Applied Source Rock Geochemistry

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Abstract

Applied organic geochemistry provides the information needed to make maps of the richness, type, and thermal maturity of a source rock. These maps are a necessary step toward determining the stratigraphic and geographic extent of a pod of active source rock in a petroleum system, and they are based on geochemical analyses of rock samples from outcrops and wells that are displayed on logs. These geochemical well logs are based on Rock-Eval pyrolysis, total organic carbon, vitrinite reflectance, and other rapid, inexpensive "screening" methods. The logs define (1) potential, effective, and spent petroleum source rock; (2) the thermal maturation gradient, including immature, mature, and postmature zones, and (3) in situ and migrated petroleum shows. Useful geochemical logs require proper sample selection, preparation, analysis, and interpretation. Useful studies, including oil-source rock correlations by biomarker and supporting techniques, are undertaken on selected samples only after the screening methods are completed.

INTRODUCTION

The goal of this chapter is to show how geochemical "screening" technology is applied to petroleum exploration. This chapter provides a conceptual framework for later discussions in this book by defining key terms used to describe source rock characteristics and reviewing principles and recent developments in source rock geochemistry. Major emphasis is placed on (1) criteria for sampling, preparation, and analysis of rocks and oils; (2) geochemical logs; and (3) geochemical maps.

The main contribution of organic geochemistry to sedimentary basin analysis is to provide analytical data to identify and map source rocks. These maps include the richness, type, and thermal maturity of a source rock and are a necessary step toward determining the stratigraphic and geographic extent of a pod of active source rock in a petroleum system. The volume, richness, and thermal maturity of this pod of active source rock determines the amount of oil and gas available for traps. Because of this, maps that show the pod of active source rock reduce exploration risk (e.g., Demaison, 1984).

Geochemical well logs are essential for mapping active source rocks. These logs plot various geochemical parameters versus depth and can be made from surface sections and during or after drilling. Certain criteria that are largely omitted from the literature must be met to ensure useful geochemical logs. These criteria include well site sampling, type of samples (core, sidewall, cuttings), sample spacing, sample preparation procedures, and methods of analysis and interpretation.

SOURCE ROCK PROPERTIES AND TERMS

Sedimentary rocks commonly contain minerals and organic matter with the pore space occupied by water, bitumen, oil, and/or gas. Kerogen is the particulate fraction of organic matter remaining after extraction of pulverized rock with organic solvents. Kerogen can be isolated from carbonate- and silicate-bearing rocks by treatment with inorganic acids, such as HCl and HF (e.g., Durand, 1980). This is only an operational definition because the amount and composition of insoluble organic matter or kerogen remaining after extraction depends on the types and polarities of the organic solvents. Kerogen is a mixture of macerals and reconstituted degradation products of organic matter. Macerals are the remains of various types of plant and animal matter that can be distinguished by their chemistry and by their morphology and reflectance using a petrographic microscope (Stach et al., 1982). This term was originally applied to components in coal but has been extended to sedimentary rocks. Palynomorphs are resistant, organic-walled microfossils such as spores, pollen, dinoflagellate cysts, and chitinozoa.

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Bitumen in rocks is that fraction of the organic matter that is soluble in organic solvents. Small amounts of bitumen originate from lipid components in once-living organisms, but most is generated by cracking (thermal dissociation) of the kerogen. Lipids are oil-soluble, water-insoluble organic compounds, including fats, waxes, pigments, steroids, and terpenoids, that are major precursors for petroleum (Peters and Moldowan, 1993).

Petroleum is a complex mixture of gas, liquid, and solid hydrocarbons and nonhydrocarbons occurring naturally in the earth (Magoon and Dow, Chapter 1, this volume). The term hydrocarbon is commonly used in the petroleum industry to indicate crude oil or natural gas. In the chemical sense, hydrocarbons are compounds containing only carbon and hydrogen. Nonhydrocarbons contain elements in addition to hydrogen and carbon. For example, NSO compounds contain nitrogen, sulfur, or oxygen, and porphyrins contain metals such as vanadium or nickel. For this volume, petroleum, oil, and gas, and hydrocarbons, used without modifiers, have similar meanings.

Depositional Environment

Descriptions of oils or source rocks using the terms marine or terrigenous are unclear without specifying whether these terms refer to provenance (origin) or depositional environment. Geochemists commonly use these terms to refer to organic matter derived from marine and land plants, respectively, whereas geologists usually refer to marine or terrigenous depositional environments. For example, when geologists refer to a "marine" sedimentary rock, they are discussing depositional environment, not provenance of the mineral grains. Likewise, a geologist might equate a marine source rock with marine depositional conditions, although the included organic matter or kerogen might be of marine, terrigenous, or mixed origin. For similar reasons, the meaning of the terms marine oil, lacustrine oil, or terrigenous oil is unclear without further explanation. Misunderstandings can occur because a marine oil might be (1) generated from land plant organic matter deposited in a marine environment, (2) generated from marine organic matter, or (3) produced from a reservoir rock deposited in a marine environment. Rather than just "marine" oil, it must be specified whether the oil is derived from a source rock deposited under marine conditions or from marine organic matter.

Various factors play a role in the preservation of organic matter, notably the oxygen content of the water column and sediment (oxic versus anoxic), primary productivity of new organic matter by plants, water circulation, and sedimentation rate (Demaison and Moore, 1980; Emerson, 1985).

For ancient sediments, the oxygen content of the overlying water column is unknown, but it can be interpreted from the presence or absence of laminated or bioturbated sediments and organic matter content in the sediment (Demaison and Moore, 1980). The oxygen content of water is determined by availability and solubility of oxygen (which depends upon the temperature, pressure, and salinity). Oxic water (saturated with oxygen) contains 8.0–20.0 mL O₂/L H₂O (Tyrrell and Pearson, 1991). Dysoxic water contains 2.0–0.2 mL O₂/L H₂O, suboxic, 0.2–0.0 mL O₂/L H₂O, and anoxic water lacks oxygen. When referring to biofacies, the corresponding terms are aerobic, dysoxic, quasi-anaerobic, and anaerobic.

Below the 0.5 mL O₂/L H₂O threshold, the activity of multicellular organisms as agents in the oxidative destruction of organic matter is severely limited (Demaison and Moore, 1980). Anoxic sediments are typically thinly laminated (distinct alternating layers <2 mm thick) because of the lack of bioturbation by burrowing, deposit-feeding organisms. Pederson and Calvert (1990) contend that anoxia is less important than primary productivity in determining quantities of organic matter preserved. However, Peters and Moldowan (1993) stress the effect of anoxia on the quality rather than quantity of organic matter preserved, that is, anoxia favors preservation of all organic matter, including hydrogen-rich, oil-prone organic matter. This may explain the positive relationship between petroleum source rocks and the faunal, sedimentologic, and geochemical parameters indicating anoxia.

Alteration of Organic Matter

Diagenesis refers to all chemical, biological, and physical changes to organic matter during and after deposition of sediments but prior to reaching burial temperatures greater than about 60°–80°C. The quantity and quality of organic matter preserved and modified during diagenesis of a sediment ultimately determine the petroleum potential of the rock (Horsfield and Rullkötter, Chapter 10, this volume).

Catagenesis can be divided into the oil zone, which corresponds to the oil window, where liquid oil generation is accompanied by gas formation, and the more mature wet gas zone, where light hydrocarbons are generated through cracking and their proportion increases rapidly (Tissot and Welte, 1984). Wet gas (<98% methane) contains methane and significant amounts of ethane, propane, and heavier hydrocarbons. The gas window corresponds to the interval from the top of the wet gas zone to the base of the dry gas zone.

Metagenesis corresponds to the dry gas zone where dry gas is generated (2.0–4.0% R₀). Dry gas consists of 98% or more of methane (Tissot and Welte, 1984). Dry gas is also found as deposits of bacteriogenic (microbial) gas generated during diagenesis of organic matter by methanogenic bacteria under anoxic conditions (Rice and Claypool, 1981).

Thermal maturity refers to the extent of temperature-time driven reactions that convert sedimentary organic matter (source rock) to oil, wet gas, and finally to dry gas and pyrobitumen. Thermally immature source rocks have been affected by diagenesis without a pronounced effect of temperature (<0.6% R₀) and are where microbial gas is produced. Thermally mature organic matter is (or was) in the oil window and has been affected by thermal processes covering the temperature range that generates
Table 5.1. Geochemical Parameters Describing the Petroleum Potential (Quantity) of an Immature Source Rock

<table>
<thead>
<tr>
<th>Petroleum Potential</th>
<th>TOC (wt. %)</th>
<th>Rock-Eval Pyrolysis</th>
<th>Bitumen^c (wt. %)</th>
<th>Hydrocarbons (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor</td>
<td>0–0.5</td>
<td>0–0.5</td>
<td>0–0.25</td>
<td>0–0.10</td>
</tr>
<tr>
<td>Fair</td>
<td>0.5–1</td>
<td>0.5–1</td>
<td>2.5–5</td>
<td>0.05–0.10</td>
</tr>
<tr>
<td>Good</td>
<td>1–2</td>
<td>1–2</td>
<td>5–10</td>
<td>0.10–0.20</td>
</tr>
<tr>
<td>Very Good</td>
<td>2–4</td>
<td>2–4</td>
<td>10–20</td>
<td>0.20–0.40</td>
</tr>
<tr>
<td>Excellent</td>
<td>&gt;4</td>
<td>&gt;4</td>
<td>&gt;20</td>
<td>&gt;0.40</td>
</tr>
</tbody>
</table>

^a mg HC/g dry rock distilled by pyrolysis.
^b mg HC/g dry rock cracked from kerogen by pyrolysis.
^c Evaporation of the solvent used to extract bitumen from a source rock or oil from a reservoir rock causes loss of the volatile hydrocarbons below about n-C_15. Thus, most extracts are described as “C_15 hydrocarbon.” Lighter hydrocarbons can be at least partially retained by avoiding complete evaporation of the solvent (e.g., C_10+).

Table 5.2. Geochemical Parameters Describing Kerogen Type (Quality) and the Character of Expelled Products

<table>
<thead>
<tr>
<th>Kerogen Type</th>
<th>HI (mg HC/g TOC)</th>
<th>S_2/S_3</th>
<th>Atomic H/C</th>
<th>Main Expelled Product at Peak Maturity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>&gt;600</td>
<td>&gt;15</td>
<td>&gt;1.5</td>
<td>Oil</td>
</tr>
<tr>
<td>II</td>
<td>300–600</td>
<td>10–15</td>
<td>1.2–1.5</td>
<td>Oil</td>
</tr>
<tr>
<td>II/III^b</td>
<td>200–300</td>
<td>5–10</td>
<td>1.0–1.2</td>
<td>Mixed oil and gas</td>
</tr>
<tr>
<td>III</td>
<td>50–200</td>
<td>1–5</td>
<td>0.7–1.0</td>
<td>Gas</td>
</tr>
<tr>
<td>IV</td>
<td>&lt;50</td>
<td>&lt;1</td>
<td>&lt;0.7</td>
<td>None</td>
</tr>
</tbody>
</table>

^a Based on a thermally immature source rock. Ranges are approximate.
^b Type II/III designates kerogens with compositions between type II and III pathways (e.g., Figure 5.1) that show intermediate HI (see Figures 5.4–5.11).

5. Applied Source Rock Geochemistry

Source Rock Terms

Sedimentary rocks that are, or may become, or have been able to generate petroleum are source rocks (Tissot and Welte, 1984). An effective source rock is generating or has generated and expelled petroleum. This definition excludes the requirement that the accumulations be "commercially significant," because (1) the terms significant and commercial are difficult to quantify and change depending on economic factors, and (2) oil-source rock relationships are never proven because some level of uncertainty always exists depending on the available data. Nonetheless, effective source rocks satisfy three geochemical requirements that are more easily defined (Tables 5.1–5.3):

- Quantity, or amount of organic matter (Table 5.1)
- Quality, or type of organic matter (Table 5.2)
- Thermal maturity, or extent of burial heating (Table 5.3).

A potential source rock contains adequate quantities of organic matter to generate petroleum, but only becomes an effective source rock when it generates bacterial gas at low temperatures or it reaches the proper level of thermal maturity to generate petroleum. An active source rock is generating and expelling petroleum at the critical moment, most commonly because it is within the oil window (Dow, 1977a). An inactive source rock has stopped generating petroleum, although it still shows petroleum potential (Barker, 1979). For example, an inactive source rock might be uplifted to a position where temperatures are insufficient to allow further petroleum generation. A spent oil source rock has reached the postmature stage of maturity and is incapable of further oil generation, but may still be capable of generating wet and dry gas.

Active source rocks include rocks or sediments that are generating petroleum without thermal maturation. For example, a peat bog might produce microbiologically generated gas (marsh gas consisting mostly of bacterio-
Table 5.3. Geochemical Parameters Describing Level of Thermal Maturation

<table>
<thead>
<tr>
<th>Stage of Thermal Maturity for Oil</th>
<th>Ro (%)</th>
<th>Tmax (°C)</th>
<th>TAIa</th>
<th>Bitumen/TOCb</th>
<th>Bitumen (mg/g rock)</th>
<th>Pi (S1/(S1 + S2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immature</td>
<td>0.2–0.6</td>
<td>&lt;435</td>
<td>1.5–2.6</td>
<td>&lt;0.05</td>
<td>&gt;50</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Mature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early</td>
<td>0.6–0.65</td>
<td>435–445</td>
<td>2.6–2.7</td>
<td>0.05–0.10</td>
<td>50–100</td>
<td>0.10–0.15</td>
</tr>
<tr>
<td>Peak</td>
<td>0.65–0.9</td>
<td>445–450</td>
<td>2.7–2.9</td>
<td>0.15–0.25</td>
<td>150–250</td>
<td>0.25–0.40</td>
</tr>
<tr>
<td>Late</td>
<td>0.9–1.35</td>
<td>450–470</td>
<td>2.9–3.3</td>
<td>—</td>
<td>—</td>
<td>&gt;0.40</td>
</tr>
<tr>
<td>Postmature</td>
<td>&gt;1.35</td>
<td>&gt;470</td>
<td>&gt;3.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

aTAI, thermal alteration index.
bMature oil-prone source rocks with type I or II kerogen commonly show bitumen/TOC ratios in the range 0.05–0.25. Caution should be applied when interpreting extract yields from coals. For example, many gas-prone coals show high extract yields suggesting oil-prone character, but extract yield normalized to TOC is low (<30 mg HC/g TOC).
cPi, production index.

genic methane) without significant heating due to shallow burial. By this definition, trapped methane and nearby unconsolidated swamp muds from which it was derived represent a petroleum system.

Criteria for describing the quantities of extractable organic matter in source rocks (Tables 5.1 and 5.3) can be used to map the pod of active source rock where data are available from several wells. For example, source rock bitumen yields normalized by weight of rock or by total organic carbon (TOC) generally increase from immature to peak thermal maturity (Table 5.3). The principal regions of oil accumulation in many petroleum provinces are confined to areas showing the greatest normalized bitumen yields (e.g., figure 21 in Kontorovich, 1984).

Organic Matter Classifications

Kerogen Type

The amount and maceral composition of kerogen determine petroleum potential and can differ vertically or laterally within a source rock. No universally accepted classification for kerogen types exists in the literature. In this chapter, we use types I, II, III (Tissot et al., 1974), and IV (Demaison et al., 1983) to describe kerogens (see Chapter Appendix A).

Kerogen types are distinguished using the atomic H/C versus O/C or van Krevelen diagram (Figure 5.1A), originally developed to characterize coals (van Krevelen, 1961; Stach et al., 1982). Tissot et al. (1974) extended the use of the van Krevelen diagram from coals to include kerogen dispersed in sedimentary rocks. Modified van Krevelen diagrams (Figure 5.1B) consist of hydrogen index (HI) versus oxygen index (OI) plots generated from Rock-Eval pyrolysis and TOC analysis of whole rock. HI versus OI data can be generated more rapidly and at less expense than atomic H/C versus O/C data for van Krevelen diagrams.

Higher relative hydrogen content in kerogen (atomic H/C, HI) generally corresponds to higher oil-generative potential. Gas (methane, or CH4) and oil are enriched in hydrogen compared to kerogen. During thermal maturation, generation of these products causes the kerogen to become depleted in hydrogen and relatively enriched in

Figure 5.1. (A) Atomic H/C versus O/C or van Krevelen diagram based on elemental analysis of kerogen and (B) HI versus OI diagram based on Rock-Eval pyrolysis of whole rock can be used to describe the type of organic matter in source rocks. TAI, thermal alteration index (Jones and Edison, 1978). The type IV (inertinite) pathway is not shown. (From Peters, 1986.)
carbon. During catagenesis and metagenesis, all kerogens approach graphite in composition (nearly pure carbon) near the lower left portion of both diagrams (Figure 5.1).

**Maceral Groups**

The three principal maceral groups in coal and sedimentary rocks are liptinite (exinite), vitrinite, and inertinite (Stach et al., 1982). Liptinite macerals, such as alginites, sporinite, cutinites, and resinite, generally mature along the type I or II kerogen pathways on the van Krevelen diagram (Figure 5.2). Preserved remains of the algae *Botryococcus* and *Tasmanites* are examples of structured alginites. Vitrinite macerals originate from land plants and mature along the type III kerogen pathway. *Collinite* is the structureless constituent of vitrinite, whereas *telinite* is the remains of cell walls of land plants. Figure 5.2 shows two types of collinite: telocollinite contains no inclusions and is the maceral recommended for vitrinite reflectance measurements, whereas desmocollinite shows submicroscopic inclusions of liptinite and other materials. Because of the inclusions, desmocollinite shows a higher atomic H/C, has a lower reflectance (Figure 5.3), and commonly fluoresces under ultraviolet light, unlike telocollinite. Inertinitic macerals, such as semi-fusinite and fusinite, mature along the type IV kerogen pathway. Because of the combined effects of diagenesis, thermal maturity, and differing organic matter input, a kerogen can plot anywhere on the van Krevelen diagram and need not fall on any of the indicated maturation curves.
Petrography alone is too imprecise to evaluate the petroleum potential of a source rock, primarily because hydrogen-rich and hydrogen-poor kerogen is difficult to distinguish. "Amorphous" kerogen is commonly presumed to be hydrogen rich and oil prone, but not all amorphous kerogens can generate oil. Ultraviolet-induced fluorescence microscopy of samples of low thermal maturity distinguishes hydrogen-rich, oil-prone amorphous (fluorescent) from hydrogen-poor, non-generative amorphous (nonfluorescent) kerogen, suggesting that petrographic methods might be further refined to better predict generative potential (Senftle et al., 1987).

Organic Facies

Various workers have used the term organic facies as a synonym for kerogen facies (based on chemical data) or palynofacies or maceral assemblage facies (based on petrographic data). Jones (1984, 1987) propose a concise definition:

An organic facies is a mappable subdivision of a designated stratigraphic unit, distinguished from the adjacent subdivisions on the basis of the character of its organic constituents, without regard to the inorganic aspects of the sediment.

Jones (1984, 1987) has defined organic facies using a combination of three types of kerogen analyses: atomic H/C ratios, Rock-Eval pyrolysis and TOC, and transmitted-reflected light microscopy. He showed that all organic facies can exist in either carbonates or shales and that there is little evidence that TOC requirements are lower for carbonate than for shale source rocks. Integration of organic facies studies with the concepts of sequence stratigraphy is a step toward improving our ability to predict the occurrence of a source rock (e.g., Pasley et al., 1991).

When used together, elemental analysis, Rock-Eval pyrolysis and TOC, and organic petrography are powerful tools for describing the richness, type, and thermal maturity of organic matter. Jones and Edison (1978) and Jones (1984) have shown how maceral composition and thermal maturity from microscopy can be used to estimate the atomic H/C ratio of a kerogen (Figure 5.2). If the measured atomic H/C differs by more than 0.1 from the estimated value, both analyses are suspect and are repeated. These maturity and atomic H/C results are commonly supported by $T_{\text{max}}$ and HI data obtained from each whole rock sample using Rock-Eval pyrolysis and TOC.

Coal

Coal is a rock containing more than 50% organic matter by weight. Both coals and sedimentary rocks can contain any combination of macerals. Various classifications of these organic-rich rocks are found in the literature (e.g., Cook and Sherwood, 1991). Not all coals are composed of humic organic matter (higher plant, type III kerogen). Humic and sapropelic coals contain less than 10% and more than 10% lipinite, respectively. Humic coal has long been recognized as a source for gas, primarily methane and carbon dioxide. However, boghead and cannel coals are dominated by type I and II kerogens, respectively, are oil prone, and thus show high oil potential.

Coals can generate oil, as exemplified by major accumulations in Indonesia and Australia. Two principal limitations for coals as effective source rocks are (1) expulsion efficiency and (2) organic matter type (sufficient hydrogen). Because of the physical properties of thick coal seams, generated liquid products are usually adsorbed and generally escape only when cracked to gas and condensate (Snowdon, 1991; Teerman and Hwang, 1991). Coals that can generate and release oil must contain at least 15-20% by volume of lipinite macerals prior to catagenesis, corresponding to an HI of at least 200 mg HC/g TOC and an atomic H/C ratio of 0.9 (Hunt, 1991).

Kerogen and Bitumen Composition

Detailed structural information on kerogen is limited because of its heterogeneous composition and difficulties associated with the chemical analysis of solid organic matter. Kerogen has been described as a geopolymer, which has been "polymerized" from a random mixture of monomers. These monomers are derived from the diagenetic decomposition of biopolymers, including proteins and polysaccharides (e.g., Tissot and Welte, 1984). This view has led to many publications showing generalized chemical structures for kerogen, none of which are particularly informative.

The discovery of insoluble biopolymers in living organisms, sediments, and sedimentary rocks has led to a reappraisal of the structure of kerogen (Rullkötter and Michaelis, 1990). In the modified scheme, more emphasis is placed on selective preservation of biopolymers and less on reconstitution of monomers. Progress has been achieved by the application of specific chemical degradation (Mycke et al., 1987), pyrolysis (Larter and Senftle, 1985), and spectroscopic techniques (Mann et al., 1991). Structural elucidation techniques are beyond the scope of
this chapter, although the reader should be aware that these studies are likely to impact our understanding of kerogen.

Asphaltenes in bitumen are lower molecular weight fragments of kerogen and may be intermediates between kerogen and bitumen. For example, although asphaltenes are soluble in polar solvents, they show elemental compositions similar to associated kerogens (Orr, 1986) and similar distributions of hydrocarbons (Bandurski, 1982; Pelet et al., 1985), including steranes and triterpanes (Cassani and Eglinton, 1986).

Lipids can be incorporated into kerogen during diagenesis, but many survive as free constituents in the bitumen and are known as molecular fossils, biological markers, or biomarkers. Biological markers are complex organic compounds composed of carbon, hydrogen, and other elements which show little or no change in structure from their parent organic molecules in living organisms (Peters and Moldowan, 1993).

**Expelled Products**

Petroleum expelled from an active source rock, (primary migration) (Lewan, Chapter 11, this volume) can migrate along a fault plane or permeable carrier bed (secondary migration) (England, Chapter 12, this volume) to a porous reservoir rock (Morse, Chapter 6; Jordan and Wilson, Chapter 7, this volume) capped or surrounded by a comparatively impermeable seal (Downey, Chapter 8, this volume) that together form a trap (Biddle and Wielchowsky, Chapter 13, this volume). Examples of how this happens are described in the case studies in this volume. Factors controlling the quantities of petroleum needed to saturate the pore space in a source rock prior to expulsion and the efficiency of expulsion are poorly understood and represent active research topics (e.g., Wilhelms et al., 1990; Mackenzie and Quigley, 1988). Accurate estimates of these quantities will improve mass balance calculations.

Shows of petroleum are proof of a petroleum system and when encountered during drilling are useful exploration clues, particularly when they can be quantified and regionally mapped. Cutting or cores that bubble or bleed oil and gas during removal from the well are called "live" shows, in contrast to the asphaltic staining of "dead" shows. The quality of shows can be evaluated by their fluorescence under ultraviolet light, by the color of organic solvent extracts, or by the geochemical screening methods described later. Quantitative bitumen or hydrocarbon yields from reservoir rocks assist in distinguishing between commercial and noncommercial subsurface petroleum occurrences (Swanson, 1981).

Oils inherit biomarker distributions similar to those in the bitumen from the source rock, thus allowing oil-oil and oil-source correlation or "fingerprinting" and paleo-reconstruction of source rock depositional conditions (Peters and Moldowan, 1993). An advantage of biomarkers is their resistance to biodegradation by aerobic bacteria in the reservoir. For heavily biodegraded oils where biomarkers have been partially altered, correlation sometimes requires sealed tube pyrolysis of asphaltenes, followed by biomarker analysis of the generated bitumen (e.g., Cassani and Eglinton, 1986). Biomarker and other correlation technologies, such as stable carbon isotope analysis and pyrolysis-gas chromatography, are among the most powerful tools for mapping petroleum systems to reduce exploration risk, particularly when oils migrate large distances from their pod of active source rock or when more than one source rock pod exists in the basin fill. Based on these fingerprinting techniques, the level of certainty for a petroleum system is determined. This level of certainty indicates the confidence that the petroleum from a particular accumulation came from a specific pod of active source rock.

**SCREENING METHODS**

Sedimentary basin analysis (Magoon and Dow, Chapter 1, this volume) of frontier areas begins with geologic and geophysical reconnaissance. Early evaluations focus on sample and data collection to assess the presence of thick sedimentary sequences, regional hydrocarbon seals, and appropriate reservoir lithologies. Maps using well control, outcrop, and geophysical data must be prepared or revised.

Geochemical screening analyses are practical exploration tools for rapid and inexpensive evaluation of large numbers of rock samples from outcrops and wells. Outcrop samples from measured stratigraphic sections are better than random outcrop samples because they can easily be made into a geochemical log that can be compared to nearby geochemical logs of wells. Rock samples from wells include drill cuttings, sidewall cores, and conventional cores, in order of decreasing abundance. Large numbers of analyses of these rock samples are used to make geochemical logs to evaluate the thickness, distribution, richness, type, and thermal maturity of source rocks in the basin fill. Evaluating the source rock in the basin fill is an important part of sedimentary basin analysis. The next step is to identify the pod of active source rock, which is the first step in evaluating a petroleum system.

The most effective screening method for large numbers of rock samples from wells and outcrops combines Rock-Eval pyrolysis and TOC measurements. These data are usually supplemented by vitrinite reflectance and spore coloration results to construct detailed geochemical logs (see Figures 5.4-5.11).

Chapter Appendix B describes key criteria for useful geochemical logs. These include proper (1) sample spacing, (2) sample quality and storage, and (3) sample preparation.

**Rock-Eval Pyrolysis and Total Organic Carbon**

Total organic carbon (TOC, wt. %) describes the quantity of organic carbon in a rock sample and includes both kerogen and bitumen. TOC can be determined in several ways, and geologists should be familiar with the advantages and disadvantages of each (Chapter
Appendix C). TOC is not a clear indicator of petroleum potential. For example, graphite is essentially 100% carbon, but it will not generate petroleum. Some Tertiary deltaic marine shales contain up to 5 wt. % TOC but generate little if any petroleum because the organic matter is gas prone or inert. The theory and pitfalls of Rock-Eval pyrolysis interpretation are discussed by Peters (1986) and are not repeated here. Key parameters are defined in Chapter Appendix D.

**Gas Analysis**

Residual gas (C₁-C₄) and heavier hydrocarbons in drill cuttings and mud arriving at the shaker table can be liberated with a blender and analyzed by gas chromatography (GC) at the well site as part of a process called hydrocarbon mud logging. Some systems use a simple hot wire detector to make only two measurements, methane and ethane-plus hydrocarbons. Hydrocarbon mud log gas curves are commonly available from wildcard wells and provide useful information on hydrocarbon shows (e.g., see Figure 5.7).

Alternatively, gaseous hydrocarbons can be detected at the well site or in the laboratory using an oil show analyzer (Espitalié et al., 1984) or by hydrogen stripping GC (Schaefer, et al., 1978). In GC, an inert carrier gas (mobile phase) passes through a column coated with a nonvolatile, high molecular weight liquid (stationary phase). The temperature of the column is gradually raised using a temperature-programmed oven. Petroleum components are separated depending on their volatility and affinity for the mobile versus stationary phases as they pass through the column. A plot of detector response versus time shows separated peaks representing single or multiple components and is called a chromatogram.

**Headspace gas analysis** is sometimes used as a screening tool because it assists in quantitative show detection (Tissot and Welte, 1984). For this method, cuttings are frozen or canned with water and a bactericide. Agitation and/or heating releases some of the hydrocarbons from the cuttings into the headspace over the water, which can be sampled through a septum with a syringe and analyzed by GC (e.g., Bernard, 1978; Whelan, 1984). Many choose not to use this technique because it is costly and time consuming and metal cans rust or leak in storage. Furthermore, this method is not particularly useful for establishing maturity profiles because gas readily migrates. Vitrinite reflectance and Rock-Eval pyrolysis are more reliable methods for establishing thermal maturity profiles than gas analysis.

Light hydrocarbon gas distributions combined with isotopic compositions can be used to describe the origin and level of maturity of the gas (e.g., Rice and Claypool, 1981; James, 1983; Schoell, 1984). Reliable sampling methods are important because sample handling can alter these gas compositions. For example, drill cuttings used for headspace gas analyses should be kept in gas-tight containers at deep freeze temperatures to avoid evaporative loss of components. Examples of procedures for sampling gases in drilling muds and cuttings are given in Schaefer et al. (1978), Reitsema et al. (1981), and Whelan (1984). Other procedures are used for sampling gases under pressure (Gas Processors Association, 1986). The more advanced aspects of gas geochemistry are beyond the scope of this chapter, which deals primarily with rapid screening methods for evaluating oils and source rocks. However, readers should be aware that analysis of gases is likely to become increasingly important as future exploration shifts from oil to gas.

**Organic Petrography**

**Thermal Alteration Index**

*Thermal alteration index* (TAI) is a numerical scale based on thermally induced color changes in spores and pollen. Strew-mount slides of kerogen are examined in transmitted light, typically using a split-stage comparison microscope. The analyst matches the color of the specimen under one ocular with that of a standard under the other ocular of the microscope. Several TAI scales have been published (e.g., Staplin, 1969; Jones and Edison, 1978). An advantage of TAI is that the greatest color changes occur in the oil window. TAI measurements are imprecise because description of color is subjective, palynomorph thickness and type affect results, and many samples contain few palynomorphs. Quantitative spore color measurements (Marshall, 1991) offer the possibility of more precise assessment of thermal maturity. Despite limitations, TAI commonly provides useful data, even when other maturity parameters fail.

**Vitrinite Reflectance**

*Vitrinite reflectance* (Rₒ) increases during thermal maturation due to complex, irreversible aromatization reactions. Approximate Rₒ, TAI, and Tₘₐₓ values have been assigned for the beginning and end of oil generation (Table 5.3). Rₒ versus depth plots generally show linear trends on semi-log paper. Dow (1977b) showed how these plots can be used to support the existence of faults, intrusions, and changes in geothermal gradient and how to estimate the thickness of a section lost at an unconformity. This information provides valuable calibration for reconstructing burial histories.

For vitrinite reflectance, kerogen isolated from sedimentary rocks is embedded in epoxy on a slide or in an epoxy plug and polished to a flat, shiny surface (Bostick and Alpern, 1977; Baskin, 1979). Measurements are made of the percentage of incident light (usually at a wavelength of 546 nm) reflected from vitrinite particles (preferably telocollinite) under oil immersion (Stach et al., 1982). The subscript “o” in Rₒ refers to oil immersion. Some old papers refer to Rₘ and Rₘₒ, reflectance in air and water, respectively. Vitrinite becomes anisotropic at high levels of maturity (above about 1% Rₒ), resulting in the terms Rₘᵦ and Rₘₐₓ for the minimum and maximum reflectance values obtained upon rotation of each particle. Most kerogen studies report random mean Rₒ rather than Rₘᵦ or Rₘₐₓ because rotation of the microscope stage is not required.
Several factors based on the experience of the analyst are weighed in the process of selecting vitrinite particles. $R_o$ trends established above and below the sample can be used to eliminate certain populations of macerals from consideration. Because TAI and $R_o$ are related (Jones and Edison, 1978), a measured TAI can be used to estimate the $R_o$ of the vitrinite population. This process is not always reliable, however, because TAI is commonly measured on less than a dozen palynomorphs and these might represent recycled organic matter or contamination from drilling mud.

Reliability of $R_o$ measurements from single samples increases when supported by independent maturity parameters (e.g., TAI and $T_{max}$) and $R_o$ versus depth trends established by multiple samples in a well. For example, $T_{max}$ can be used to support $R_o$, particularly in the thermally mature stage. In situ vitrinite in some samples can be overwhelmed by recycled (high maturity) or caved (low maturity) particles. Selection of these particles as the "true" vitrinite might result in anomalous values compared to the $R_o$ trend established by samples from other depths. As an extreme example, some Alaskan wells show little change or even a decrease in $R_o$ with increasing depth at shallow well depth due to shedding of recycled (high $R_o$) organic matter from Mesozoic highlands into thermally "cool" Tertiary basins.

$R_o$ cannot be measured in rocks that lack vitrinite. Vitrinite is derived from land plants and is not common in rocks older than Devonian because abundant land plants had not yet evolved. Reflectance can be measured on graptolites in lower Paleozoic rocks (Link et al., 1990). Some oil-prone source rocks that formed on broad marine carbonate shelves (e.g., Jurassic of Saudi Arabia) or in large lakes (e.g., Lower Cretaceous of West Africa) contain only small amounts of vitrinite due to limited terrigenous organic matter input. The reflectance of solid bitumen has been calibrated to $R_o$ and is particularly useful in vitrinite-poor carbonate rocks (Jacob, 1989). Evidence suggests that large amounts of bitumen (Hutton et al., 1980) and oil-prone macerals (Price and Barker, 1985) retard the normal increase of vitrinite reflectance with maturity. Low $R_o$ values can result from poor polishing, whereas high values are typical of oxidized vitrinite.

$R_o$ Histograms

$R_o$ histograms show the frequency distribution of reflectance measurements determined on about 50–100 vitrinite particles in each polished kerogen preparation. The random mean $R_o$ is determined from these histograms. $R_o$ versus depth plots use the random mean value and refer only to the population of organic particles identified by the analyst as vitrinite. Likewise, the standard deviation for these $R_o$ values represents the repeatability by which the analyst can select these particles. Because $R_o$ values based on fewer than 50 particles can be unreliable, we recommend that $R_o$ histograms be examined for all samples.

Reflectograms

Reflectograms (Figure 5.3) are frequency plots of the reflectance of all macerals measured in the polished kerogen slide. Unlike $R_o$ histograms, reflectograms may provide an idea of the difficulty in selecting vitrinite particles for measurement. Selection of the correct particles for measurement may be difficult when there is no clearly predominant population of telocollinite (Figure 5.3). $R_o$ must be determined using vitrinite because other macerals mature at different rates (e.g., Dow, 1977b). However, $R_o$ can be extrapolated from reflectance measurements of some macerals other than telocollinite, such as exinite (Alpern, 1970).

INTERPRETIVE TECHNIQUES

Source Potential Index

During the source rock assessment phase of sedimentary basin evaluation, geologists commonly rely on the quantity, type, and thermal maturity of organic matter as criteria to indicate favorable risk for significant petroleum charge. However, source rock volumetrics (thickness and lateral extent) must not be ignored. An oil-prone source rock dominated by type I or II kerogen and showing excellent genetic potential (e.g., $S_1 + S_2 > 10$ mg HC/g rock) may be too thin to charge economically significant oil accumulations. Source potential index (SPI) (Demaison and Huizinga, 1991) is defined as the quantity of hydrocarbons (metric tons) that can be generated in a column of source rock under one square meter of surface area (Demaison and Huizinga, Chapter 4, this volume). SPI (or "cumulative hydrocarbon potential," according to Tissot et al., 1980) is a simple method for ranking source rock productivity because it integrates both source rock richness and thickness. A relative source rock ranking system has been developed by compiling the average SPI values for source rock units from around the world.

The SPI is relevant only where a pod of active source rock has been established. The entire source rock interval must be sampled and systematically logged at closely spaced intervals using Rock-Eval pyrolysis. Samples that were positively picked (Chapter Appendix B) or affected by substantial caving should be avoided. Gross thickness of the source rock must be corrected for well deviation, structural complexities, and nonsource units lacking significant hydrocarbon generative potential ($S_1 + S_2 < 2$ mg HC/g rock) to get net source rock thickness. The samples should be representative of the organic facies in the area of interest. Samples should show no evidence of contamination or migrated oil (Chapter Appendix B) and should be from thermally immature or early mature portions of the source rock. SPI values determined from thermally mature or postmature sections can be low because of petroleum expulsion. Although specific source rock densities should be used, a density of 2.5 t/m³ is used for most SPI calculations.

Laterally drained petroleum systems tend to accumu-
late petroleum from larger drainage areas compared to vertically drained systems. For this reason, lower limits are used to define SPI categories for laterally drained systems (low, SPI < 2; moderate, 2 ≤ SPI < 7; high, SPI ≥ 7) than for vertically drained petroleum systems (low, SPI < 5; moderate, 5 ≤ SPI < 15; high, SPI ≥ 15) (see figure 4.4 of Lewan, Chapter 4, this volume).

SPI is a measure of the petroleum potential of a source rock and ideally is determined from thermally immature rock. After a source rock shows a favorable SPI rating, maps of SPI and thermal maturity are used to evaluate which areas of a basin have the highest petroleum charge. Areas with the highest charge are most likely to be nearest the source rock where it is the most thermally mature, or nearest the pod of active source rock. Conversely, areas most likely to have the lowest charge are farthest from the mature source rock, or farthest from the pod of active source rock. Whether this charge is mostly gas or mostly oil is determined from the kerogen type and maturity. Demaison and Huizinga (1991; Chapter 4, this volume) provide a complete discussion of migration drainage and entrapment styles for different petroleum systems and show how to estimate the SPI for source rocks, even when they have undergone thermal maturation beyond the immature stage.

**Mass Balance Calculations**

Mass balance calculations, either by accumulation (or prospect) or petroleum system, can be used to provide another comparison of the amount of petroleum generated with the amount that has accumulated. The geochemical data for screening can also be used for SPI calculations (Demaison and Huizinga, Chapter 4, this volume) and for mass balance calculations as suggested by Schmoker (Chapter 19, this volume), whose technique is used in many of the case studies in this volume.

**EXAMPLES**

**Geochemical Logs**

Geochemical logs are among the most valuable tools for basin analysis, yet few examples are given in the literature (e.g., Clementz et al., 1979; Espitalié et al., 1977, 1984, 1987; Peters, 1986; Magoon et al., 1987, 1988). Proper use of geochemical logs allows identification of the following features in penetrated intervals:

- Occurrence of potential, effective, and spent as well as active and inactive source rocks
- Main stages of thermal evolution: diagenesis (immature), catagenesis (mature), and metagenesis (postmature) zones
- Occurrence of varying amounts of in situ and migrated petroleum

When geochemical logs are unavailable, geophysical wireline logs and interpretive techniques can be used as qualitative indicators of organic content (e.g., Passey et al., 1990; Schmoker and Hester, 1983; Stocks and Lawrence, 1990; Hester et al., 1990). These methods are most reliable within small areas where wireline response has been calibrated to geochemical data.

Geochemical logs for eight exploratory wells are included to show their usefulness for detecting free hydrocarbons and identifying source rocks. The first three geochemical logs (Figures 5.4-5.6) are from three wells (I, II, and III) that are in the same area and demonstrate the lateral continuity of two different source rocks. The last five geochemical logs (Figures 5.7-5.11) are from wells that are in different areas, but are used as examples of different ways to identify and evaluate a source rock.

**Wells I through III**

The high-quality geochemical log for well I is based on closely spaced Rock-Eval pyrolysis and TOC data supplemented by vitrinite reflectance (Figure 5.4). Closely spaced samples allow a critical evaluation of source and reservoir rock intervals (note the wider sample spacing in the C formation, a Lower Cretaceous reservoir rock). The penetrated section contains two source rocks. The Upper Cretaceous B formation source rock interval at 780-1540 m is a potential source rock that has the capacity to generate significant quantities of oil (SPI = 42 t HC/m²). The Tₘₕ versus depth trend is slightly depressed through this interval, probably because this sulfur-rich kerogen undergoes thermal degradation at lower temperatures than many type II kerogens. Because the Lower Cretaceous is at maximum burial depth, the F formation source rock at 3120-3620 m is an active source rock that is presently generating oil (SPI ≥ 8 t HC/m²). The production or productivity index (PI) gradually increases below about 3200 m, reflecting the onset of generation, which is also indicated by Tₘₕ and Rₒ data. Vitrinite is generally absent in the carbonate section and in the strata containing particularly hydrogen-rich kerogen. PI anomalies (e.g., at 100-600 m and 1600-3050 m) are "mathematical artifacts" caused by relatively low S₂ yields where S₁ yields may be slightly elevated by small quantities of organic drilling additives or minor shows. The F formation penetrated in well I is presently an active source rock.

The geochemical log for well II, which is located in the same basin about 120 km southeast of well I (Figure 5.5), shows that the Upper Cretaceous potential source rock is thicker than in well I. This potential source rock is still immature and shows a similar source potential index (SPI = 40 t HC/m²) to that in well I. The Lower Cretaceous source rock in well II is thicker and shows more discrete zones of higher and lower source potential than in well I. The total thickness of the Lower Cretaceous interval in well II is 700 m, but the net source rock thickness is only about 550 m and shows an SPI of 25 t HC/m². Only the deeper portions of the Lower Cretaceous source rock are actively generating petroleum (because the onset of petroleum generation for this source rock occurs at 0.6% Rₒ). Stratigraphically equivalent Lower Cretaceous source rocks buried more deeply adjacent to this trap are the probable source for hydrocarbon shows in the Lower Cretaceous sandstone in well
II. High productivity indices (at 100–600 m and 1820–2600 m) are an artifact of low $S_1$ and $S_2$ values in rocks containing highly oxidized organic matter.

Well III is located about 80 km northwest of well I (Figure 5.6). Sidewall cores are indicated by dotted bars, while ditch cuttings are indicated by solid bars. Only the Upper Cretaceous potential source rock was penetrated in this well. This unit is less oil prone than in wells I and II, but it is approaching the onset of oil generation ($R_o$, equivalent 0.5% for this unit). Because it is very thick, the Upper Cretaceous source rock still shows a high SPI of 15 t HC/m$^2$. Variations in TOC and HI in the Upper Cretaceous source rock in this well are more obvious than in wells I and II and can be explained by local sea level fluctuations. Geochemical parameters on the logs in Figures 5.4–5.6 allow individual units to be correlated among these three wells, similar to conventional correlations using wireline logs and paleontology.
Wells IV through VIII

The geochemical log for well IV shows a largely poor source section above 3500 m (Figure 5.7). Tick marks in the sample location column to the left of the hydrocarbon yield column ($S_2$) in the figure show locations of samples. The hydrocarbon yield column shows that most samples above 3500 m contain kerogen with little or no petroleum potential. PI data indicate the presence of hydrocarbon shows in the sandstone and siltstone interval between 2400 and 3500 m. Deeply buried shale below 3500 m represents an active source rock that is presently generating oil ($\text{SPI} \geq 8 \text{ t HC/m}^2$). $T_{max}$ values increase with depth in this shale, establishing a thermal maturity trend that is consistent with that in the poor source shale above about 2400 m. The thermal maturity of the sandstone and siltstone interval between 2400 and 3500 m can be extrapolated from the $T_{max}$ trend established by the overlying
Figure 5.6. Geochemical log for well III, located about 80 km northwest of well I (Figure 5.4). The Upper Cretaceous section in well III is not as oil prone as in wells I or II and is more thermally mature, approaching the onset of oil generation. Geochemical parameters on the logs in Figures 5.4 to 5.6 allow individual units to be correlated among the wells. Sidewall cores indicated by dotted bars, drill cuttings by solid bars.

and underlying shales. Measured $T_{\text{max}}$ values are either anomalously high or low in the sandstone and siltstone interval compared to the established trend based on $T_{\text{max}}$ in the shales. The anomalously high $T_{\text{max}}$ values result from dominance of recycled organic matter in these coarse-grained, organic-poor rocks. The low $T_{\text{max}}$ values correspond to zones impregnated by migrated oil or where $S_2$ peaks are too small (<0.2 mg HC/g rock) to yield reliable $T_{\text{max}}$ values. High molecular weight components in oil commonly generate a spurious $S_2$ peak with a corresponding low $T_{\text{max}}$ (e.g., Peters, 1986). Note the good correlation in the deeper shale between free hydrocarbon indications ($S_2$) and the mud log gas.

Well V penetrates Mesozoic marine shale and sandstone and Tertiary carbonate rocks (Figure 5.8). Some fine-grained marine rocks are relatively lean in
organic matter, but still may be source rocks for petroleum accumulations because they are thick and/or widespread. The geochemical log for well V shows organic-lean Jurassic source rock from 2880 m to total depth. In situ bitumen in this presently active source rock has been geochemically correlated with oils in the area. An SPI of 2 t HC/m² has been calculated for this Jurassic source rock using samples that have a genetic potential $(S_1 + S_2) > 1$ mg HC/g rock.

The geochemical log for well VI shows a depressed trend in $T_{\text{max}}$ in the Lower Cretaceous lacustrine rocks below 2500 m (Figure 5.9). Organic petrography data

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**Figure 5.7.** Geochemical log for well IV shows a clear thermal maturity trend established by $T_{\text{max}}$ for shales above 2400 m (poor source) and below 3500 m (presently active source rock). The intermediate zone consists of sandstones and siltstones where $T_{\text{max}}$ values are either anomalously high or low compared to the above trend. The high $T_{\text{max}}$ values result from a dominance of recycled kerogen in coarse-grained, organic-poor rocks. The low $T_{\text{max}}$ values correspond to zones impregnated by migrated oil. Heavy ends in the oil generate a spurious $S_2$ peak with an anomalously low $T_{\text{max}}$ (Peters, 1986).

Sidewall cores indicated by dotted bars, drill cuttings by solid bars.
indicates a significant alginite component in the kerogen from these rocks. Espitalie et al. (1985) and Huizinga et al. (1988) have shown that $T_{\text{max}}$ is seldom useful as a maturation parameter for oil-prone algal kerogens because, unlike other kerogens, it shows little to no increase throughout the oil window. Facies effects on $T_{\text{max}}$ are discussed in Peters (1986). In this case, vitrinite reflectance represents a more useful thermal maturity parameter than $T_{\text{max}}$.

Well VII penetrates Mesozoic and Tertiary marine shales and sandstones, reaching Precambrian basement at total depth (Figure 5.10). The geochemical log shows the results for sidewall cores (dotted bars) and drill cuttings (solid bars). Thin shale beds sampled by sidewall cores are more organic-rich than nearby samples, but are too thin to generate significant quantities of petroleum. When mixed with adjacent lithologies in drill cuttings composited over 10-20 m intervals, these
thin organic-rich shales are difficult to recognize. If the drill cuttings samples had been used alone, these source rocks would have been overlooked in the penetrated section. These thin beds could represent the feather-edge of a source rock that thickens and is more deeply buried somewhere else in the basin fill. Based on the results in this well, more of these types of geochemical analyses in nearby wells could be obtained to determine if this source rock does thicken and become more mature where it is more deeply buried. If these thin shale beds do not increase in thickness and maturity, there is little chance they could charge nearby traps. In this case, other source rocks must be identified if this area is to remain prospective for oil exploration.

Well VIII penetrates a thick Cretaceous marine sequence dominated by gas-prone organic matter
5. Applied Source Rock Geochemistry

Geochemical Maps

Geochemical maps are made from geochemical logs. The properly designed and implemented geochemical log allows the geologist and geochemist to evaluate a source rock in one dimension. The power of the geochemical log is obvious when several logs in the same area are used to make source rock maps and cross sections. An example is a series of maps and a cross-
section for the fictitious Deer Shale source rock.

The fictitious Deer-Boar(.) petroleum system was introduced by Magoon and Dow (Chapter 1, this volume) through four figures and a table (Figures 1.2-1.5 and Table 1.4). The map and cross section were drawn to show the essential elements of the petroleum system at the critical moment, or at the end of the Paleozoic. At that time, the Deer Shale was an active source rock, whereas now, because of uplift, it is inactive. In addition, a rift graben formed on the right (east) side of the cross section during the Tertiary. To elaborate on this example, four source rock maps and one cross section (Figure 5.12) that represent the present-day geology show how a source rock is evaluated and placed into the context of a petroleum system that was operating in late Paleozoic time. Sedimentary basin analysis techniques are used to evaluate the source rock, whereas the petroleum system is used to evaluate the hydrocarbons.
Figure 5.12. Source rock maps and cross section used in sedimentary basin analysis showing thickness, richness, and thermal maturity of the fictitious Deer Shale. (A) Index map. (B) Isopach map. (C) TOC content map. (D) % R<sub>0</sub> base reservoir rock map. (E) Source potential index (SPI) map, which is used in studies of petroleum systems to classify a system and to determine its petroleum potential. (F) Cross section showing extent of petroleum system.
Table 5.4. Geochemical Information on the Fictitious Deer Shalea

<table>
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<th>Well No.</th>
<th>(R_o) (%)</th>
<th>(h) (m)</th>
<th>(S_1^b)</th>
<th>(S_2^b)</th>
<th>(S_1 + S_2^b)</th>
<th>(p) (g/cm³)</th>
<th>SPI (t HC/m²)</th>
<th>TOC (wt. %)</th>
<th>HI (mg HC/g TOC)</th>
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aSee equation 1 in text for definition of terms.
bmg HC/g dry rock.

Sedimentary Basin Analysis

The data used to construct this hypothetical example might include geochemical logs for the 32 exploratory wells, as well as other types of geologic and geophysical information that are not shown (Figure 5.12A). Information from geochemical logs is summarized for 17 of these wells in Table 5.4. The symbols in Figure 5.12A indicate that the exploratory well is a dry hole, encountered gas or oil shows, or is an oil well. A dry hole indicates that from well site drill cuttings examination, mud log, Rock-Eval pyrolysis, or other geochemical analyses, there is a lack of petroleum. Oil and gas shows indicate that some petroleum was encountered. The oil wells correlate with the fields shown on the Deer-Boar petroleum system map and table (Figure 1.3 and Table 1.3, Chapter 1). The dashed line represents the geographic extent of the same map and table (Figure 1.3 and Table 1.3, Chapter 1). The dashed line represents the geographic extent of the same petroleum system, and the wavy unconformity line represents the erosional edge of the source rock.

The isopach map of the Deer Shale indicates that it thickens from 25 to 150 m (Figure 5.12B). Because of essentially uniform lithology vertically through the shale, this is both a gross and net source rock thickness. The contours trend in a northwesterly direction and indicate that before or during the deposition of the overlying reservoir rock erosion stripped away the source rock east of the unconformity line.

The TOC contour map of the Deer Shale source rock ranges from 2.0 to >6.0 wt. % (Figure 5.12C and Table 5.4). The average TOC contoured is derived from the net source rock thickness, that is, TOC data is first averaged over 20 m intervals then these 20 m intervals are averaged. This procedure is used to average TOC because the frequency with which each 20 m interval is sampled and analyzed is different. For example, a 10-m core may be sampled and analyzed every 1 m, whereas drill cuttings samples may be sampled every 10 m. The lowest TOC values are nearest the unconformity at the top of the map, and the highest TOC values are where the source rock is immature at the bottom of the map. From right to left, TOC values increase to 5.0 wt. %, but then decrease with burial depth to about 3.0 wt. % because of thermal maturity. This TOC map suggests that the Deer Shale is a very good to excellent source rock (Table 5.1).

To determine the present-day thermal maturity of the Deer Shale source rock, a vitrinite reflectance value was determined for the base of the overlying Boar Sandstone reservoir rock, and this value was contoured (Figure 5.12D). The isoreflectance map indicates that the base of the reservoir rock was buried enough to be in the oil window (>0.6 % \(R_o\)) in two areas and has reached the gas window (>1.35 % \(R_o\)) on the left. Because the source rock is only present in the west (left) and is thermally mature, it is logical to conclude that the oil and gas shows and oil accumulations originated from this pod of mature source rock. When the thermal maturity pattern is compared with the TOC map, the TOC is interpreted to decrease where the thermal maturity is highest.

Rock-Eval pyrolysis data are summarized for 17 of the 32 wells (Table 5.4) to determine the hydrogen index (HI) and (SPI). The HI shows the present-day amount of hydrogen in the source rock organic matter and indicates the kerogen type or quality (Table 5.2). HI is the \(S_2\) peak (mg HC/g rock) divided by the TOC (mg TOC/g rock).
The average HI values were determined in the same way as the average TOC values, that is, over 20-m intervals. The average HI contours range from 400 to 583 mg HC/g TOC, indicating type II kerogen.

The source potential index requires Rock-Eval pyrolysis data as well as the thickness and density of the source rock unit, as discussed by Demaison and Huizinga (Chapter 4, this volume). If the density, net thickness, and quality of a source rock remain constant, SPI decreases as thermal maturity increases. Because these SPI values indicate remaining potential, they are called “residual SPI” (Figure 5.12E). Residual SPI values for the Deer Shale increase to the southwest (lower left), but are interpreted to be less than 4 where the source rock is buried deepest. The source rock density is constant (Table 5.4). If prior to increased thermal maturity, the SPI values all increased to the southwest from 2 to 10, then along strike there is a decrease of up to 8 SPI units caused by thermal maturity. These are moderate to high SPIs (Figure 4.4).

These maps indicate that the Deer Shale is a very good to excellent source rock that contains type II kerogen and that there is a pod of thermally mature source rock in the west-central part of the map. Additional information, such as paleontology, indicates that the Deer Shale was deposited in a marine environment, and organic petrography indicates that the kerogen macerals are in part waxy pollen (terrigenous), but mostly marine algal debris.

The cross section that represents present-day geology indicates that the overburden rock to the east in the rifted graben is Tertiary in age, whereas the overburden rock in the foreland basin to the west is late Paleozoic (Figure 5.12F). Because the source rock is absent from either side of the graben, and the graben is filled with nonmarine siliciclastics, the conclusion is that the hydrocarbons originated from the west side of the cross section from the pod of mature source rock mapped earlier.

The maps and interpretations outlined here are part of sedimentary basin analysis because organic and rock matter are investigated. The thickness, TOC content, % Ro, and SPI are all mappable properties of the source rock. However, the well control shown on the base map indicates that hydrocarbons have been detected in the area (Figure 5.13). These hydrocarbons are proof that in this area a petroleum system exists. To determine the origin and economic significance of these hydrocarbons, a petroleum system study is carried out.

**Petroleum System Study**

The presence of hydrocarbons in such close proximity to a pod of mature source rock strongly suggests that the two are genetically related, that is, the oil came from the Deer Shale source rock. This makes the Deer Shale an effective source rock.

Oil has been discovered to the east of the graben, whereas the pod of mature source rock is on the west side of the graben. Unless the oil came from the east, south, or north of the rift graben, it had to migrate before the rift graben formed in Tertiary time. This observation

*Figure 5.13. Maps indicating the oil and gas shows encountered inexploratory wells penetrating the Deer Shale and Boar sandstone. Few shows were detected in (A) the overburden rock and (B) the seal rock, whereas numerous shows were detected in (C) the reservoir rock horizon, indicating that this is the interval through which the oil migrated.*
indicates that the Deer Shale was an active source rock sometime in pre-Tertiary time. Burial history charts (Figure 1.2, Chapter 1) in several places in the area confirm that the source rock was active in late Paleozoic time.

Because the hydrocarbon shows in the wells are proof of the petroleum system, an understanding of the distribution of these shows is important to determine the geographic and stratigraphic extent of the system. Most of the wells were drilled to basement. Where the basement rock, underburden rock, and source rock intervals were penetrated, shows were not detected. Hydrocarbon shows were detected in the overburden rock and seal rock intervals.

Slight oil shows (streaming cut-fluorescence) were detected near the base of the overburden rock in the north-central part of the area, and gas shows were detected at a depth of 350 m in the central part of the area (Figure 5.13A). Well site evaluation of the gas shows indicated substantial gas on the hot wire that was 99.7% methane on the GC (dry gas). Laboratory analyses of headspace gas from canned cuttings collected through this interval indicate a carbon isotope value of −71.6‰, or biogenic gas. The conclusion is that this gas is part of a separate petroleum system probably related to Carboniferous coals in the overburden rock.

Within the seal rock, two shows were detected near the base of the unit (Figure 5.13B). The show in the north-central part of the area underlies the oil show in the overburden rock. Both shows are interpreted to be vertically migrating oil from the reservoir rock below. South of this show is another show in the seal rock, which is also interpreted to be oil that migrated from the reservoir rock below.

The reservoir rock interval, the Boar Sandstone, has the most abundant oil shows of any interval investigated (Figure 5.13C). Of the 32 wells that penetrated the reservoir horizon, 7 have oil shows and 6 recovered oil when drill-stem tested. Based on the distribution of these oil shows and their proximity to the pod of mature source rock, there is little doubt that the oil originated from this source rock. If this is true, the pattern of oil shows should give some indication as to the migration path of the oil. Two east-west bands of shows are shown, one at the top and one in the middle of the map with five wells in between that lack shows. These bands are good circumstantial evidence that the oil migrated from the mature source rock on the west through the reservoir rocks along two corridors to the east (Figure 1.3, Chapter 1). The distribution of these oil shows and the pod of mature source rock provide a basis for the geographic extent of the petroleum system.

Gas chromatography of the Deer Shale source rock extract shows that the pristane–phytane ratio is above 1.5 and the carbon preference index (CPI) is 1.2. Organic petrography indicates that the organic matter is mostly marine amorphous material with up to 35% terrigenous material.

The API gravity of the oil ranges from 32° to 43° and sulfur content is less than 0.3%. The pristane–phytane ratio is 1.6 and the CPI is 1.1. A more definitive oil-source rock correlation using biomarkers was not completed. Based on the rock extract and oil geochemistry, the oil probably originated from the Deer Shale, therefore the level of certainty for the Deer–Boar petroleum system is hypothetical.

The maps and cross sections in Figures 1.2–1.5 (Chapter 1) and in Figures 5.12 and 5.13 indicate the stratigraphic and geographic extent of the Deer–Boar petroleum system. Based on the burial history chart, the Deer Shale was an active source rock in late Paleozoic time. The oil show map of the Boar Sandstone reservoir rock interval indicates the oil migrated along two corridors into anticlinal and stratigraphic traps. In Tertiary time, a rift graben formed, isolating the oil accumulations on the east from those on the west side of the graben and the pod of inactive source rock. Oil samples from the shows and accumulations were used in an oil-oil correlation. Results showed that all these oils originated from the same source rock. The confidence that this oil originated from the Deer Shale is based on the similarity of certain geochemical parameters for both the oil and rock extract even though a detailed oil-source rock correlation was not completed.

After the source rock is demonstrated to be effective, that is, it generated and expelled hydrocarbons, then the question remains as to how effective. Decreased TOC and pyrolysis yields of source rocks resulting from thermal maturation must be taken into account to assess their original generative potential accurately and to make volumetric estimates of petroleum generated (Dow, 1977b; Schmoker, Chapter 19, this volume). For example, TOC is little affected by maturation of rocks containing type IV kerogen, but TOC can be reduced by 12–20 wt. % for type III and by as much as 50 and 70 wt. % for types II and I, respectively (Daly and Edman, 1987). Failure to account for these effects on mature or spent source rocks can cause source intervals to be overlooked on geochemical logs and can result in underestimates of original source rock potential or oil generated.

The volume of hydrocarbons generated and accumulated can be demonstrated in many ways. The case studies in this volume use a mass balance method (Schmoker, Chapter 19), and Demaison and Huizinga (1991; Chapter 4) use the SPI. Because the case studies adequately explain the mass balance method, only the SPI method is outlined here.

The residual SPI map is constructed from the net source rock thickness map and the genetic potential (S₁ + S₂) (Table 5.4) of the source rock from Rock-Eval pyrolysis (Figure 5.12E). The SPI ranges from 0.6 to 11.3. The residual SPI where the source was buried deepest suggests that up to 8 SPI units were lost as the source rock generated oil. Based on the preliminary SPI classification (Figure 4.4), the burial of this source rock indicates a large drainage area with moderate to high potential. Using regional geology and SPI, this petroleum system can be classified as a supercharged, low impedance, laterally drained petroleum system.
SUMMARY

Source rock characterization using geochemical logs and maps is an exercise in sedimentary basin analysis with the objective of identifying the pod of active source rock. The pod of active source rock contributes hydrocarbons to the petroleum system.

This chapter emphasizes (1) terms used to describe source rocks; (2) sampling, preparation, and analysis criteria; (3) geochemical logs and their use to describe source rocks and petroleum shows in one dimension; and (4) geochemical maps and their use for interpolating between one-dimensional control points for a three-dimensional understanding of the petroleum system.

Proper use of terms is critical for clearly describing petroleum systems. Some examples of source rock terms include richness, kerogen type, thermal maturity, product generated, time generated, and provenance or depositional environment. Source rock organic richness can be poor, fair, good, very good, or excellent (Table 5.1). Kerogen can be described as type I, II, III, or IV based on elemental analysis (Table 5.2). Organic petrography provides information on organic matter type and thermal maturity, but is currently too imprecise to describe generative potential. Thermal maturity is divided into immature, mature, and postmature based on such parameters as vitrinite reflectance, T_max, and thermal alteration index (Table 5.3). A source rock can be described as potential (could generate oil), effective (generated or currently generating oil), or spent (generated oil). A spent source rock can still generate gas. An inactive source rock is not generating oil today, but in the past it was an active source rock. The term “marine source rock” implies marine deposition, while the terms “marine organic matter” and “marine kerogen” could imply an origin from marine organisms. A marine source rock might contain dominantly land plant organic matter.

Geochemical logs of closely spaced Rock-Eval pyrolysis and TOC, vitrinite reflectance, lithology, mud log gas, and related data are indispensable tools in the sedimentary basin evaluation process. Useful geochemical logs require adherence to proper procedures for sample selection, preparation, analysis, and interpretation. These logs identify petroleum source rocks (as potential, effective, or spent), the thermal maturation gradient (including immature, mature, and postmature zones), and in situ and migrated petroleum shows.

Because of the rapid and inexpensive screening methods used, it is practical to generate libraries of geochemical logs that progressively reduce the risk associated with petroleum exploration as a petroleum province becomes more thoroughly sampled. Logs from various locations can be used to map the pod of active source rock, regional variations in organic facies, and the volume of generated petroleum. This information can be used as input to refine mathematical basin models. Finally, the two-step procedure consisting of screening followed by detailed geochemical analyses on selected samples reduces cost and simplifies interpretation.

Acknowledgments We thank L. B. Magoon and W. G. Dow for their invitation to prepare this paper and G. J. Demaison for his suggestion that it be written. The following people contributed timely reviews that improved the manuscript: L. B. Magoon, S. C. Teerman, D. K. Baskin, T. A. Edison, G. J. Demaison, J.T. Smith, and W.G. Dow. Tables 5.1, 5.2, and 5.3 were improved by input from D. K. Baskin, L. B. Magoon, and J. Miles. Concepts for Figures 5.2 and 5.3 were provided by T. A. Edison and S. C. Teerman, respectively. S. D. Northam and B. R. Barden coordinated the production of figures and text. We thank E. L. Couch and N. Schneidermann for their support and the management of Chevron Overseas Petroleum Inc. for permission to publish this work.

References Cited


5. Applied Source Rock Geochemistry


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CHAPTER APPENDIX A:
Kerogen Types

There are four principal types of kerogens found in coals and sedimentary rocks which are defined using atomic H/C versus O/C or Rock-Eval HI versus OI diagrams (see Figures 5.1 and 5.2.)

Type I
Immature type I kerogens are oil prone, show high atomic H/C (>1.5), low O/C (<0.1) (Figures 5.1 and 5.2), and generally have low sulfur content. These kerogens are dominated by liptinite macerals, but vitrinites and inertinites can be present in lesser amounts. Type I kerogens appear to be derived from extensive bacterial reworking of lipid-rich algal organic matter, commonly, but not always, in lacustrine settings (e.g., Eocene Green River Formation). Botryococcus and similar lacustrine algae and their marine equivalents, such as Tasmanites, can be major contributors to type I kerogens.

Type II
Immature type II kerogens are oil-prone (e.g., Jurassic of Saudi Arabia) and show high atomic H/C (1.2-1.5) and low O/C compared to types III and IV. Sulfur is generally higher in type II compared to other kerogens. Type II S kerogens (e.g., Miocene Monterey Formation) show high sulfur (e.g., 8-14 wt. %; atomic S/C > 0.04) and appear to generate petroleum at lower thermal maturity than other type II kerogens (Orr, 1986; Baskin and Peters, 1992). Type II kerogens are also dominated by liptinite macerals.

Type III
Immature type III kerogens show low atomic H/C (<1.0) and high O/C (≤0.3). Type III kerogen is called gas-prone because it yields some hydrocarbon gas but little oil during maturation. This term is misleading because type III kerogens actually yield less gas than types I and II. Some thick deltaic deposits dominated by type III kerogen have generated substantial oil (e.g., Mahakam Delta in Indonesia, U.S. Gulf Coast, and offshore West Africa), primarily from liptinite macerals that may represent only a small portion of the kerogen.

Type IV
Type IV kerogen is “dead carbon” showing very low atomic H/C (about 0.5-0.6) and low to high O/C (≤0.3). These kerogens are dominated by inertinite macerals that generate little or no hydrocarbons during maturation. Type IV kerogens can be derived from other kerogen types that have been reworked or oxidized.

CHAPTER APPENDIX B:
Key Factors Affecting Accuracy of Geochemical Logs

We recommend Rock-Eval pyrolysis and TOC analyses every 10-20 m and vitrinite reflectance data every 100-200 m throughout each well. Closer sample spacing results in better geochemical logs. The strength of the pyrolysis and TOC screening approach lies in sheer numbers of analyses. Trends are established by statistically significant amounts of data, and occasional anomalies become obvious (e.g., Figure 5.6). Incomplete geochemical logs based on isolated measurements are of little exploration value.

Because screening analyses are inexpensive, it is practical to generate libraries of detailed geochemical logs. As provinces become better explored, libraries of logs progressively reduce exploration risk by clarifying the three-dimensional distributions of organic facies, thermal maturity, and prospective reservoirs. Consistent scales for geochemical logs simplify comparisons of source rock intervals between wells.

Rock Sample Preparation
Rock sample quality generally decreases in the following order: conventional whole core, sidewall core, drill cuttings, and outcrops. Cuttings can be contaminated by particulate or fluid (e.g., oil-based mud) drilling additives or can contain rock chips “caved” from higher in the section during drilling. Cuttings polluted with diesel can be cleaned with a solvent, but the residue lacks useful volatile compounds and only the kerogen can be analyzed reliably. Samples stored for long periods are generally reliable, provided they are clean and were stored under conditions restricting the growth of fungus. Core, sidewall, and outcrop samples can be brushed or scraped to remove mudcake, residues from marking pens, or weathered surfaces.

Outcrops are commonly weathered, resulting in altered organic matter. Outcrops should be systematically collected (e.g., every 2 m vertically) from fresh cuts, such as cliffs, roadcuts, or river banks. In general, outcropping rocks with high dips are more deeply weathered than those with low dips. Fist-sized samples (5 × 5 × 8 cm) are sufficient for most source rock analyses. Accurate positioning (within about 10 m) can be obtained using a commercially available hand-held satellite positioning system. Sample locations should be recorded on a measured section, outcrop sketch, or photograph.

Samples can be screened in the field by sedimentologic features or using a commercially available portable pyrolysis system. Shales or dense, fine-grained micritic carbonates are the best candidates for source rocks. Good source rocks containing type I or II kerogen are commonly thinly laminated and range from yellowish brown to grayish brown or brownish black (GSA Rock Color Chart, 1979). However, good source rocks can
be light-colored on weathered surfaces. Burrows and abundant benthic macrofossils indicate poor conditions for preservation of organic matter. When in doubt, it is better to sample a candidate source rock for laboratory confirmation.

Most geochemical logs are based on cuttings, complemented by sidewall cores and conventional cores. The following discussion is directed toward cuttings, although the same general criteria for preparation and interpretation apply to cores and outcrop samples. Each sample should weigh about 50 g. Cuttings are best washed at the well site prior to shipment and storage because mudcake can become more difficult to remove with time. Cuttings are washed of mudcake using fresh or salt water, and in the process, wet-sieved with a 2-mm top sieve and a 180-μm bottom sieve. Cuttings must not be washed with organic solvents, which remove soluble components. Many particulate additives can be floated off by panning in an evaporating basin. Samples are air-dried at about 40°C.

After arrival in the geochemical laboratory, cuttings are rehashed and described for lithology. Washed and air-dried cuttings are examined using a binocular microscope, and contaminants, such as walnut hulls, woodchips, metal, and obvious caved material, are removed by “negative picking.” We do not recommend “positive picking,” where an inferred representative lithology is selected for analysis from a mixture of lithologies in a sample. Positive picking generally results in nonrepresentative samples. We do not recommend composite samples of cuttings from several intervals. Natural mixing of cuttings in the mudstream during drilling is a form of compositing that need not be compounded in the laboratory. When severe, caving or bypass of lithologies on the shaker table can cause problems in interpretation. We have found that natural mixing is reasonably representative of significant rock lithologies. For example, thin, organic-rich beds that might be sampled by sidewall cores are “averaged” and do not appear as organic-rich spikes on geochemical logs (Figure 5.10).

A small portion of the dried cuttings is crushed to fine sand particle size (0.125-0.25 mm). Grinding to a smaller size is not recommended because powdered samples can result in anomalous Rock-Eval results, including poor S2 peak definition, low S2 yield, and erroneous T<sub>max</sub> values. The crushed samples (100 mg) are analyzed using Rock-Eval pyrolysis where every twentieth sample is a rock standard. If very rich in organic matter (>10 wt. % TOO, sample size is reduced and the sample is Soxhlet extracted for 24 hr with dichloromethane:methanol (9:1), dried for 2-3 hr, and pyrolyzed.

We recommend that both pyrolysis and TOC be completed on every sample. Rock-Eval pyrolysis is more expensive than TOC, so many prefer to complete Rock-Eval pyrolysis only on samples exceeding 0.3% TOC. Alternately, TOC can be performed only on samples with S2 ≥ 0.05 mg HC/g rock.

Sidewall and conventional cores are better than cuttings for outcrop samples for both screening and detailed geochemical analyses. However, caution must be applied where these samples represent organic-rich beds of insufficient thickness to serve as regionally significant source rocks. Sidewall or core samples for source rock analysis should be taken at 15-30 m intervals in fine-grained lithologies. Although not recommended for cuttings, composites of sidewalls or cores at 15-30 m intervals may be a useful supplement for analyses of isolated samples, particularly where organic matter in the source rock varies nonsystematically with depth (Figure 5.10).

Critical information that should be included with rock samples includes well name, operator, location, formation, age, depth, and type of sample. Good quality paper or zip-lock plastic sample bags are recommended. Paraffin coatings are not recommended for storing rock samples. Maps and lithology logs assist in evaluating sample quality and geologic relations. If additives or migrated oil could represent contaminants, samples of these materials are helpful.

**Oil Sample Preparation**

Oils are best collected in quart-sized or smaller glass containers with teflon cap liners. Oil can leach contaminants, such as phthalates, from plastic containers or rubber-lined caps. Fill only to the shoulder of the container to minimize contact of oil with the cap. Each sample container should be carefully labeled using waterproof ink. Bottled oils do not appear to undergo biodegradation for several years in storage. However, metal containers react with emulsified water and can leak.

Care must be taken in collecting production oils because they may represent mixtures from several zones. Surface exposure diminishes the information content of seeps due to evaporation, biodegradation, and possible contamination. It may be necessary to dig into seeping rock exposures to obtain the freshest possible samples.
APPENDIX C:
Methods for Measuring TOC

Direct Combustion
Weighed, pulverized rock (1–2 g) is treated with hydrochloric acid (6 N HCl) in Leco filtering crucibles. Spent acid and wash water are removed by vacuum filtration. The dried residue (100°C, 30 min.) is mixed with metal accelerator (elemental iron and copper), combusted using a high-frequency induction furnace (1200°C), and measured as carbon dioxide. Direct combustion is the most commonly used method for TOC. However, certain samples that contain immature oil-prone organic matter can lose from 10% (Peters and Simoneit, 1982) to 44% (Roberts et al., 1973) TOC as hydrolyzate with the acid filtrate prior to combustion.

Modified (Nonfiltering) Direct Combustion
Pulverized rock is weighed into Leco nonfiltering crucibles and treated dropwise with HCl until all CO2 evolution ceases, followed by reaction overnight. Spent acid and wash water are decanted, the residue is dried, mixed with accelerator, and analyzed as described for direct combustion. Although prohibiting loss of hydrolyzate, this method is laborious, and difficulties in removing all acid can result in corrosion of the drying oven.

Indirect (by Difference)
Two weighed aliquots of a pulverized, homogeneous sample are treated separately. One aliquot is mixed with accelerator and combusted to yield total carbon (TC = organic plus carbonate carbon). Another aliquot is treated dropwise with HCl and the evolved CO2 is measured. Total organic carbon is the difference between TC and carbonate carbon. Indirect TOC is generally more accurate for organic-poor (<0.5 wt. % TOC), carbonate-rich samples than direct TOC. However, for samples with TOC values over about 0.5 wt. %, cumulative errors resulting from measurements for two aliquots make this approach less satisfactory than other methods.

Pyrolysis plus Combustion Products
Some pyrolysis systems allow determination of TOC by summing the carbon in the pyrolyzate with that obtained by oxidizing the residual organic matter at 600°C. For small samples (100 mg), this method provides more reliable TOC data than conventional combustion methods, which require about 1–2 g of ground rock. However, mature samples, in which vitrinite reflectance (R0) exceeds about 1%, yield poor TOC data because the temperature is insufficient for complete combustion.

CHAPTER APPENDIX D:
Key Rock-Eval Pyrolysis and TOC Parameters

S1 measures hydrocarbon shows as the amount of free hydrocarbons that can be volatilized out of the rock without cracking the kerogen (mg HC/g rock). S1 increases at the expense of S2 with maturity.

S2 measures the hydrocarbon yield from cracking of kerogen (mg HC/g rock) and heavy hydrocarbons and represents the existing potential of a rock to generate petroleum. S2 is a more realistic measure of source rock potential than TOC because TOC includes "dead carbon" incapable of generating petroleum.

S1 + S2 is a measure of genetic potential (Tissot and Welte, 1984) or the total amount of petroleum that might be generated from a rock.

Production or productivity index [PI = S1/(S1+S2)] gradually increases with depth for fine-grained rocks as thermally labile components in the kerogen (S2) are converted to free hydrocarbons (S1). Reservoir rocks show anomalously high PI values compared to adjacent fine-grained rocks. For T\textsubscript{max} values of <435°C and T\textsubscript{max} in the range 435°–445°C, PI values exceeding 0.2 and 0.3, respectively, are considered anomalous.

Hydrogen index [HI = (S2/TOC) × 100, mg HC/g TOC] and S2/S3 are proportional to the amount of hydrogen in the kerogen and thus indicate the potential of the rock to generate oil. High hydrogen indices indicate greater potential to generate oil. Although HI versus OI plots are generally reliable indicators of kerogen type, gas-prone coals and coaly rocks can give anomalously high HI values that must be confirmed by elemental analysis (Peters, 1986). The average HI in a rock interval is best determined from the slope of a regression line on a graph of S2 versus TOC (Langford and Blanc-Valleron, 1990).

Oxygen index [OI = (S3/TOC) × 100, mg CO\textsubscript{2}/g TOC] is related to the amount of oxygen in the kerogen. In general, the S3 measurement is not as reliable as other Rock-Eval parameters, partially because of interference of carbonate minerals or kerogen oxidation resulting from pulverizing the sample. When S3 results are suspected to be unreliable, HI versus T\textsubscript{max} (Espitalié et al., 1984) can be substituted for the HI versus OI plot.

T\textsubscript{max} measures thermal maturity and corresponds to the Rock-Eval pyrolysis oven temperature (°C) at maximum S2 generation. T\textsubscript{max} should not be confused with geologic temperatures. T\textsubscript{max} is partly determined by the type of organic matter (Figure 5.9) (Peters, 1986).