

Article

Gas Generation and Its Carbon Isotopic Composition during Pyrite-Catalyzed Pyrolysis of Shale with Different Maturities

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Abstract: In this study, two shale samples with different maturities, from Geniai, Lithuania ($R_o = 0.7\%$), and Wenjiaba, China ($R_o = 2.7\%$), were selected for open-system pyrolysis experiments at 400 °C and 500 °C, respectively. The generation of isotopic gases from the shales with different maturities was investigated, and the effects of pyrite catalysis on the carbon isotopic compositions were also studied. It was found that CO₂, CH₄ and their isotopic gases were the main gaseous products of the pyrolysis of both shales, and more hydrocarbon gases were generated from the low-maturity Geniai shale. The $\delta^{13}C_1$ values fluctuated from -40% to -38% , and $\delta^{13}C_2$ showed higher values (-38% ~ -34%) for the Geniai shale. In addition, its $\delta^{13}C_{CO_2}$ values ranged from -28% to -26% . Compared with the Geniai shale, lower $\delta^{13}C_1$ values (-43% ~ -42%) and higher $\delta^{13}C_{CO_2}$ values (-19% ~ -14%) were detected for the Wenjiaba shale. As temperature increased, CH₄ became isotopically lighter and C₂H₆ became isotopically heavier, which changes were due to the mass-induced different reaction rates of ¹²C and ¹³C radicals. Furthermore, the pyrite made the kinetic isotope effect stronger and thus made the CH₄ isotopically lighter for both shales, especially at the lower temperature of 400 °C.

Keywords: shale pyrolysis; thermal maturity; carbon isotope; pyrite catalysis



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1. Introduction

As an unconventional natural gas, shale gas has been considered as a vital transitional fuel for the shift to renewable energy due to its abundant reserves and low carbon emissions. Most shale reservoirs exhibit high gas adsorption capacities and extremely low permeabilities, which are the main factors restricting shale gas recovery [1]. Recently, thermal recovery technologies, such as in situ combustion, have been studied for the exploitation of unconventional oil and gas reservoirs [2–4]. Previous studies have proved that high-temperature heat treatment can significantly enhance shale permeability and promote gas desorption [5,6]. Additionally, the generation of various gases from the thermal decomposition of organic matter in shale also has important implications for shale gas production and has not been sufficiently studied.

The natural maturation of kerogen in shale involves several processes, including kerogen generation, secondary cracking and recombination into residual solids [7]. The generation of thermogenic gases in shale formation (e.g., CH₄, C₂–C₅ and CO₂) is strongly related to the cleavage of chemical bonds in organic matter [8]. As kerogen matures, long-chain organic molecules (e.g., kerogen and residual oil) crack into simpler molecules, such as light hydrocarbons [9]. This leads to the relatively weak gas generation potential of overmatured kerogen in shale [10,11].

During shale pyrolysis, the gas generation behavior also follows the mechanisms of thermal cracking of chemical bonds and the combination of radical fragments [12]. Pyrolysis conditions, such as the temperature, residence time and catalyst used, have

been found to significantly affect gas generation characteristics [13]. At low temperatures ($<300\text{ }^{\circ}\text{C}$), weak C–O and –OH bonds (covalent bonds) break first to generate water, CO_2 and CO [8,14]. With increasing temperatures ($<500\text{ }^{\circ}\text{C}$), the breakage of C–C and C–H bonds in long-chain organic compounds leads to significant generation of $\text{C}_1\text{--C}_5$ [15]. At higher temperatures, dehydrogenation and aromatization–condensation of organic matter into solid bitumen occur, and residual over-mature kerogen remains limit gas generation potential [16,17].

The carbon isotopic compositions of shale gas have been found to vary with multiple factors, such as temperature, maturity and type of kerogen, as well as other geochemical properties. Given this consideration, carbon isotopic geochemistry has become a promising tool in tracing the origin and evolution of hydrocarbon gas, even shale maturity and gas migration patterns [18,19]. Researchers found that with increasing pyrolysis temperatures, the $\delta^{13}\text{C}$ values of CH_4 became more negative first, then became less negative [18,20]. Gases were also found to become isotopically heavier as shale matures [21]. This can be chemically explained by the kinetic isotope effect (KIE), the preferential cracking and recombination of ^{12}C bonds in kerogen leading to different generation rates of hydrocarbon carbon isotopes [22,23]. However, the effect of heating temperature on the carbon isotopic composition of gas generated from heated shale has not been well analyzed, which has potential engineering applications in the monitoring of formation heat treatments during thermal recovery processes.

Additionally, minerals enriched in shale, such as clays (e.g., kaolinite), carbonates (e.g., calcite) and pyrite, have been considered as geological catalysts due to their positive effects on hydrocarbon generation [24–27]. Kaolinite-type minerals were found to have low catalytic activities and to slightly increase CO_2 yields during kerogen pyrolysis [28]. Numerous studies have shown that the addition of pyrite can increase yields of bitumen and gases, including $\text{C}_1\text{--C}_5$, CO_2 and H_2S [25,29–31]. Previous studies have indicated that the nascent sulfur generated from the transformation of pyrite into pyrrhotite operates as a catalyst for radical production in kerogen [25]. S–S bonds can contribute to the generation of free radicals, and active sulfur has a strong affinity for hydrogen to form H_2S [32]. In hydrogen-deficient environments, sulfur can react with the active sites of hydrocarbons in shale to form organic sulfur compounds [24,29,33].

However, relevant studies have mainly focused on the catalytic role of pyrite in promoting hydrocarbon production. Limited attention has been paid to its catalytic role in influencing carbon isotope composition during shale pyrolysis [30,34,35]. The effects of factors such as pyrolysis temperature and shale maturity on kerogen–pyrite interactions still need further investigation. The study of Gai et al. indicated that pyrite has different catalytic effects on the production of oil and gas at different temperatures [31]. At $500\text{ }^{\circ}\text{C}$, pyrite improved the yields of both oil and gas, while pyrite catalysis at higher temperatures only increased gas yield [31]. The effect of pyrite catalysis on the carbon isotopic composition of gas from shale pyrolysis at different temperatures has not been well-studied. In addition, the studies that have been carried out have mainly been performed in closed or semi-closed systems. In these pyrolysis conditions, secondary and tertiary cracking occur after the primary cracking of organic matter in shale, leading to difficulties in distinguishing gas sources [36,37], while in open systems the gaseous products from the primary cracking of kerogen are instantly removed from the pyrolysis system, which can minimize the influence of secondary cracking. Therefore, it is necessary to investigate the carbon isotopic compositions of gases due to the primary cracking of organic matter in shale, especially considering the influence of shale maturity and mineral catalysis.

In this study, two shale samples with different thermal maturities were selected for an open-system pyrolysis experiment. The shale samples were pyrolyzed at different temperatures. The chemical compositions and carbon isotopic compositions of the generated gases were measured. The effects of maturity, temperature as well as pyrite catalysis were analyzed based on the carbon isotopic compositions of generated gases.

2. Materials and Methods

2.1. Sample Properties

In this study, shale samples with different thermal maturities were selected to explore the evolution of pyrolysis gas and the effect of pyrite catalysis on carbon isotopic composition. Shale with high thermal maturity was collected from Wenjiaba, Guizhou Province, China, where it was buried at a depth of 635 m. Shale with low thermal maturity was obtained from Geniai, Lithuania, at a depth of 1754 m.

Shale geochemical properties, such as chemical composition, vitrinite reflectance (R_o) and total organic carbon (TOC), were measured before the experiments. The property tests of the Geniai shale sample were conducted by a commercial laboratory. The properties of the shale sample from Wenjiaba were obtained based on the studies of Chen et al., given in Table 1 [38]. The components were expressed on an air-dried basis.

Table 1. Geochemical properties of the shale samples [38].

	Proximate Analysis/wt.%				Ultimate Analysis/wt.%					R_o /%	TOC/%
	M	A	VM	FC	C	O	H	N	S		
Geniai	1.31	79.58	14.01	5.10	13.54	1.31	1.34	0.40	2.52	0.7	10.8
Wenjiaba	2.59	87.58	7.44	2.39	5.36	1.04	0.48	0.26	2.69	2.7	5.4

M: Moisture; A: Ash; VM: Volatile Matter; FC: Fixed Carbon; C: Carbon; O: Oxygen; H: Hydrogen; N: Nitrogen; S: Sulfur.

2.2. TG-FTIR Test

Thermogravimetric analysis coupled with Fourier transform infrared spectrometry analysis (TG-FTIR) was conducted to study the pyrolysis behavior of the shale samples. The TG-FTIR analysis was performed on an STA6000-Frontier analyzer (PerkinElmer, Waltham, MA, USA). The two shale samples with different maturities were heated from 25 °C to 800 °C at a rate of 15 °C/min in a N_2 environment. The mass loss curve and gaseous products released during the heating process were recorded.

2.3. Shale Pyrolysis Experiments

Before the experiments, the shale samples were first crushed into 0.15–0.355 mm diameter particles. The shale samples were then dried and degassed at 105 °C to remove moisture and residual adsorbed gases. Shale samples fully mixed with pyrite particles (0.71–1 mm) at a mass ratio of 3:1 were also prepared.

Figure 1 shows the setup for the open-system pyrolysis experiments. The tube furnace was preheated to the desired temperature. Based on the TG results, the temperatures were set at 400 °C and 500 °C, respectively. Meanwhile, N_2 was supplied as a carrier gas at a constant flow rate of 10 mL/min, using a gas flow controller. Then, the samples (3 g of shale sample, with or without 1 g of pyrite particle) were inserted into the furnace to conduct the pyrolysis experiments. The pyrolysis time was set to 15 min.

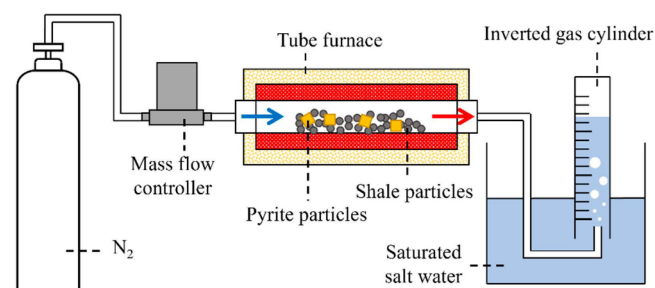


Figure 1. This is a figure. Schemes follow the same formatting.

During shale pyrolysis, the gases generated from primary cracking of organic matter were immediately carried out of the reaction system by the N_2 . The gases were quantitatively collected using the saturated brine displacement method [39]. The gas-filled sample bottles were stored in inverted positions. The collected gases were analyzed using a gas chromatography system (SCION-456-GC, Bruker, Billerica, MA, USA) and gas chromatography (MAT 253, Finnigan MAT, Bremen, Germany) to measure the gaseous product components and carbon isotope values of CH_4 , C_2H_6 and CO_2 .

2.4. XRD Test

The minerals in shale, such as pyrite and carbonates, are usually considered to play a catalytic role in the pyrolysis of shale and coal [31,40]. In this study, X-ray diffraction (XRD) was used to identify mineral compositions in raw and pyrolyzed shale samples. The XRD tests were carried out with a D8 ADVANCE X-ray diffractometer (Bruker, Billerica, MA, USA). The scattering angle of this machine ranged from 10° to 80° , and the scan speed was $5^\circ/\text{min}$, with a step size of 0.02° .

3. Results and Discussion

3.1. Shale Properties

Table 1 gives the geochemical analysis results for the shale samples, including proximate analysis, ultimate analysis, vitrinite reflectance (R_o) and total organic carbon (TOC). The low vitrinite reflectance of the Geniai shale (0.7%) shows its low thermal maturity, lying within the oil window, while the Wenjiaba shale has a high thermal maturity, with an R_o value of 2.7%, which is in the dry gas window. In addition, the higher TOC (10.8%) and volatile matter contents (14.01%) of the Geniai shale indicate that it has a higher gas generation potential than the Wenjiaba shale [41,42]. According to the H/C ratios (1.19) and O/C ratios (0.07) of the Geniai shale and the H/C ratios (1.07) and O/C ratios (0.15) of the Wenjiaba shale, the predominant type of organic matter in these two shale samples is hydrogen-rich type II kerogen [43].

3.2. Mineralogical Composition Analysis

Based on the XRD spectra of the minerals shown in Figure 2a, it can be identified that the main minerals in the Geniai shale are quartz (PDF #46-1045, 20.8° , 26.6° , 50.0° , 59.9° and 68.2°), kaolinite (PDF #29-1488, 12.4°), calcite (PDF #47-1743, 29.4° and 39.4°) and illite (PDF #43-0685, 19.8° and 34.8°) [44]. The strong diffraction peak intensities show high contents of brittle minerals, such as quartz and calcite, in the Geniai shale. Additionally, kaolinite and illite were observed to be the most abundant clay minerals in the Geniai shale.

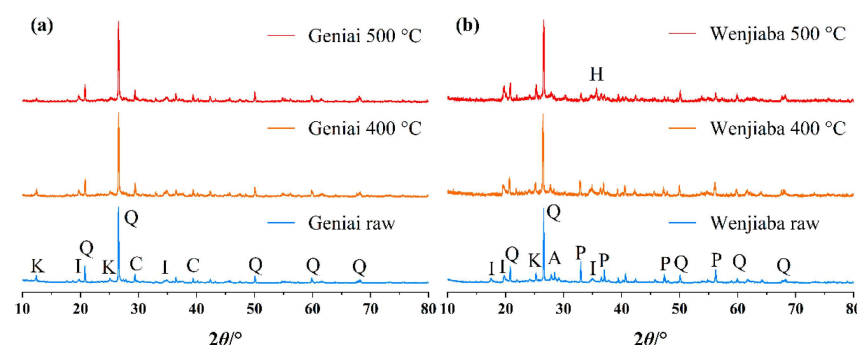


Figure 2. XRD spectra of (a) the Geniai shale and (b) the Wenjiaba shale. A: Albite; C: Calcite; H: Pyrrhotite; I: Illite; K: Kaolinite; P: Pyrite; Q: Quartz.

According to the spectra of the raw and pyrolyzed Geniai samples, it can be found that most mineral compositions were stable during pyrolysis. These mineral compositions, such as quartz and illite, acted as inorganic frameworks rather than catalysts in the shale

pyrolysis. The diffraction peaks of kaolinite slightly decreased in the sample pyrolyzed at 500 °C due to dehydroxylation reactions [16].

Compared with the Geniai shale, more types of minerals, such as albite (PDF #09-0466, 27.8°) and pyrite (PDF #42-1340, 28.5°, 32.9°, 37.0°, 47.4° and 56.2°), were identified in the Wenjiaba shale (Figure 2b) [16]. The mineral compositions in the Wenjiaba shale did not show significant changes at low temperatures. However, in the sample pyrolyzed at 500 °C, some of the diffraction peaks of pyrite were attenuated and the diffraction peak of pyrrhotite (PDF #25-0411) was identified, showing the transformation of pyrite into pyrrhotite [45].

3.3. TG-FTIR Analysis

TG curves of the shale samples were obtained to study their mass loss behaviors in a N₂ environment, as shown in Figure 3. At low temperatures, no significant mass loss was observed in the Geniai shale, while a mass loss peak for the Wenjiaba shale was found around 100 °C due to the evaporation of moisture. As temperature increased (>300 °C), both shale samples experienced significant mass loss. The two decomposition peaks shown in the mass loss rate curves correspond to the cracking of organic matter at 400–500 °C and the decomposition of minerals at around 700 °C, respectively [38]. It can be seen that the cracking of organic matter in the Geniai shale (300–625 °C) occurred at a lower temperature than in the Wenjiaba shale (400–650 °C). This was due to the release of labile volatile organic compounds from the Geniai shale, which are released at lower temperatures compared with other products. However, there were fewer labile volatile compounds in the Wenjiaba shale, due to the evolution of kerogen during its maturation process.

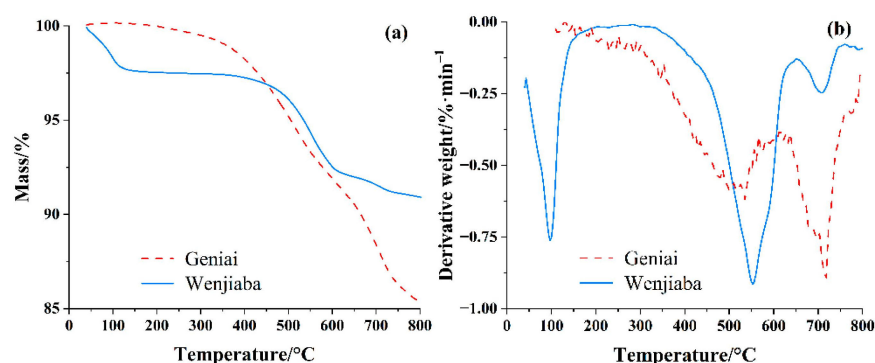


Figure 3. (a) Mass loss and (b) mass loss rate curves for the shale samples in nitrogen conditions.

The FTIR results for a temperature range of 300–500 °C were selected to analyze gas generation behavior during shale pyrolysis, as shown in Figure 4. The generated gases were identified based on the standard FTIR characteristic adsorption bands of different substances and previous studies [16,24,46–49].

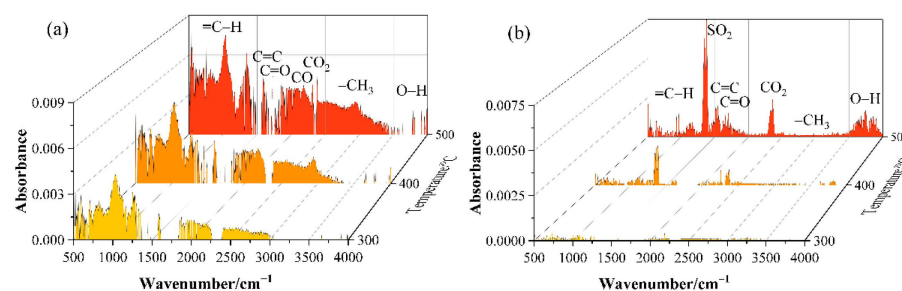


Figure 4. FTIR spectra of gaseous products from the pyrolysis of (a) the Geniai shale and (b) the Wenjiaba shale at 300 °C, 400 °C and 500 °C.

Various products were detected during the pyrolysis of the Geniai shale, such as aromatic and aliphatic hydrocarbons. Aromatic =C-H bonds ($670\text{--}860\text{ cm}^{-1}$ and $966\text{--}1096\text{ cm}^{-1}$) and aromatic C=C bonds (1586 cm^{-1}) were identified at all selected temperatures, indicating a high content of aromatic-compound-bearing organic matter in shale [16]. In addition, the cracking of kerogen also contributed to the generation of aliphatic hydrocarbons containing -CH_3 radicals ($2875\text{--}2965\text{ cm}^{-1}$) [9]. The characteristic bands at $3500\text{--}4000\text{ cm}^{-1}$ were identified as the stretching vibrations of O-H bonds from the organic hydroxides and the decomposition of clay minerals [49,50].

High pyrolysis temperatures not only increased the peak intensities of the functional groups but also contributed to the evolution of pyrolysis products. With increasing temperatures, higher peak intensities of CO_2 (2360 cm^{-1}) and -CH_3 were detected. The band around 1716 cm^{-1} is related to C=O stretching of carbonyl and carboxyl groups [40,51]. Additionally, the emission of CO (2182 cm^{-1}) was observed above $400\text{ }^\circ\text{C}$, which was mainly derived from phenolic hydroxyl groups and ether-bridged bonds [46].

The characteristic bands of aromatic =C-H , aromatic C=C , O-H bonds and CO_2 were detected in both the Geniai shale and the Wenjiaba shale during pyrolysis. However, compared with the Geniai shale, fewer functional groups and lower absorbance intensities of bonds were detected in the Wenjiaba shale, due to its lower gas generation potential. With temperature increasing to $400\text{ }^\circ\text{C}$, a significantly high-intensity absorbance SO_2 band ($1342\text{--}1374\text{ cm}^{-1}$) was observed, which was derived from the cracking of organic sulfur compounds and the decomposition of pyrite.

3.4. Gas Composition Analysis

Based on the GC tests, the accurate compositions of the gases generated from shale pyrolysis at $400\text{ }^\circ\text{C}$ and $500\text{ }^\circ\text{C}$ were obtained, as shown in Figure 5. The concentration of N_2 was subtracted as the carrier gas, and the rest of the gas concentrations were normalized to 100%.

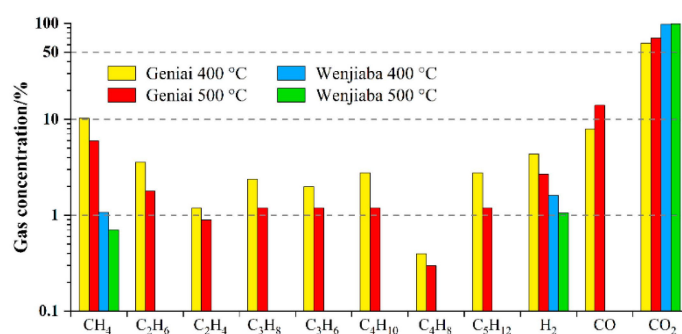


Figure 5. The concentrations of gases generated from shale pyrolysis at different temperatures.

Various gases were detected during the Geniai shale pyrolysis, including CH_4 , $\text{C}_2\text{--C}_5$, H_2 , CO and CO_2 . The thermogenic alkanes, such as $\text{C}_1\text{--C}_5$, originate mainly from the cleavage and polymerization of C-C chains attached to aromatic rings and aliphatic structures [52]. The likely sources of CO_2 mainly include the cracking and reformation of the ether, carbonyl and carboxyl groups from kerogen [24,50,53]. In addition, CO_2 took up the highest percentage of the total products, and CH_4 accounted for the highest percentage of the generated alkanes. These were consistent with the TG-FTIR results.

Compared with the Geniai shale, there were fewer types of gas that could be measured in the Wenjiaba shale pyrolysis, the main ones being CO_2 , H_2 and CH_4 . H_2 was mainly derived from condensation reactions between free radicals, as well as condensation reactions and aromatization reactions of pyrolysis products [54]. The low percentage of CH_4 indicates the low gas generation potential of the high-maturity Wenjiaba shale, in which many hydrocarbons had been cracked into gases during the maturation process. Furthermore, although the total yields of gaseous products increased at higher temperatures, according to the FTIR results, the GC results showed a lower CH_4 percentage at $500\text{ }^\circ\text{C}$. This was

due to the difference between the generation rates of CO_2 and CH_4 during the primary cracking of organic matter.

3.5. Carbon Isotopic Composition Analysis

Figure 6 shows the measured $\delta^{13}\text{C}$ values of CH_4 , C_2H_6 and CO_2 generated from shale pyrolysis. It was found that the $\delta^{13}\text{C}_1$ values fluctuated from -40‰ to -38‰ , and $\delta^{13}\text{C}_2$ showed higher values (-38‰ – -34‰) for the Geniai shale. The carbon isotope distribution of $\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2$ is due to the enrichment of ^{13}C in C_{2+} hydrocarbons during thermal maturation. Compared with the Geniai shale, lower $\delta^{13}\text{C}_1$ values (-43‰ – -42‰) were detected for the Wenjiaba shale. Unfortunately, the gas yields for the Wenjiaba shale were too low to allow measurement of the isotopic compositions of C_2H_6 .

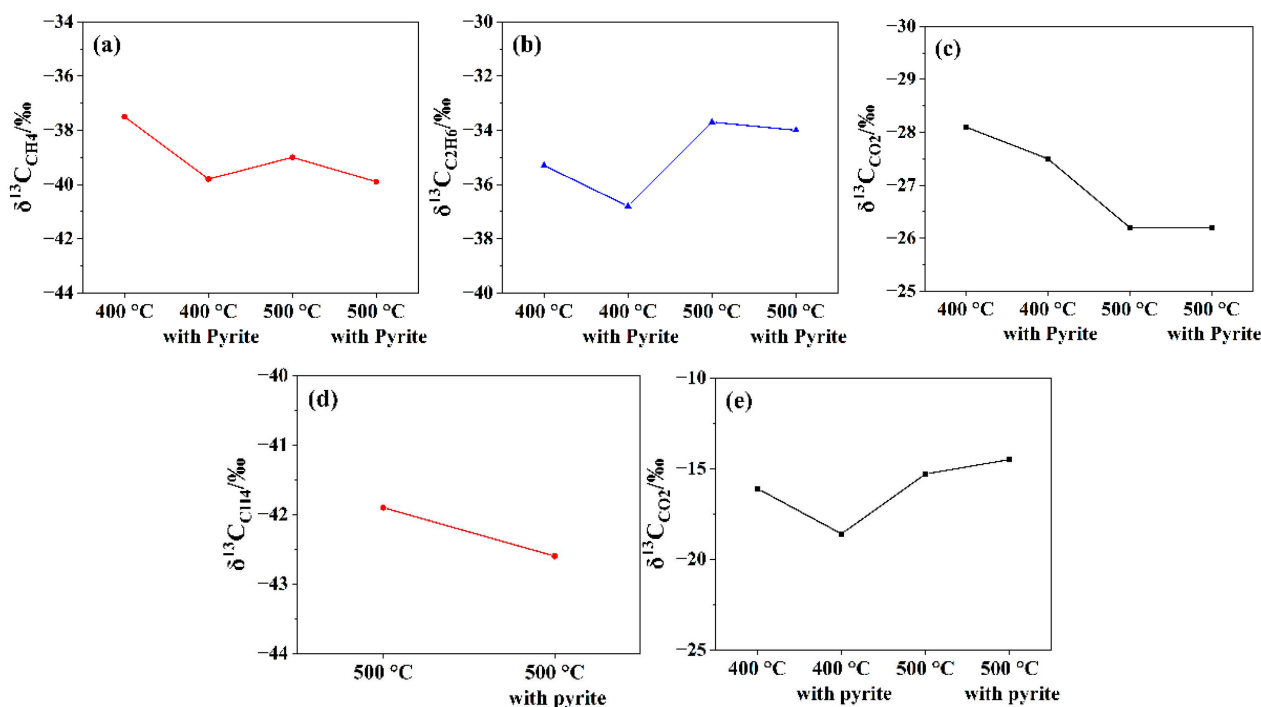


Figure 6. Measured $\delta^{13}\text{C}$ values of (a) CH_4 , (b) C_2H_6 and (c) CO_2 for the Geniai shale and (d) CH_4 and (e) CO_2 for the Wenjiaba shale.

The pyrolysis behavior of organic matter in shale varies with temperature, resulting in changes in the carbon isotopic compositions of the generated gases. It was found that the higher temperature (500 °C) led to a more negative $\delta^{13}\text{C}$ value for CH_4 (i.e., enrichment in ^{12}C) and a less negative $\delta^{13}\text{C}$ value for C_2H_6 (i.e., enrichment in ^{13}C) in the Geniai shale pyrolysis. These changes with temperature were mainly due to the kinetic isotope effect (KIE), which demonstrates that the weaker bond strength leads to the preferential cracking of ^{12}C – ^{12}C bonds compared with stronger ^{12}C – ^{13}C and ^{13}C – ^{13}C bonds [22,55–57]. However, the previous studies conducted in closed-system conditions showed that the CH_4 and C_2H_6 generated become isotopically heavier at higher temperatures [30,34]. This difference is due to the closed-system conditions of these experiments. In closed-system pyrolysis, more organic matter is cracked, and the pyrolysis products undergo secondary or further cracking, resulting in higher yields of light hydrocarbons containing ^{13}C at higher temperatures. In contrast, during open-system pyrolysis, the secondary cracking of organic matter is very limited and can be neglected. Therefore, during the primary cracking of organic matter, the high temperature of 500 °C promoted the enrichment of ^{12}C in the CH_4 and ^{13}C in the C_{2+} hydrocarbons generated.

The change in $\delta^{13}\text{C}$ values also demonstrated the catalytic effect of pyrite. Previous studies have demonstrated that the active sulfur generated from the transformation of

pyrite can promote the generation of free radicals by abstracting hydrogen atoms and thus accelerating the thermal decomposition of kerogen [25,29,31]. In this study, under pyrite-catalyzed conditions, more negative $\delta^{13}\text{C}$ values of CH_4 and C_2H_6 were found with the pyrolysis of both the Geniai shale and the Wenjiaba shale at all temperatures. These results indicate that the addition of pyrite can lead to stronger kinetic isotope effects, as shown in Figure 7. The radicals containing ^{12}C had faster reaction rates when catalyzed by the active sulfur in pyrite, leading to the more negative $\delta^{13}\text{C}$ values of CH_4 and C_2H_6 .

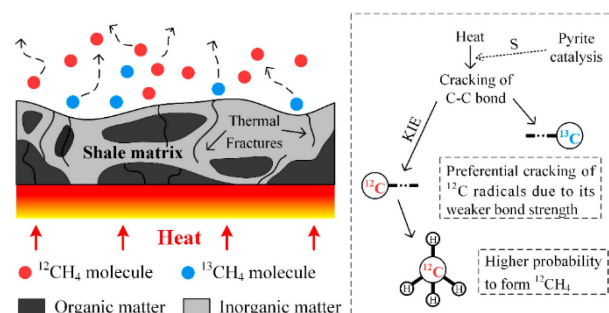


Figure 7. Carbon isotopic fractionation during shale pyrolysis.

It was found that, when catalyzed by pyrite, the $\delta^{13}\text{C}$ values for CH_4 and C_2H_6 at 400 °C underwent greater declines than at 500 °C. The weaker catalytic effect of pyrite at 500 °C is due to the more complete cracking of kerogen at higher temperatures. According to the TG results, the thermal decomposition rate of organic matter in the Geniai shale increased to a maximum as the temperature increased to 500 °C. At this temperature, most of the organic matter in the Geniai shale underwent thermal cracking, including the hydrocarbons containing ^{13}C radicals.

However, no obvious relationships between $\delta^{13}\text{C}_{\text{CO}_2}$ values and temperature or pyrite catalysis could be determined. The $\delta^{13}\text{C}_{\text{CO}_2}$ values for the Geniai shale decreased at the higher temperature of 500 °C, while the $\delta^{13}\text{C}_{\text{CO}_2}$ values for Wenjiaba shale showed different trends. These phenomena were also observed in previous studies. Although the XRD results indicated that no significant decomposition of carbonate minerals occurred below 500 °C to produce CO_2 , the possible sources of CO_2 remain complex, such as decomposition of organic matter and thermochemical sulfate reduction [30,58].

3.6. Implications for Shale Gas Thermal Recovery

In this study, the chemical compositions and carbon isotopic characteristic of gases generated from shale pyrolysis exhibited changes with temperature and pyrite catalysis. The results contribute to better understanding of gas generation behavior during shale gas thermal recovery. A key advantage of thermal recovery is that the organic matter in shale can be converted into valuable gases, such as CH_4 . More gases were generated from the pyrolysis of the low-maturity Geniai shale than the high-maturity Wenjiaba shale, indicating that the gas generation potential of shale is one of the key factors affecting the effectiveness of shale gas thermal recovery. Additionally, the changes in $\delta^{13}\text{C}$ values for CH_4 and C_2H_6 with different temperatures and pyrite catalysis all followed the mechanism of the kinetic isotope effect. This mechanism may contribute to potential engineering applications of gas carbon isotope characteristics in the monitoring and control of the heating temperature of shale formation and the decomposition degree of kerogen during the thermal recovery process. The effect of mineral catalysis on carbon isotopes also shows the necessity of mineral composition analysis for engineering applications of carbon isotopes in shale gas thermal recovery.

4. Conclusions

In this study, two shale samples with different maturities were selected to investigate gas generation and pyrite-catalyzed carbon isotopic compositions in shale pyrolysis. The main conclusions reached are as follows:

- (1) During the pyrolysis of the low-maturity Geniai shale, numerous radicals of aromatic and aliphatic hydrocarbons were identified, indicating its high gas generation potential. In contrast, CO₂, SO₂ and a small amount of CH₄ were the main gaseous products of the high-maturity Wenjiaba shale.
- (2) For the Geniai shale, the $\delta^{13}\text{C}_1$ values fluctuated from -40‰ to -38‰ , while $\delta^{13}\text{C}_2$ showed higher values from -38‰ to -34‰ , due to the enrichment of ^{13}C in C₂H₄ during thermal maturation. Lower $\delta^{13}\text{C}_1$ values for the Wenjiaba shale (-43‰ ~ -42‰) were also detected compared with the Geniai shale.
- (3) At the higher temperature of 500 °C, the CH₄ generated from the Geniai shale pyrolysis became isotopically lighter, while the C₂H₆ became isotopically heavier. For both shales, the addition of pyrite made the kinetic isotope effect stronger, resulting in more negative $\delta^{13}\text{C}$ values for CH₄. It was also found that the changes in $\delta^{13}\text{C}$ values caused by the catalysis of pyrite were smaller at 500 °C.

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Conflicts of Interest: The authors declare no conflict of interest.

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