carbon assessment is followed by other screening procedures such as pyrolysis and vitrinite reflectance analysis. These tests allow rapid evaluations for large numbers of rock samples and may be supplemented by more extensive test methods.

TOC values can be obtained using a direct-combustion technique that requires only 1-g [0.0022-lbm] samples of rock.[31] The samples are pulverized and treated to remove any carbon found in carbonate samples, or other contaminants. They are then combusted at 1,200°C [2,192°F] using a high-frequency induction furnace. Carbon contained in the kerogen is converted to CO and CO_2. The evolved carbon fractions are measured in an infrared cell, converted to TOC and recorded as mass weight percent of rock.[32]

The TOC measurement assesses three components. Carbon from extractable organic matter (EOM) is derived mostly from the thermal cracking of kerogen. This carbon is found within the oil and gas that the rock has generated but has not yet expelled. At the other extreme is residual carbon, which makes up that portion of kerogen having no oil- or gas-generating potential because its highly condensed chemical structure contains so little hydrogen. Convertible carbon contained within the kerogen represents the remaining petroleum-generating potential of a rock. The capacity to generate petroleum depends largely on the chemical composition of this convertible carbon fraction.[33]

The TOC measurement is the first screen for quantifying organic richness. TOC values provide only a semiquantitative scale of petroleum-generating potential. TOC indicates the quantity, but not the quality, of the organic matter. If this initial screening test demonstrates sufficient organic content, the rock should undergo additional tests to ascertain organic matter quality and maturity.

One of these tests was developed by the Institut Français du Pétrole, whose Rock-Eval pyrolysis analyzer has become an industry standard in source rock assessment.[34] A major breakthrough in petroleum geochemistry, this programmed pyrolysis technique subjects rock samples to high temperatures, enabling researchers to obtain results that would have taken millions of years in a sedimentary basin. This technique requires only 100 mg [0.00022 lbm] of pulverized rock and can analyze a sample in a matter of minutes (above right). The latest version of the Rock-Eval apparatus uses both pyrolysis and oxidation ovens to heat samples in a programmed series of stages ranging from 100°C to 850°C [212°F to 1,562°F].[35] Sample analyses are automated, and results are computed before they are tabulated and output to a log.

During Rock-Eval pyrolysis, samples are heated under an inert atmosphere of helium or nitrogen. A flame ionization detector (FID) senses organic compounds emitted during each stage of heating. Sensitive infrared (IR) detectors

^ Pyrolyzer. This Rock-Eval 6 pyrolysis analyzer records gases evolved from the source rock during a programmed heating process. (Photograph courtesy of Vinci Technologies SA.)

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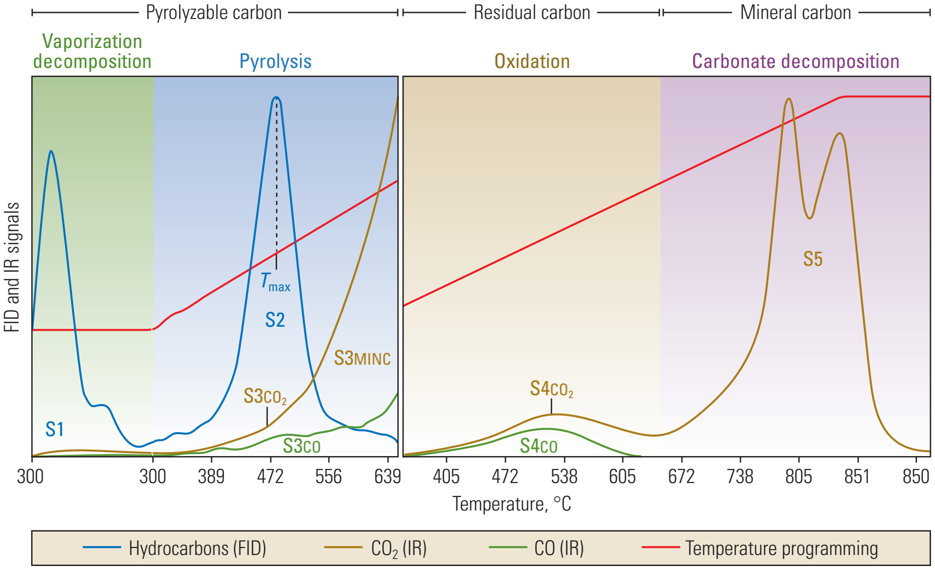
19. Baskin DK: "Atomic H/C Ratio of Kerogen as an Estimate of Thermal Maturity and Organic Matter Conversion," *AAPG Bulletin* 81, no. 9 (September 1997): 1437–1450.
20. Hood A, Gutjahr CCM and Heacock RL: "Organic Metamorphism and the Generation of Petroleum," *AAPG Bulletin* 59, no. 6 (June 1975): 986–996.
21. For more on diagenesis: Ali SA, Clark WJ, Moore WR and Dribus JR: "Diagenesis and Reservoir Quality," *Oilfield Review* 22, no. 2 (Summer 2010): 14–27.
22. Peters et al, reference 2.
23. Rice DD and Claypool GE: "Generation, Accumulation, and Resource Potential of Biogenic Gas," *AAPG Bulletin* 65, no. 1 (January 1981): 5–25.
24. Peters et al, reference 2.
25. Cracking is a process in which high temperature and pressure act upon large, heavy hydrocarbon molecules, causing them to split into smaller, lighter components. Under such conditions, oil can be transformed into a gas.
26. Peters et al, reference 2.
27. Peters KE and Cassa MR: "Applied Source Rock Geochemistry," in Magoon LB and Dow WG (eds): *The Petroleum System—From Source to Trap.* Tulsa: The American Association of Petroleum Geologists, AAPG Memoir 60 (1994): 93–120.
28. Barker C: "Pyrolysis Techniques for Source-Rock Evaluation," *AAPG Bulletin* 58, no. 11 (November 1974): 2349–2361.
29. Fresh cores work best; outcrop samples tend to be degraded through weathering and are less desirable.
30. By definition, organic compounds are those that contain carbon (with the exception of carbides, carbonic acid, carbonates, carbon oxides and cyanides). Within the realm of geochemistry, carbon is divided into a number of classes. Geochemists define organic carbon as that which is derived from biogenic matter, whereas inorganic carbon is derived from mineral matter. For more on the organic carbon model: Jarvie DM: "Total Organic Carbon (TOC) Analysis," in Merrill RK (ed): *Source and Migration Processes and Evaluation Techniques*. Tulsa: AAPG (1991): 113–118.
31. For a description of other techniques used for measuring TOC, see Appendix C of Peters and Cassa, reference 27.
32. A TOC of 1% means there is 1 gram of organic carbon in 100 grams of rock.
33. Jarvie, reference 30.
34. Pyrolysis involves heating of organic matter in the absence of oxygen. In this application, pyrolysis causes hydrocarbons to crack into simpler, lighter compounds. For more on this technique: Espitalié J, Madec M, Tissot B, Mennig JJ and Leplat P: "Source Rock Characterization Method for Petroleum Exploration," paper OTC 2935, presented at the Ninth Annual Offshore Technology Conference, Houston, May 2–5, 1977.
35. Other variations on this method use different temperature ranges and heating times. For more on the Rock-Eval 6 technique: Lafargue E, Espitalié J, Marquis F and Pillot D: "Rock-Eval 6 Applications in Hydrocarbon Exploration, Production and in Soil Contamination Studies," *Oil & Gas Science and Technology—Revue de l'Institut Français du Pétrole* 53, no. 4 (July–August 1998): 421–437.



^ Programmed pyrolysis results. Free hydrocarbons are measured by the S1 peak, and residual hydrocarbons are measured by the S2 peak. T_{max} of 472°C [882°F] corresponds to the temperature recorded when the S2 peak was achieved. CO, CO_2 and mineral carbon components of the S3 measurement are also displayed. CO_2 is proportional to the amount of oxygen present in organic matter and provides input for calculating an important index used in determining maturity and kerogen type. Pyrolysis results are computed to determine amounts of pyrolyzable carbon, residual carbon, mineral carbon and TOC. (Illustration courtesy of Vinci Technologies SA.)

measure CO and CO_2 during pyrolysis and oxidation. A thermocouple monitors temperatures. These measurements are recorded on a chart known as a pyrogram (above). The results help geochemists characterize the type of organic matter in a source rock and determine the thermal evolution of a sample and its residual hydrocarbon-generating potential.[36]

Rock samples are heated in stages, initially held at a constant 300°C [572°F] for several minutes, followed by programmed heating at 25°C [45°F] per minute to a peak temperature of about 850°C [1,562°F]. During the first stage, any free oil and gas previously generated by the bitumen are distilled and released from the rock. During the next stage, hydrocarbon compounds are generated through thermal cracking of the insoluble kerogen. As temperatures rise, the kerogen releases CO_2 in addition to hydrocarbons.[37] This controlled heating program is illustrated by a series of peaks on the pyrogram.[38]

The first peak, S1, corresponds to free oil and gas that evolve from the rock sample without cracking the kerogen during the first stage of heating at 300°C. These hydrocarbons were generated in the subsurface but came to be expelled from the rock only during pyrolysis. S1 represents how many milligrams of free hydrocarbons can be thermally distilled out of one gram of the sample.[39]

The second peak, S2, corresponds to the hydrocarbons that evolve from the sample during the second programmed heating stage of pyrolysis. These hydrocarbons result from the cracking of heavy hydrocarbons and from the thermal breakdown of kerogen. S2 represents milligrams of residual hydrocarbons in one gram of rock, thus indicating the potential amount of hydrocarbons that the source rock might still produce if thermal maturation continues. This reading can have important implications for the evaluation of oil shales.

The Rock-Eval technique yields a variety of CO_2 measurements. The S3 peak corresponds to CO_2 that is evolved from thermal cracking of the kerogen during pyrolysis, expressed in milligrams per gram of rock. Following pyrolysis, residual organic carbon is oxidized in a separate oven to produce the S4 peak. The S4 measurement can be broken down into carbon dioxide and carbon monoxide components to yield the $S4CO_2$ and S4CO peaks. A separate CO_2 peak, designated S5, reflects carbon dioxide derived from decomposition of carbonate minerals in the sample.

Pyrolysis temperatures are also recorded and produce a T_{max} peak that corresponds to the pyrolysis oven temperature during maximum generation of hydrocarbons. T_{max} is reached during the second stage of pyrolysis, when cracking of the kerogen and heavy hydrocarbons produces the S2 peak.[40] Knowing the amount of heat necessary to create various chemical compounds in the rock can help geochemists understand the history of the rock and the extent of thermal maturation it has already undergone. T_{max} should not be confused with geologic temperatures, but it can be useful in characterizing thermal evolution of the organic matter.

Source rock quality	TOC, %	Pyrolysis S2, mg hydrocarbons/g rock	EOM weight, %	Hydrocarbons, ppm
None	< 0.5	< 2	< 0.05	< 200
Poor	0.5 to 1	2 to 3	0.05 to 0.1	200 to 500
Fair	1 to 2	3 to 5	0.1 to 0.2	500 to 800
Good	2 to 5	5 to 10	> 0.2	> 1,200
Very good	> 5	> 10		

Product type	Hydrogen index
Gas	50 to 200
Gas and oil	200 to 300
Oil	> 300

Stage	T_{max}
Onset of oil	
Type I kerogen	~445°C
Type II kerogen	~435°C
Type III kerogen	~440°C
Onset of gas	~460°C

^ Source rock evaluation criteria. Evaluation of source rock potential must be based on the appraisal of multiple factors.

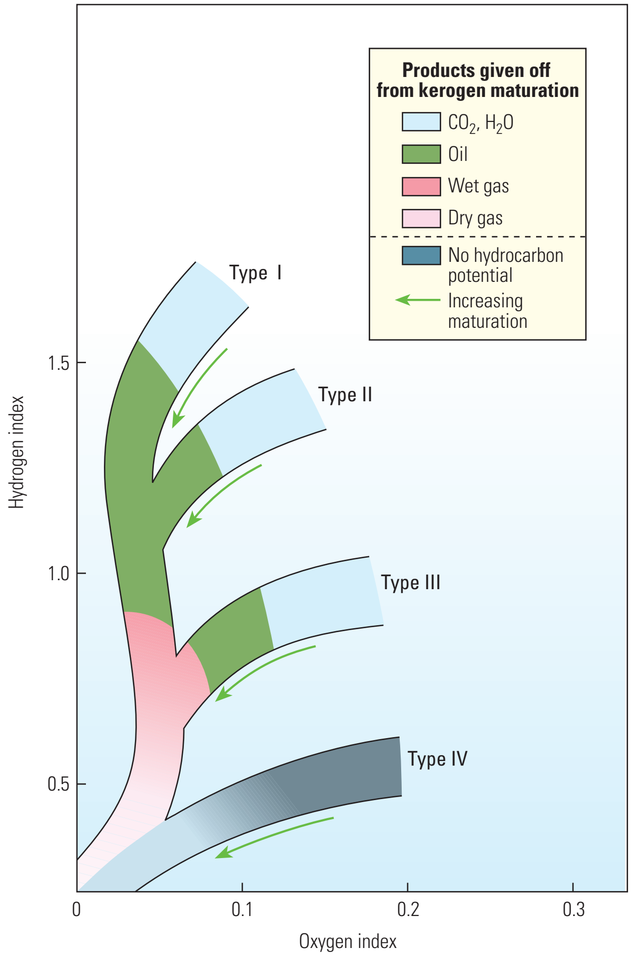
Important Indices

Taken together, these pyrolysis measurements provide insight into the chemical makeup and maturity of the organic matter contained within the source rock (previous page, bottom left). The relationship between these components forms the basis for various indices used in the interpretation of rock characteristics.[41]

- The hydrogen index, HI, is derived from the ratio of hydrogen to TOC; it is defined as 100 × S2/TOC. The HI is proportional to the amount of hydrogen contained within the kerogen, and high HI indicates a greater potential to generate oil. Kerogen type can be inferred from this index as well.
- The oxygen index, OI, is derived from the ratio of CO_2 to TOC; it is defined as 100 × S3/TOC. The OI is related to the amount of oxygen contained in the kerogen and can be useful in tracking kerogen maturation or type.
- The production index, PI, is derived from the relationship between hydrocarbons generated during the first and second stages of pyrolysis; it is defined as S1/(S1 + S2). This relationship is used to characterize the evolution of the organic matter because PI tends to gradually increase with depth for fine-grained rock. It also tends to increase with source rock maturation prior to hydrocarbon expulsion, as thermally degradable components in kerogen are converted to free hydrocarbons. Anomalously high values of S1 and PI can also be used to identify petroleum accumulations or stained carrier beds.
- The petroleum potential represents the maximum quantity of hydrocarbons that a sufficiently matured source rock might generate; it is defined as the sum of S1 + S2. It therefore accounts for the quantity of hydrocarbons that the rock has already generated (S1) and those that the rock could still produce if maturation continues (S2). It is expressed as kilograms of hydrocarbons per metric ton of rock.

These indices are particularly useful in tracking kerogen type and maturation. When plotted on a Van Krevelen diagram, Type I kerogens have a high HI and low OI (right). Type III kerogens are characterized by low HI and high OI. Between these two extremes lie the Type II kerogens. During maturation, the OI tends to decrease while HI initially remains nearly constant. As the kerogen enters the oil window, HI decreases. PI tends to increase with burial depth.[42] This type of information provides geochemists with valuable clues for evaluating a rock's potential for oil and gas generation by determining the quantity, type and maturation of organic matter.

The power of Rock-Eval and TOC analyses in wellbores is a direct function of close sample spacing, thus requiring samples at every 10 m [33 ft] of depth, regardless of lithology.[43] However, pyrolysis is not intended for use without supporting geochemical analysis. For critical samples, interpretations from pyrolysis results should be verified by other methods.



^ Kerogen maturation. A modified Van Krevelen diagram shows changes to kerogen brought on by increased heat during burial. The general trend in the thermal transformation of kerogen to hydrocarbon is characterized by generation of nonhydrocarbon gases; it then progresses to oil, wet gas and dry gas. During this progression, the kerogen loses oxygen primarily as it gives off CO_2 and H_2O; later, it begins to lose more hydrogen as it evolves hydrocarbons.

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36. Espitalié J and Bordenave ML: "Rock-Eval Pyrolysis," in Bordenave ML (ed): *Applied Geochemistry.* Paris: Éditions Technip (1993): 237–261.
37. Peters KE: "Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis," *AAPG Bulletin* 70, no. 3 (March 1986): 318–329.
38. Early papers sometimes referred to these peaks as P1, P2 and P3. For example, Espitalié et al, reference 34, distinguished between the P1, P2 and P3 peaks and the area beneath each peak, designated as S1, S2 and S3, respectively. However, modern pyrolysis analyzers automatically calculate these areas and annotate them on the pyrogram, and the peaks are now commonly referred to as S1, S2 and S3.
39. Espitalié et al, reference 34.
40. Peters and Cassa, reference 27.
41. Espitalié et al, reference 34.
42. Espitalié et al, reference 34.
43. Peters and Cassa, reference 27.

Vitrinite in bituminous coal. The amount of light reflected by vitrinite macerals is a key test for determining the thermal maturity of a rock. The intensity of light reflected from a sample is measured at hundreds of points along a microscopic sampling area, then a statistical analysis determines the amount of vitrinite in the sample and its thermal maturity. This photograph was taken in incident white light, with the sample in an oil immersion. [Photograph courtesy of the US Geological Survey Energy Resources Program: "2011 Photomicrograph Atlas," http://energy.usgs.gov/Coal/OrganicPetrology/PhotomicrographAtlas.aspx (accessed July 7, 2011).]

Other Evaluation Methods

Vitrinite reflectance is a key diagnostic tool for assessing maturation. Vitrinite, a maceral formed through thermal alteration of lignin and cellulose in plant cell walls, is found in many kerogens (above). As temperature increases, vitrinite undergoes complex, irreversible aromatization reactions that increase reflectance.[44] Vitrinite reflectance was first used to determine the rank, or thermal maturity, of coals. This technique is now used to help geochemists evaluate kerogen maturity over temperatures corresponding to early diagenesis through metamorphism—a range spanning the sequence of petroleum generation, preservation and destruction in rocks.[45]

Reflectivity (R) is measured by a microscope equipped with an oil-immersion objective lens and photometer.[46] Vitrinite reflectance measurements are carefully calibrated against glass- or mineral-reflectance standards, and reflectance measurements represent the percentage of light reflected in oil, designated as R_o. When a mean value of vitrinite reflectivity is determined from multiple samples, it is commonly designated as R_m.

As indicators of thermal maturity, R_o values vary with the type of organic matter. And because the temperature range of the gas window extends beyond that of oil, R_o values for gas will show a corresponding increase over those of oil. Thus, high maturation values ($R_o > 1.5\%$) generally indicate the presence of predominantly dry gas; intermediate maturation values ($1.1\% < R_o < 1.5\%$) indicate gas with a tendency toward oil generation at the lower end of the range. Wet gas can be found still lower in the range ($0.8\% < R_o < 1.1\%$). Lower reflectivity values ($0.6\% < R_o < 0.8\%$) indicate predominantly oil, while $R_o < 0.6\%$ points to immature kerogen.

By themselves, R_o values can sometimes be misleading and should be weighed with other measurements. Some of these measures of maturity are based on the color of ancient pollens and plant spores, or on the color of tiny fossilized teeth. Due to the prevalence of vitrinite reflectance, these indicators are often correlated to R_o values. Because vitrinite is present only in sediments younger than the Carboniferous age, which experienced the onset of woody plants, the maturity of older kerogens relies on the presence of bitumen to derive a vitrinite reflectance equivalent (VRE).

The thermal alteration index (TAI) is determined through microscopic examination of spore color.[47] Carbonization causes a change of color in palynomorphs such as spores and pollen. Thermally immature palynomorphs are yellow but change to orange or yellow-brown during diagenesis. With increased heat, they change to brown during catagenesis and then to black during metagenesis.[48] The TAI has five alteration ratings (below left).

Thermal alteration index	Color of organic matter	Associated hydrocarbons
1: none	Yellow	Liquid hydrocarbons to dry gas
2: slight	Orange to brownish yellow	Liquid hydrocarbons to dry gas
3: moderate	Brown	Liquid hydrocarbons to dry gas
4: strong	Black	Dry gas
5: severe	Black, with additional evidence of metamorphism	Dry gas to none

Thermal alteration ratings. Maturity of source rocks can be ascertained through changes in the color of spores and pollen contained in the rock. (Modified from Staplin, reference 47.)

The conodont alteration index (CAI) is based on color changes seen in fossil teeth.[49] Conodonts are tiny fossilized dental remains of eel-shaped chordates. These fossils contain trace amounts of organic matter. Their small size and carbonate-apatite composition make them highly resistant to weathering and metamorphic temperature regimes; they have even been recovered from marbles and garnet-mica schists.

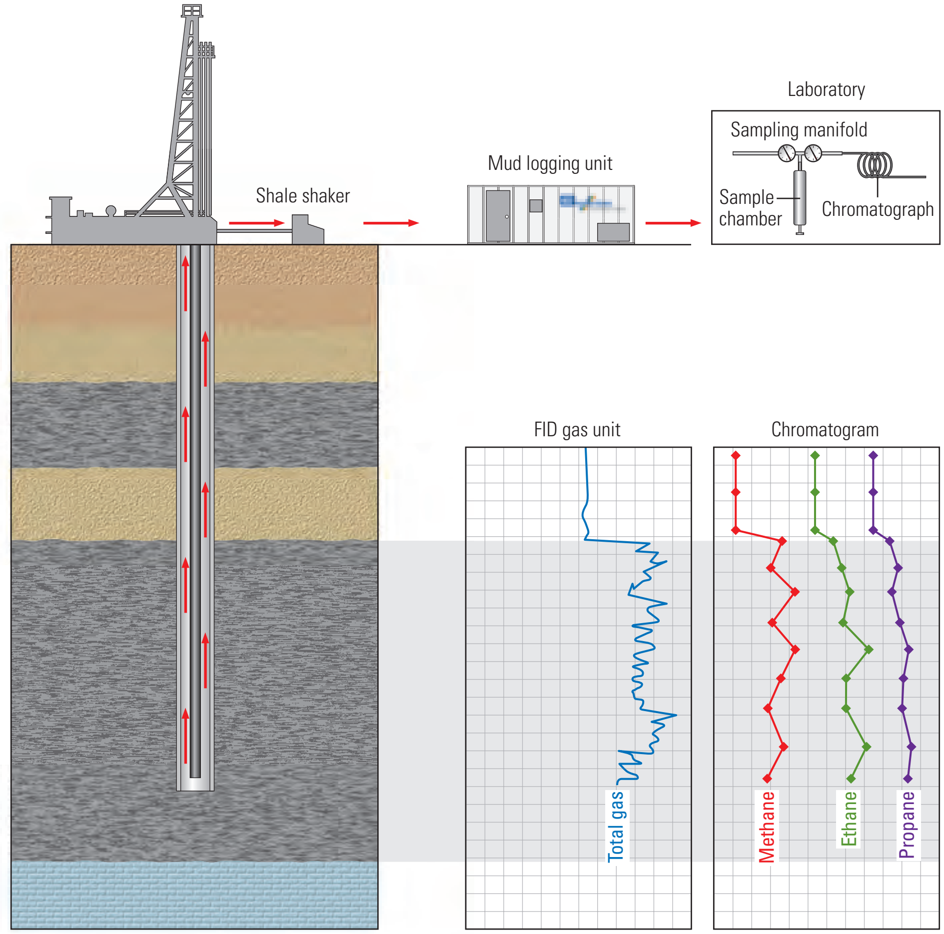
Their color alteration follows a sequence that can be reproduced by laboratory heating experiments. Conodont color alteration is time and temperature dependent, and is progressive, cumulative and irreversible, thus making it a good correlation tool for maximum temperatures.[50] Unweathered conodonts are pale yellow;

with heat they change progressively to light brown, then dark brown, black, opaque white and crystal clear. Alteration from pale yellow to black is thought to result from carbon fixing within the organic matter contained in the fossil structure. The color changes with carbon loss and release of water from the crystal structure. Experimental data show that color alteration begins at about 50°C [122°F] and continues to about 550°C [1,022°F]. The CAI can be determined by comparing samples against a set of laboratory-produced conodont color standards to estimate a temperature range. Conodont color alteration has been correlated with other optical indices and with percent fixed carbon (above right).

Another screening method measures the composition and concentration of light hydrocarbons released from drill cuttings.[51] Fine-grained formation cuttings, typical of those produced by source rocks, may retain hydrocarbons even after they arrive at the surface, making good samples for this type of analysis. This technique, known as gas chromatography, can be carried out at the wellsite or under strictly controlled conditions at a laboratory (right).

Conodont alteration index	Conodont temperature, °C	Vitrinite reflectance	Percent fixed carbon
1	< 50 to 80	< 0.80	< 60
1.5	50 to 90	0.70 to 0.85	60 to 75
2	60 to 140	0.85 to 1.30	65 to 73
3	110 to 200	1.40 to 1.95	74 to 84
4	190 to 300	1.95 to 3.60	84 to 95
5	300 to 400	> 3.60	> 95

^ Conodont alterations. Conodonts change color with heat; their color can be linked to vitrinite reflectance. (Data from Harris, reference 50.)



^ Formation cuttings analysis. At the well, cuttings are collected from the drilling mud after circulating to the surface (red arrows) and passing over the shale shaker. In the mud logging unit, the cuttings are evaluated under a microscope, and mud gas is analyzed by an FID and gas chromatograph. Gas from the cuttings may also be analyzed in a laboratory. For transport to the laboratory, the cuttings are sealed in sample jars containing water. Gas expelled from the cuttings will accumulate above the liquid surface. This gas is commonly referred to as headspace gas. At the laboratory, the gas is drawn from the container then injected into the sampling port of a gas chromatograph. As the gas passes through the chromatograph's capillary column, it splits into separate compounds, with each compound taking a little longer to move through the system than its predecessor. Each compound exits the column individually, to be analyzed by an FID or other detector. The results are recorded on a chart known as a chromatogram (*bottom right*).

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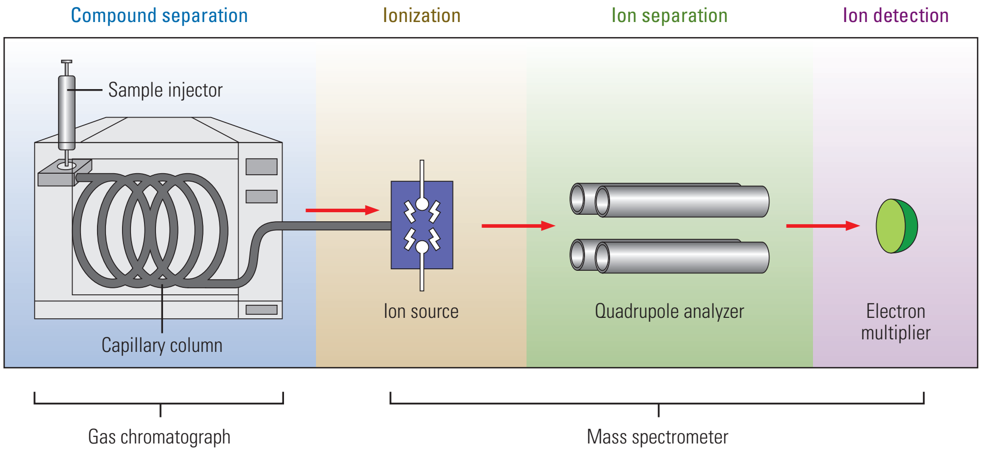
44. Peters and Cassa, reference 27.
45. Senftle JT and Landis CR: "Vitrinite Reflectance as a Tool to Assess Thermal Maturity," in Merrill RK (ed): *Source and Migration Processes and Evaluation Techniques*. Tulsa: AAPG (1991): 119–125.
46. The terms reflectance and reflectivity tend to be used interchangeably, with the former being more common. However, reflectance is a ratio of the light reflected from a surface to the light directed onto that surface—the ratio of reflected radiation to incident radiation. This value can change, up to a point, depending on the thickness, and hence, opacity, of a surface. If that surface is thick enough to prevent light from being transmitted through the surface, then reflectance reaches a maximum. This is the reflectivity of a surface.
47. The TAI is set forth in Staplin FL: "Sedimentary Organic Matter, Organic Metamorphism, and Oil and Gas Occurrence," *Bulletin of Canadian Petroleum Geology* 17, no. 1 (March 1969): 47–66.
48. Anders D: "Geochemical Exploration Methods," in Merrill RK (ed): *Source and Migration Processes and Evaluation Techniques*. Tulsa: AAPG (1991): 89–95.
49. Found in Late Cambrian and Triassic formations, conodonts were long suspected of being fossilized teeth. In the early 1990s, this supposition was verified through the aid of electron microscopy. For more on conodont research: Zimmer C: "In the Beginning Was the Tooth," *Discover* 14, no. 1 (January 1993): 67–68.
50. Harris AG: "Conodont Color Alteration, An Organo-Mineral Metamorphic Index, and Its Application to Appalachian Basin Geology," in Scholle PA and Schluger PR (eds): *Aspects of Diagenesis*. Tulsa: Society of Economic Paleontologists and Mineralogists, SEPM Special Publication 26 (1979): 3–16.

    For the seminal paper on CAI, see: Epstein AG, Epstein JB and Harris LD: "Conodont Color Alteration—An Index to Organic Metamorphism," Washington, DC: US Government Printing Office, US Geological Survey Professional Paper 995, 1977.
51. Noble RA: "Geochemical Techniques in Relation to Organic Matter," in Merrill RK (ed): *Source and Migration Processes and Evaluation Techniques*. Tulsa: AAPG (1991): 97–102.



^ Biomarker analysis. Biomarker carbon structures are directly related to precursor molecules of specific biological substances. The smallest markers are found at a molecular level and can only be determined through GCMS. With this method, separate compounds are drawn through the gas chromatograph capillary column then pass to an ionizer. There, a metallic filament ionizes each compound. The quadrupole analyzer filters the ions based on their mass/charge ratio. The electron multiplier detects every ion of the selected mass filtered through the quadrupole analyzer.

A gas chromatograph evaluates gas liberated during the drilling process and records individual peaks for methane (C_1), ethane (C_2), propane (C_3), isobutane (iC_4) and normal butane (nC_4); a single peak is typically recorded for pentanes (iC_5 and nC_5) and heavier hydrocarbons (C_{5+}). Determining the composition and concentration of these gases helps geoscientists evaluate the types of hydrocarbons that may be produced within a prospective reservoir.

Gas chromatography (GC), when supplemented by mass spectrometry (MS), can provide a detailed analysis of organic compounds found in trace amounts (above). Geochemists commonly use this technique, referred to as GCMS, for identifying the masses and relative concentrations of organic compounds known as biological markers. Biomarkers constitute molecular fossils and are synthesized only through biogenic processes.[52] Their organic structures can be classified into basic groups, which, in turn, contain members having variations of the same basic structure. These groups can be related to certain types of organisms and can help geochemists ascertain the environment in which such an assemblage might have been deposited.

Biomarker compositions reflect the type of organic matter incorporated into the sediment as well as chemical changes that occurred subsequent to deposition. The combination of precursor molecules and their chemical reactions varies from one basin or field to another, producing a biomarker distribution that can be unique to a particular location. By comparing oil to samples of potential source rock, this chemical fingerprint can help link oil to its source.[53] Because biomarker patterns tend to change systematically with respect to time and temperature, they can help geochemists infer maturation trends.

When potential source rocks have not been encountered in a basin, indirect correlations between oil and source rock may be obtained through source-related biomarker ratios.[54] These biomarker ratios help geochemists infer source rock thermal maturity, lithology, depositional environment, organic matter input and age. For example, the biomarkers contained in a specific crude oil might indicate that its source rock was a marginally mature, clay-poor marine carbonate of Devonian age that contained algal and bacterial organic matter deposited under anoxic conditions. Biomarkers can also supplement maturity indicators such as vitrinite reflectance and spore coloration.[55]

Beyond the Basic Toolkit

Though source rocks have been studied extensively for the past 50 years, the recent move to exploit plays centered on gas shales and oil shales has spurred a resurgence of geochemical research and development. This resurgence has prompted expanded utilization of established techniques as well as the development of new tools.

The past decade, in particular, has seen a renaissance in petroleum system modeling tools. Source rock kinetics, a key input for these models, characterizes the chemical reactions and petroleum compounds generated during thermal maturation of a rock. Two pyrolysis techniques that have proved useful in simulating maturation processes are microscale sealed vessel and gold tube confined pyrolysis.[56] Using these techniques, scientists are able to scrutinize processes such as oil-to-gas cracking (OTGC), in which application of temperatures greater than 150°C causes existing oil to break down into gas. OTGC investigations have, in turn, led to the tracking of thermally resistant carbon molecules, known as diamondoids, for determining how gas is generated from oil under high-temperature conditions.[57]

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[52] Noble, reference 51.

[53] This type of geochemical fingerprint can also be used to compare one oil to another; it has proved useful in tracking "mystery" oil slicks at sea to the vessels responsible for discharging oil wastes.

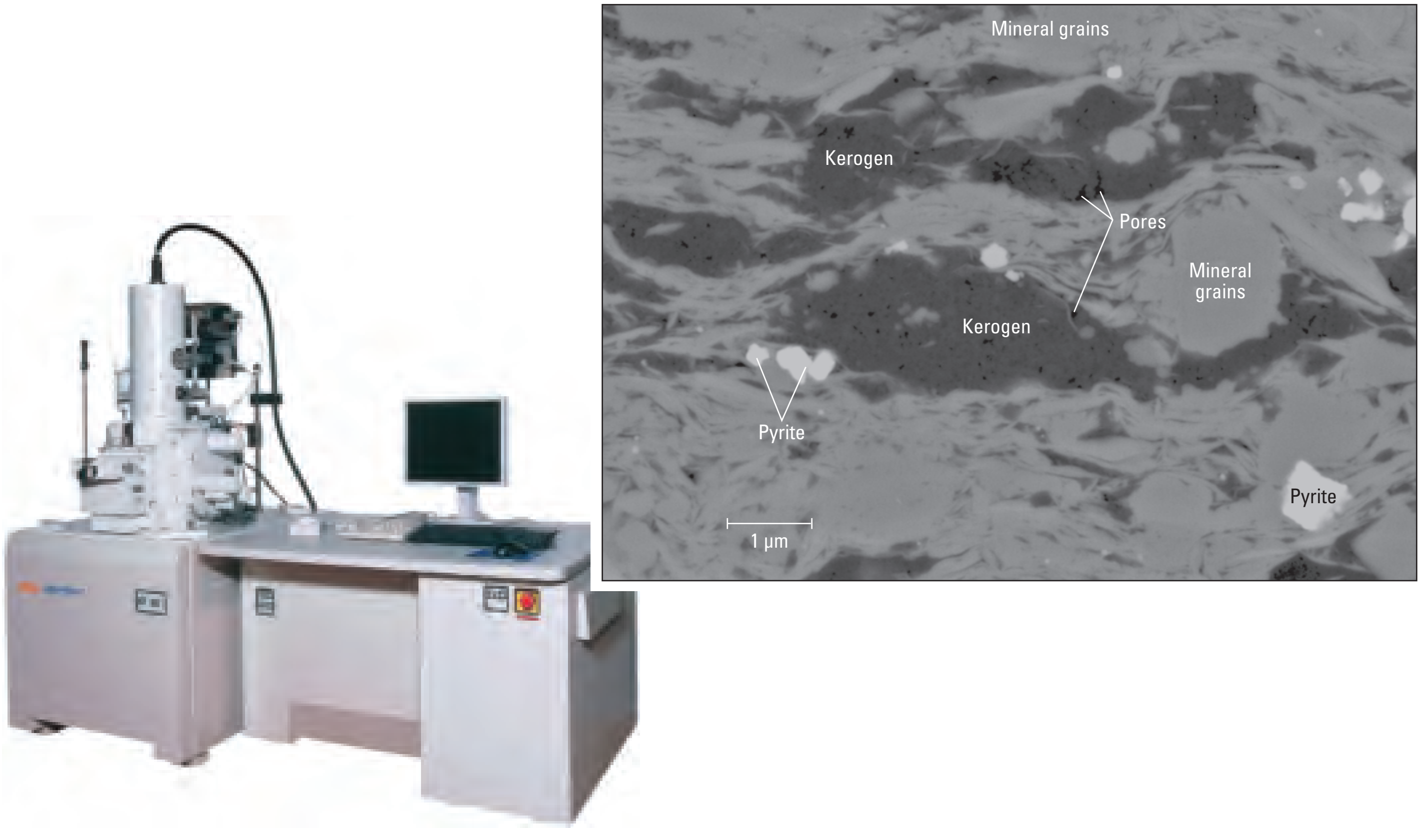
[54] Peters KE and Fowler MG: "Applications of Petroleum Geochemistry to Exploration and Reservoir Management," *Organic Geochemistry* 33, no. 1 (2002): 5–36.

[55] Noble, reference 51.

[56] Horsfield B, Disko U and Leistner F: "The Micro-Scale Simulation of Maturation: Outline of a New Technique and Its Potential Applications," *Geologische Rundshau* 78, no. 1 (1989): 361–374.

Hill RJ, Tang Y, Kaplan IR and Jenden PD: "The Influence of Pressure on the Thermal Cracking of Oil," *Energy & Fuels* 10, no. 4 (1996): 873–882.

[57] Dahl JE, Moldowan JM, Peters KE, Claypool GE, Rooney MA, Michael GE, Mello MR and Kohnen ML: "Diamondoid Hydrocarbons as Indicators of Natural Oil Cracking," *Nature* 399, no. 6731 (May 6, 1999): 54–57.



^ Scanning electron microscope with a backscatter image of a Barnett Shale sample at 1,000× magnification. In the shale sample (*right*), amorphous organic matter (dark gray), consisting primarily of kerogen is seen as large continuous lenses or small, finely dispersed packets interwoven in a complex mineral matrix (lighter gray components). Pyrite, a product of shale thermochemical maturation, is also present (small white crystals). Pores of varying size and shape (small black spots) can be seen in both the kerogen and mineral components, but are more prevalent in the former. The sample was milled using an argon ion polisher then imaged using a scanning electron microscope (*left*) to reveal the complex organic-mineral-pore architecture characteristic of such mudrock deposits. (Graphic courtesy of Nicholas Drenzek, Schlumberger-Doll Research Center and Natasha Erdman, JEOL USA, Inc.)

The analysis of stable isotopes of carbon and other elements such as hydrogen, oxygen or sulfur is also seeing increased application in organic geochemistry. Recent observations of ethane carbon isotopes have led to interesting correlations between dry gas and overpressured zones within gas shales. Isotope plots show a rollover, or reversal, in maturity that runs contrary to trends normally tied with depth. The origin of these reversals is unknown, but a trend toward high production rates has been observed in wells that exhibit rollover.

Scientists are also focusing on the physical structure of kerogen within the mineral matrix of source rocks. The formation of secondary permeability and porosity in organic-rich shales during in situ maturation is believed to be a key enabler for production of shale gas in many source rocks (above). Organic petrography, utilizing basic and advanced microscopy techniques to focus on organic matter, is therefore seeing a revival in kerogen evaluation.

Beyond the laboratory, new techniques for monitoring gases encountered during drilling are helping geoscientists determine the composition of hydrocarbons, locate fluid contacts and aid in the identification of compositional gradients in reservoirs. The FLAIR fluid logging and analysis service extracts gas from drilling mud under constant pressure, flow, volume and temperature conditions. Part of the Schlumberger Geoservices suite of mud logging services, the FLAIR system first samples gas that has been circulated to surface then separates it into individual components to provide a quantitative analysis of gases from C_1 to C_5 and semiquantitative information on the C_6 to C_8 components. Isotope analysis can provide information regarding the origins and characteristics of the hydrocarbons encountered during drilling. Using $\delta^{13}C/CH_4$ ratios, which are originally related to petroleum generation,mud logging analysts can provide E&P companies with preliminary information concerning the source rock, including its kerogen type and thermal maturity.

While operators devote much of their exploration efforts to studying the depositional and structural characteristics of a prospect, many are also concerned with the processes that control the formation of oil and gas. Geochemical reactions and the conversion of organic matter are integral to petroleum generation; the characterization of organic matter, in turn, is becoming increasingly critical for the development of new plays. These tools are proving instrumental in opening new frontiers of exploration. —MV