Influencing factors of the Tmax parameter in Rock-Eval pyrolysis

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Abstract. The rock pyrolysis parameter Tmax is an important index to evaluate the maturity of organic matter in source rocks. However, during the use of Tmax, it is found that the Tmax value of some samples does not conform to the thermal evolution law of organic matter when evaluating the maturity of organic matter, which affects the accuracy of geological applications. Studying the influencing factors of the rock pyrolysis parameter Tmax analysis data is beneficial to improve the experimental method to ensure the accuracy of the experimental data, and it is of great significance to the correct evaluation of the source rock type and maturity of the source rock. In this paper, the effects of sample mixing uniformity, sample weight, soluble organic matter and minerals on the rock pyrolysis parameter Tmax are analyzed experimentally. It is concluded that the degree of sample uniformity and the amount of sample will affect the results. Soluble organic matter will lead to a decrease in Tmax. With the change of kerogen/clay mineral ratio, the influence of clay mineral on the pyrolysis parameter Tmax.

1. Introduction

Organic carbon and rock pyrolysis analysis is one of the most basic analytical techniques in organic geochemistry research. For the reasons of rock pyrolysis parameters, the former has been studied. Zhang Zhenduo and others believe that the soluble organic matter enters the S2 peak, which leads to an increase in the S2 value and a decrease in the Tmax value. Clay minerals have an adsorption effect on heavy hydrocarbons, resulting in a decrease in S2 value and an increase in Tmax. Liang Jimin and others believe that too small a sample size will result in a low S2 value and an increase in the Tmax value. For samples with low abundance of limestone and organic matter, a more accurate Tmax value can be obtained by changing the heating rate. By studying the influencing factors of the pyrolysis parameter Tmax, the influence of high soluble organic matter in source-storage source rocks on pyrolysis parameters can be clarified, and it is proved that the amount of pyrolysis hydrocarbons is closely related to the type and content of mineral matrix. The influence of Tmax on the pyrolysis of kerogen was determined to determine the range of sample sizes of three types of source rocks: mudstone, carbonaceous mudstone and coal in rock pyrolysis analysis.

In this paper, 25 samples of low-to-high organic carbon content in the Junggar Basin were collected, and five basic analyses of organic carbon, pyrolysis, chloroform asphalt A extraction, group components, elements and isotopes were carried out on the rock samples. Appropriate rock samples
and kerogen samples were tested for rock pyrolysis, sample uniformity, sample weight, soluble organic matter, and clay minerals.

2. Factors affecting rock pyrolysis parameters Tmax

2.1 Effect of sample uniformity on pyrolysis parameters Tmax

Under normal circumstances, after the rock sample is selected by 100 mesh after being pulverized, it is analyzed by pyrolysis instrument. Whether the sample is evenly mixed and affects the pyrolysis results needs further analysis. In this paper, the samples from XJC1 well, DX8 well and C58 well were selected, and their TOC values were 1.55, 6.18 and 13.80. The three mudstone samples with low, medium and high organic carbon values were elected to rock pyrolysis experiments to analyze the sample uniformity and pyrolysis parameters. The samples were separately mixed for over 3 minutes using an XH-C type vortex mixer, and then each of them was conducted by parallel analysis of rock pyrolysis five times.

The Tmax values of the mud samples in the XJC1 well before and after being mixed were all distributed between 470 °C and 472 °C, with an average of 471 °C. 471 °C was used as the standard value of the mudstone sample, and the Tmax value of the sample before being mixed needed deviation calculation. The maximum deviation of the Tmax value of the XJC1 well was 1 °C. The mud samples’ Tmax values of the DX8 well before being mixed were between 451 °C and 453 °C, and the average value was 452 °C. The Tmax values of the samples after being mixed were between 451 °C and 452 °C, and their average value was 451 °C. Take 451 °C as the standard value of the mudstone sample, and the Tmax value of the sample before being mixed was calculated in the way of deviation. The maximum deviation of the Tmax value of the DX8 well was 2 °C. The mud samples’ Tmax values of the C58 well before being mixed were all distributed between 457 °C and 458 °C. The Tmax values of the samples after being mixed were between 458 °C and 459 °C, with an average of 459 °C. Identically 459 °C was used as the standard value of the mudstone sample, and the Tmax value of the sample before being mixed needed deviation calculation. The maximum deviation of the Tmax value of the C58 well was 2 °C. The rock pyrolysis experiment before and after being mixed of the samples show that the Tmax of the pyrolysis parameter before and after being mixed conforms to the relative double difference and deviation, which requires the GB/T 18602-2012 of rock pyrolysis analysis standard, with its deviation Should be ≤ 5 °C. That is to say, the current mixing method of the sample can fully meet the standard requirements (Table 1).

| Well number | XJC1 | DX8 | C58 |
|-------------|------|-----|-----|
| Tmax(°C)    | 471  | 471 | 453 |
|             | 472  | 471 | 451 |
|             | 472  | 472 | 453 |
|             | 470  | 470 | 451 |
| average(°C)| 471  | 471 | 452 |
| maximum deviation(°C) | 1    | 2   | 2   |

2.2 The effect of sample weight on Tmax

Rock pyrolysis analysis sample size is generally specified as 100mg. If the sample amount is too small, it will affect the accuracy of the data. If the sample amount is too large, the pyrolysis hydrocarbon peak S2 will be too large, exceeding the detection range of the hydrogen flame ionization detector. The sample weight should be adjusted according to the organic matter abundance of the rock sample. The stable S2 and Tmax should be regarded as the true S2 and Tmax values within a certain range of sample weight. In this paper, seven mudstones, carbonaceous mudstones, coal and standard samples...
with different organic carbon contents were selected. From 5mg or 10mg as the starting point, 100mg was sequentially determined, and the influence of the sampled amount on the pyrolysis parameters $S_2$ and $T_{max}$ was analyzed (Table 2).

According to the experimental results, the $S_2$ value is low when the sample amount is too small. For mudstone or tuff samples with $S_2$ value less than 30mg/g, the $S_2$ value does not vary with the sample volume. The sample size is greater than 40mg. For carbonaceous mudstone samples with $S_2$ value greater than 30mg/g, the $S_2$ value does not follow the sample weight. The variation range of the sample is from 20 mg to 35 mg. The range of $S_2$ value of coal sample varies greatly. From the experimental data, for coal samples with $S_2$ value less than 100mg/g, the suitable sample size ranges from 15mg to 30mg, for coal with $S_2$ value greater than 100mg/g and less than 200mg/g. For example, the suitable sample size ranges from 5 mg to 15 mg. For coal samples of M006 well with $S_2$ value greater than 200 mg/g, the sample weight exceeds 5 mg, and the $S_2$ exceeds the detection range of the hydrogen flame ion detector. As the amount of sample increases, the value of $S_2$ decreases. Therefore, a suitable amount of weighing is less than 5 mg. For $T_{max}$, when the sample quantity does not exceed the $S_2$ detection limit, the sample quantity has no effect on $T_{max}$, but when the sample quantity is too much, it exceeds the detection limit of $S_2$, for example, the coal sample of M006 well increases with the sample quantity. The value of $S_2$ decreases, and $T_{max}$ rises first and then decreases.

**Table 2.** The table of relationship between injection volume and $T_{max}$ value

| Well name | Lithology       | Injection mg | $S_2$ mg/g | $T_{max}$ °C | $S_2$ mg/g | $T_{max}$ °C | $S_2$ mg/g | $T_{max}$ °C | $S_2$ mg/g | $T_{max}$ °C | $S_2$ mg/g | $T_{max}$ °C |
|-----------|-----------------|--------------|------------|--------------|------------|--------------|------------|--------------|------------|--------------|------------|--------------|
| C58       | Carbonaceous mudstone | 5           | /          | /           | /          | /            | /          | /            | /          | /            | /          | /            |
| JT2       | Black coal      | 10          | 0.7        | 471         | 3.4        | 438          | 5.8        | 452          | 18.8       | 442          | 24.6       | 457          |
| C55       | Carbonaceous mudstone | 15          | /          | /           | /          | /            | /          | /            | /          | /            | /          | /            |
| C58       | Carbonaceous mudstone | 20          | 0.9        | 473         | 3.8        | 438          | 7.2        | 451          | 21.6       | 441          | 31         | 458          |
| JT2       | Black coal      | 25          | /          | /           | /          | /            | /          | /            | /          | /            | /          | /            |
| C58       | Carbonaceous mudstone | 30          | 1          | 472         | 4          | 437          | 8.7        | 452          | 22.8       | 442          | 31.6       | 457          |
| JT2       | Black coal      | 35          | /          | /           | /          | /            | /          | /            | /          | /            | /          | /            |
| C58       | Carbonaceous mudstone | 40          | 0.9        | 471         | 4.1        | 437          | 9.4        | 451          | 23.7       | 442          | 32.6       | 458          |
| JT2       | Black coal      | 45          | /          | /           | /          | /            | /          | /            | /          | /            | /          | /            |
| C58       | Carbonaceous mudstone | 50          | 1          | 472         | 4.2        | 437          | 9.3        | 449          | 24.2       | 442          | 32.2       | 458          |
| JT2       | Black coal      | 60          | 1          | 471         | 4.1        | 438          | 9.9        | 450          | 24.3       | 442          | 32.6       | 458          |
| C58       | Carbonaceous mudstone | 70          | 1          | 471         | 4.2        | 438          | 9.6        | 451          | 24.8       | 443          | 34.2       | 459          |
| JT2       | Black coal      | 80          | 1.1        | 471         | 4.2        | 439          | 10         | 452         | 24.6       | 441          | 34.1       | 458          |
| C58       | Carbonaceous mudstone | 90          | 1.1        | 471         | 4.1        | 438          | 10         | 450         | /          | /            | /          | /            |
| JT2       | Black coal      | 100         | 1.1        | 471         | 4.2        | 438          | 10         | 450         | /          | /            | /          | /            |

2.3 Effect of soluble organic matter on $T_{max}$

$T_{max}$ is the peak temperature of the pyrolysis $S_2$ peak, which is the temperature at which the hydrocarbon generation rate of the pyrolysis hydrocarbon is the largest. Therefore, $T_{max}$ is closely related to the pyrolysis peak. The incorporation of soluble organic matter increases the $S_2$ value and affects the determination of the $T_{max}$ value. In this paper, the source rock samples of the source and reservoir in the Jimusaer area were selected, and the soluble organic matter in the rock was removed by chloroform extraction. The $T_{max}$ value of the rock pyrolysis parameters was compared before and after being extrated. The experimental results show that the soluble organic matter in the source rock will enter the $S_2$ peak, resulting in a large $S_2$ value and a decrease in the $T_{max}$ value. This is because under the conditions of conventional pyrolysis analysis, $S_2$ is heavy at the initial analysis temperature
of 300 °C. The soluble organic matter fails to fully evaporate, and some of them enter the pyrolysis hydrocarbon $S_2$, while the Tmax of the soluble organic matter is low, so the Tmax value is lowered. It can be seen that when the chloroform pitch A is less than 1%, the Tmax value of samples varies by less than 2 °C, within the tolerance of the Tmax value. When the chloroform pitch A is greater than 1%, the Tmax value ranges from 1 °C to 11 °C, the Tmax of most samples varies by more than 2 °C. Overall, the Tmax value of the sample after extraction is increased (Figure1 and Figure2). Therefore, when the chloroform pitch A is greater than 1%, it is necessary to extract the sample and then perform pyrolysis analysis to obtain an accurate Tmax value.

2.4 Effect of minerals on Tmax

Select the common clay minerals in the Junggar Basin, kaolinite, illite, and chlorite are mixed with type I, type II, and type III kerogens at a ratio of 1:20, 1:60, and 1:100. Pyrolysis experiments were carried out to analyze the effect of different clay minerals on the Tmax value of rock pyrolysis parameters. The experimental results show that, the three clay minerals have no effect on the pyrolysis Tmax value of type I kerogen, for type II kerogen, as the clay content increases, the Tmax value decreases, of which chlorite to Tmax The value of the value is greater than that of illite and kaolinite, and the type III kerogen increases with the increase of kaolinite content, and the Tmax value increases first and then decreases with the increase of illite and chlorite content (Figure3).
3. Conclusion

(1) Before and after being mixed, the pyrolysis parameter Tmax meets the standard double difference and deviation requirement, and the mixed sample method has little effect on the result.

(2) If the sample weight is too small, the $S_2$ value will be low. For mudstone, the appropriate sample weight is greater than 40mg, for carbonaceous mudstone samples with $S_2$ value greater than 30mg/g, the sample weight is 20mg ~ 35mg, for coal samples with $S_2$ value less than 100mg/g, the appropriate sample weight ranges from 5mg to 15mg. For coal samples with $S_2$ value greater than 200mg/g, the appropriate sample weight range is less than 5mg.

(3) Soluble organic matter leads to an increase in $S_2$, and a decrease in Tmax.

(4) Clay minerals have an effect on the pyrolysis analysis of Tmax, but different types of clay minerals have different effects on different types of kerogen, and with the ratio of kerogen/clay minerals changing, the Tmax will change.

References

[1] Liu Quanyou, Liu Wenhui, Wang Xiaofeng, et al. Comparison of experimental evaluation methods for different source rocks[J]. Petroleum Geology, 2007, 29(1): 88-94.

[2] Wang He. Discussion on the influence of dissolution time on the analysis results of total organic carbon samples in sedimentary rocks[J]. Petrochemical Applications, 2015, 34(10): 87-92.

[3] Huang Dizhen, Li Jinchao, Zhang Dajiang. Validity, Limitations and Correlation of Types of Kerogen and Their Classification Parameters[J]. Acta Sedimentologica Sinica, 1984, 2(3): 18-33.

[4] Gao Xianzhi, Zhang Wanxuan, Zhang Houfu. Study on the effect of minerals on pyrolysis[J]. Petroleum Experimental Geology, 1990, 12(2): 201-205.

[5] Liang Jimin. Several conditions in pyrolysis analysis of oil-bearing rocks[J]. Petroleum Experimental Geology, 1988, 10(4): 377-381.

[6] Zhang Zhenbiao, Zhai Liyan, Shu Nianzu. Causes of abnormal Tmax of pyrolysis analysis parameters of source rocks[J]. Petroleum Exploration and Development, 2006, 33(1): 72-75.

[7] Zhang Zhenbiao, Zhai Liyan, Bou Qi, et al. Reduction of Tmax anomaly values of pyrolysis analysis parameters of source rocks [J]. Petroleum Exploration and Development, 2007, 34(5): 580-584.

[8] Zhang Zhihuan, Gao Xianzhi, Fang Chaoliang. Effect of clay minerals on pyrolysis products of kerogen and its action mechanism [J]. Journal of the University of Petroleum, 1995, 19(5): 11-17.

[9] Zhang Zhihuan, Zhang Houfu, Gao Xianzhi. Effects of clay minerals on pyrolysis hydrocarbon generation process of kerogen[J]. Petroleum Exploration and Development, 1994, 21(5): 29-377.

[10] Yao Yongmei, Liu Ming. Analysis of the Influence of Oil Immersion on the Geochemical Index of Source Rocks_Taking the Oil-dipped Mudstone of Wangyun 12 Well as an Example[J]. Petroleum Geology and Engineering, 2015, 29(3): 13-20.
[11] Zhai Liyan, Ding Lian, Li Bin, et al. Rapid quantitative evaluation of pyrolysis of raw oil rock [M]. Beijing: Science Press, 1986.