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Organic Metamorphism and the Generation of Petroleum[1]

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Abstract A scale referred to as "Level of Organic Metamorphism" (LOM) describes how far the thermal metamorphism of sedimented organic matter has progressed during subsurface burial. It represents a single, continuous numerical scale which is applicable to the entire thermal range of interest in the generation and destruction of petroleum. It is based on coal rank and is convenient for interrelating other useful scales of organic metamorphism.

A relation of temperature to time for petroleum generation is based on LOM values of sedimentary rocks in the 9- to 16-LOM range with reasonably dependable *maximum* temperatures and *effective* heating times. The relation is nearly equivalent to a doubling of the reaction rate for each additional 10°C, and the apparent activation energies increase from about 18 to 33 kcal/mole as LOM increases from 9 to 16.

The principal metamorphic stages of petroleum generation and a zone of initial oil-source-rock maturity are superimposed on graphs of LOM versus depth for two wells to illustrate the prediction of specific depths where oil, gas condensate, and high-temperature methane would be generated in petroleum source rocks at any given location.

INTRODUCTION

The origin of petroleum can be described generally by four successive stages: (1) the formation of organic-rich, fine-grained sediments through the photosynthesis, deposition, and preservation of abundant organic matter; (2) the thermal degradation of that organic matter during burial to increasing temperatures, with the formation of petroleum molecules; (3) the expulsion of oil and gas from its fine-grained source rock, and its migration through and entrapment in porous, permeable, reservoir rock; and (4) the physical, thermal, and/or biologic alteration of petroleum in reservoir rock. The second of these four stages—the thermal metamorphism of organic matter—is the subject of this paper.

Publications by Stevens et al (1956) and Bray and Evans (1961) provided the stimulus for renewed interest in the importance of heat in the generation of petroleum. They were the first to point out that the small amounts of hydrocarbons in recent sediments typically have distributions of n-alkanes which are significantly different from those of crude oils or postulated source beds. They concluded that shales and limestones with odd-to-even carbon-number ratios significantly greater than those of crude oils could not have generated enough hydrocarbons to form petroleum-like mixtures and thus to expel crude oil. Subsequently, Philippi (1965) demonstrated for Miocene source sediments of the Los Angeles and Ventura basins of California that most of the oil in those basins is generated at burial temperatures exceeding 115°C (239°F) and that shale hydrocarbon compositions become crude-oil-like or "mature" in those basins only after burial to temperatures of about 150°C (302°F).

The generation of petroleum hydrocarbons from thermally reactive organic matter (mainly kerogen) during burial is a part of the overall process of thermal metamorphism of organic matter. We refer to this process as "organic metamorphism." It also has been called "transformation" (Dobryansky, 1963), "eometamorphism" (Landes, 1966, 1967), "thermal alteration" (Henderson et al, 1968; Staplin, 1969), "incipient metamorphism" (Baker and Claypool, 1970), "katagenesis" (Vassoyevich et al, 1970), and frequently just "maturation." Dobryansky (1963) and subsequently many others have described the process as a series of thermocatalytic reactions leading to products of lower free energy by (1) *degradation,* leading to smaller molecules of increasing volatility, mobility, and hydrogen content (with methane as the end product in sedimentary rocks), and (2) *condensation,* leading to a carbonaceous residue of decreasing hydrogen content (with graphitic carbon as the end product).

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There are many published scales (e.g., coal rank, spore and pollen carbonization, elemental composition of kerogen, vitrinite reflectance, electron spin resonance, and chemical maturity indicators) which reflect irreversible effects of organic metamorphism. For application to petroleum exploration problems, however, there has been a need for a single numerical scale which is applicable over the entire thermal range of interest in the generation and destruction of petroleum. This paper describes the development of such a scale for indicating how far the organic metamorphic process has gone at any given location, its dependence on temperature and time, and its application to the study of petroleum generation.

CONTINUOUS NUMERICAL SCALE OF ORGANIC METAMORPHISM

Desired Characteristics

The coal-rank scale has for many years provided the basic framework for studying the coalification process and recently has been used for comparing stages of organic metamorphism in petroleum source rocks (Brooks and Smith, 1967, 1969; Brooks, 1970; Hacquebard and Donaldson, 1970; Vassoyevich et al, 1970; Teichmüller, 1971; Shibaoka et al, 1973). None of the various coal ranking properties such as calorific value, moisture content, volatile matter (or fixed carbon), hydrogen content, and vitrinite reflectance, however, is satisfactorily applicable over the entire range of interest for petroleum generation. Thus the coal-rank scale is not a single numerical scale but, in effect, represents a series of two or more partly overlapping numerical scales. The main new characteristic needed in a scale of organic metamorphism, therefore, is that it is a numerical scale continuous over the whole range of generation and destruction of petroleum compounds.

Another desired characteristic is that the scale can be correlated with other available scales of organic metamorphism. This means mainly that it should be correlative with coal rank and the major coal-rank parameters, to which most scales have been compared.

Still another characteristic which we desired is that the scale be approximately linear with maximum burial depth in any given geographic location where the sedimentary column exhibits no major time hiatus or temperature-gradient anomaly. Such a scale would be convenient for geologists to use in relating organic metamorphism to depth on subsurface cross sections. As we shall see later, however, probably no single scale can be linear with maximum burial depth for subsurface sections of widely differing burial histories.

Inasmuch as temperature is considered to be the main defining factor in the process of organic metamorphism (Kartsev et al, 1971), it would seem that a scale of maximum temperature might serve the desired purpose. The effect of time, however, is too great to allow the use of maximum temperature alone as a general measure of organic metamorphism. For example, for subsurface organic matter which has reached an organic metamorphic level equivalent to the high-volatile/medium-volatile bituminous coal-rank boundary, we have observed maximum burial temperatures as low as 220°F (105°C) for Paleozoic rocks of West Texas and as high as 400°F (205°C) for Tertiary sediments of the Los Angeles and San Joaquin basins of southern California. A suitable scale, therefore, should reflect both temperature and time effects—thus temperature history.

Development of LOM Scale

With the above characteristics in mind, we developed a scale which we call "Level of Organic Metamorphism," or just "LOM." For this purpose we desired (1) a single subsurface section of organic-rich sediments which was buried at essentially a constant rate and a constant temperature gradient, and (2) a linear scale (zero to 20) to replace the depth scale of that ideal section. Of the subsurface sections considered at that time, it appeared that the New Zealand (Tertiary-Cretaceous) coal-rank column reported by Suggate (1959, p. 90) was the most suitable, and we used a modification of that column as our standard. Suggate included a numerical scale ("rank number") which was linear with maximum burial depth for the coal column. His scale, however, was simply maximum depth (in feet) divided by 1,000. To avoid any connotation of absolute maximum depth in the LOM scale, we used a numerical scale—from zero at no burial to 20 at the anthracite/meta-anthracite boundary—which was intentionally different from Suggate's rank number.

The defined relation of the LOM scale to Suggate's coal-rank column is shown in Figure 1. The only modifications which we added to Suggate's original coal-rank column are subdivisions within the subbituminous and high-volatile bituminous coal ranks in accordance with the ASTM classification.

Recently Bostick and Damberger (1971) reported a relative-depth column which is a composite from coalification studies (mainly Carboniferous) of several geographic areas of overlapping coal ranks. This composite coal-rank column, in which we have defined arbitrarily the anthracite/meta-anthracite boundary as LOM 20 for convenience of comparison, is compared with the Sug-

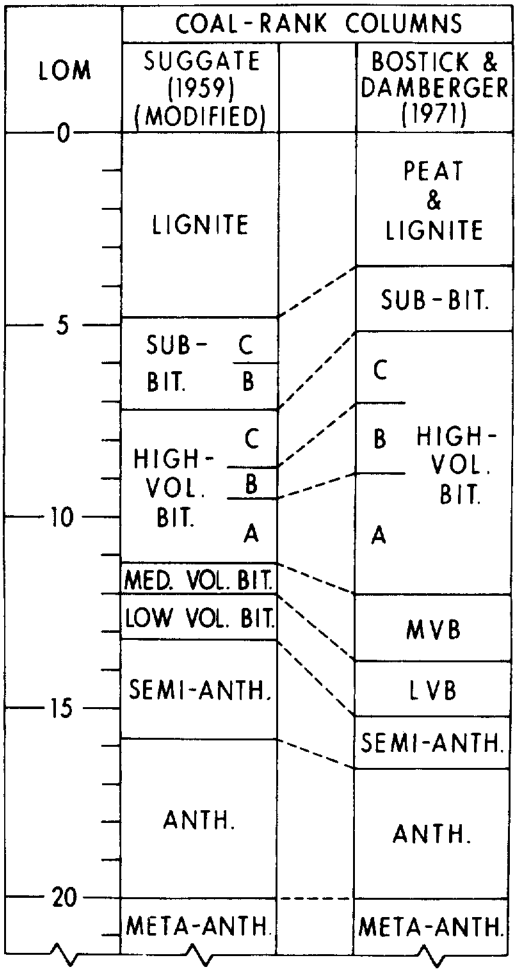

FIG. 1—Definition of LOM scale on basis of modification of Suggate's (1959) coal-rank column. Comparison with composite column (Bostick and Damberger, 1971) also thought to be approximately linear with depth.

gate column in Figure 1. The two depth columns are not in very good agreement. The lack of agreement may reflect problems such as difficulties in the proper geologic reconstruction of the sections, differences in ages of the coal sections, and irregular conditions of burial rates and temperature gradients within a single coal section. Without sufficient information to decide that either coal-rank column is clearly better than the other as a subsurface relative-depth standard, we are continuing to use the LOM scale as originally defined in terms of Suggate's coal-rank column, but we are keeping in mind the inferred possible limitations of the standard.

Correlation with Other Scales

Other useful scales of organic metamorphism which have been reported in the literature are compared with LOM in Figure 2. The figure includes coal rank, carbonization of structured organic matter, and vitrinite reflectance, and these scales are described briefly. Other indicators of increasing organic metamorphism which are useful but have not yet been correlated numerically with coal rank or LOM, include the elemental (C-H-O) composition of kerogen (Seyler, 1948; Van Krevelen, 1950; Van Krevelen and Schuyer, 1957; McIver, 1967; Durand and Espitalié, 1973; Tissot et al, 1974), paleotemperature based on electron spin resonance (Pusey, 1973a, b), and chemical maturity indicators (Stevens et al, 1956; Bray and Evans, 1961; Philippi, 1965; Tissot et al, 1974). In addition the combination of temperature and time has been used to predict levels of organic metamorphism, and this will be discussed in a later section of this paper.

Coal rank—The coal-rank scale shown in Figure 2 is the modified Suggate (1959) column. Shown together with the ASTM rank nomenclature are ranking properties of calorific value (BTU) for low-rank coals and percent volatile matter (VM) for higher rank coals. The part of the VM scale which we extended into the lower rank range (VM $>$ 31) is suitable only for humic, vitrinitic coals, and numerical values are shown in parentheses.

Changes in palynomorphs—Gutjahr (1966) has used a color scale (yellow through brown to black) based on the carbonization of spores and pollen. He showed that the intermediate color range of brownish yellow to dark brown accounted for only a small but important part of the LOM scale. Staplin (1969) reported a similar scale, "Thermal Alteration Index," based on the microscopic observations of both color and structure alteration of organic debris—mainly leaf cuticle and plant pollen. In 1974 Staplin et al reported the correlation of this index with coal rank. A similar scale, the state of preservation of palynomorphs, was reported by Correia (1967) but is not shown here.

Vitrinite reflectance—Probably one of the most useful measures of organic metamorphism is the reflectance of vitrinite (McCartney and Teichmüller, 1972; Shibaoka et al, 1973). Vitrinite is found not only in humic coals but also in coaly inclusions in many shales. Therefore, it is directly applicable to the study of temperature histories of petroleum source rocks (Teichmüller, 1971; Castaño, 1973; Castaño and Sparks, 1974). Furthermore, it provides a continuous numerical

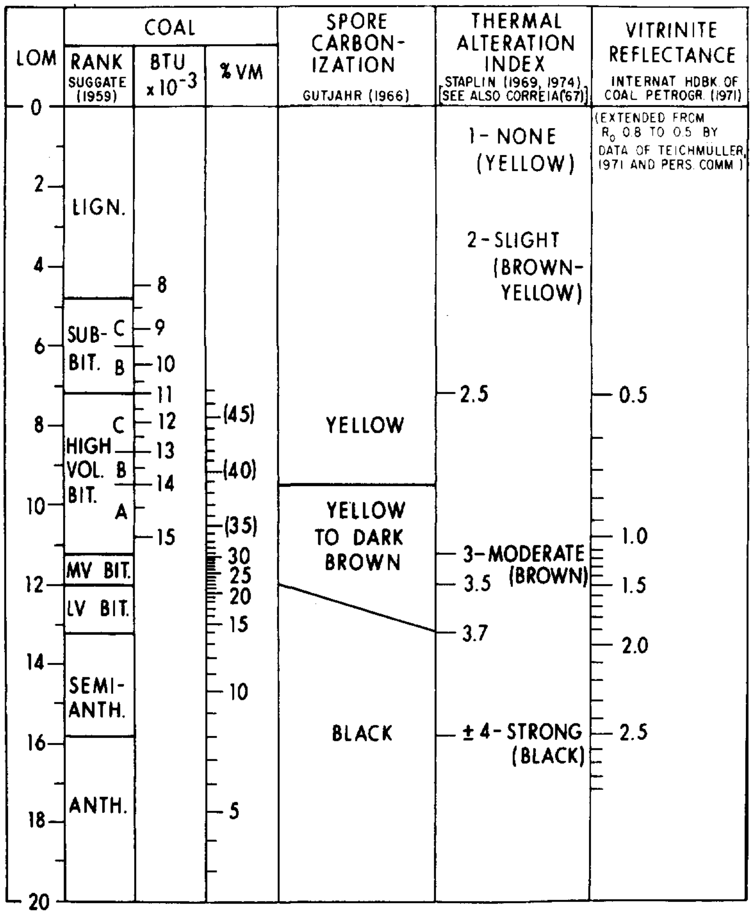

FIG. 2—Some scales of organic metamorphism. Part of volatile matter (VM) scale extended from 31 to 47 percent is suitable only for humic, vitrinitic coals; numerical values are shown in parentheses.

scale from about LOM 7 or 8 (high-volatile C bituminous) to LOM 17 or 18 (within the anthracite coal-rank range). The major part of the scale shown in Figure 2 ($R_o \geq 0.8$) was derived from the curve of vitrinite reflectance versus vitrinite volatile matter reported in Internat. Handbook on Coal Petrography, 1971, Rank, p. 3. The low-reflectance part of the scale ($R_o < 0.8$) represents an extension to values of 0.5 percent R_o at the subbituminous/high-volatile-bituminous-A boundary and 0.6 percent R_o at the braunkohle/steinkohle boundary (R. and M. Teichmüller, 1973, personal commun.) based on the data of Teichmüller (1971).

RELATION BETWEEN TEMPERATURE AND TIME

Although Figure 2 shows the correlation of several useful scales of organic metamorphism versus LOM, no simple scale of temperature is included. The reason for not including it is, as pointed out in many publications (e.g., Huck and Karweil, 1955; Teichmüller and Teichmüller, 1966, 1968; Lopatin, 1971; Bostick, 1973; Demaison, 1974), that both temperature and time are important factors of organic metamorphism. Neither temperature nor time alone, therefore, is a suitable single measure of the level of organic metamorphism present.

Because of the desirability of being able to use observed burial histories to estimate stages of the organic metamorphic process for oil source rocks and coals, the relative effects of temperature and time have been studied and reported by several investigators. Some of these will be discussed, together with our results from studies of maximum temperature and effective heating time.

Karweil Relation for Coal

The Karweil (1955) nomogram for predicting coal rank from burial history is probably the most widely publicized relation of time to temperature for subsurface organic metamorphism. It is based mainly on the properties of coals of the Ruhr area and makes use of an activation energy of 8.4 kcal/mole for coalification over the entire coal-rank range (Huck and Karweil, 1955). This value is lower than those reported since then by most authors and appears to overemphasize the importance of time, with respect to temperature, required to produce a given level of organic metamorphism. Recently Bostick (1973) has suggested a modification of Karweil's nomogram in an effort to overcome that problem.

Doubling of Rate for Each Increase of 10°C

Lopatin (1971), Laplante (1972), and Momper (1972) concluded that doubling the reaction rate with each increase in temperature of 10°C provides a suitable model of the relative effects of temperature and time in subsurface organic metamorphism. In addition Lopatin (1971) described a temperature-time index, τ, which represents an integrated burial history—a sum of the temperature-adjusted durations of burial—based on doubling the reaction rate for every increase in temperature of 10°C. Lopatin illustrated the use of the temperature-time index by means of data from the deep Münsterland-1 core hole, about 40 mi north of the Ruhr area of Germany. His graph of log τ versus vitrinite reflectance is linear over the range of 1.1 to 5 percent R_o and has a very high correlation coefficient ($r = 0.999$).

Maximum Temperature and Effective Heating Time

Most of the published studies of the time-to-temperature relation in organic metamorphic processes have been concerned either with heating at constant temperature or with integrating the temperature effects over the whole burial history. We have combined *maximum* temperature (T_{max}) with an *effective* heating time (t_{eff}) to develop a simplified method of predicting LOM for petroleum source rocks. Although approximate, the method is adequate in view of the uncertainties in the geologic data. Using a variety of typical burial histories and a wide range of activation energies (8.4 to 55 kcal/mole), we concluded that the time (t_{eff}) during which a specific rock has been within 15°C (27°F) of its maximum temperature (T_{max}) represents a reasonably suitable, though somewhat arbitrary, definition of effective heating time for use in graphs of T_{max} versus t_{eff}. A simple illustration may help to clarify the definition of t_{eff}. If a sediment which was formed 150 m.y. ago required 100 m.y. to reach a temperature of 120°C, and if at sometime during the remaining 50 m.y. the temperature of the sediment reached a maximum of 135°C and did not drop below 120°C, the last 50 m.y. is counted as the effective heating time.

The observed relations of maximum temperature to effective heating time are shown in Figure 3 for values of LOM in the range of 9 to 16. The relations were based on (1) measured LOM values of 40 fine-grained rocks of reasonably well-known and varied burial histories, and (2) the observed increase of LOM with depth for 8 deep wells in Colorado and Wyoming basins ($t_{eff} \sim 20$-40 m.y.) and 5 deep wells in the Anadarko basin of Oklahoma ($t_{eff} \sim 200$-400 m.y.). The relations of 1/T versus t_{eff} in Figure 3 are drawn as straight lines on the assumption of first-order reactions that obey the Arrhenius equation.

Also shown in Figure 3 are activation energies which were determined from the slopes of the lines. E_A was found to range from about 18 kcal/mole at LOM 9 to about 33 kcal at LOM 16. By comparison Weitkamp and Gutberlet (1968) reported an increase in apparent activation energy from about 20 to 60 kcal as kerogen conversion increased from zero to 80 percent in laboratory studies of microretorting of shales.

Figure 3 is intended for use in estimating LOM from maximum temperature and effective heating time. There are some practical problems in both calibration and application which represent limitations to general applicability. One of these problems is the lack of sufficient knowledge of paleotemperatures—particularly in the case of older sediments. Furthermore, even present-day formation temperatures are not always dependable. When the only temperature available for a given well was recorded under standard logging conditions within a few hours after mud circulation was discontinued, we add corrections of about 15, 30, and 35°C to recorded logging temperatures of 50, 100, and 150°C, respectively. Other problems in estimating LOM from T_{max} and t_{eff} include (1) those involved in reconstruction of burial history, and (2) occasional disagreement among methods of determining LOM

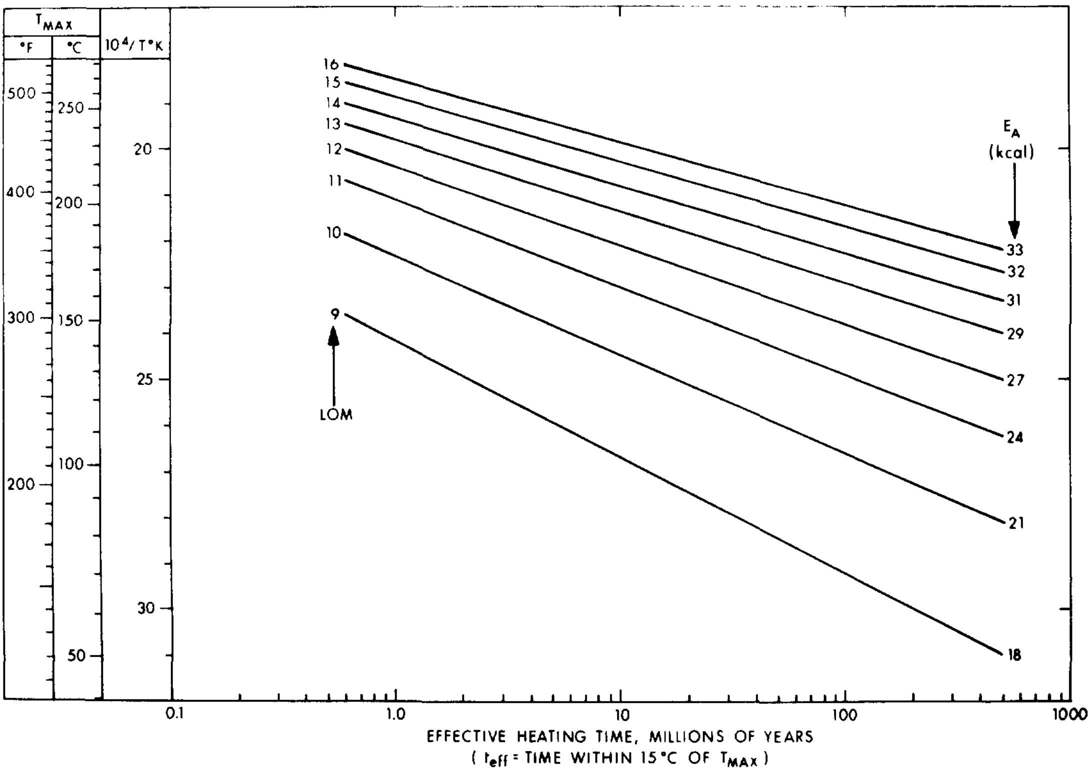

FIG. 3—Relation of LOM to maximum temperature and effective heating time.

of fine-grained rocks. In addition, the degree of conversion of kerogen to petroleum compounds at a given LOM is not necessarily constant but may vary significantly from one rock type to another (Vassoyevich et al, 1970). Because of such limitations, Figure 3 is probably most useful as a *relative* tool when using time and temperature data to estimate LOM values for fine-grained rocks. That is to say, the figure is utilized best as a tool for extrapolating LOM from dependable, measured values in a given subsurface section.

The relative importance of time with respect to temperature shown in Figure 3 (derived from subsurface data of T_{max} and t_{eff} at a given LOM) is essentially equivalent to a doubling of the reaction rate for each temperature increase of 10°C. This is illustrated in Figure 4 for three of the straight, constant-LOM lines of Figure 3 (i.e., LOM 9, 11, 16). Starting arbitrarily at $t_{eff} = 20$ m.y. on each straight line, a second line was drawn by repeatedly adding 10°C and cutting the heating time in half—or subtracting 10°C and doubling the time. In each case the resulting slightly curved line has an average slope (over the range of about 0.6 to 300 m.y.) similar to that of the related straight line. Thus the apparent activation energies which we have inferred for given LOM values are in good agreement with those required to cause the doubling in rate per 10°C temperature increase as recommended by Lopatin (1971). The Karweil (1955) diagram, on the other hand, typically requires higher temperatures for Tertiary rocks and lower temperatures for Paleozoic rocks to attain a given LOM value as compared with temperatures shown in Figure 3.

APPLICATION TO PETROLEUM GENERATION

One of the important applications of studies of organic metamorphism of potential petroleum source rocks is the determination of subsurface depths at which oil and gas are generated from the kerogens of those rocks. Such information in turn provides useful limitations on the timing of oil and gas expulsion, on the floor of oil in reser-

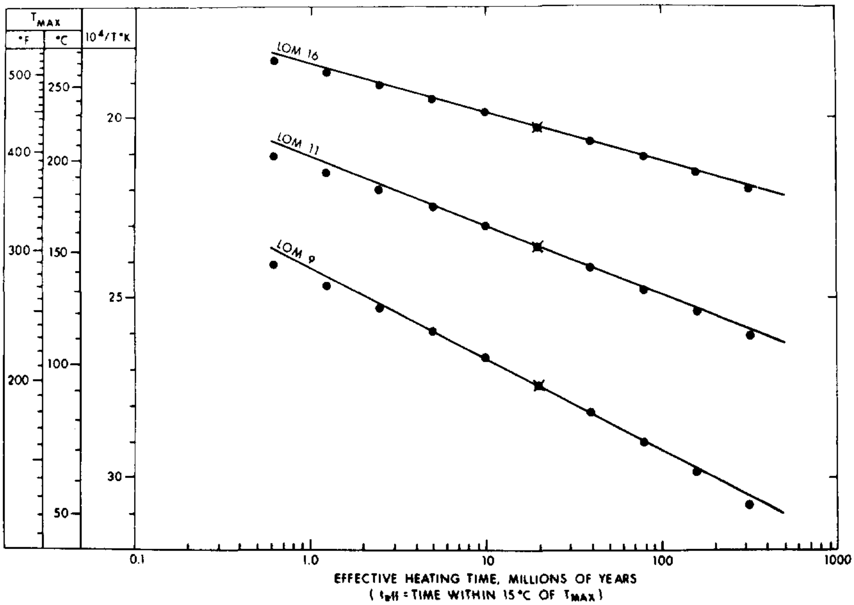

FIG. 4—Relation of LOM to maximum temperature and effective heating time: agreement with concept of doubling reaction rate for each increase in temperature of 10°C. Constant LOM values of 9, 11, and 16 derived from T_{max} and t_{eff} (Fig. 3) are shown as straight, solid lines. Three series of solid black dots related to three constant-LOM lines were obtained by starting arbitrarily on each line at t_{eff} 20 m.y. and then halving (or doubling) heating time for each temperature increase (or decrease) of 10°C.

voirs, and on other related questions. The application of the LOM scale to petroleum generation will be discussed.

As summarized by Vassoyevich et al (1970), the specific stage of the organic metamorphic process (thus the value of LOM) at which oil is generated in a given fine-grained source rock depends to some extent on the type of source rock. Those authors, however, defined a *principal* stage of oil generation in terms of coal rank—a stage which includes oil generation from a wide variety of source rocks. Similarly, they indicated principal stages of generation of gas condensate and late-katagenetic (high-temperature) methane. They referred to the whole stage prior to oil generation as a stage of formation of early diagenetic methane, which includes methane of biologic origin. The correlation of Vassoyevich's stages with the LOM scale via percent volatile matter is shown in Figure 5. According to that correlation the stage of formation of diagenetic methane and the three principal stages of generation of oil, condensate plus wet gas, and high-temperature katagenetic methane fall in LOM ranges of < 7.8, 7.8-11.6 (mainly 9-10), 11.6-13.5, and > 13.5 respectively.

Another indicator of oil generation is the maturation of source-rock hydrocarbons. On the basis of compositions of high-boiling n-paraffins (method of Bray and Evans, 1961) and naphthenes (method of Philippi, 1965) in both crude oils and source rocks, the compositions of source-rock hydrocarbons first become crude-oil-like (mature) in the LOM range of about 9 to 11.5 (Fig. 5). As seen in the figure, this zone of initial maturity occupies essentially the high-LOM two-thirds of Vassoyevich's principal stage of oil generation. This suggests that at least the low-LOM one-third of Vassoyevich's oil stage typically represents oil generation without reaching maturity—therefore without effective oil expulsion from the source rock.

Examples of the observed relations of LOM and petroleum generation to depth are shown for two wells—one in the Anadarko basin of Oklahoma (Fig. 6) and one in the Piceance basin of Colorado (Fig. 7). In both figures the LOM values were determined by vitrinite reflectance and, for comparison, by the use of T_{max} and t_{eff} in accordance with Figure 3. Vassoyevich's principal stages of petroleum generation and the zone of

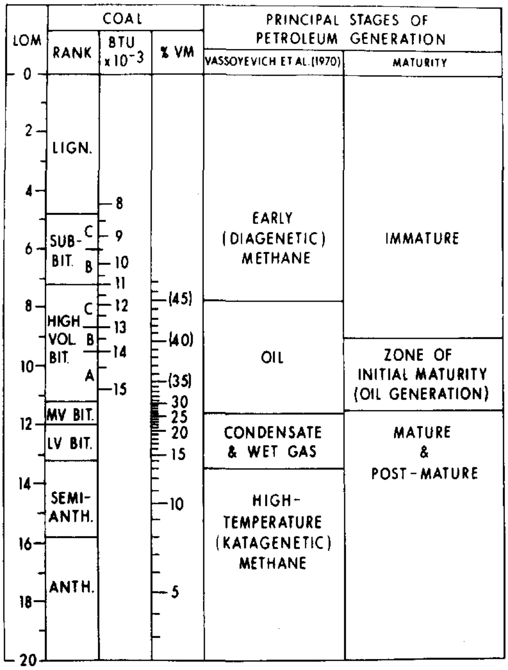

FIG. 5—Organic metamorphic stages of petroleum generation.

initial maturity have been superimposed on both figures on the basis of the relation shown in Figure 5 and utilizing LOM values derived from vitrinite reflectance. Figures 6 and 7, therefore, illustrate the prediction of specific depths at which oil, gas condensate, and methane would be generated by source rocks at any given location.

The two examples do not show linear relations of LOM with depth. Both figures, however, do show a similar type of nonlinearity; i.e., at shallower depths the observed LOM values are significantly greater than those defined by linear relations of LOM to depth. Pusey (1973a, p. 24) has reported a strikingly similar nonlinearity in his graph of "paleotemperature" versus depth for a well in the Anadarko basin—actually in the same county in Oklahoma as the well of Figure 6. Pusey derived the paleotemperature values from electron-spin-resonance (ESR) parameters of aromaticity. Because of the similarity between the graph of LOM versus depth and the graph of paleotemperature versus depth, and because a paleotemperature greater than 250°F near the surface in Beckham County, Oklahoma, seems quite unlikely, we conclude that Pusey's paleotemperature scale is not simply temperature but, instead, a combined temperature-time scale which is relatable to LOM.

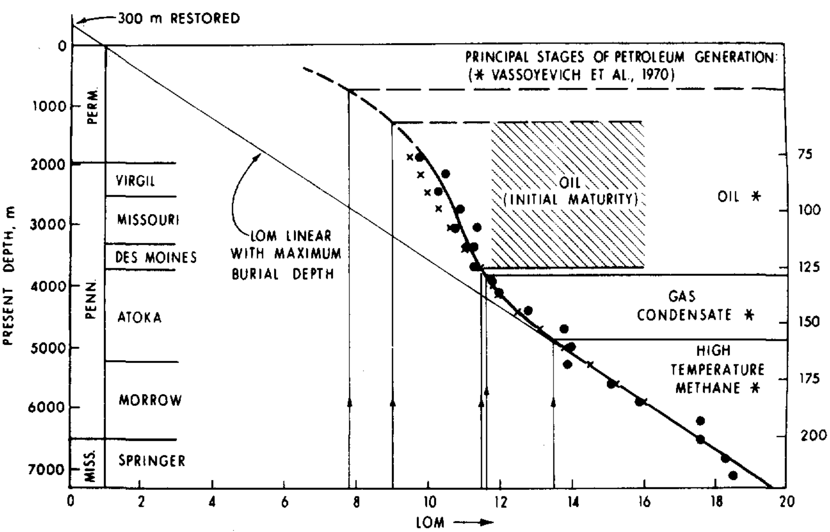

FIG. 6—Relations of LOM and petroleum generation to depth: Shell Rumberger 5, Beckham County, Oklahoma, Anadarko basin. LOM is based on vitrinite reflectance (●); for comparison, LOM values based on T_{max} and t_{eff} (see Fig. 3, using 260 × 10^6 years for t_{eff}) are shown as x's.

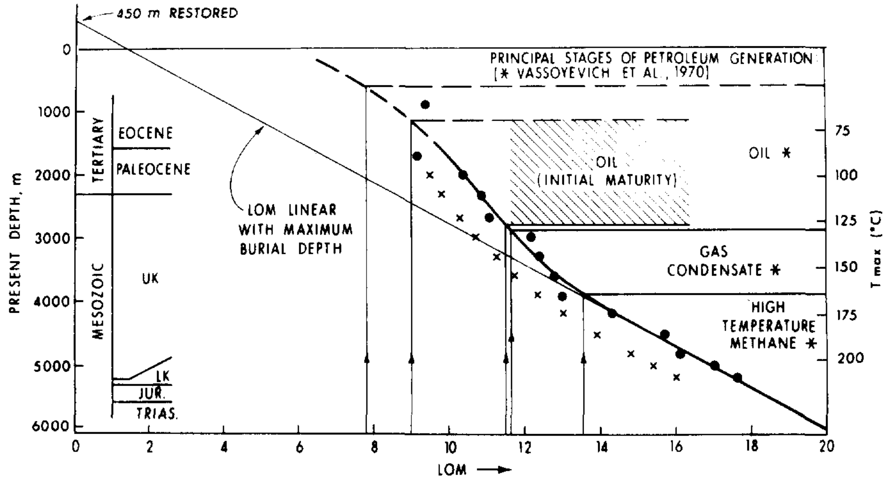

FIG. 7—Relations of LOM and petroleum generation to depth: Mobil Unit T-52-19G, Rio Blanco County, Colorado, Piceance basin. LOM is based on vitrinite reflectance (●); for comparison, LOM values based on T_{max} and t_{eff} (see Fig. 3, using 35×10^6 years for t_{eff}) are shown by x's.

Possibly the nonlinearity of both LOM and "paleotemperature" with depth is mainly a result of the observed increase in apparent activation energy with increasing LOM. The lower activation energies (at low LOM values) indicate a greater importance of time with respect to temperature. This results in a significantly greater importance of total burial time at lower levels than at higher levels of organic metamorphism, and therefore a greater nonlinearity of the type observed would be expected for Paleozoic than for Mesozoic or Cenozoic rocks. This appears to be borne out by a comparison of the curves of Figure 6 (mainly Pennsylvanian) and Figure 7 (Upper Cretaceous to Eocene), and it suggests that no single scale of organic metamorphism can be expected to be linear with maximum depth for subsurface sections of widely varying ages.

Conclusions

The LOM scale is a scale of organic metamorphism applicable to the organic matter in fine-grained sedimentary rocks. The scale simply represents a way of exhibiting the relative thicknesses of the various ranks of a standard subsurface coal-rank column—essentially that of Suggate (1959). However, it has proved to be a convenient one for use in geologic studies of temperature histories of petroleum source rocks. Probably its main advantage is that it is a single numerical scale covering the entire thermal range of interest in petroleum generation and destruction. Although not a primary measurement, it correlates with coal rank and other scales or measures of organic metamorphism; therefore, LOM can be determined by any of these other techniques and can be applied to problems such as petroleum generation in fine-grained rocks and thermal destruction of crude oil accumulations in reservoir rock.

The reported relation of maximum temperature (T_{max}) and effective burial time (t_{eff}) to LOM provides a suitable approximate method for estimating levels of organic metamorphism within the LOM range of about 9 to 16. For such estimates accurate formation temperatures are essential.

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