DENSITY FUNCTIONAL THEORY STUDY ON THE ADSORPTION OF METHANE ON KEROGEN WITH DIFFERENT FUNCTIONAL GROUPS

WANG, Z-H.[1*] – LI, Y.[1] – MENG, W-J.[1] – GUO, P.[1] – LUO, Q.[2] – RAN, Z-L.[3]

[1]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
(phone: +86-139-8203-6861)

[2]College of Science, Southwest Petroleum University, Chengdu 610500, China

[3]Key Laboratory of Optical Fiber Sensing & Communication of the Ministry of Education, University of Electronics Science & Technology of China, Chengdu 611731, China

*Corresponding author
e-mail:wangzhouhua@126.com

Abstract. Organic matter plays a vital role in the adsorption of shale gas. The current study about adsorption capacity and adsorption law of organic matter have made abundant achievements, but the effect of functional groups on the adsorption of shale gas is still not clear. In this paper, the adsorption of CH_4 on the surface of kerogen fragments with different functional groups (OH, CH_2OH, COOH, CH_3, NH_2, O) was studied based on first principles density functional theory (DFT). The structures, electronic properties were calculated by the generalized gradient approximation (GGA). The result shows that the existence of oxygen and nitrogen in functional groups makes kerogen has greater methane adsorption capacity. The fragment of kerogen with NH_2- has strongest methane adsorption capacity and the adsorption energy is -5.959eV, while the adsorption energy of the fragments of kerogen with OH, CH_2OH, COOH, O is between -0.274eV~-0.395eV, which is close to each other, but far less than the former; the adsorption effect is very weak for methane on the surface of kerogen fragments RH、 RCH_3; Difference value of the adsorption energy is less than 0.03eV on the surface of same fragment of kerogen, indicating that adsorption site has little influence on methane adsorption and methane is easy to spread on the same surface.
Keywords: *first principles, fragments, adsorption energy, electronic state density, shale gas*

Introduction

Shale gas is an important unconventional natural gas resource, widely distributed in the world. The success of the development of shale gas in North America, stimulates and promotes the exploitation of the shale gas worldwide. From the perspective of geochemistry, organic rich shale is a kind of granular material, which is composed of organic-phase kerogen that dispersed in the nonorganic matrix (such as quartz, clay minerals, etc.) (Collell et al., 2014). Because of the existence of organic phase, the connectivity of the pore networks is very poor, and about the 50% of shale gas is adsorbed on organic-phase kerogen in shale gas reservoir (such as Barnett Shale) (Wang et al., 2009). The main components of shale gas are alkanes. In addition to a small number of ethane, propane and butane, the number of methane accounted for the vast majority (Zou et al., 2011). Therefore, the study on the adsorption of methane in organic-phase kerogen is the main direction in shale gas research area.

At present, the research on the adsorption of methane in organic matter has two sides, experimental study and theoretical study. In the experimental study, the researchers mainly used the physical and chemical method to separate the sample from the shale, and used the method of volume or weight to test the adsorption capacity of methane (Hu, 2014; Zhang et al., 2012). However, in the aspect of theoretical research, the adsorption of methane in carbon nanopores, such as kerogen, carbon nanotubes and graphene, were studied by Monte Carlo method (Collell et al., 2014; Bartuś and Bródka, 2011; Billemont et al., 2010; Billemont et al., 2013). Previous research was mainly on the description and analysis for adsorption isotherm which could reflect the adsorption capacity of kerogens for methane, and has already obtained many achievements. But few scholars have applied the density functional theory (DFT) to study the effect of functional groups of organic matter on the adsorption of methane.

The application of first principles calculation for the adsorption of gas molecules on the surface of materials has been reported. Leenaerts et al. (Leenaerts et al., 2008; Leenaerts et al., 2009) researched the adsorption of H_2O, NH_3, NO_2 and some else gas molecules on the surface of graphene by using the DFT. Based on applying the ideal grapheme surface to construct the structure of the coal seam, Y. Liu et al. (Liu and Wilcox, 2009) analyzed the adsorption law of CO_2 in different scale space with the DFT. However, the results of these studies can hardly be applied to explain the adsorption of shale gas on organic matter surface. In this paper, it calculates the adsorption structure and properties of methane on the surface of kerogen fragments with different functional groups (Behar and Vandenbroucke, 1987) (OH, CH_2OH, COOH, CH_3, NH_2, O) by using the first principle method, compares the adsorption of CH_4 on different sites on the same kerogen fragment surface, and analyzes the structure, adsorption energy and electronic properties of the kerogen fragment after the adsorption of CH_4. Thus, the quantum mechanical mechanism of the interaction between CH_4 and organic matter is understood, which provides a certain theoretical support to the development of shale gas reservoir.

Methods and models

Based on the density functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965), the first principle method was used to calculate the ground state geometries and electronic properties of methane adsorbed on the surface of kerogen fragments with different functional groups. Calculation was implemented in the CASTEP, a program that was developed by the condensed state physics research group of University of Cambridge. The reliability of the program had been verified by a large number of practical calculations. The structure of the kerogen is a kind of aromatic structure, which is composed by functional groups and a kind of aromatic unit with cross-linked alkyl chains. In order to study the effect of different functional groups on the adsorption of CH_4 in kerogen, we referred to the method of constructing the structure of kerogen by Yiannourakou et al. in this work (Yiannourakou et al., 2013). Functional group was connected to the symmetrical site of polycyclic aromatic structures to construct a fragment of kerogen, which was used to simulate the surface of organic matter. When the aromatic structure (R) is connected with hydrogen atom, it is called the kerogen fragment RH. Similarly, when R is connected with OH, it is called the kerogen fragment ROH, and the rest is the same as the law. The structures of kerogen fragments after optimization are shown in *Fig. 1*.

The calculation of the CASTEP program which requires the system to have the periodicity is based on the total energy pseudopotential method and the plane wave expansion (Blöchl, 1994; Kresse and Joubert, 1999). When calculated, it was the first to optimize the structure of different kerogen fragments. In order to simulate the adsorption of CH_4 on the surface of organic matter, the hydrogen atoms in the aromatic structure were fixed, while the position of carbon atoms in aromatic structure, functional groups and the adsorbed CH_4 were variable in structure optimization calculation. On the optimization of the surface structure, the vacuum region was left on the surface of the kerogen with thickness of 1.7nm, to avoid the interference between the layers.

The single kerogen fragment was treated as a single cell. In this work, the p(1×1) cell was used. It optimized the structure of cell before the calculation of adsorbing CH_4 in different high symmetry sites (the bridge, the top and the hole). The results showed that wherever the site of hydrogen atom in CH_4 changed on the surface of the kerogen, the effect on the adsorption for CH_4 was little. So the change of the site of hydrogen atom was not considered. To make the result better convergence in the process of optimizing structure, the BFGS optimization algorithm proposed by Broyden et al. (Broyden, 1970; Fletcher, 1970; Goldfarb, 1970; Shanno, 1970) was used for geometry optimization. Exchange-correlation energy was obtained by using generalized gradient approximation (GGA-PBE), which was proposed by Perdew et al. (Perdew et al., 1996). Using a 240.0eV plane wave set the cutoff. The value of self-consistent field (SCF) tolerance was $1.0×10^{-5}$ eV. 1×1×1 k point sampling was used (Monkhorst and Pack, 1976). The value of maximum force tolerance was 0.1eV/nm.

(a)RH   (b) ROH   (c) RCH$_3$ (d) RCH$_2$OH

(e) RNH$_2$ (f) RCOOH   (g) RO
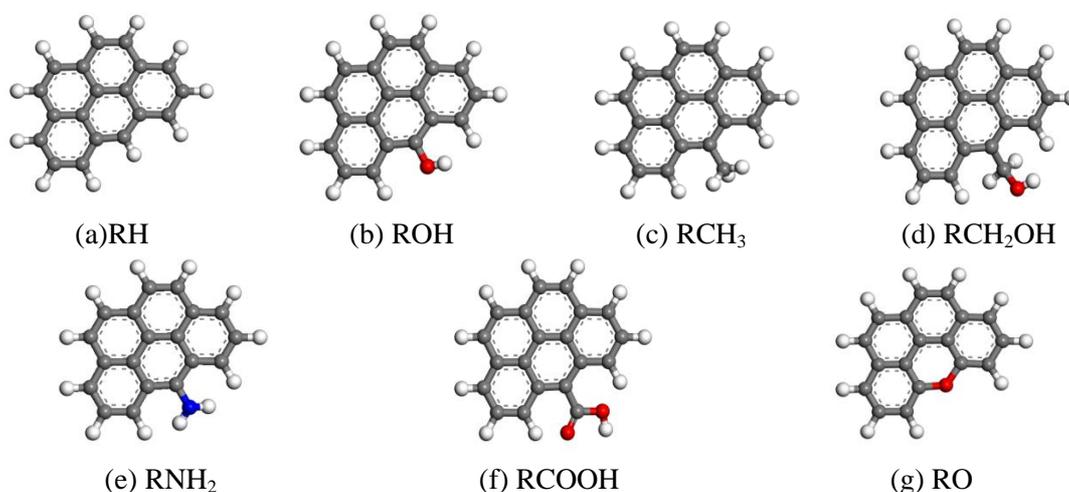
Figure 1. Kerogen fragments after optimization (Atoms representation: gray is for carbon atoms, white for hydrogen, red for oxygen, and blue for nitrogen).

Results and discussion

Herein, the adsorption of methane on the surface of different organic-phase kerogen fragments was studied. As shown in *Fig. 2*, the high symmetry sites on the surface of the kerogen fragment include the top site (T), the bridge site (B) and the hole site (H). The position of T site is over the atom which connected with aromatic structure in functional group.
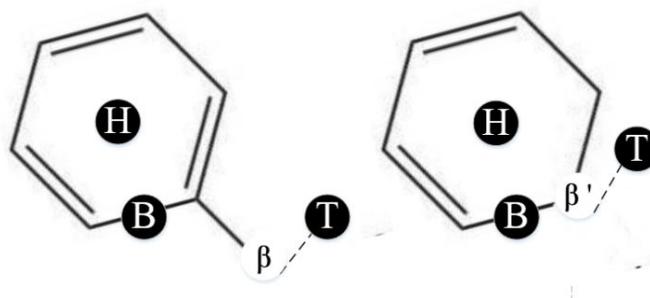
Figure 2. High-symmetry adsorption sites on the surface of Kerogen fragments (β represents H, OH, CH₂OH, COOH, CH₃, NH₂; β' represents O).

In *Fig. 3* the cases of methane molecules adsorbed on the surface of RNH_2 (B), (T) and (H) are showed as structure (a), (b) and (c), respectively. The pink atoms in picture (a) represent the fixed atoms, and the dark gray atoms the non-fixed.

(a)	(b)	(c)
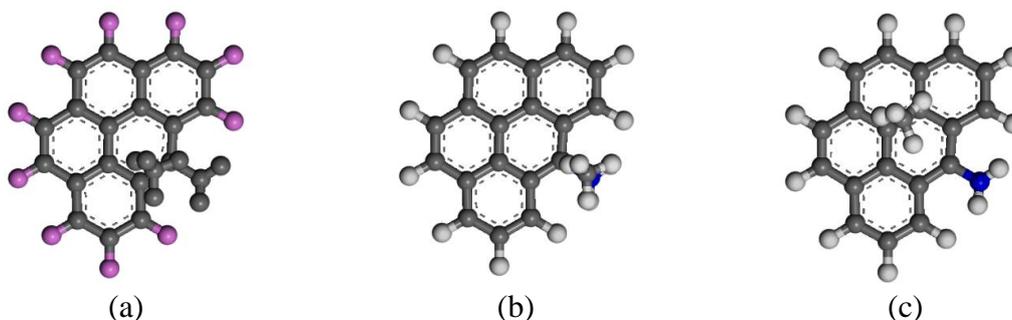
Figure 3. Structure of Kerogen fragments with NH₂ after adsorbing methane on different adsorption sites.

In order to analyze the stability of methane molecules adsorbed on different positions of the kerogen fragment, the adsorption energy of methane molecules at each position was calculated. Adsorption energies (E_{ad}) are calculated from

$$E_{ad} = E_{CH_4/Kero} - \left(E_{Kero} + E_{CH_4} \right) \qquad (Eq.1)$$

where $E_{CH4/Kero}$, E_{Kero} and E_{CH4} are energies of the adsorption system, the isolated kerogen molecule, the isolated methane molecule, respectively. The formula shows that the adsorption energy is negative, and the process of adsorption is exothermic. The smaller the value is, the easier the adsorption process occurs.

Adsorption energy and location of methane on the surface of different kerogen fragments are showed in (*Table 1*). By comparison, it is found that the distance (d_0) between the carbon atoms in methane and the plane of the kerogen fragment is changed. In the H site of kerogen fragment ROH and RO, d_0 is less than 0.4nm. In the B, T sites, d_0 is between 0.4~0.45nm, and in the rest position of kerogen fragment, d_0 is between 0.5~0.6nm. So the correlation between the size of d_0 and the adsorption energy E_{ad} is not strong.

Table 1. *Adsorption energy and location of methane on the surface of different segments of kerogen.*

Kerogen fragment	T（top）		B（bridge）		H（hole）	
	E_{ad}/ev	d_0/nm	E_{ad}/ev	d_0/nm	E_{ad}/ev	d_0/nm
RH	0.051	0.504	0.037	0.574	0.058	0.504
ROH	-0.351	0.415	-0.373	0.439	-0.363	0.387
RCH_3	0.046	0.592	0.036	0.557	0.05	0.504
RCH_2OH	-0.376	0.507	-0.396	0.503	-0.395	0.502
RCOOH	-0.377	0.501	-0.395	0.505	-0.393	0.523
RO	-0.274	0.446	-0.25	0.445	-0.254	0.363
RNH_2	-5.959	0.522	-5.939	0.58	-5.946	0.505

Adsorption energies of the most stable adsorption site of methane after adsorbed on different kerogen fragments are showed in (*Fig. 4*). When the methane is adsorbed on the T site of kerogen fragment RNH_2, the adsorption energy for a minimum of -5.959eV is far less than that of other types of kerogen fragments, which indicating the adsorption on kerogen fragment RNH_2 is the strongest. The methane on the B site of ROH, RCH_2OH, RCOOH has the most stable adsorption. The adsorption energies are -0.373eV, -0.396eV, -0.395V, respectively. The difference is very small, and it illustrates that their adsorption capacity for methane is close. While the most stable adsorption site on kerogen fragment RO is the T site, and the adsorption energy is -0.274eV, showing that the adsorption capacity of methane is slightly weaker than that of the above three kinds of kerogen. On the T, B, H sites of kerogen fragment RH and RCH_3, the adsorption energies are both close to zero, explaining the adsorption capacity for methane of two kerogens are very weak. By comparing the elements of the functional groups, it is not difficult to find that the presence of oxygen and nitrogen element makes the adsorption of kerogens more powerful.
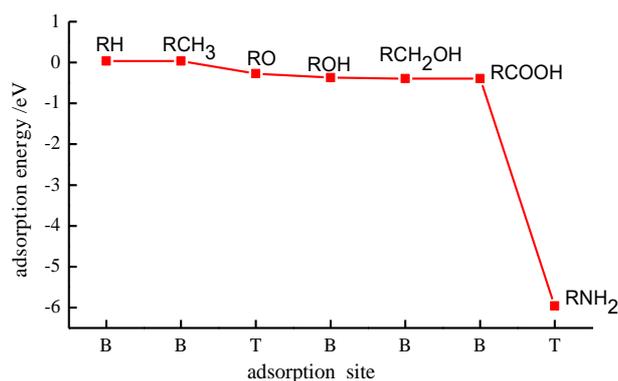
Figure 4. *Adsorption energy of the most stable adsorption site of kerogen fragments.*

Fig. 5 shows both the density of states of CH_4 before and after it is adsorbed on the surface of kerogen fragment RNH_2. Before the adsorption, three isolated peaks appear nearby the energy of -7.5eV, 0, 9eV in black curve. However, the distribution of three peaks significantly moves to the lower energy region once the adsorption occurs. At the

same time, the value of peaks is lower than that of the former too. It indicates that CH_4 molecule has been adsorbed on the surface of the kerogen fragment with the energy reduced. But after the adsorption in the different site on kerogen surface, the change of the density of states distribution of CH_4 is not obvious. Combined with *Table 1*, it can be seen that the difference of adsorption energy is very small when CH_4 adsorbed on the three high symmetry sites in the same kerogen, and the maximum is no more than 0.03eV. This means that CH_4 is easy to diffuse on the surface of the same kerogen. In *Fig. 3(c)*, CH_4 appears in the B site after adsorbed on H site. So it is proved that the diffusion phenomenon of CH_4 does exist.
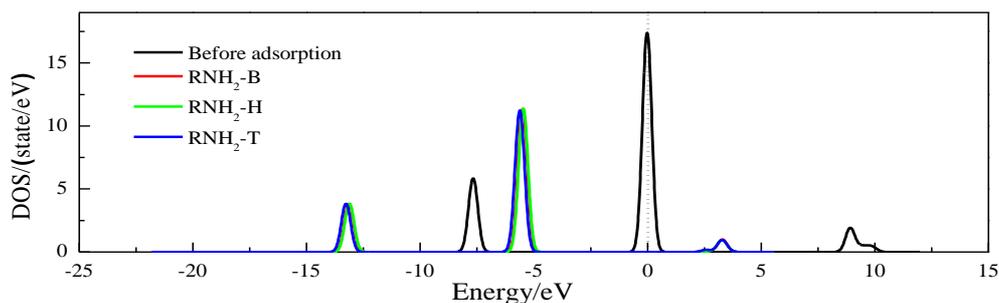
Figure 5. Density of states of methane before and after it adsorbing on the surface of kerogen fragment RNH_2.

Fig. 6 shows the density of states of CH_4 after it is adsorbed on the B site of kerogen fragments RH, RCH_3, ROH and RNH_2. Compared to the density of states before adsorbed, the distribution of the density of states obviously moves to the lower energy region when the adsorption occurs on the surface of different kerogens. However, the distribution regions of the density of states of CH_4 are almost coincident.
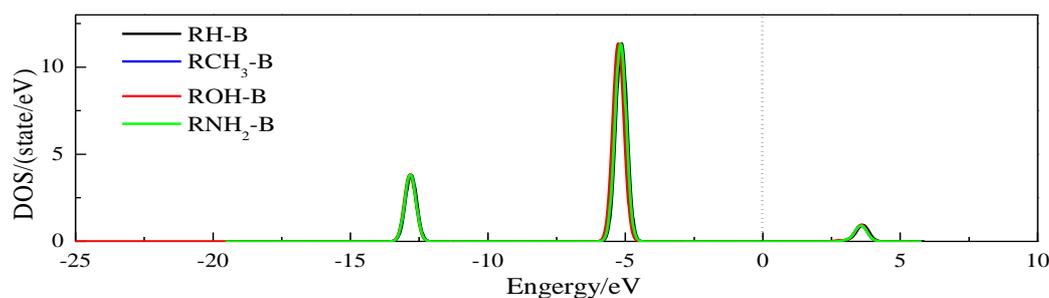
Figure 6. Density of states of methane after it adsorbing on B site of different kerogen fragments.

In order to further analyze the influence of different functional groups on the adsorption of methane, we compared the density of states of aromatic structure (R) after the adsorption of methane in the B site of kerogen fragments RCH_3, ROH, RNH_2 and RH. In *Fig. 7(a)*, the density of states of aromatic structure R in RCH_3 and RH are both continuously distributed in the region of the energy -18.5eV~5eV, and the two curves are close to coincidence, which indicates that the functional groups CH_3 have little effect on the adsorption of methane to the kerogen. In *Fig. 7(b)*, the energy distribution

regions of the density of states with different R are arranged in order of RNH_2 (the green curve), ROH (the red curve), RH (the black curve) from low to high. This shows that the energy of aromatic structure of RNH_2 becomes smaller and the structure becomes more stable after adsorption. From another point of view, it also explains that the presence of oxygen and nitrogen in functional groups enhances the adsorption capacity of RNH_2 and ROH, and the adsorption capacity of the functional group RNH_2 is more than that of functional groups OH.
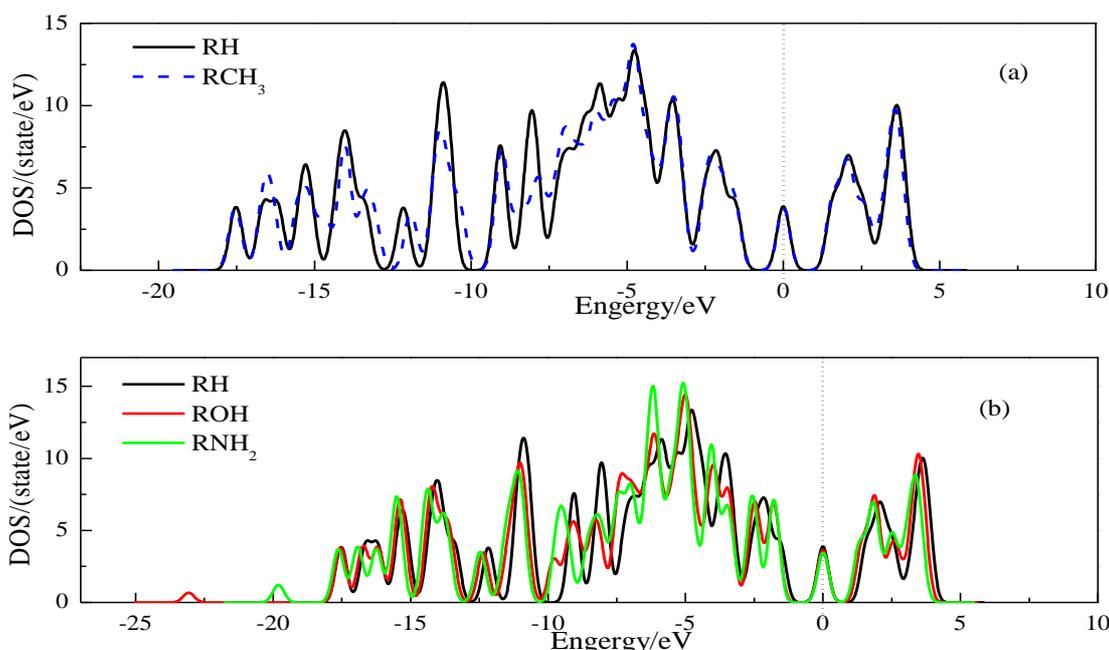
Figure 7. Density of states of the aromatic structure after methane adsorbing on B site of different kerogen fragments.

Conclusions

In this article, the problem that the adsorption of CH_4 on the surface of fragments RH, ROH, RCH_3, RCH_2OH, RCOOH, RNH_2 and RO of kerogen was studied in first-principle theory based on the density functional theory. The structure, electronic state density and adsorption energy properties while CH_4 is adsorbed on the surface of kerogen are obtained. Meanwhile, the sorption behavior of CH_4 on the surface of different fragments of kerogen was analyzed. Conclusions are as follows.

(1) In kerogen, the existence of the functional group that contains oxygen and nitrogen element will strengthen its ability of adsorbing CH_4.

(2) The adsorption ability of fragment RNH_2 is the strongest for the adsorption of CH_4, while the adsorption ability of other fragments ROH, RCH_2OH, RCOOH and RO are nearly the same and far less than that of the former.

(3) The adsorption energy of kerogen fragments RH and RCH_3 are both close to zero on the T site, B site and H site. The adsorptive action to CH_4 is very weak.

(4) The difference value of adsorption energy of CH_4 on the T site, B site and H site in the same fragment of kerogen is less than 0.03eV. It indicates that the effect of adsorption site on the adsorption of CH_4 is small and the diffusion of CH_4 on the surface of the same kerogen fragment is easy to happen.

Although the ability of functional group RNH_2 to adsorb CH_4 is the strongest, its effect on the ability of kerogen to adsorb CH_4 is limited as the content of nitrogen in kerogen is quite few. However, oxygen is the important constituent element of kerogen (Vandenbroucke and Largeau, 2007). Therefore, the content of oxygen in kerogen can significantly influence its ability to absorb CH_4. In other words, the bigger the atomic ratio of O/C is, the stronger the adsorption ability of kerogen should be. In experimental test, the ability of different types of kerogen to adsorb CH_4 is (Zhang et al., 2012): Type I kerogen < Type II kerogen < Type III kerogen, and the corresponding O/C atomic ratios are 0~0.1, 0.1~0.2 and 0.2~0.3 respectively (Tissot et al., 1974). The results of experiment are consistent with the conclusions obtained in this article and the conclusions can also explain the results in micro-scale. Therefore, the O/C atomic ratio as an important indicator to evaluate the adsorption capacity of kerogen can be further studied in the future.

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