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Estimations of the upper and lower depth limits for kerogen to generate oil/gas worldwide: A hypothesis

Shuheng Du [a,b], Ya-Pu Zhao [a,b,*], Fuqiang Sun [c], Yongmin Shi [d]

[a] State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing, 100190, China

[b] School of Engineering Science, University of Chinese Academy of Sciences, Beijing, 100049, China

[c] The University of Hong Kong, Hong Kong, 999077, China

[d] School of Earth and Space Sciences, Peking University, Beijing, 100871, China

HIGHLIGHTS

- The upper and lower depth limits for kerogen to generate oil/gas worldwide are estimated by the equations with clear physical significance.
- The ratio of dissociation energy and molar mass of kerogen is one of the most critical factors for the upper and lower depth limits of oil/gas generated by kerogen.

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ABSTRACT

This study focuses on the upper and lower depth limits for kerogen to generate oil/gas worldwide. For the first time, the upper and lower depth limits of the conversion process from kerogen to oil/gas are given by the equations with clear physical significance. The method for obtaining the parameters in the equations is also proposed. The results show that the upper limit of hydrocarbon generation of kerogen mainly depends on the ratio of the minimum dissociation energy and initial molar mass of hydrocarbon generation. The smaller the ratio is, the shallower the upper limit of hydrocarbon generation of kerogen is. The upper depth limit of hydrocarbon generation ranges from 688 m to 4925 m, with an average of 1944 m. The lower limit of hydrocarbon generation mainly depends on the ratio of the dissociation energy and molar mass at the end of hydrocarbon generation. The lower depth limit of hydrocarbon generation is proportional to the above ratio. The lower limit of hydrocarbon generation of kerogen ranges from 2539 m to 16 337 m, with an average of 6926 m. This study not only solves a major controversial issue which is the minimum and maximum depth of drilling required to capture oil/gas but also helps select the location of carbon storage. It will be conducive to the effective utilization of fossil energy and the early realization of global carbon neutralization.

* *Corresponding author*. State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China.

E-mail addresses: dushuheng@imech.ac.cn (S. Du), yzhao@imech.ac.cn (Y.-P. Zhao).

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Introduction

As indispensable fossil energy and chemical raw materials, oil and natural gas are known as the blood of the industry, and their strategic position is self-evident. Many large oil and gas fields have been found worldwide based on organic genesis theory. In fact, this theory constantly guides the discovery of new oil and gas fields [1–4].

The global energy consumption and development trend forecast results show that fossil energy will play an indispensable role in the energy consumption of the whole 21st century and will also be the top priority of energy research (Fig. 1).

Kerogen is one of the core concepts in the theory of the organic genesis of oil and gas. It mainly refers to the dispersed organic matter insoluble in alkali, non-oxidizing acid and non-polar organic solvents in sedimentary rocks. It is widely recognized as the source material of hydrocarbon generation [5]. A large number of studies have been carried out on the source analysis, molecular construction and evolution of kerogen, and accordingly a series of achievements have been obtained [6,7]. However, many core issues still remain unresolved. The difficulties related to the burial depth of kerogen have existed for a long time. Most of the related studies are based on qualitative discussions, such as giving the approximate depth range of each stage of kerogen evolution, but detailed data are not provided. Furthermore, a relatively quantitative calculation method has yet to be provided so far [5,8,9].

The temperature at which organic matter begins to be transformed into hydrocarbon is called the threshold temperature of hydrocarbon generation, and the corresponding depth is the threshold depth of hydrocarbon generation [8,9,11].A large number of studies on threshold depth show that kerogen can start to be decomposed into oil and gas only when the energy provided by the crust is higher than the activation energy required for the oil and gas formation reaction. Similarly, only when the temperature or burial depth exceeds the threshold values can a large amount of oil be

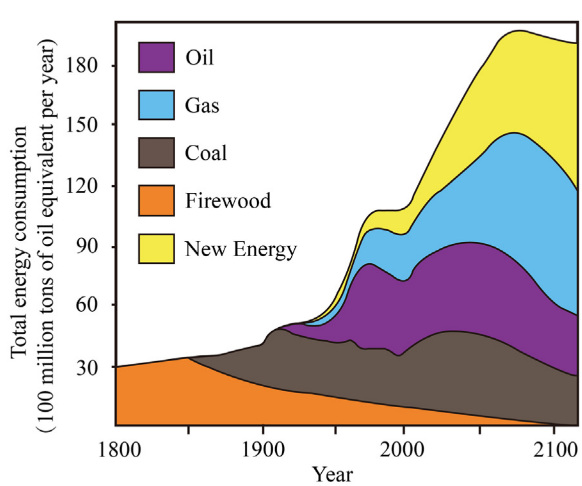

Fig. 1 – Forecast of global energy consumption and development trend (Revised according to Ref. [10]).

generated. Therefore, the time for kerogen to reach the activation energy as well as threshold temperature and depth should be highly consistent. It is due to the different chemical bond combinations of different types of kerogen that different activation energies are required for pyrolysis reaction, so the thresholds of oil formation of different types of kerogen are also different. Therefore, it can be said that when a type of kerogen in the source layer reaches its activation energy, the formation temperature and its corresponding depth are the threshold temperature and threshold depth of the kerogen, respectively [12–16]. In this study, it is called the upper limit of hydrocarbon generation of kerogen.

The lower limit of hydrocarbon generation of kerogen is also called the bottom limit of hydrocarbon supply and the depth limit of active source rock. The lower limit of hydrocarbon generation is defined as the maximum burial depth of the active source rock. When the burial depth exceeds the lower limit, the source rock can no longer produce or discharge hydrocarbons and becomes inactive. In addition to the burial depth, the lower limit of hydrocarbon generation can also be characterized by other physical parameters (such as thermal maturity %R_o) of source rocks. The conversion rate of kerogen with depth in the Songliao Basin in Northeast China indicates that the maximum burial depths of kerogen oil and gas are about 1875 m and 2875 m, respectively [17].

Determining the upper and lower limits of hydrocarbon generation is significant for the exploration and development of fossil energy. Theoretical derivation, experiment, computation and validation for estimating the origin and extinction of fossil energy are shown in Fig. 2. Generally speaking, for oil and gas exploration, the upper and lower limits of hydrocarbon generation can be helpful to solve the problems of the depth of layer from which there is oil and gas and no petroleum. For oil and gas exploitation, the upper and lower limits of hydrocarbon generation can be conducive to solving the problems of how deep oil and gas drilling is required, at least in different areas, and the maximum drilling depth is required for oil and gas drilling in different regions. Therefore, determining the upper and lower limits of hydrocarbon generation not only provides a crucial engineering practice basis for the exploration and development of global fossil energy but also helps select the location of carbon storage, which is conducive to the early realization of global carbon neutralization.

In essence, the burial, evolution and hydrocarbon generation of kerogen is a dynamic process, and in this process, the reaction characteristics of different kerogen molecules will be different. Therefore, the upper and lower limits of kerogen hydrocarbon generation should be computed by selecting specific real-time parameters in the dynamic process to ensure the accuracy of the data. At the same time, the study of kerogen should pay close attention to the properties of kerogen themselves, including its original chemical composition and the possible changes of material composition and structure in the reaction process. It also indicates that only by digging out the key parameters affecting the hydrocarbon generation potential of kerogen and reasonably determining some critical thresholds for the depletion of the hydrocarbon generation potential of kerogen can we reasonably grasp the upper and lower limits.

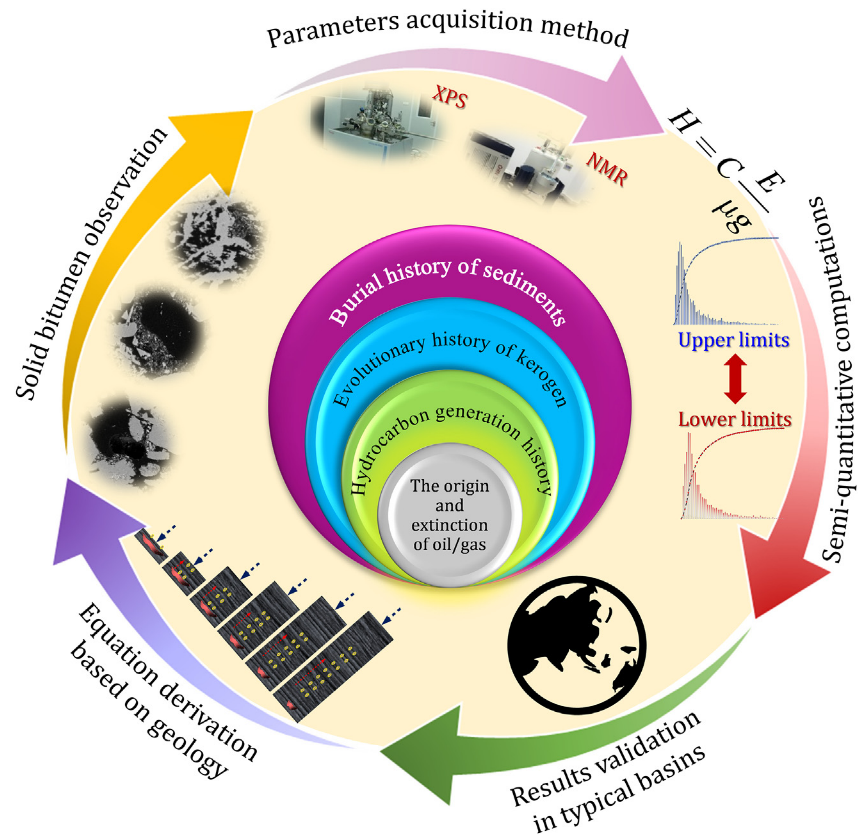

Fig. 2 – Theoretical derivation, experiment, computation and validation for estimating the origin and extinction of oil and gas.

Generally speaking, the problem of determining the upper and lower limits of the kerogen hydrocarbon generation has not been solved completely; *i.e.* there is still no semi-quantitative or quantitative computation method with a clear physical significance and simple form. Therefore, further study is urgently needed.

Theoretical analysis

Equation derivation

The determination of the upper and lower limits of hydrocarbon generation needs a theoretical basis from geosciences. Previous research results and Fig. 3 show that with the increase of burial depth, the formation temperature, kerogen maturity, and oil and gas in main oil and gas forming periods also gradually increase. The processes of hydrocarbon generation, kerogen organic matter evolution and the burial of sediments are interdependent and mutually restrictive [9].It should be pointed out that the authors only consider the oil and gas directly generated by kerogen molecules here. Actually, a small part of the oil generated by kerogen will be cracked into gas. This oil–gas transformation may influence the accurate evaluation of the hydrocarbon generation ability of kerogen. Therefore, this transformation effect is not considered in this study.

By taking the stable structural kerogen as the research object and assume that there is no late tectonic uplift in the process of deposition, we can try to calculate the upper and lower limits of hydrocarbon generation of this type of kerogen theoretically.

After the initial stable structure of kerogen molecules undergoes the burial process, the kerogen maturity increases, and a series of depolymerization, cracking and polycondensation reactions begin to occur gradually. The chemical bonds break, and different types of asphaltene, glia, heavy hydrocarbon and light hydrocarbon are gradually formed.

From the point of view of element composition, with the increase of burial depth and the promotion of thermal evolution, the changes of kerogen molecules mainly include deoxidation, hydrogen loss and carbon enrichment. Generally speaking, the evolution of kerogen is the process of redistribution of hydrogen and the ordering of carbon in organic matter and the process of the decomposition of complex kerogen macromolecules into smaller and simpler compounds. With the increase of the molecular metamorphism of kerogen, the proportion of different chemical bonds in the molecule changes. The total average bond energy of all chemical bonds of kerogen changes because of the different bond energy. In addition, the larger the molar mass of the stable kerogen molecule, the more branched chain the fat and the higher the weightlessness during pyrolysis. Therefore, the total average bond energy of the main chemical bonds and the

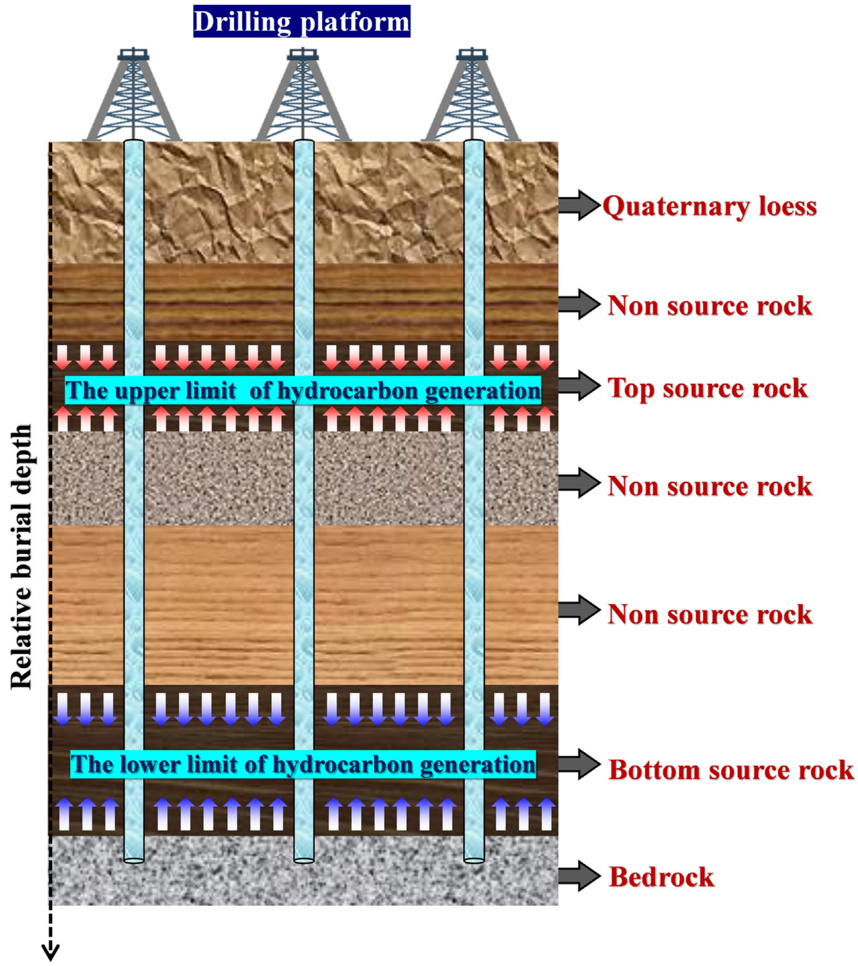

Fig. 3 – Diagram of the history of sediment burial, organic matter evolution and hydrocarbon generation.

molar mass of kerogen are the key factors that restrict the potential of kerogen to generate oil and gas. Among them, the main chemical bonds include C_{ar}–C_{al}, C_{ar}–C_{ar}, C_{al}–C_{al} and C–X. Here, C_{ar} and C_{al} represent aromatic carbon and fatty carbon, respectively; X represents O, S, N, H and other atoms, and there are about 11 connection modes. Although kerogen can be buried for a long time, the breakage of aromatic carbon and other chemical bonds may eventually evolve into graphite, but hydrocarbon generation stops in this process. Therefore, the bond energy of the aromatic structure fracture is not considered in this study.

Temperature plays a vital role in the hydrocarbon generation of kerogen [3]. Therefore, it is necessary to discuss the upper and lower limits of hydrocarbon generation in detail. Most of the research results show that there is a strong dependence between formation temperature and burial depth, in which there is the concept of geothermal gradient. Moreover, the temperature at different depths in the formation is basically constant [19,29]. As a matter of fact, the origin of geo-temperature has not yet been determined. Some scholars believe that a large amount of heat left over from the formation of the earth and the heat generated by the continuous thermonuclear reaction inside the earth continuously conducts to the surface, thus forming the geothermal field [20]. If the stratum plane where the kerogen begins to be buried is taken as the initial datum plane, the strata gradually stack above the datum plane with time, resulting in the overlying gravity of the stratum where the datum plane is located gradually increasing. In this process, due to the compressibility of the rock, part of the gravitational potential energy of the rock is continuously converted into internal energy. It will also increase the internal temperature of sedimentary strata, thus promoting the continuous evolution of kerogen. Therefore, there is a strong dependence between temperature and the earth's gravity field (mainly determined by burial depth and gravity acceleration). The above analysis will be the most crucial theoretical hypothesis used to explore the upper and lower limits of kerogen hydrocarbon generation in this study.

Dimensional analysis is widely used as one of the most effective methods to analyze the main control factors of complex problems [22]. The above theoretical method has inspired the exploration of the upper and lower limits of hydrocarbon generation depth of kerogen in this study.

The main factors related to the upper limit of kerogen hydrocarbon generation (H_{min})include the dissociation energy of kerogen (E_s), the molar mass of kerogen (μ_s), the intensity of gravity field (*i.e.* gravity acceleration) (g) and the formation temperature (T).

The dimensions of each physical quantity are as follows (Eq. (1)):

$$\begin{aligned}&[H_{min}] = L\\&[T] = \theta\\&[E_s] = ML^2T^{-2}n^{-1}\\&[\mu_s] = Mn^{-1}\\&[g] = LT^{-2}\end{aligned} \tag{1}$$

According to the fast matching method of dimensional analysis proposed by Zhao [23], since the dimension of the upper limit and lower limit of kerogen hydrocarbon generation with dependent variables has only length term, the quantity n of substance in the independent variable dimension expression must be eliminated by the separation of the minimum dissociation energy and initial molar mass:

$$\left[\frac{E_s}{\mu_s}\right] = \frac{ML^2T^{-2}n^{-1}}{Mn^{-1}} = L^2T^{-2} \tag{2}$$

The time T in Eq. (2) can be eliminated by combining Eq. (2) with the acceleration of gravity g.

Eq. (3) is obtained.

$$\left[\frac{E_s}{\mu_s g}\right] = \frac{L^2T^{-2}}{LT^{-2}} = L \tag{3}$$

The results are as follows,

$$H_{min} \sim \frac{E_s}{\mu_s g} \tag{4}$$

$$H_{min} = C\frac{E_s}{\mu_s g} \tag{5}$$

In Eq. (5), C is the dimensionless coefficient, which is usually taken as 1 for the order of magnitude estimation. Eqs. (4) and (5) indicate that the formation temperature T does not appear, which does not mean that the temperature T has no effect on the hydrocarbon generation process of kerogen. As a matter of fact, the effect of temperature is implied in the earth's gravity field parameters (*i.e.* stratum depth and gravity acceleration). It can be seen from Eq. (5) that the upper limit of hydrocarbon generation of kerogen mainly depends on the ratio of the minimum dissociation energy of hydrocarbon generation to the initial molar mass of hydrocarbon generation.

Similarly, for the lower limit of hydrocarbon generation of kerogen, its influencing factors include dissociation energy at the end of hydrocarbon generation, molar mass at the end of hydrocarbon generation, gravity field intensity (*i.e.* gravity acceleration) and formation temperature. The process of dimensional analysis is similar to the upper limit of hydrocarbon generation.

$$H_{max} = C'\frac{E_e}{\mu_e g} \tag{6}$$

In Eq. (6), C' is the dimensionless coefficient, which is usually taken as 1 when estimating the order of magnitude. Similarly, the formation T does not appear in the expression of the lower limit of hydrocarbon generation. Eq. (5) shows that the lower limit of hydrocarbon generation of kerogen mainly depends on the ratio of the dissociation energy at the end of hydrocarbon generation to the molar mass at the end of hydrocarbon generation.

FE-SEM characterization

To illustrate the fact that organic matter remains in shale in the form of residual bitumen, we collected shale oil reservoir samples (sampling depth: 3500 m) from the Junggar Basin in Western China, made rock slices and used field emission scanning electron microscopy (FE-SEM) for high-resolution imaging.

Fig. 4 shows that organic matter occurs in shale in the form of massive (Fig. 4a, e, f and g), strip (Fig. 4b, d and h) and block-strip mixed (Fig. 4c). The kerogen in different positions develops different degrees of organic pores, but the overall development degree is low. This strongly proves that there is still residual organic matter at a depth of 3500 m in the Junggar Basin, which has not reached the lower limit of hydrocarbon generation. To a certain extent, it indicates that there must be great potential for oil and gas exploration at a depth of 3500 m in this area. Actually, the depth of the target layer in the Junggar Basin has far exceeded 3500 m.

Parameter acquisition method

To obtain the relevant parameters in Eqs. (4) and (5) and then estimate the upper and lower limits of the kerogen hydrocarbon generation, it is essential to combine the experiment with simulation. A series of fruitful studies about the construction and pyrolysis simulation of kerogen macromolecules have been performed. The relevant parameters in Eqs. (4) and (5) could be obtained based on previous studies [7,24]. The specific method is divided into the following three steps.

The first step is the construction of kerogen macromolecules. The percentages of major elements such as C, H, O, N and S are obtained by elemental analysis. The main functional groups in shale kerogen are qualitatively and quantitatively analyzed by X-ray photoelectron spectroscopy (XPS) and ^{13}C nuclear magnetic resonance (NMR), and the main structural parameters of kerogen are clarified. Based on the principle of minimum energy, the two-dimensional molecular structure of kerogen is constructed by molecular mechanics software, and then a relatively realistic three-dimensional model is constructed by molecular dynamics structure optimization and simulated annealing to calculate the proportion of main chemical bonds.

The second step is to simulate the hydrocarbon generation reaction of the kerogen. The molecular dynamics and quantum mechanics simulation of kerogen pyrolysis is carried out, and the chemical bond order and other parameters are calculated to predict the hydrocarbon generation process of kerogen.

The third step is to estimate the upper and lower limits of hydrocarbon generation. When the hydrocarbon molecular generation process starts, the dissociation energy of kerogen at the moment of the start-up is taken as the minimum dissociation energy, and the molecular molar mass of kerogen at this state is taken as the initial molar mass of hydrocarbon

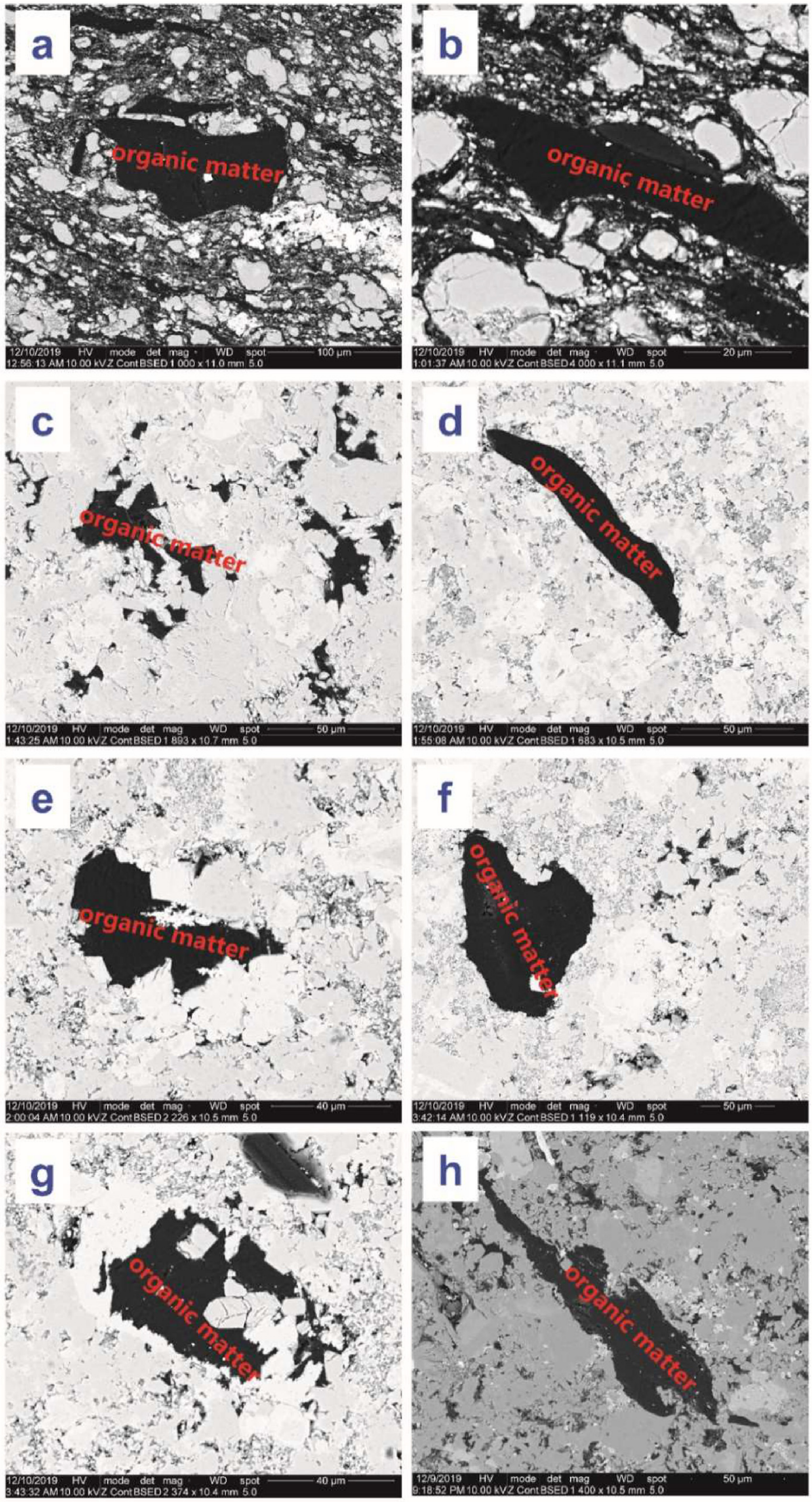

Fig. 4 – Distribution characteristics of residual organic matter (solid bitumen) in shale oil reservoirs in Western China.

generation. When the ratio of hydrogen to carbon tends to zero, it can be considered that kerogen loses its hydrocarbon generation potential. At this time, the dissociation energy of the kerogen molecule in this state is calculated as the dissociation energy at the end of hydrocarbon generation, and the molar mass of the kerogen molecule at the end of hydrocarbon generation is calculated as the molar mass at the end of hydrocarbon generation. Finally, the upper and lower limits of kerogen generation can be estimated by substituting the relevant parameters into Eqs. (4) and (5), respectively, and the dimensionless coefficient is around 1.

Semi-quantitative computation

In fact, it is extremely difficult to involve a large number of parameters in the computation of the upper and lower limits of hydrocarbon generation of kerogen. To have a general understanding of the numerical distribution of the upper and lower limits of kerogen, based on the published studies, the numerical distribution intervals of the parameters in Eqs. (4) and (5) are determined, and several groups of calculation results were obtained by using the method of random number generation. Although the results are semi-quantitative, the total distribution will have scientific significance.

The upper depth limit of the conversion process from kerogen to oil/gas

To obtain the semi-quantitative results of the upper limit of hydrocarbon generation of kerogen, it is essential to determine the numerical distribution range of the relevant parameters designed in Eq. (4).

In this study, combined with the conclusions of a published study [25], we found the initial molar mass distribution of kerogen to be 10 000–30 000 g/mol and the minimum dissociation energy of hydrocarbon generation to be 200–500 kJ/mol. According to the value ranges of the above parameters, we obtained 5000 groups of kerogen parameters via random number generation. The maximum burial depth of 5000 groups of kerogen was calculated, and the depth was statistically analyzed (Fig. 5).

Fig. 5 demonstrates that the upper limit of hydrocarbon generation of kerogen ranges from 688 m to 4925 m, and there is a prominent peak range (1414–1536 m). It should be pointed out that this does not mean that oil/gas could only be found below the depth of about 688 m. The upward migration of oil/gas is likely to lead to the existence of oil/gas at the depth less than about 688 m. The upper limits of hydrocarbon generation of the Songliao Basin, Ordos Basin, Sichuan Basin, Bohai Bay Basin, Junggar Basin and Tarim Basin are put into Fig. 5, where the corresponding cumulative probabilities are 28%, 40%, 66%, 78%, 85% and 97%, respectively.

The lower depth limit of the conversion process from kerogen to oil/gas

Similarly, to obtain the semi-quantitative results of the lower limit of hydrocarbon generation of kerogen, it is essential to determine the numerical distribution range of the relevant parameters designed in Eq. (4).

In this study, combined with the research results of a published study [25], the molar mass distribution of kerogen at the end of hydrocarbon generation locates at 3000–8000 g/mol, and the dissociation energy distribution at the end of hydrocarbon generation locates at 200–500 kJ/mol. We also obtained 5000 groups of kerogen parameters via random number generation.

The maximum burial depth of 5000 groups of kerogen is calculated, and the depth is statistically analyzed in Fig. 6. The lower limit of hydrocarbon generation of kerogen ranges from 2539 m to 16 337 m, and the distribution of kerogen has an obvious peak range (6000–6500 m). It should also be pointed out that this does not mean that oil/gas could not be found below the depth of about 16 337 m. The downward migration of oil/gas is also likely to lead to the existence of oil/gas at the depth more than about 16 337 m. When the lower limits of hydrocarbon generation of the Songliao Basin, Bohai Bay Basin, Ordos Basin, Sichuan Basin, Junggar Basin and Tarim Basin in the published studies [17] are put into Fig. 6, the corresponding cumulative probability is 31%, 37%, 52%, 67%, 72% and 80%, respectively.

Pang et al. proposed an empirical equation based on the statistics of experimental data as follows [17]:

$$H'_{\max} = 16448 - 3.61HI - 139.46HF \tag{7}$$

In Eq. (7), HI is the hydrogen index, which is the mass of hydrocarbon generated by pyrolysis of a unit mass of organic carbon (in mg HC per g TOC) and is also a quantitative proxy for the characterization of kerogen types and is easily obtained through the Rock–Eval analysis. HF is the present average heat flow value of a basin (in mW/m^2). In order to get the distribution of the lower limit value of hydrocarbon generation defined by Eq. (6) and compare with Fig. 6, according to the former experimental test data [17], the hydrogen index value is set at 200–600 mg/g, the present average heat flow value is set at 40–70 mW/m^2, and 5000 groups of kerogen parameters are obtained via random number generation. The lower limits of hydrocarbon generation of 5000 groups of kerogen are calculated, as shown in Fig. 7.

Fig. 7 indicates that there is no obvious peak range in the distribution of the lower limit value of hydrocarbon generation of kerogen calculated by Eq. (7). When the lower limit values of hydrocarbon generation of the Songliao Basin, Bohai Bay Basin, Ordos Basin, Sichuan Basin, Junggar Basin and Tarim Basin in the published study are put into Fig. 7 [17], the corresponding cumulative probabilities are 6%, 12%, 32%, 58%, 69% and 91%, respectively.

Validation of results

It can be seen from Figs. 5 and 6 that the upper limit values of hydrocarbon generation of the six major basins in China obtained from published studies are all included in Fig. 5, and the lower limit values of hydrocarbon generation are all included in Fig. 6.

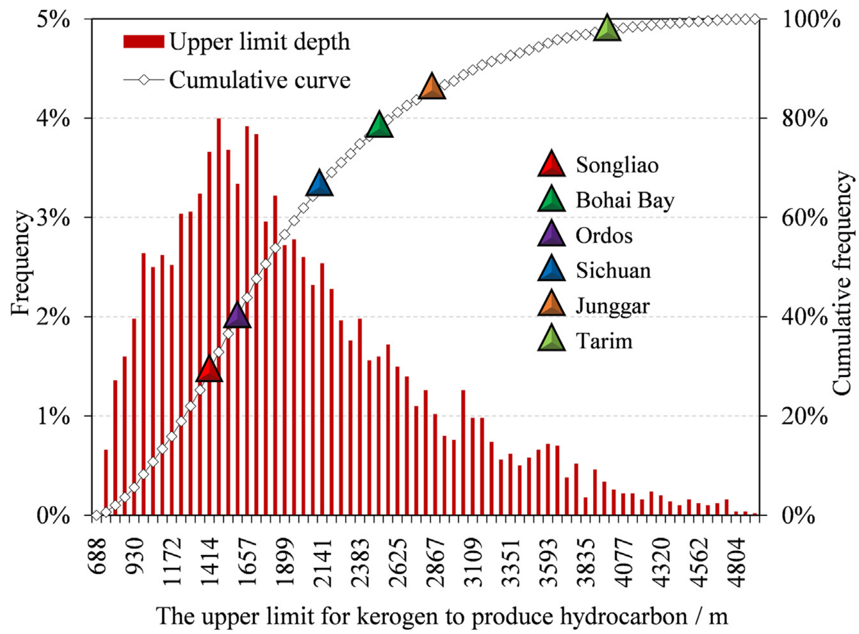

Fig. 5 – Statistics of the upper depth limit of converting kerogen into oil and gas.

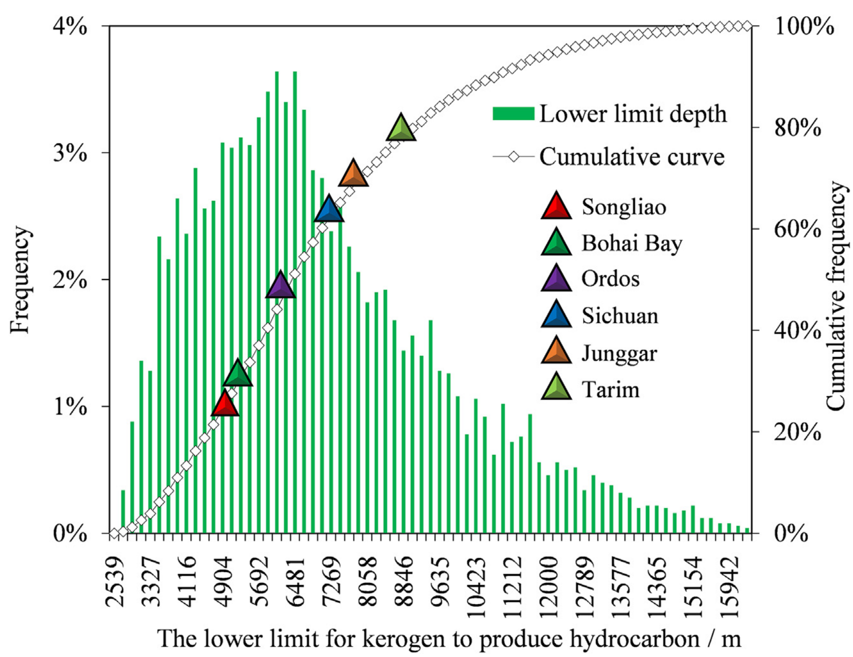

Fig. 6 – Statistics of the upper depth limit of converting kerogen into oil and gas.

Using the empirical equation (7), the lower limit ranges from 4520 to 10 148 m, and the average is 7307 m (Fig. 7). The lower limit value calculated by the equation proposed in this study ranges from 2539 to 16 337 m, and the average value is 6926 m (Fig. 6). The globally available geochemical data show that the upper and lower limits of kerogen hydrocarbon generation range from 3000 m to 16 000 m. There is no denying that the overall distribution range of the predicted values obtained by this method is more suitable for the range of 3000–16 000 m, and the physical meaning of the equation is clear. From the average value, the results obtained in this study are generally consistent with those obtained by equation (7).

At the same time, we use the cumulative probability of the lower limit of hydrocarbon generation in each basin in Figs. 6 and 7 to carry out the comparative analysis in Fig. 8. The results show that there is a significant linear correlation between the two prediction methods.

Therefore, the rationality of the proposed equation is proved from many aspects. Actually, the above achievements

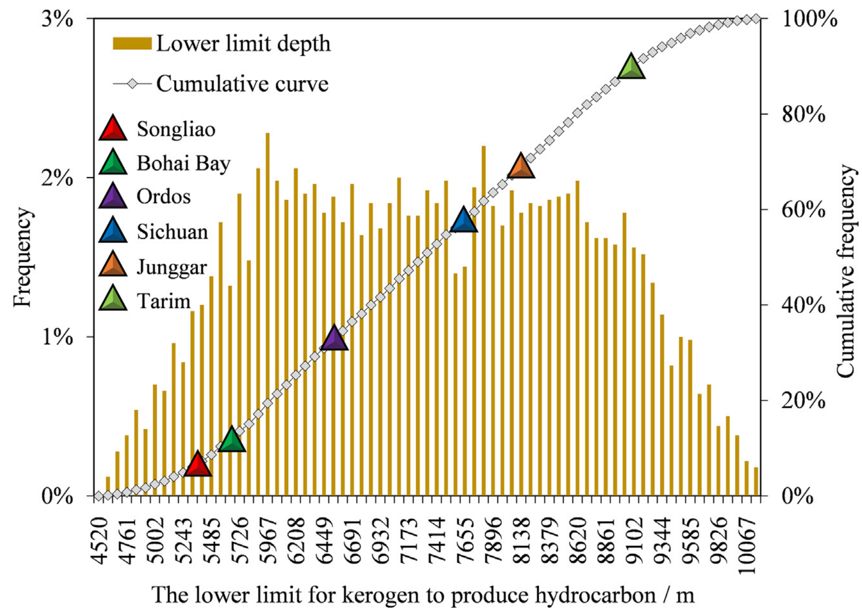

Fig. 7 – Statistics of the lower limit of hydrocarbon generation of global kerogen using the equation (7).

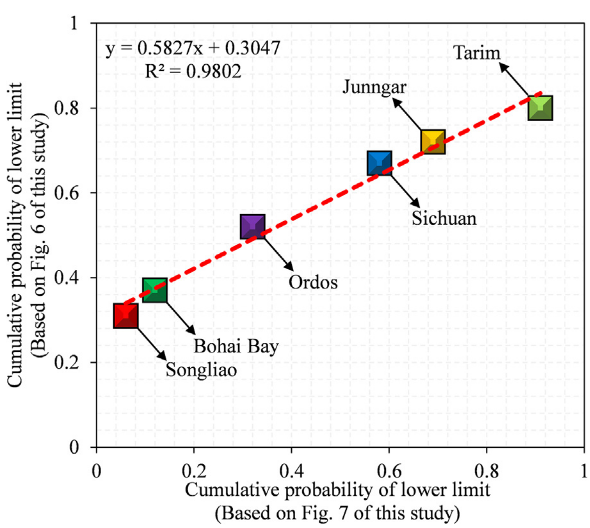

Fig. 8 – Comparison of cumulative probability prediction results of lower limit values in Chinese basins.

could be used to uncover the mystery of the generation and extinction of unconventional resources such as tight oil [31–34], shale oil [35–38], shale gas [39–42], oil shale [26–28] and so on.

Conclusions

The upper limit of hydrocarbon generation of kerogen is proportional to the ratio of the minimum dissociation energy to the initial molar mass of hydrocarbon generation. The upper limit of hydrocarbon generation of kerogen ranges from 688 m to 4925 m, with an average of 1944 m. The lower limit of hydrocarbon generation of kerogen is proportional to the ratio of dissociation energy at the end of hydrocarbon generation to the molar mass at the end of hydrocarbon generation. The lower limit of hydrocarbon generation ranges from 2539 m to 16 337 m, with an average of 6926 m.

This study reveals the maximum molecular weight of the initial kerogen in different regions and the range of the minimum molecular weight that can be reached after the pyrolysis of kerogen. The above results are indispensable in the construction studies of kerogen macromolecular structures. When the average bond energy is the maximum of all types of chemical bond energies related to hydrocarbon generation and the depth is the upper limit of hydrocarbon generation obtained from actual drilling, then the theoretical maximum molecular weight of the original kerogen could be computed. Similarly, when the average bond energy is taken as the minimum of all types of chemical bond energy related to hydrocarbon generation and the depth is taken as the lower limit of hydrocarbon generation obtained from actual drilling, the theoretical minimum molecular weight of kerogen after the maximum pyrolysis could also be calculated.

Frankly, the molecular structure of kerogen is extremely complex. At present, to obtain the accurate values of minimum dissociation energy and initial molar mass of hydrocarbon generation, dissociation energy and molar mass of kerogen at the end of hydrocarbon generation, it is necessary to accurately clarify the molecular equation, structure and specific reaction process of kerogen in the early stage of evolution. In recent years, the first principle calculation, molecular dynamics simulation and other numerical means could be used to simulate the hydrocarbon generation process preliminarily, which still depends on the further development of experimental and simulation technology. In addition, due to the different types of initial kerogen (types I, II and III), there are differences in the initial oil and gas forming potential. The upper limit of oil (or gas) generation and lower limit of oil (or gas) generation could also be calculated in future studies.

Finally, the viewpoint put forward in this study is still a hypothesis, which is a potential answer to the mystery of hydrocarbon generation. Meanwhile, it should be pointed out that the upper and lower limits of hydrocarbon generation of kerogen proposed in this study are still theoretical values, which need to be modified in conjunction with the study of basin ascending and descending history, burial history and thermal history, and there is still a lot of research work worth doing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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