

# Basic Geochemical Evaluation of Unconventional Resource Plays

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## Introduction

Basin-centered petroleum accumulations such as the Bakken Formation in the Williston Basin of North Dakota have recently been recognized as being important in the future development of energy resources. There are several features that these petroleum systems have in common. The systems typically include the deposition of organic-rich rocks that form the core of the petroleum system when subjected to elevated temperatures for sufficient periods of time. This allows for the source rock to “mature” to the point that oil is generated. Once a sufficient amount of generation has occurred the oil is expelled into neighboring rocks and, in instances when these rocks are poorly permeable, the oil accumulates under high pressures. The three interconnected processes of deposition, maturation, and expulsion may all be studied using various types of geochemical analyses.

Deposition of a potential source rock involves a tightly constrained set of circumstances. These include high rates of biological activity that produce organic carbon compounds that following death accumulate, are buried, and preserved. High levels of organic productivity are associated with many environments. However, the efficient preservation of organic matter produced in these environments is limited to only a few depositional settings. In general these settings contain low levels of free oxygen that prevent the deposited organic matter from being destroyed by biological activity or chemical processes. Environments that meet these criteria include lakes, seas, and marshes in which water depth, bottom topography, and the absence of currents prevents near-surface oxygenated waters from mixing with bottom waters. When large amounts of organic debris are added to stagnant water, bottom waters become depleted in dissolved oxygen and under extreme conditions may become oxygen-free (anoxic). In this environment, proteins, carbohydrates, and other organic compounds accumulate and may be buried as the depositional environment subsides and sediment is added. Following burial, organic compounds deteriorate and reform into large, complex organic molecules that are insoluble in organic solvents. This material, known as kerogen, undergoes a continuous series of temperature- and pressure-driven chemical reactions that remove hydrogen, oxygen, sulfur, and nitrogen from the kerogen. Over time, and with sufficient heat, these reactions “mature” the kerogen to the point that oil and gas is generated. As petroleum generation proceeds, newly formed oil and gas expel water contained in the source-rock. With sufficient maturation, possibly in conjunction with source rock compaction, oil is injected into the pore space of the surrounding non-source rock units. If there are no permeable avenues of escape this oil and gas will collect close to the source bed, frequently under high pressure, and form an “unconventional resource.” Throughout this process, changes in the composition of the kerogen occur.

These changes provide clues that may answer questions such as:

- 1) Is a given kerogen capable of producing petroleum?
- 2) If so, what are the likely types of petroleum that may result?
- 3) Did a given source rock generate petroleum?
- 4) If so, how fast and possibly how much?

## Source Rock Evaluation

Probably the most important aspect of evaluating a potential source rock involves determining the amount and character of organic matter that could have been available, given the proper conditions, to generate oil and gas. One of the first things to consider is just how much organic carbon is currently present in the rock. Secondary concerns include evaluating the organic carbon with respect to the likely products that may be generated, as well as the subsurface conditions for the generation of oil and gas. Understanding these aspects of a source rock provides a basis for evaluating the resource potential of individual formations on a basin-wide basis.

## Determination of Total Organic Carbon

The amount of total organic carbon (TOC) present in a potential source rock is one of the first analyses that need to be made. One of the more popular methods of doing this makes use of the LECO® TOC method. This method is preferred because it can differentiate between organic carbon and inorganic carbon using samples that weigh less than a gram. One of the important aspects of this method is that inorganic carbon compounds, mostly carbonate minerals, are removed with acid prior to analysis. The remaining organic carbon is combusted in an oxygen atmosphere releasing the organically bound carbon in the form of CO<sub>2</sub>. The mass of CO<sub>2</sub> measured is converted into a percent (% TOC) using the dry weight of the original sample. In the absence of other information, the richness of a source rock may be classified by weight% TOC as follows:

Poor	0 to 1%
Fair	>1 – 2.5%
Good	> 2.5 to 5%
Excellent	> 5%

The total organic carbon (TOC) measured with the LECO® method includes carbon compounds capable of generating petroleum (“live” carbon) as well as carbon compounds that are not (“dead” carbon). Unfortunately the LECO® method alone cannot distinguish between “live” and “dead” organic carbon. Therefore,

the TOC content of a source rock must be combined with some way of determining how much of the TOC consists of “live” organic carbon.

### Rock Eval Pyrolysis

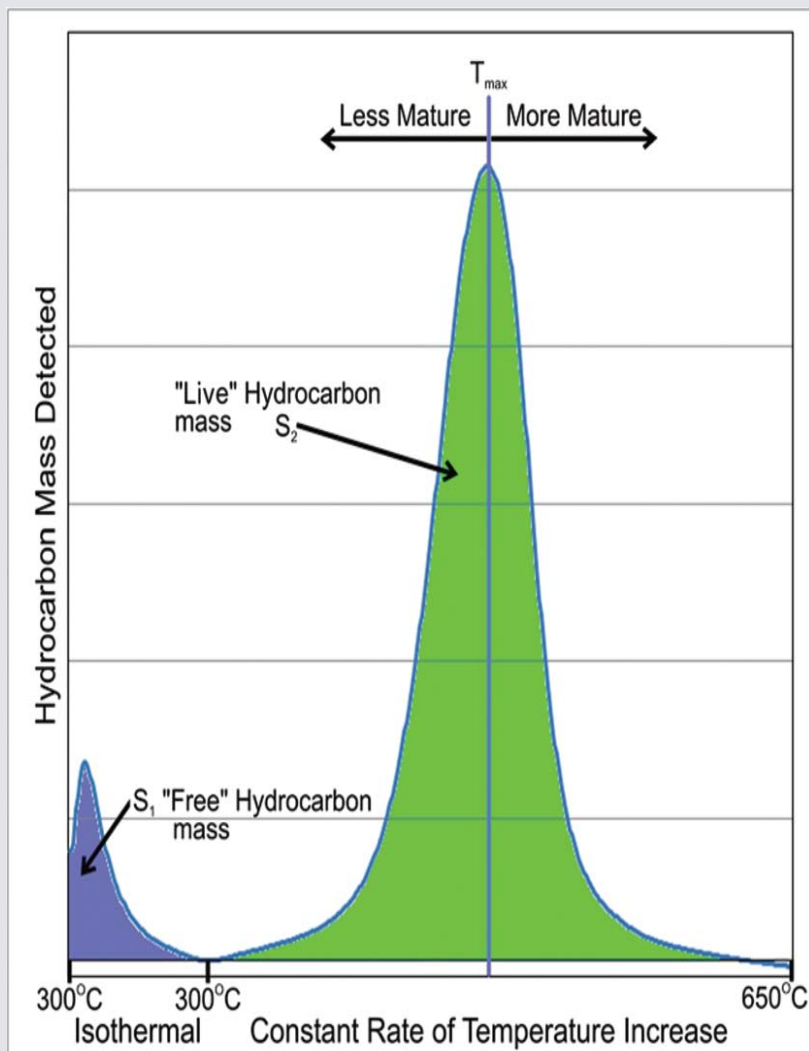
One of the most robust and least complicated methods of analyzing “live” organic carbon makes use of the programmed pyrolysis method known as Rock Eval analysis. This method artificially matures source rock kerogen by subjecting it to elevated temperatures. At high temperatures (400°-500°C) the chemical reactions that produce petroleum or petroleum-like substances are greatly accelerated so that the maturation of a sample can be accomplished in as little as 20 minutes. Under natural subsurface conditions, millions of years would likely be needed to achieve a similar result.

In the Rock Eval method a small sample (~0.1 g) is placed in an oven and heated. During heating, free oil and “live” organic matter in the kerogen convert to hydrocarbon vapors that are collected by a carrier stream of chemically inert helium or, in older units, nitrogen gas. In most Rock Eval systems the carrier stream is split into one that feeds a flame ionization detector and a second stream that flows to a detector that measures the mass of oxygen-bound carbon (CO, CO<sub>2</sub>). The stream passed to the flame ionization detector flows into an oxygen-hydrogen flame that burns (ionizes) the hydrocarbons and results in a voltage that is calibrated to the mass of hydrocarbons present in the carrier gas stream.

The Rock-Eval method consists of two heating periods. During the first period, temperatures are held constant at 300°C for two or three minutes, depending on the Rock Eval method. At this temperature, free oil vaporizes and is recorded as the S<sub>1</sub> curve on the standard Rock Eval presentation (fig. 1). The mass of free oil from the integrated S<sub>1</sub> curve has the potential of being a direct measurement of the oil generated in the subsurface. However, its utility is often compromised when other hydrocarbons, such as diesel-based drilling fluids, contaminate the sample. When contamination is not involved, the value of S<sub>1</sub> is good evidence of past oil generation. The mass of free hydrocarbons obtained from the S<sub>1</sub> peak is frequently used to estimate the extent of oil generation through the use of the production index (PI). The production index is found from the free hydrocarbon mass (S<sub>1</sub>) and the mass of “live” carbon compounds (S<sub>2</sub>) present in the kerogen as follows:

$$\text{Eq. 1} \quad \text{PI} = S_1 / (S_1 + S_2)$$

During the second heating phase the sample is heated from 300°C to 650°C at a rate of 25°C per minute. Between these temperatures “live” kerogen decomposes into hydrocarbon vapor. The total hydrocarbon mass produced during this interval is reported as S<sub>2</sub>. The ratio of “live” hydrocarbon mass (S<sub>2</sub> in mg) to the total mass of carbon in the sample (TOC in g) is given by the Hydrogen Index or HI (Eq. 2). The HI provides a standardized measure of the relative amount of “live” carbon within a sample.



**Figure 1.** An example of a Rock Eval program showing the amount of free oil (S<sub>1</sub>) and the mass of “live” carbon bearing kerogen (S<sub>2</sub>) as a function of temperature (°C). T<sub>max</sub> corresponds with the maximum rate of hydrocarbon release (maximum S<sub>2</sub>) during the phase in which temperatures increase 25°C per minute.

$$\text{Eq. 2} \quad \text{HI} = S_2 \text{ (mg)} / \text{TOC (g)} \times 100$$

Between 300°C and 390°C oxygen-bearing kerogen compounds decompose into carbon dioxide and carbon monoxide. The mass of these components is recorded as S<sub>3</sub> (mg) and is a measure of the amount of organic oxygen that is contained in a sample. The relative mass of the oxygen-bearing hydrocarbons (S<sub>3</sub> in mg) relative to the total carbon mass (g) is called the Oxygen Index or OI (Eq. 3).

$$\text{Eq. 3} \quad \text{OI} = S_3 \text{ (mg)} / \text{TOC (g)} \times 100$$

One problem that Rock Eval analysis seeks to address involves the interrelated issue of kerogen quality and quantity. The question of the quantity of potential hydrocarbon-generating material in a source rock may be addressed by combining the results from the LECO® TOC analysis with the value S<sub>2</sub> from the Rock Eval method. In this way, the relative contribution of “live” kerogen (S<sub>2</sub>) to the overall carbon content of a sample (“live”+“dead” carbon) may be evaluated. The classification scheme proposed by

Dembicki (2009) uses this idea to evaluate the quantity of organic carbon susceptible to oil generation by cross-plotting TOC versus  $S_2$  (fig. 2). This classification scheme illustrates the existing oil-generation potential of a kerogen.

The interpretation of this classification scheme can lead to errors without some knowledge of the kerogen's past oil generation history, as oil generation causes kerogen to lose "live" carbon and hydrogen. This results in reduced values for the HI and TOC and raises the possibility that the original oil-generating potential of a given source bed is underestimated. This means that during maturation, an original kerogen that might be classified as being "excellent" could lose enough carbon and hydrogen during the formation of oil or gas that the remaining kerogen would be classified as only "good" or "fair." On the other hand, very high values of TOC and HI are no assurance that oil generation has taken place. It is important to understand that this classification refers to the current potential of a kerogen to generate additional hydrocarbons and should not be strictly viewed as an indicator of past petroleum generation. The determination of TOC and OI may provide clues concerning the "richness" of a potential source rock; the more important question that needs to be addressed involves the source rock's history of oil generation.

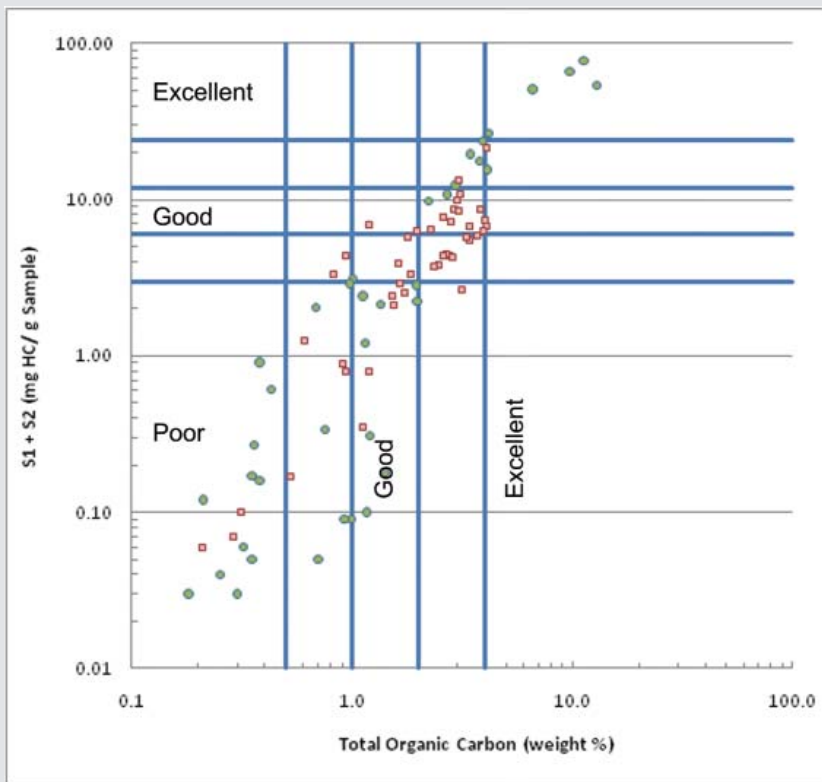
The question as to how much oil has been generated might be answered in part with the Production Index (PI). This index (Eq. 1) is the ratio of the amount of oil contained in a sample relative to the amount of oil and "live" carbon in the sample. If all of the oil generated by a source rock is still contained in the sample when it is analyzed then the value of  $S_1$  would be an excellent measure of the extent of oil generation. However, free oil in even the most confined conditions, may escape, either in the subsurface, during

drilling, or at the surface following drilling. Measurement of  $S_1$  also suffers from issues of sample contamination during drilling, sampling and handling. This is especially true when diesel-based muds are used as drilling fluids. Unfortunately, the use of the PI in the Williston Basin is limited because the prevalent use of oil-based drilling muds masks the true oil content of potential source rocks. However, there are other methods provided by the Rock Eval method that can be used to evaluate the oil generating history of a given source rock.

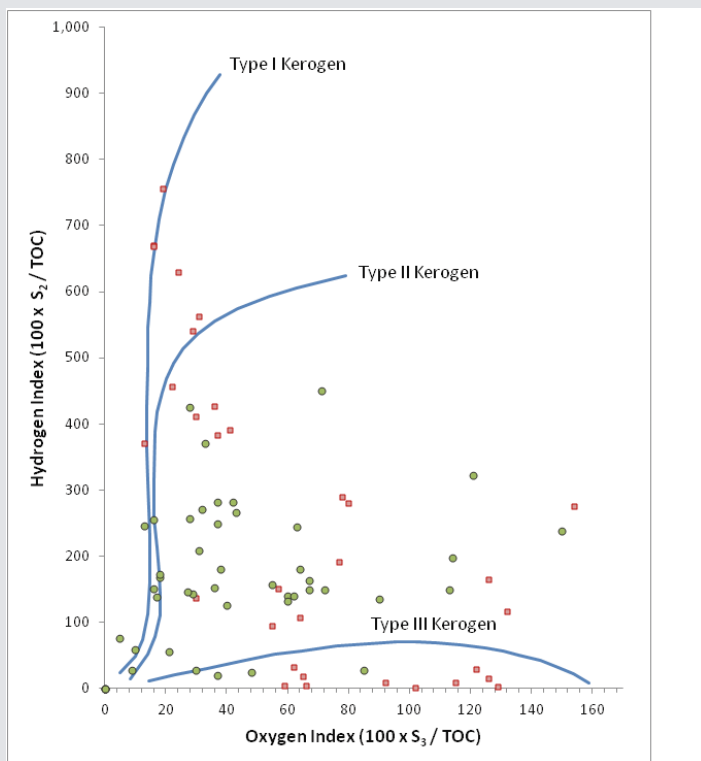
In the absence of direct evidence of oil generation, the question as to how much (if any) oil a given source rock has generated is best answered by establishing the kinetic behavior of the "live" carbon that is present in the source rock. The term "kinetics" refers to the relationship between temperature and the speed with which kerogen chemically breaks down into petroleum, either oil or gas or some combination of the two. The controlling factor, referred to as the "activation energy," depends upon the chemical composition of the kerogen as well as other factors that contribute to, or hinder the reactions that produce petroleum from the original kerogen. These factors are, in part, inherited from the environment that produced the original organic matter.

Depositional environments that generate large amounts of organic matter favor the formation of good source rocks. These include tropical regions where high rates of solar input coupled with large amounts of water provide ideal conditions for photosynthesis to initiate the fixation of carbon into organic compounds that eventually become kerogen. Kerogen is a confused mixture of very large, complex organic molecules. Unlike rock-forming minerals, it has no fixed chemical composition. However, the composition of kerogen is, to some degree, related to the original biological community that existed during deposition. In particular,

the relative amounts of hydrogen and oxygen are broadly related to the dominant types of persistent cellular matter (algae, pollen, spores, leaf cuticle and cellulose) present during deposition (Horsfield and Rullkotter, 1994). Four broad categories can be distinguished on this basis. These categories, Type I through Type IV, are differentiated by the amount of oxygen and hydrogen that the kerogen contains. Biological communities that produce waxy compounds (Type I) are associated with kerogen that contains large amounts of hydrogen and very little oxygen. Communities that produce kerogen rich in proteins and other lipids (Type II) typically contain a little less hydrogen and more oxygen than Type I kerogen. These kerogens tend to produce oil (Type I) or both oil and gas (Type II). Gas-generating kerogen (Type III) typically contains carbohydrate-rich matter and lignin derived from land plants deposited in environments that have larger amounts of oxygen-bearing organic compounds relative to the hydrogen-bearing compounds. Type IV kerogen is essentially "dead" organic carbon because there is too little hydrogen to allow for oil or gas generation. Type IV kerogen may result either as a happenstance of deposition or as the final residue of a pre-existing kerogen that has completely matured. In extreme cases, this "dead" carbon is crystallized into the mineral graphite.



**Figure 2.** Classification of kerogen quantity for samples of the Tyler Formation using Dembicki's (2009) scheme.



**Figure 3.** A modified Van Krevelen diagram show that the kerogen in the Tyler Formation consists of Types I and II as well as Type III. Significant mixing between kerogen types seems likely. The square data points (red) are from the Gov't.-Taylor #1-449 (NDIC: 4789; API: 33-007-00135-00-00) drilled by the Mule Creek Oil Company, Inc. in the Square Butte Field (SE 1/4, SE 1/4, Sec. 9, T139N, R103W). The data presented as circles (green) are from State of North Dakota 41-36 (NDIC: 4627, API: 33-033-00018-00-00) drilled by Shell Oil Co. in the NE 1/4, NE 1/4, Sec. 36, T137N, R100W in the Rocky Ridge field.

The HI and OI are frequently used to classify kerogen composition. One way involves the so-called pseudo-Van Krevelen diagram in which a set of type curves is used to differentiate between the kerogen types using a plot of HI versus OI. Application of this method to Tyler Formation is presented in figure 3.

Like the TOC-HI plots, interpretation of pseudo Van Krevelen diagrams requires care as during oil generation, kerogen bound hydrogen is lost to newly formed petroleum products and oxygen is also lost. Rock Eval analysis of samples that have undergone some level of oil generation will therefore yield HIs that are lower than, and in more mature samples much lower than, the original HI of the sampled source rock. At the same time hydrogen is being lost, organically bound oxygen is also being lost. The combined effect of these processes changes the HI and OI so that with increasing maturity the HI and OI descend roughly parallel to the kerogen type curves. One of the primary benefits of being able to classify kerogen is that by knowing the kerogen type one might be able to predict the likely product of petroleum generation and gain a bit of an understanding concerning the kinetics of petroleum generation.

#### **$T_{max}$ as a Source Rock Maturation Index**

$T_{max}$  is the temperature that produces the most hydrocarbon vapor during the programmed heating portion of the Rock Eval method.

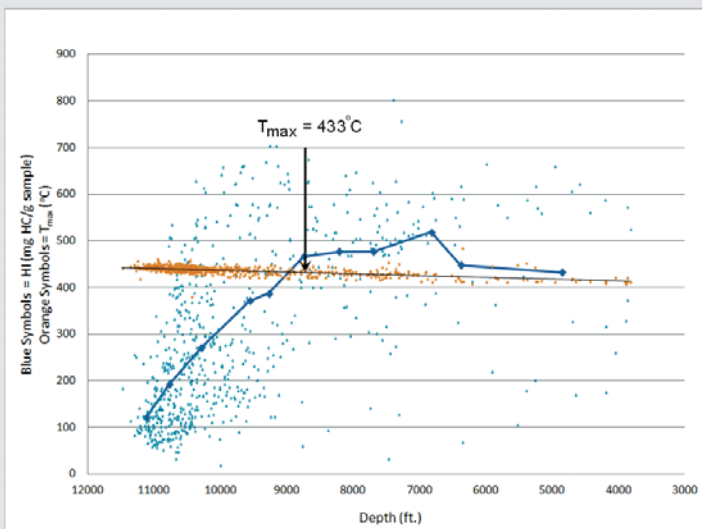
This temperature depends not only on the kinetic character of the kerogen but is also sensitive to the specific rate at which the sample is heated. In fact, the change in  $T_{max}$  as a function of heating rate is one way to determine the activation energy of a sample. Therefore, in order to compare  $T_{max}$  values it is imperative that the heating rate for each sample be the same. This is sometimes difficult to achieve and is frequently noted as a potential source of error when results from different laboratories or even different machines are compared.

Other sources of error result when comparing results from different versions of the Rock Eval method. Early generations of Rock Eval machines measured temperature with a thermocouple mounted on the outside of the sample chamber. This resulted in temperatures that were about 40°C lower than the actual temperature that the sample experienced. Modern Rock Eval machines eliminate this problem by placing the thermocouple directly below the sample. However, in order to make the newer Rock Eval data consistent with older data, the recorded sample temperature is “corrected” by subtracting about 40°C. Consequently, a reported  $T_{max}$  of 435°C actually corresponds to a sample temperature of about 475°C depending upon the exact machines and methods involved.

One of the more useful parameters provided by the Rock Eval method is the temperature that corresponds with the maximum release of hydrocarbons during the  $S_2$  phase of pyrolysis. These hydrocarbons are released by the thermally induced decomposition of the kerogen within the sample.  $T_{max}$  is significant because it is directly related to the activation energy of the “live” carbon contained in a kerogen. The activation energy is the amount of energy that must be added to a chemical system before a chemical reaction begins. The addition of energy in the form of heat (elevated temperature) results in exponentially accelerated reaction rates that are tied to the activation energy. Therefore the significance of  $T_{max}$  with regard to the maturation of a source can be understood by realizing that organic compounds with smaller activation energies generate petroleum faster than organic compounds with larger activation energies. In this way the process of kerogen “maturation” during oil generation involves the loss of organic compounds with small activation energies while leaving behind organic compounds with larger activation energies. This progressive removal of more easily reacted organic compounds from the mixture of organic material in a maturing kerogen increases the average activation energy of the remaining kerogen, which results in an increase in  $T_{max}$ . Hence, the maturation level of a kerogen may be estimated from  $T_{max}$ .

As a rule of thumb, a  $T_{max}$  of 435°C is frequently used to define a level of maturation that corresponds with intense oil generation. In many cases this threshold reasonably defines regions in which intense oil generation has probably occurred. However, better interpretations are possible when  $T_{max}$  is calibrated in some way to kerogen maturity. One way of doing this uses the variation in the hydrogen index (HI) with the depth of burial. Because the HI typically decreases as oil is generated, a rapid decline in the HI with depth could reasonably be interpreted to reflect the depth at which oil generation occurs (fig. 4).





**Figure 4.** Plot of  $T_{max}$  (orange dots) and HI (blue dots) versus depth using data from the Bakken Formation in North Dakota. The depth averaged value of HI suggests that oil generation is occurring at a depth of at least 8,700 feet with a corresponding  $T_{max}$  of 433°C.

In a similar fashion, calibration of  $T_{max}$  to HI may be accomplished by overlaying maps of  $T_{max}$  with a map that illustrates the lateral change in HI (Nordeng et al., 2010). In both cases, the  $T_{max}$  that corresponds with rapid changes in HI provides the basis for developing a “custom” value of  $T_{max}$  that is consistent with the indication of intense oil generation provided by the HI. The advantage gained by using  $T_{max}$  rather than trends in HI is that a single calibrated  $T_{max}$  is capable of providing the same or a better measure of source rock maturity that would otherwise require several HIs. Where wells are few and far between, a single point maturation indicator may be the only way to establish the level of source rock maturity with any confidence.

### Conclusion

The use of Rock Eval data in conjunction with LECO® TOC analyses is capable of providing essential information that may

be used to evaluate the oil generation potential of source rocks. These data include the means to estimate the type and quantity of organic matter present in a source bed as well as data that bear on the degree of oil generation that has occurred. The inclusion of these data with other indicators of accumulated oil, such as high shale resistivities and overpressured formation pressures, are the building blocks needed to construct and calibrate a predictive three-dimensional model of oil and gas generation in North Dakota.

### References

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## Staff changes at the Dept of Mineral Resources

### Geological Survey

Ned Kruger – Subsurface Geologist

### Oil and Gas Division

Steve Thuner – Production Technician – Minot District  
 Dan Wells – Production Technician – Williston District  
 Marc Binns – Field Inspector – Williston District  
 Ashleigh Day – Field Inspector – Dickinson District  
 Allen Christensen – Field Inspector – Williston District  
 Joyce Eversvik – Field Inspector – Dickinson District

### Support Staff

Alison Ritter – Public Information Specialist – Bismarck Office  
 Linda Llewellyn – Office Assistant – Bismarck Office  
 Robyn Loumer – Accounting Budget Specialist – Bismarck Office

Karen Gutenkunst – retired after 35 years as the Business Manager for the Department of Mineral Resources