Molecular Thermal Maturity Indicators in Oil and Gas Source Rocks

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Abstract

Many detailed chemical parameters have been proposed as indicators of thermal maturity in oil and gas source rocks. Certain classical maturity parameters involving carbon preference indices and compound class ratios, such as hydrocarbons/extract yield and extract yield/total organic carbon, are less commonly used today, having been complemented with detailed molecular parameters. Among these parameters, the molecular distributions of metalloporphyrins, cyclic hydrocarbons, low-molecular-weight hydrocarbons, and gases are most commonly used. Recent instrumental advances have allowed the routine measurement of molecular ratios in geochemical organic matter, stimulating the development and use of biological markers, such as steranes, hopanes, and metallated tetrapyroles, as thermal maturity indicators. Increased chromatographic resolution of source rock hydrocarbons has also led to the use of low-molecular-weight hydrocarbons, methylphenanthrenes, and aromatized steranes as maturity indicators. In this paper, we discuss these developments, emphasizing the applications and the pitfalls of using molecular maturity indicators.

Measurements of source rock thermal maturity attempt to describe the progress of the sum of the chemical reactions that convert sedimentary organic matter into oil and gas. Such measurements can be made on a molecular basis, using both soluble organic matter (C₁₅⁺ hydrocarbons) and gases/gasoline range hydrocarbons (C₁₅⁻). The biological markers, including both aliphatic and aromatic hydrocarbons, are probably the most "ideal" molecular maturity indicators currently available, although their range of applicability is generally limited. Gases and gasoline range molecules (particularly their isotopic characteristics) also have great potential as thermal indicators, although an understanding of migrational fractionation is critical. While no single thermal maturity indicator will ever be the ultimate "ideal" parameter, molecular indicators will undoubtedly increase in importance in coming years, owing largely to their specificity and to the increasing ease of obtaining this type of data.

Introduction

The presence of thermally mature source rocks is a necessary element for the existence of a petroliferous basin. The maturity of an organic rich sediment is commonly used as a necessary criterion for distinguishing actual oil and gas source rocks from merely potential source rocks. Recognizing the need for thermal input in the generation of commercial quantities of petroleum from fine-grained sediments, source rock geochemists have developed numerous methods for assessing thermal maturity levels in a basin. Recently, the traditional "bulk" techniques involving compound class distributions, vitrinite reflectance, and spore coloration, to name a few, have been complemented by detailed molecular parameters, involving ratios and distributions of specific compounds. As instrumental technology for analytical chemistry advances, use of such molecular approaches to the problem of thermal maturity measurement will undoubtedly increase, hopefully leading to increasingly refined maturity indicators.

The purpose of this chapter is to present a synthesis of current thinking concerning molecular thermal maturity indicators that derive from the extractable organic matter of petroleum source rocks, in light of the strengths and weaknesses of...
Figure 4.1. Values of maturity parameters versus true “maturity” (SOM = sedimentary organic matter). Line A illustrates an ideal maturity parameter—potential values are proportional to maturity over the entire possible range. Lines B (e.g., biomarker ratios) and C (e.g., graphite crystallinity) are typical of real maturity parameters, where the parameter's value is proportional to “maturity” over only a limited range.

the classical approaches using bulk measurements. Although practical applications are discussed to illustrate various points, the emphasis is mainly conceptual. Consequently, no attempt is made to document exhaustively every molecular indicator used to date. Rather, specific molecular indicators are reviewed in terms of their strengths and weaknesses, with an eye toward infusing some fresh ideas into the discussion of those thermal maturity parameters that are currently in vogue. We concentrate on hydrocarbon molecular indicators, including gases and gasoline range hydrocarbons as well as the C15+, fraction. Kerogen, because of its role as a progenitor of most of the hydrocarbons, is discussed also. We begin with an overview of the use of thermal maturity as a conceptual approach to petroleum exploration.

An adequate definition of thermal maturity, as the term is used by petroleum geochemists, is unavailable in the literature. Maturity, as used in this chapter, describes the position or extent of the chemical reactions that convert sedimentary organic material (SOM) into gas and graphite. One end member of this evolutionary pathway is bacterial and plant debris (mostly kerogen and bitumen, following diagenetic conversion), which are generally low in hydrocarbons. At the other extreme is dry thermal gas and hydrogen-deficient carbonaceous residue (graphite). “Maturity” is the extent to which this reaction complex has proceeded. Part way along this reaction coordinate axis, liquid and gaseous hydrocarbons are produced, then destroyed.

Figure 4.1 illustrates this concept of maturity. The x axis varies from 100% SOM on the left to 100% gas and graphite on the right. The objective of measuring chemical maturity parameters is to determine where on this reaction coordinate scale a kerogen, bitumen, oil, or gas sample lies. In this regard, the choice of maturity parameter is critical.

The ideal maturity parameter would derive from a reaction of the form

$$A \rightarrow^k B$$

where k is the rate constant in units of 1/time. In order to use such a reaction to derive an ideal maturity parameter, the following conditions must be satisfied:

1. A and B should be single compounds, and the reaction should be irreversible.
2. A should have no fate other than transformation to B.
3. B should be stable and have no source other than A.
4. The reaction should not proceed to completion in less than the full range of maturity of interest.

The best parameter for assessing maturity using such a reaction would be the ratio of the concentration of B to the sum of the concentrations of A and B, as this ratio would be independent of the initial concentration of A. Ideally, this ratio would be a linear function of maturity, varying from zero to one, and would represent the previously discussed reaction coordinate.

Many reactions related to the genesis of oil and gas from kerogen are conceptually of form $A \rightarrow B$ but have significant problems as indicators of maturity. In reality, most reactions are more similar to that shown in Figure 4.2. In this case, B is neither stable nor the unique product of A. Also, A is not conserved in reacting to form B, but has sources and sinks that are external to the reaction of interest.