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The Dynamic Evolution Model of Chemical and Carbon Isotopic Composition of $C_{1\text{-}3}$ during the Hydrocarbon Generation Process

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Abstract: A new approach is presented for dynamic modeling of chemical and isotopic evolution of $C_{1\text{-}3}$ during the hydrocarbon generation process. Based on systematic data obtained from published papers for pyrolysis of various hydrocarbon sources(type I kerogen/source rock, type II kerogen/source rock, type III kerogen/source rock, crude oil, asphalt, etc), the empirical evolution framework of chemical and isotopic composition of $C_{1\text{-}3}$ during the hydrocarbon generation process was built. Although the empirical framework was built only by fitting large amount of pyrolysis data, the chemical and isotopic composition of $C_{1\text{-}3}$ derived from the pyrolysis experiments all follow the evolution laws, convincing us that it is applicable to the thermal evolution process of various hydrocarbon sources. Based on the simplified formula of the isotopic composition of mixed natural gas at different maturities ($\delta^{13}C_{\text{mixed}}$). $\delta^{13}C_{\text{mixed}}=\frac{X*n_{iA}*\delta^{13}C_{iA}+Y*n_{iB}*\delta^{13}C_{iB}}{X*n_{iA}+Y*n_{iB}}$, it can be derived that the cumulative isotopic composition of alkane generated in certain maturity interval can be expressed by the integral of the product of instantaneous isotopic composition and instantaneous yield at certain maturity point, and then divided by the cumulative yield of alkane generated in corresponding maturity interval. Thus, the cumulative isotopic composition(A(X)), cumulative yield(B(X)), instantaneous isotope(C(X)),and instantaneous yield(D(x)) in the dynamic model comply with the following formula during the maturity interval of (X_0-X). $A(X)=\frac{\int_{X_0}^{X} C(X)*D(X)dx}{B(X)}$, where A(X) and B(X) can be obtained by fitting of pyrolysis data, and D(x) can also be obtained from the derivation of B(X). The dynamic model was applied on the pyrolysis data of Pingliang Shale to illustrate the quantitative evolution of cumulative yield ,instantaneous yield, cumulative isotope and instantaneous isotope of $C_{1\text{-}3}$ with increasing maturity. The dynamic model can quantify the yield of methane, ethane and propane as well as $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ respectively during the hydrocarbon generation process. This model is of great significance to evaluate the natural gas resources of hydrocarbon source rock with different maturity and to identify the origin and evolutionary process of hydrocarbons by chemical and isotopic data. Moreover, this model provides an approach to study the dynamic evolution of isotope series of $C_{1\text{-}3}$ (including reversed isotopic series), which is hopeful to reveal the mechanism responsible for isotopic reversal when combined with post-generation studies.

Keywords: dynamic evolution model; yield; carbon isotope; hydrocarbon genereation; $C_{1\text{-}3}$; geochemistry

1. Introduction

Chemical and isotopic composition of light hydrocarbons have long been used to study the origins, generation, accumulation and degradation process of hydrocarbons in the past decades (Schoell, 1980; Rooney et al., 1995; Tang et al., 2000; Galimov, 2006; Liu et al., 2013; Zhao et al., 2019, 2020, 2021; Pei at al., 2023). However, with the large-scale exploration & development and intensive isotopic geochemistry study of natural gas resources in high evolution strata of superimposed basin, it is increasingly difficult to clearly identify the origin and evolutionary process of hydrocarbons by chemical and isotopic characteristics of alkanes. This is because there are many factors and geochemical processes responsible for chemical and isotopic compositions of hydrocarbons in geological conditions, such as the inheritance of isotopic signatures from precursor organics, kinetic isotope fractionations, equilibrium isotope fractionations and the mixing of hydrocarbons from different origins/maturities. Combined, these factors can readily lead to overlapping of bulk isotopic signatures of hydrocarbons of different origins and history, obscuring their origins and evolutionary processes. The mechanism responsible for the evolution of isotopic composition of alkanes, for example, the cause for the reversed alkane $\delta^{13}C$ values in many natural gas plays, is still controversial and remains an open question(Hunt et al. , 2012; Tilley et al., 2011; Dai et al., 2016;Shen et al., 2022).

The problems in the application of traditional natural gas isotope geochemistry can be attributed to the following two aspects: a) For current isotope analysis technology of monomer hydrocarbon, the isotopic information of the internal functional groups of the monomer hydrocarbon disappears in the process of oxidizing the target component to CO_2 or reducing it to H_2, accordingly, the intra-molecular isotope distribution information which can disclose the formation and evolution process of natural gas is not fully obtained (Zhao et al., 2020; Liu et al., 2019;Wen et al., 2023); b) The dynamic evolution laws of isotope composition of monomer hydrocarbon and corresponding mechanism during the formation and evolution process of natural gas are still in disputes(XiaXinyu and Tang Yongchun, 2012; Dai et al., 2016; Wang et al., 2015; Zhao et al., 2019). Efforts to explore the intra-molecular isotope distribution of hydrocarbons, including position-specific isotope and clumped isotope, have been made in the past decades (Stolper et al., 2014;Gilbert et al., 2016; Piasecki et al., 2016; Liu et al., 2019; Zhao et al., 2020). These isotopic information with higher dimensions are expected to provide unique constrains on their formation and migration-degradation processes, however, the theoretical studies and applications of intra-molecular isotope distribution are still in its infancy, and can't be widely used to date. Traditional monomer hydrocarbon isotope is still the main research method of natural gas isotope geochemistry, accordingly, research on the dynamic evolution of chemical and isotopic composition of alkanes still needs to be strengthened, especially the dynamic evolution during hydrocarbon generation process.

Efforts to study the dynamic evolution of chemical and isotopic composition of alkanes (especially C_{1-3}) during hydrocarbon generation process have been made in the past decades. Many empirical models have been put forward to study the compositional and isotopic variation of natural gas(Stahl et al.,1975; Schoell, 1980;Prinzhofer et al.,1995; Liu et al.,1999). However, these empirical models are developed based on statistic analysis of massive data, the mechanisms responsible for the compositional and isotopic variation of alkanes were not fully understood. Rayleigh model is the first semi-quantitative model to study the compositional and isotopic variation of alkanes (Clayton, 1991; Berner et al., 1992; Lorant etal., 1998). But Rayleigh model can not exactly study the compositional and isotopic variation of alkanes either, the obvious defects of Rayleigh model are as follows (Tang et al., 2000): one is the assumption that methane and the higher hydrocarbons can be modeled using a single extent of reaction parameter; the other is the assumption that the fractionation factor of each first-order reaction is constant. Hydrocarbon generation kinetic model based on various pyrolysis experiments are widely be applied to quantitative study the yield evolution of methane and total gaseous hydrocarbon (C_1-C_5) , while carbon isotope kinetic model based on various pyrolysis experiments are widely be applied to quantitative study the isotopic evolution of methane during the hydrocarbon generation process(Tang et al.,2000, 2005;Wang et al. 2006; Tian et al . 2007; Pan et al., 2010; Jia et al., 2014; Liu et al.,2016).Whereas, hydrocarbon generation kinetic model and carbon isotope kinetic model are only applicable to the first order reaction in the hydrocarbon generation process. The yield of total gaseous hydrocarbon (C_{1-5}) can also reach a plateau in hydrocarbon generation simulation experiments, so C_{1-5} can be considered as a whole to calculate its yield evolution using hydrocarbon generation simulation data. However, the yield of individual heavy hydrocarbon components initially increase and then decrease after reaching maximum yield in the hydrocarbon generation simulation experiments, indicating that the heavy hydrocarbon components have undergone pyrolysis. In addition, the heavy hydrocarbon components may involve Fischer-Tropsch reaction in the high evolution stage, so individual heavy hydrocarbon components cannot be regarded as a first-order reaction and are not suitable for hydrocarbon generation kinetic model and carbon isotope kinetic model. Tang et al.(2000) predicted the evolution of cumulative yield of methane, instantaneous yield of methane, instantaneous $\delta^{13}C_1$

and cumulative $\delta^{13}C_1$ by hydrocarbon generation kinetic model and carbon isotope kinetic model based on the pyrolysis of n-octadecan. Shuai et al.(2005,2006) carried out the hydrocarbon generation kinetic and carbon isotope kinetic study of ethane by dividing the evolution process of ethane into two stages: the generation dominated stage and the cracking dominated stage. However, each stage simultaneously involves the generation and cracking of ethane, and there may be ethane generated by the Fischer Tropsch reaction in the cracking dominated stage. To sum up, there is no valid model to quantitatively study the chemical and isotopic variation of C_{1-3} during the hydrocarbon generation process to date, making it very difficult to identify the origin, source and resources of natural gas by chemical and isotopic data.

To address this limitation, a quantitative model was built to illustrate the chemical and isotopic variation of C_{1-3} during the process of hydrocarbon generation.

The objective of this work is multifold:

(1) Summarize the universal evolution laws of chemical and isotopic composition of C_{1-3} in hydrocarbon generation process on the basis of fitting systematic data obtained from published papers for pyrolysis of various hydrocarbon sources.

(2)Introduce the theoretical approach and detailed steps to built the dynamic model of chemical and isotopic evolution of C_{1-3} during the hydrocarbon generation process.

(3)Illustrate the application of the dynamic model on the pyrolysis experiment of the Ordovician Pingliang Shale from Ordos Basin, China (Jia et al., 2014) to study its chemical and isotopic evolution of C_{1-3} during the hydrocarbon generation process.

2. Theoretical Approach

2.1. The Universal Chemical and Isotopic Evolution Laws of C_{1-3}in Hydrocarbon Generation Simulation Experiments

The universal evolution laws of hydrocarbon composition and isotope were summarized by data fitting of massive hydrocarbon generation simulation experiments involving various hydrocarbon sources obtained from available literature, including type I kerogen/source rock, type II kerogen/source rock, type III kerogen/source rock, crude oil, asphalt, etc (Lorant et al.,1998; Xiong et al.,2002,2004; Hill et al.,2003; Gong et al.,2004; Shuai et al.,2005; Wang et al.,2006; Yin etal.,2010; Li et al.,2011; Liu et al.,2012; Pan et al., 2012; Tian et al., 2012; Li et al.,2013;Tang et al.,2013, 2014;Cao et al.,2017;Wang et al.,2013;Gao et al., 2014; Jia et al., 2014;Wang et al., 2014; Chen,2015;Gai et al., 2015; Xiang et al., 2016; Shao et al., 2018)(Figure 1). For the yields evolution laws of C_{1-3}, C_1 yields increase continuously with rising maturity; while C_2 and C_3 yields initially increase and then decrease with increasing thermal maturity, reaching maximum yields at certain intermediate maturity. As regards the evolution laws of $\delta^{13}C_{1-3}$, $\delta^{13}C_1$ present obvious isotope rollover , initially shifting negatively and then shifting positively with increasing maturity; while $\delta^{13}C_2$ and $\delta^{13}C_3$ in certain simulation experiments also present isotope rollover with increasing maturity, but the variation amplitude is much lower than that of $\delta^{13}C_1$.Overall, the $\delta^{13}C_2$ and $\delta^{13}C_3$ generally shift positively with increasing maturity(Figure 1).

Since the samples adopted in the hydrocarbon generation simulation experiments are of different organic matter type and different maturity, the yields and isotope compositions of C_{1-3} may vary greatly from each other, however, the yields and isotope compositions of C_{1-3} present universal variation trends. Although these universal laws are empirical models summarized from massive data statistics (only the variation of C_1 yields and $\delta^{13}C_1$values are verified by hydrocarbon generation kinetics and isotope kinetics), massive hydrocarbon generation simulation data of various hydrocarbon sources all comply with these universal laws, convincing us that these universal laws are applicable to hydrocarbon generation process of various organic matter.

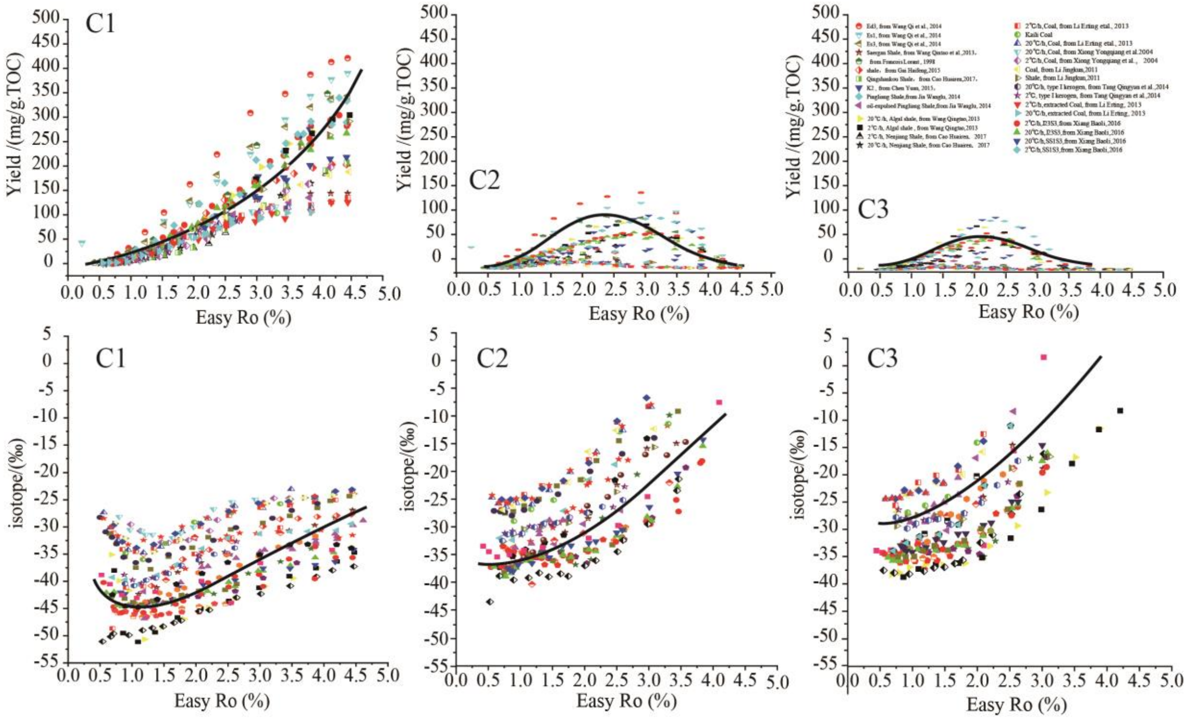

Figure 1. The universal evolution laws summarized from massivehydrocarbon generation simulation experiments.

2.2. *The Calculation of the Isotopic Composition of Mixed Natural Gas from Different Maturities ($\delta^{13}C_{mixed}$)*

The carbon isotope of mixed natural gas at different maturities can be formulated by equation (1) and equation (2) according to the definition of natural gas isotope.

$$\delta^{13}\mathrm{C}=[\frac{\mathrm{R_{sample}}}{\mathrm{R_{standard}}}-1]*1000(\text{‰}) \qquad (1)$$

where R denotes the isotope ratio of $^{13}C/^{12}C$ of PDB standard.

$$\delta^{13}\mathrm{C_{mixed}}=\frac{X*n_{iA}*\Delta_{iA}*(1+\Delta_{iB})+Y*n_{iB}*\Delta_{iB}*(1+\Delta_{iA})}{X*n_{iA}*(1+\Delta_{iB})+Y*n_{iB}*(1+\Delta_{iA})} \qquad (2)$$

A, B represent different natural gas end member; X,Y represent the proportion of A,B in mixed natural gas, respectively; n_i represents the concentration of alkane component i in natural gas; $\delta^{13}C_i$ represents the carbon isotope of component i;$\Delta=\delta^{13}C/1000+1$;R represents the $^{13}C/^{12}C$ ratio of PDB standard. However, too many parameters in equation (2) make it too complex to calculate$\delta^{13}C_{mixed}$.

$$\delta^{13}\mathrm{C_{mixed}}=\frac{X*n_{iA}*\delta^{13}C_{iA}+Y*n_{iB}*\delta^{13}C_{iB}}{X*n_{iA}+Y*n_{iB}} \qquad (3)$$

Xia et al.(1998) put forward a simplified formula to studied the influence of mixture on natural gas isotope(equation(3)).Although the simplified formula proposed by Xia et al.(1998) has been widely applied to the isotopic study of natural gas, some researchers are still skeptical of this formula and insist that it is only applicable to limited proportions of end members and may lead to obvious mistakes beyond limited proportions.Comparative study of the definition formula of mixed natural gas (equation (2)) and the simplified formula (equation (3)) were conducted under different proportions (A:B=1:9999-9999:1) to verify the validity of the simplified formula. To strengthen reliability and persuasion, the scope between $\delta^{13}C_{iA}$ and $\delta^{13}C_{iB}$ should cover the variation range of $\delta^{13}C_i$ in geological and experimental conditions, in addition, the difference of $\delta^{13}C_{iA}$ and $\delta^{13}C_{iB}$ should be big enough. Accordingly, we assign$\delta^{13}C_{iA}$ and$\delta^{13}C_{iB}$ to be -10‰ and -50‰, respectively. As shown in Table 1, the $\delta^{13}C_{mixed}$ values calculated according to simplified formula are very close with those calculated according to the definition formula under obviously different proportions, with only minor difference on the fifth significant digit To date, the precision of one digit after decimal point for $\delta^{13}C$ is sufficient to meet the requirement of isotope study of natural gas. So the simplified formula of $\delta^{13}C_{mixed}$ can be widely applied to the isotopic study of natural gas under diverse proportions of different end member.

Table 1. The $\delta^{13}C_{mixed}$ value of mixed natural gas with different proportions of end member A and B.

Proportion of end member A (%)	Proportion of end member B(%)	$\delta^{13}C_{mixed}$ according to definition formula(‰)	$\delta^{13}C_{mixed}$ according to simplified formula(‰)
0.01	99.99	-49.996	-49.996
0.1	99.9	-49.960	-49.960
1	99	-49.600	-49.600
5	95	-48.001	-48.000
10	90	-46.002	-46.000
20	80	-42.003	-42.000
30	70	-38.004	-38.000
40	60	-34.004	-34.000
50	50	-30.004	-30.000
60	40	-26.004	-26.000
70	30	-22.004	-22.000
80	20	-18.003	-18.000
90	10	-14.002	-14.000
95	5	-12.001	-12.000
99	1	-10.400	-10.400
99.9	0.1	-10.040	-10.040
99.99	0.01	-10.004	-10.004

2.3. Dynamic Modeling of Chemical and Isotopic Variation of $C_{1\text{-}3}$ during hydrocarbon Generation Process

2.3.1. Nomenclature

Cumulative yield: The total yield of certain alkane gas in certain maturity interval or geological period;

Instantaneous yield: The yield of certain alkane gas at certain single maturity point or single point of geological time;

Cumulative Isotope: The isotopic composition of alkane generated in certain maturity interval or geological period;

Instantaneous Isotope: The isotopic composition of alkane generated at certain single maturity point or single point of geological time;

Supposing the cumulative isotope function of X(maturity) is A(X); the cumulative yield function of X(maturity) is B(X); the instantaneous isotope function of X(maturity) is C(X); the instantaneous yield function of X(maturity) is D(x).

2.3.2. Calculations

According to the simplified formula of $\delta^{13}C_{mixed}$ (formula(3)), we can infer that A(X), B(X), C(X), D(x) comply with the formula (4) in the maturity interval of (X_0-X) based on the theory of integration and differentiation.

$$A(X)=\frac{\int_{X_0}^{X} C(X)*D(X)dx}{B(X)} \quad (4)$$

From equation (4), we have

$$A(X)*B(X)=\int_{X_0}^{X} C(X)*D(X)dx \quad (5)$$

Derivatives were taken on both sides of formula (5), we have

$$C(X)=\frac{d[A(X)*B(X)]}{D(X)} \quad (6)$$

The cumulative isotope function (A(X)) and cumulative yield function (B(X)) can be obtained by data fitting of the yield and isotope data from pyrolysis experiments using Origin software. The conventional viewpoints insist that the yield and isotope of alkanes collected at certain temperature/maturity point in open pyrolysis experiments can represent the instantaneous yield and instantaneous isotope, respectively. However, the alkanes collected at certain temperature/maturity

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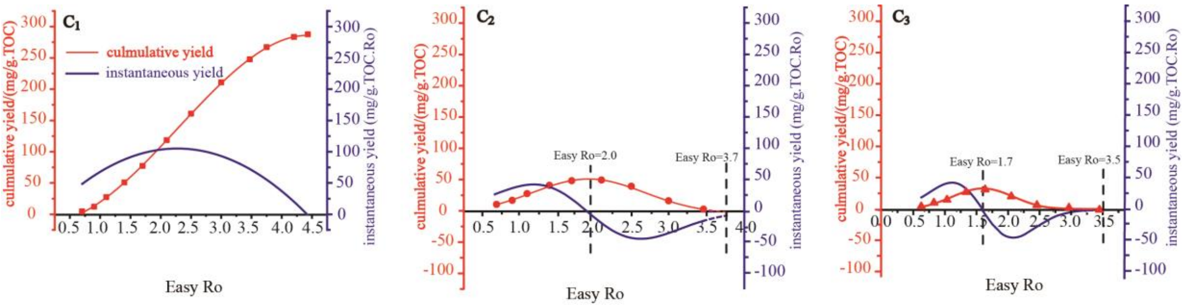
in open pyrolysis experiments are actually the cumulative pyrolysis product during the maturity interval of two sampling points (except using on-line pyrolysis -GC- IRMS method). Although alkanes collected at certain maturity in open pyrolysis experiments can reflect the variation trend of instantaneous yield and instantaneous isotope when the sampling interval is very small, they cannot accurately represent the instantaneous yield and instantaneous isotope. In this study, the instantaneous yield function (D(x)) can be obtained by taking derivative of cumulative yield function (B(X)), and the instantaneous isotope function (C(x)) can be calculated by formula(6). The calculation and plotting of formula(6) were conducted by Maple software.

It has been documented that the hydrocarbon generation history (including heating rate (subsidence rate), geothermal gradient, primary/secondary hydrocarbon generation) also impose significant influence on the component and isotopic characteristics of hydrocarbon(Tang et al., 2000; Qin et al., 2000; Jin et al., 2008). But for simplicity, it is assumed in this study that the hydrocarbon generation history does not influence the instantaneous yield and isotope characteristics of hydrocarbon at each maturity. The above-mentioned cumulative yield function (B(X)) and cumulative isotope function (A(X)) are obtained based on the fact that all pyrolysis products are preserved in confined pyrolysis system. For natural gas systems which experienced hydrocarbon expulsion, the calculation of cumulative isotope (A(X)) must take consideration of the expulsion ratio on the basis of formula (4), which are discussed elsewhere (Zhao et al., in prep).

3. Results and Discussion

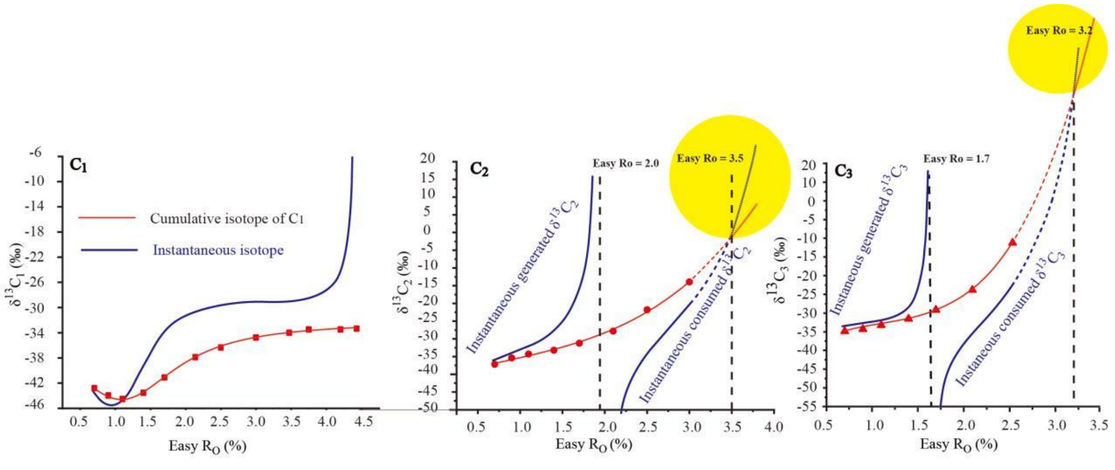
The quantitative model was applied on the anhydrous confined pyrolysis data of the kerogen extracted from the Ordovician Pingliang Shale from Ordos Basin, China (Jia et al., 2014) to study its chemical and isotopic evolution of C_1-C_3 during the hydrocarbon generation process. The detailed information of Ordovician Pingliang Shale are as follows: marine shale, type II kerogen, TOC 18.1%, vitrinite reflectance (R_O) 0.7%. The δ^{13}C of the isolated kerogen is 30.1‰. The detailed procedures of anhydrous confined pyrolysis experiment are as follows: the kerogen samples were introduced into gold tubes and were sealed under argon; the tubes containing fresh kerogen were loaded into the stainless vessel; pyrolysis was performed under a constant pressure of 50 MPa, and the pyrolysis temperatures ranged from 250–600°C at heating rates of 2 °C/h(Liu and Tang (1998)).The simulation temperatures was converted to “Easy Ro” to represent the evolutionary maturity of Pingliang Shale (Sweeney and Burnham,1990).

The cumulative isotope function (A(X)) and cumulative yield function (B(X)) of kerogen from Pingliang Shale are obtained by data fitting of confined pyrolysis experiments (Figures 2 and 3). The instantaneous yield function (D(x)) can be obtained by taking derivative of cumulative yield function (B(X)), and the instantaneous isotope function (C(x)) can be calculated by formula (6) (Figures 2 and 3). The unit of instantaneous yield function [mg/(g.TOC.Ro)] is different with the unit of cumulative yield function[mg/(g.TOC)]，so the charts of instantaneous and cumulative yield were plotted using Dual-axis method, and there are no direct comparability between the value of instantaneous yield and cumulative yield.



(a) (b) (c)

Figure 2. The instantaneous and cumulative yield of $C_{1\text{-}3}$ from the pyrolysis of Pingliang Shale at different maturity.



(a) (b) (c)

Figure 3. The instantaneous and cumulative isotope of $C_{1\text{-}3}$from the pyrolysis of Pingliang Shale at different maturity.

3.1. Dynamic Chemical Evolution of $C_{1\text{-}3}$ During hydrocarbon Generation Process

3.1.1. Dynamic Evolution of C_1 Yield During Hydrocarbon Generation Process

The cumulative yield of C_1 originated from the pyrolysis of Pingliang Shale increase continuously with rising maturity and reach a plateau at the end of methane generation process , which is consistent with that the instantaneous yield of C_1 always keep positive during the methane generation process. The cumulative yield of C_1 increase quite mildly at two end of the curve and increase quite sharply in the middle of the curve, which is consistent with that the instantaneous yield of C_1 initially increase and then decrease with raising maturity, reaching maximum instantaneous yield at certain intermediate maturity(Easy Ro approx=2.4%).

Methane is widespread in various stages of hydrocarbon generation evolution of Pingliang Shale:immature stage, low mature stage, mature stage, high mature stage and over mature stage. At immature-low mature stage and mature stage, liquid hydrocarbons dominate the hydrocarbon generation product of sapropelic Pingliang Shale, the gaseous hydrocarbons originated mainly from the degradation of aliphatic side chain only account for very low proportion of the total hydrocarbons, so the instantaneous and cumulative yield of C_1 is quite low at the beginning of hydrocarbon generation process. At high mature stage， liquid hydrocarbons start to be extensively cracked, crude oil cracking gas become the dominate origin of gaseous hydrocarbon, while the proportion of kerogen cracking gas decrease quickly. Since the hydrocarbon-generating intensity of crude oil cracking is 3～4 times of that of kerogen cracking(Zhao et al., 2005; Li et al., 2018), the instantaneous yield of C_1 increase sharply and reach maximum at Easy Ro approx. 2.4% in this period. At over mature stage, liquid hydrocarbons are mostly cracked and the gas generation potential of kerogen is also nearly exhausted, so the instantaneous yield of C_1 decrease sharply at the end of over mature stage(Li et al., 2018). At Easy Ro approx. 4.5%, the cumulative yield of C_1 reach plateau and meantime the instantaneous yield of C_1 approach zero, implying that the hydrocarbon generation potential of Pingliang Shale is already exhausted at Easy Ro approx. 4.5%. However, the instantaneous yield of C_1 has never become negative during the whole hydrocarbon generation evolution stage, indicating that there exist no cracking of methane. Previous researches on the calculation of reaction activation energy and pyrolysis experiments of methane have also prove that methane is so thermodynamically stable that it can hardly be pyrolyzed under geological conditions and hydrocarbon generation simulation experiments(Ni et al., 1995; Zhang et al.,2012; Li et al., 2018). Previous calculations have shown that the activation energy required for methane cracking is 441kJ/mol， higher than that of ethane and propane(Ni et al., 1995; Zhang et al.,2012). Moreover, it has been verified by extensive pyrolysis experiments of methane that the threshold temperature of methane pyrolysis is 1100 °C at atmospheric pressure(equivalent Ro approx=5.0%) (Li et al., 2018). While the maximum temperature of the pyrolysis experiment of Pingliang shale is 600 °C, far lower than the threshold temperature of methane pyrolysis. It follows that the instantaneous yield of C_1 is hopeful to predict the maturity deadline of hydrocarbon generation, which has practical significance to define the upper limit of natural gas exploration.

3.1.2. Dynamic Evolution of C_{2-3} Yield During Hydrocarbon Generation Process

The variation trends of cumulative yields C_2 and C_3 are identical, the cumulative yields initially increase and then decrease with increasing thermal maturity, reaching maximum yields at certain intermediate maturity.C_2 and C_3 reach maximum cumulative yield at Easy Ro appr.2.0 and 1.7, respectively (Figure 2). At the same time, the instantaneous yield of C_2 and C_3 shift from positive values to negative values also at Easy Ro 2.0 and 1.7, respectively, which indicate the cracking threshold maturity of C_2 and C_3. Actually, there are both generation and cracking of C_2 and C_3 before and after the threshold maturity, C_2 and C_3 just shift from generation-dominated stage to cracking-dominated stage at Easy Ro 2.0 and 1.7, respectively. For simplicity, it is assumed in this study that there is only generation of C_2 and C_3 before the threshold maturity(Easy Ro 2.0% and 1.7%, respectively), and there is only cracking of C_2 and C_3 after the threshold maturity.

Propane starts cracking at Easy Ro 1.7% and ends cracking at Easy Ro 3.5%, while ethane starts cracking at Easy Ro 2.0% and ends cracking at Easy Ro 3.7%. Previous studies have shown that the activation energy required for ethane cracking is higher than that of propane (Li et al., 2018), therefore the later cracking of ethane can probably be attributed to its higher molecular stability.The variation trends of instantaneous yield of C_2 and C_3 are also identical. During the generation stage(instantaneous yield $>$ 0),the instantaneous yield initially increase and then decrease with raising maturity, reaching maximum instantaneous yield at certain intermediate maturity. The increase of instantaneous yield of C_2 and C_3 at the early generation stage mainly be attributed to that C_2 and C_3 originated from kerogen cracking and crude oil cracking begin to be extensively generated at mature stage and high mature stage. While the decrease of instantaneous yield of C_2 and C_3 at the late generation stage can mainly be attributed to that kerogen cracking and crude oil cracking are more inclined to generate C_1 rather than C_2 and C_3 at high mature stage. During the consumption stage(instantaneous yield $<$ 0), the instantaneous consumption rate initially increase and then decrease with raising maturity, reaching maximum instantaneous consumption rate at certain intermediate maturity. The increase of instantaneous consumption rate at the early consumption stage is owning to the initiation of extensive cracking of C_2 and C_3 at high mature stage and over mature stage. While the decrease of instantaneous consumption rate at the late consumption stage is owning to that the cumulative yields C_2 and $C_3$are mostly cracked and cracking potential of C_2 and C_3 is nearly exhausted.

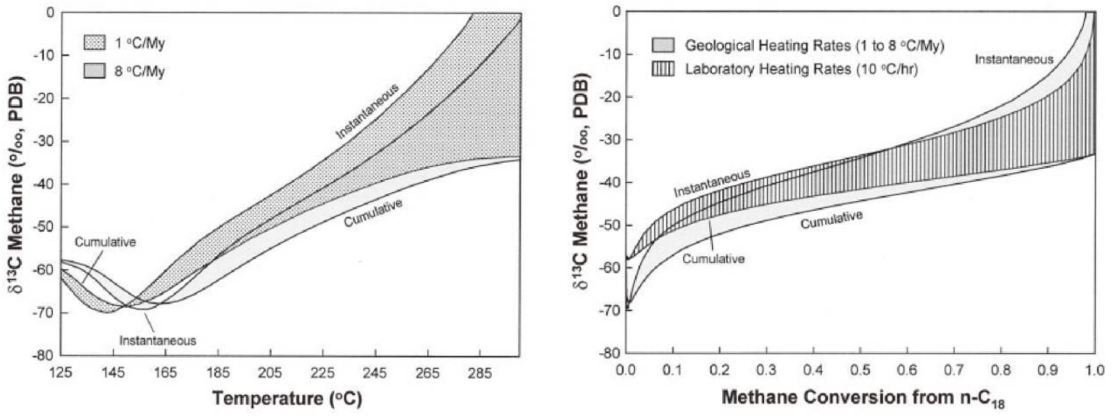
3.2. Dynamic isotopic Evolution of $\delta^{13}C_{1-3}$ During hydrocarbon Generation Process

3.2.1. Dynamic Isotopic Evolution of $\delta^{13}C_1$ During Hydrocarbon Generation Process.

The cumulative and instantaneous $\delta^{13}C_1$ from the pyrolysis of Pingliang Shale all present identical variation pattern: shift negatively at the early hydrocarbon generation stage, and then shift positively until the end of methane generation. The variation trend of cumulative $\delta^{13}C_1$ depends on the relative isotopic composition values between cumulative$\delta^{13}C_1$ and instantaneous $\delta^{13}C_1$: when instantaneous$\delta^{13}C_1$is lighter than cumulative$\delta^{13}C_1$(Easy Ro< 1.1%), the cumulative $\delta^{13}C_1$ shift negatively; when instantaneous $\delta^{13}C_1$ is heavier than cumulative$\delta^{13}C_1$ (Easy Ro> 1.1%), the cumulative $\delta^{13}C_1$ shift positively. The rollover of cumulative and instantaneous $\delta^{13}C_1$have already be verified by the study of Tang et al. (2000) using carbon isotope kinetic model(Figure 4. a). Moreover, the rollover of cumulative $\delta^{13}C_1$ from the pyrolysis of Pingliang Shale were also observed in many pyrolysis experiments (Figure 1) (Lorant, 1998;Wang et al.,2013;Tang et al.,2013;Jia et al.,2014;Chen,2015;Li et al.,2013; Tian et al., 2012).

The mechanism responsible for the isotope rollover of δ^{13}C$_1$include:(a) There are two or more precursors for methane generation with different isotopic compositions, the mixing of methane originated from different precursors lead to the isotope rollover of C$_1$(Tang et al., 2000).. Heteroatoms such as O and S are widely present in organic matter, and alkyl carbons connected to these heteroatoms are more isotopically heavier. Due to the instability of the C-O or C-S bonds, these isotopically heavier alkyl groups were preferentially decomposed to form isotopically heavier methane. When the alkyl carbons connected to heteroatoms were almost cracked, the isotopically lighter methane originated from the cracking of more tightly bound C-C bonds was extensively generated. The initial trend of decreasing δ^{13}C$_1$ values can be explained by the mixing of isotopically lighter methane. For alkyl groups connected with C-C bond, ^{12}C enriched alkyl groups were preferentially decomposed to form isotopically lighter methane. With increasing evolution degree, ^{13}C enriched alkyl groups were gradually decomposed to form isotopically heavier methane , resulting in the increase of δ^{13}C$_1$. However, the rollover of δ^{13}C$_1$were also observed in many pyrolysis experiments of pure n-alkanes which are free of heteroatoms, indicating that this theory cannot cover all the δ^{13}C$_1$rollover occurrences.(b)There are two sets of methane precursors with significantly different activation energy in hydrocarbon source, and precursor with lower activation energy typically has higher isotope fractionation factor and tends to generate isotopically lighter methane, while precursor with higher activation energy typically has lower isotope fractionation factor and tends to generate isotopically heavier methane(Tang et al., 2000). Since precursor with lower activation energy was preferentially decomposed to form isotopically heavier methane, the variation trends of δ^{13}C$_1$initially decrease with the mixing of isotopically lighter methane originated from the decomposition of precursor with higher activation. When precursor with lower activation was almost decomposed, precursor with higher activation were gradually decomposed to form isotopically heavier methane, leading to the increase of δ^{13}C$_1$ (Zhao, 2019).

A sudden and sharp increase of instantaneousδ^{13}C$_1$ was observed at the end of methane generation stage, but the cumulative δ^{13}C$_1$ shows only very gentle increase at this stage. The sharply increasing instantaneous δ^{13}C$_1$ was also observed when the methane conversion rate approaching 1.0 in the study of Tang et al.(2000) (Figure 4. b).In addition, Liu and Xu(1999) also documented the sudden and sharp increase of δ^{13}C$_1$in 106 coal-type gas samples from 10 basins of China at high mature and over mature stages, and a two-stage model of carbon isotopic fractionation was built to explain the fractionation mechanism of δ^{13}C$_1$. As mentioned in 3.1.1, methane is mainly generated from the cracking of kerogen and the instantaneous yield is very limited at the end of methane generation stage, moreover there exists no cracking of methane in this period. Accordingly, the sudden and sharp increase of instantaneous δ^{13}C$_1$ may be attributed to the sudden transform of precursor with higher activation energy and lower isotope fractionation factor. Since previous normal methane precursors have been mostly cracked at the end of methane generation stage, the continuously advancing evolutionary process may suddenly result in the cracking of unconventional precursor with higher activation energy, and lead to sudden and sharp increase of instantaneous δ^{13}C$_1$. As the instantaneous C$_1$ yield is very limited in this period, the sharp increase of instantaneous δ^{13}C$_1$did not lead to the obvious increase of cumulative δ^{13}C$_1$.



(a) (b)

Figure 4. The calculated evolution trend of instantaneous and cumulative $\delta^{13}C_1$(Tang et al. ,2000).

3.2.2. Dynamic Isotopic Evolution of $\delta^{13}C_{2\text{-}3}$ During hydrocarbon Generation Process

The cumulative $\delta^{13}C_2/\delta^{13}C_3$ and instantaneous $\delta^{13}C_2/\delta^{13}C_3$from the pyrolysis of Pingliang Shale all present identical variation pattern: the cumulative $\delta^{13}C_2/\delta^{13}C_3$

increase continuously with increasing maturity while the instantaneous $\delta^{13}C_2/\delta^{13}C_3$ present two-stage pattern(Figure 3). The instantaneous $\delta^{13}C_2/\delta^{13}C_3$ in the generation stage(instantaneous yield＞0) mainly represents the isotope of instantaneously generated C_2/C_3 ,while the instantaneous $\delta^{13}C_2/\delta^{13}C_3$ in the consumption stage(instantaneous yield＜0) mainly represents the isotope of instantaneously cracked C_2/C_3. The instantaneous generated $\delta^{13}C_2/\delta^{13}C_3$ increase with raising maturity until the end of C_2/C_3 generation, which is result from the preferential generation of ^{12}C enriched C_2/C_3. While the instantaneous consumed $\delta^{13}C_2/\delta^{13}C_3$ increase with raising maturity until the exhaustion of C_2/C_3 , which can all be attributed to the preferential decomposition of ^{12}C enriched C_2/C_3. Similar with the variation trend of instantaneous $\delta^{13}C_1$ at the end of methane generation stage, the instantaneous generated $\delta^{13}C_2/\delta^{13}C_3$ also present sudden and sharp increase at the end of C_2/C_3generation stage, which may also be attributed to the cracking of unconventional precursor with higher activation energy.

The variation trend of cumulative$\delta^{13}C_2/\delta^{13}C_3$was controlled by the relative isotopic composition values between cumulative$\delta^{13}C_2/\delta^{13}C_3$ and instantaneous generated $\delta^{13}C_2/\delta^{13}C_3$ in the generation stage as well as the relative isotopic composition values between cumulative$\delta^{13}C_2/\delta^{13}C_3$ and instantaneous consumed $\delta^{13}C_2/\delta^{13}C_3$in the consumption stage. In the generation stage, the instantaneous generated $\delta^{13}C_2/\delta^{13}C_3$ is heavier than corresponding cumulative$\delta^{13}C_2/\delta^{13}C_3$, accordingly, the cumulative $\delta^{13}C_2/\delta^{13}C_3$increase continuously with raising maturity. In the consumption stage, the instantaneous consumed $\delta^{13}C_2/\delta^{13}C_3$is lighter than corresponding cumulative$\delta^{13}C_2/\delta^{13}C_3$, accordingly, the cumulative$\delta^{13}C_2/\delta^{13}C_3$ still increase continuously with raising maturity. As common acknowledged, the bond energy of ^{12}C-^{12}C is lighter than that of ^{12}C-^{13}C and ^{12}C-^{13}C, so ^{12}C enriched C_2/C_3 should be preferential decomposed during the consumption stage. As a result, the $\delta^{13}C$ of residual $\delta^{13}C_2/\delta^{13}C_3$ (cumulative $\delta^{13}C_2/\delta^{13}C_3$) should be heavier than instantaneous consumed $\delta^{13}C_2/\delta^{13}C_3$ during the consumption stage. This is the case observed in most of the consumption stage of C_2/ C_3, but at the end of consumption stage, the instantaneous consumed $\delta^{13}C_2/\delta^{13}C_3$ reversed to be more positive than cumulative $\delta^{13}C_2/\delta^{13}C_3$(yellow labelled area in Figure 3.(b),(c)), which is unreasonable according to the bond energy theory. The reversal of instantaneous consumed $\delta^{13}C_2/\delta^{13}C_3$ and cumulative $\delta^{13}C_2/\delta^{13}C_3$ happened when the cumulative C_2/C_3 have almost been decomposed (Easy Ro above 3.5% C_2 and 3.2% for C_3,correspondingly).As shown in Figure 3, the reversal of instantaneous consumed $^{13}C_2/\delta^{13}C_3$ and cumulative $\delta^{13}C_2/\delta^{13}C_3$ can mainly be ascribed to the sudden and sharp increase of instantaneous consumed $^{13}C_2/\delta^{13}C_3$, which is similar with the sudden and sharp increase of instantaneous generated $\delta^{13}C_1$. Accordingly, it can be speculated that the sudden and sharp increase of instantaneous consumed $^{13}C_2/\delta^{13}C_3$ may also be attributed to the sudden transform of an unconventional precursor, e.g. propane analogues with unconventionally heavier intra-molecular isotope distribution and higher activation energy, when common precursors have been mostly cracked .

4. Conclusions

Based on systematic data obtained from published papers for pyrolysis of various hydrocarbon sources, the empirical evolution framework of chemical and isotopic composition of C_{1-3} generated from various organic matter was built., which laid overall foundation for the dynamic evolution model of chemical and isotopic composition of C_{1-3} in this study.

Based on the calculation of the isotopic composition of mixed natural gas at different maturities ($\delta^{13}C_{mixed}$), the quantitative relationship between cumulative isotopic composition(A(X)), cumulative yield(B(X)), instantaneous isotope(C(X)),and instantaneous yield(D(x)) were accomplished according to integration theory, which is the core of dynamic model. Moreover, the dynamic model was applied on the pyrolysis data of Pingliang Shale, and the cumulative yield ,instantaneous yield, cumulative isotope and instantaneous isotope were illustrated to study its chemical and isotopic evolution of C_{1-3} during the hydrocarbon generation process

The geological significances of the dynamic model are as follows:

(1) Quantified the yield and proportion of methane, ethane and propane during the hydrocarbon generation process by the parameters of cumulative yield of C_{1-3} and instantaneous yield of C_{1-3}, provided a basis for evaluation of natural gas resources from hydrocarbon source rock of different maturity, especially the evaluation of high mature source rock.

(2) Clarified the cracking maturity of ethane and propane, and proposes that there exists no cracking of methane below the Easy Ro of 4.5%, which may be helpful for natural gas exploration of deep formations.

(3) Quantified the evolution of δ13C1, δ13C2 and δ13C3 respectively during hydrocarbon generation processby the parameters of cumulative $^{13}C_{1-3}$ and instantaneous $^{3}C_{1-3}$, improved the accuracy to identify the origin and evolutionary process of hydrocarbons by chemical and isotopic data, and made it possible to study the dynamic evolution of isotope series of C_{1-3} (including reversed alkane series) .

The empirical evolution framework of chemical and isotopic composition of C_{1-3}, which was built on the basis of data fitting of systematic pyrolysis experiments of different hydrocarbon source, laid a factual basis for the dynamic model in this study . However, the theoretical basis is still weak, accordingly, the mechanism responsible for the evolution trends of cumulative yield ,instantaneous yield, cumulative isotope and instantaneous isotope still needs to be systematically and deeply studied.

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