Stable carbon isotope compositions of gaseous hydrocarbons produced from high pressure and high temperature pyrolysis of lignite

Jianguo Du[a,c,*], Zhijun Jin[b], Hongsen Xie[a], Liping Bai[c], Wei Liu[c]

[a]*Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[b]*University of Petroleum, Beijing 102249, China*
[c]*Center for Analysis and Prediction, China Seismological Bureau, # 63 Fuxing Road, Beijing 100036, China*

Abstract

Pyrolysis of lignite at high pressure and high temperature (HPT) was conducted to investigate the potential stable carbon isotopic fractionation of the produced gaseous hydrocarbons. The experiments were done in a closed system at temperatures of 500–700 °C and pressures of 1–3 gigapascals (GPas). Gas chromatography–combustion-isotope ratio mass spectrometric analysis (GC–C–irMS) of the produced gaseous hydrocarbons leads to two important observations. First, the distribution of the $\delta^{13}C$ values for methane, ethane, propane and butane shows a clear reversal, with $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$. The relatively ^{13}C-enriched methane and ^{13}C-depleted butane is in contrast to the widely accepted isotope distribution pattern of biogenic gases and is similar to that reported for abiogenic gases. Second, carbon dioxide produced from the pyrolysis of lignite is relatively enriched in ^{13}C, with $\delta^{13}C$ values (−18.6 to −22.3‰) that are much higher than those of the gaseous hydrocarbons and lignite itself (−26.8‰). These findings suggest a possible scenario that gaseous hydrocarbons can be generated from organic matter under the HPT conditions of the lower lithosphere, particularly in subduction regions where sedimentary organic matter might be introduced into the mantle, and that the reversal in the stable carbon isotopes of gaseous hydrocarbons may not be an exclusive indicator of abiogenic gases. Therefore, isotope criteria commonly used to differentiate biogenic from abiogenic gases should be used with caution.
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1. Introduction

Stable carbon isotope geochemistry of natural gas has been widely used in oil and gas exploration because stable carbon isotope composition carries the signature of gas origin and maturity. It is well known that the $\delta^{13}C$ values of natural gas are controlled not only by the isotopic compositions of the source organic matter, but also the temperature and mechanism of gas generation (e.g. Stahl, 1977; Schoell, 1983; Du and Xu, 1990; Whiticar, 1994; Xu, 1994).

Stable carbon isotope compositions of gaseous hydrocarbons are useful source indicators and have been used to differentiate biogenic from abiogenic natural gases (Schoell, 1988; Gold, 1993; Xu, 1994). Gaseous hydrocarbons originated from sedimentary organic matter were reported to have a "normal" isotopic distribution with $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$ (Prinzhofer and Huc, 1995; Dai et al., 1997; Rowe and Muehlenbachs, 1999). This appears to be supported by the pyrolysis of kerogen, coal, and sediments at low pressures (McCarty and Felbeck, 1986; Andresen et al, 1995; Berner et al., 1995). Abiogenic gaseous

hydrocarbons in igneous rocks and meteorites were reported to have a "reversed" distribution pattern of $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$ (Des Marais et al., 1981; Yuen et al., 1984; Jenden et al., 1993). This reversal in the isotopic compositions is commonly thought to be a unique criterion for abiogenic gases, although additional criteria, such as $C/^3He$, $^3He/^4He$, C_1/C_{2+} and $^{40}Ar/^{36}Ar$ ratios, were proposed for identifying abiogenic gaseous hydrocarbons (Marty and Jambon, 1987; Gold, 1993; Jenden et al., 1993; Guo and Wang, 1994; Xu, 1994). Secondary processes, including migration, mixing and oxidation of biogenic gases, can also result in partially reversed distribution of stable carbon isotopes of gaseous hydrocarbons (Jenden et al., 1993). In addition, such a partially reversed distribution was also observed from the gaseous hydrocarbons generated from peat and lignite upon high pressure and high temperature pyrolysis (Jiang et al., 2000), further complicating the interpretation of isotopic data in determining the sources of gaseous hydrocarbons. However, a complete "reversal" in the isotope distribution as in the case of abiogenic gases has not been reported for gaseous hydrocarbons originated from organic matter in the literature.

Pyrolysis and chemical-kinetic modeling play an important role in determining the origin and migration of natural gases and the maturity of source rocks (Des Marais et al., 1981; Andresen et al., 1995; Berner et al., 1995; Jiang et al., 1996; Berner and Faber, 1997; Rowe and Muehlenbachs, 1999). Attempts have been made to determine the kinetic parameters and stoichiometric parameters for oil and gas generation through thermal cracking of kerogen using laboratory pyrolysis experiments (Behar et al., 1997). Open system pyrolysis of coal demonstrates that methane is formed through a two-stage process and the generated methane is depleted in ^{13}C relative to the initial organic matter (Boreham et al., 1998). However, the analogy between pyrolysis in an open system and the geological process remains contentious. Genetic simulation of gaseous hydrocarbons with natural samples under conditions similar to that of high temperature and high pressure (HPT) in the lithosphere was rarely reported.

Essential to the interpretation of the variation in the isotopic ratios is knowledge of the magnitude and temperature dependence of the isotopic fractionation factor. The methods to obtain isotopic fractionation factors of hydrogen, carbon and oxygen and the key controls on the isotopic features of minerals were reviewed by O'Neil (1986). Cole and Ohmoto (1986) described kinetics of isotopic exchange reactions at elevated temperature and pressure. The role of pressure in gas-forming processes during laboratory pyrolysis or geological processes in the natural environment has not been considered in developing the gas generation models, because it is commonly assumed that temperature is the principal variable in determining equilibrium partition-

ing of the isotope, and pressure is of no importance. Nevertheless, there is also evidence that the pressure effect on the hydrogen isotope composition at HTP was too large to be ignored (Vennemann and O'Neil, 1996; Horita et al., 1999). Therefore, the objectives of this study are to investigate the stable carbon isotopic characteristics of gaseous hydrocarbons formed in laboratory experiments under HTP conditions and to evaluate the significance of these parameters as indicators of biogenic and abiogenic natural gases.

2. Samples and experiments

2.1. Samples

Lignite samples were collected from Eogene coal-bearing strata in Nanning Basin located in Guangxi Zhuang Autonomous Region of southern China. Microscopic analyses showed that the lignites typically contain approximately 77% huminite, 1.6% inertinite, 18% clay minerals, 2% quartz, and 1.4% "other". Maturity of the coal bed and lignite is low, with vitrinite reflectance value (R_0) between 0.45 and 0.48%. Collected lignite samples were dried at room temperature and ground to powder with an agate pestle and mortar.

2.2. Pyrolysis

The high temperature and high pressure pyrolysis experiments were performed in a closed system at temperatures of 500, 600, and 700 °C and pressures of 1, 2, and 3 GPas with a YT-3000t press at the Institute of Geochemistry, Chinese Academy of Science (CAS). The pressure cell (Fig. 1) was loaded into the chamber of the press and pressure was applied to the cell by six anvils through pyrophylite as the pressure transmitting media. Detailed structure of the press and the methods of temperature and pressure measurements were described in
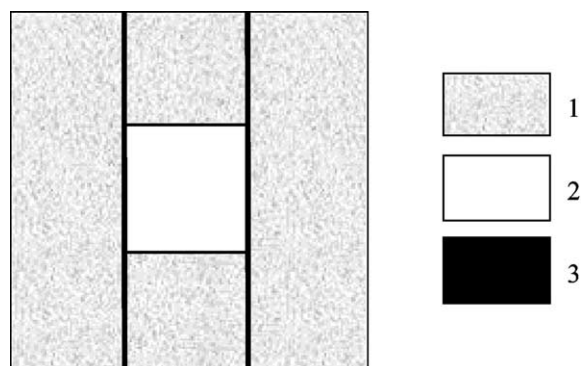

Fig. 1. A cross section of the pressure cell assembly. 1. Pyrophylite as pressure transmitting medium. 2. Copper capsule with lignite and water. 3. Stainless steel acting as a heater.

Xie (1997) and Xie et al. (1998). Prior to conducting the experiments, the pressure inside the cell was calibrated by means of quartz–coesite–stishovite phase transition at room temperature and by the pressure–temperature function of melting bronze. The calibrated apparatus has an accuracy of ± 0.01 GPa. The temperature of the pressure cell was recorded electrically, and is calibrated with a Pt–Pt$_{10}$Rh thermocouple. The temperature reading has an error of ± 5 °C. Experimental conditions are provided in Table 1.

The copper cylinder and cover were welded with silver to form a copper capsule with a volume of approximately 0.35 ml. The cover has a thickness of 5 mm and a hole of 1.5 mm in diameter was drilled in the center. After a small amount of water (about 0.1 ml) was added with a syringe, the copper capsule was filled with the lignite sample. The capsule was mechanically compacted to reduce porosity and to expel the air in pores of the lignite powder. The small opening in the cover was then mechanically plugged with copper and sealed at low temperature to prevent the sample from premature heating.

After loading the sample into the pressure cell chamber, pressure was applied at a rate of about 300 MPa/min. Once the target pressure was reached, heat was applied at the maximum rate of about 60 °C/min. It generally took about 10 min for the cell to reach the desired temperatures. The sample was then maintained isothermally at the defined temperature and pressure conditions for 120 min. After cooling, the sample container was unloaded for integrity inspection, and the unloaded copper capsules were put under water to check leakage. Samples with no visible leakage in the copper capsules were then used for stable carbon isotope analysis.

2.3. Analysis

Carbon isotope compositions of the gaseous products of the experiments were measured with a Finnigan MAT 252 isotope ratio mass spectrometer connected to a gas chromatograph through a combustion chamber (GC–C-irMS) in Lanzhou Institute of Geology, Chinese Academy of Sciences. Sample collection, separation and analysis were all carried out online in a closed system (Baylis et al., 1994; Jiang et al., 2000), as shown in Fig. 2. After crushing the copper capsule online mechanically in vacuum, gas samples were injected into the GC by switching the sample collection valve. Each separated compound from the GC was combusted to CO_2 and analyzed directly by the mass spectrometer. Samples that form part of the Chinese National Isotope Standards were routinely used to calibrate the instrument. The error margin for carbon isotope compositions is less than 0.5 per mil, and the results are reported relative to the PDB standard.

3. Results and discussion

3.1. Gas isotope compositions

The major gaseous components produced during the pyrolysis in the closed aqueous system were carbon dioxide, methane, ethane, propane and butane in the order of decreasing concentrations according to the response of mass spectrometer. Carbon dioxide concentrations in some experiments exceeded the capacity of the mass spectrometer and the isotope composition of CO_2 was not determined in such cases. The carbon isotope compositions of hydrocarbon gases and carbon dioxide produced during the HPT pyrolysis are shown in Table 1.

A measurable amount of olefin, which is often produced from cracking of organic material at high temperatures, was detected in two of the HPT pyrolysates (Experiment Nos 2 and 3). Mass spectral analysis indicates that the olefin is likely propylene. Because of low concentration, reliable isotope composition of this compound was not obtained. Olefins were not detected in other experiments.

Table 1
Experimental conditions used in the hydrous pyrolysis of a lignite and the stable carbon isotope compositions of the produced gaseous products[a]

No.	Sample	Pressure (GPas)	Temperature (°C)	Time (min)	$\delta^{13}C$ (‰)				
					C_1	C_2	C_3	C_4	CO_2
1	2	1	500	120	−22.0	−27.5	−37.7	n.d.	−22.3
2	3	1	600	120	−21.2	−32.4	n.d.	n.d.	(n.d.)
3	27	2	600	30	−23.2	−33.1	−35.1	−44.0	−20.7
4	11	2	700	120	−21.7	−34.9	−28.7	n.d.	(n.d.)
5	6	3	500	120	−20.6	−28.8	−22.8	−39.1	−21.1
6	17	3	600	120	−28.9	−44.2	−26.4	n.d.	−20.7
7	18	3	700	120	−23.7	−25.3	n.d.	n.d.	−18.6

[a] n.d., not determined due to low concentration; (n.d.), not determined due to the overloading of the system by excessive carbon dioxide generated.
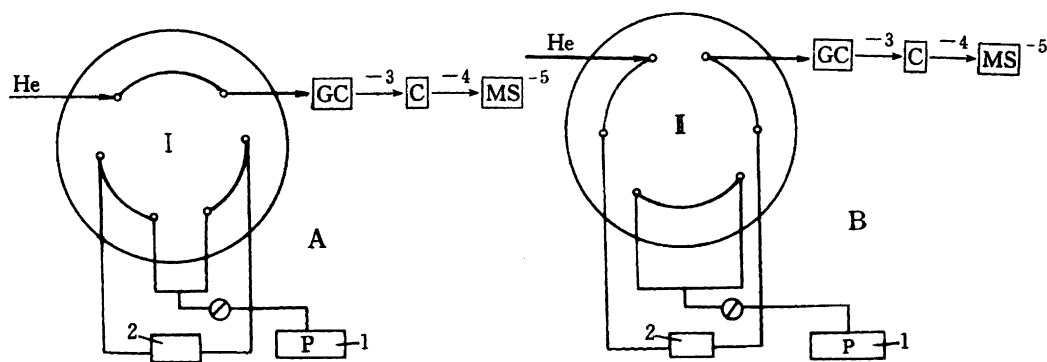
Fig. 2. Diagram illustrating the online gas sample collection and analysis for carbon isotope compositions of experimental gas (Jiang et al., 2000). A. Sample collection by crushing the copper capsule of samples in a vacuum line; B. Sample injection and analysis for carbon isotope composition. States A and B are switched by a six-port valve (I and II). 1. Mechanical vacuum pump; 2. Obturation cell for crushing specimen copper capsule; 3. Gas chromatograph; 4. Combustion chamber; 5. MAT 252 Mass spectrometer. He was used as the carrier gas.

Concentrations of the gaseous components varied substantially at different temperature and pressure conditions. Carbon dioxide was the most abundant gas produced in the HPT pyrolysis experiments. Concentration of butane was lowest among the gases analyzed. Concentration of butane was too low in several experiments for isotope composition to be determined. The compositions of gases produced at HPT conditions were similar to previously reported results of low-pressure pyrolysis of coals (Shen et al., 1991; Andresen et al., 1995).

The $\delta^{13}C$ values of the produced CO_2 also varied significantly under different experimental conditions, ranging from −22.3 to −18.6‰ (Table 1). These values are more positive than those of coals from China that are usually within the −27.6 to −23.3‰ range (e.g. coals from the Sichuan, Ordos Basin and Bohai Bay basins). The $\delta^{13}C$ values of the lignites in the Dongsheng of Inner Mongolia and in the Kedu of Yunnan Province are also within this range (Shen et al., 1991). Low-pressure hydrous pyrolysis of brown coal with a $\delta^{13}C$ value of −26‰ also produced ^{13}C-enriched carbon dioxide with $\delta^{13}C$ values as much as 5‰ more positive than that of the coal (Andersen et al., 1995).

The $\delta^{13}C$ values of the produced CO_2 tended to become less negative with increasing experimental pressure and temperature (Table 1). The change in the carbon isotope compositions was substantial when the temperature changed from 600 to 700 °C at a given pressure of 3 GPas. The enrichment of ^{13}C in the produced CO_2 compared to lignite indicates that the CO_2 was likely formed either through the cleavage of molecular moieties that are enriched in ^{13}C or through isotopic fractionation during the formation of CO_2 from lignite. It has been reported that carboxyl groups are generally enriched in ^{13}C compared to the rest of the molecule (e.g., Galimov, 1980). It is likely that the ^{13}C-enriched CO_2 was derived from the reactions between supercritical water and carboxyl groups lost from lignite. Kinetic isotope fractionation would not result in ^{13}C-enriched CO_2 because the ^{12}C–^{12}C bonds will preferentially cleave over the ^{12}C–^{13}C bonds.

The $\delta^{13}C$ values of methane produced in the HPT pyrolysis ranged from −28.9 to −20.6‰ (Table 1), much more positive than those of natural gases from the producing oil/gas fields around the world that show a normal carbon isotope distribution for C_1–C_4 alkanes (Fig. 3). The wide variation in the range of $\delta^{13}C_1$ values observed from the laboratory experiments may be caused by varying water/lignite ratios used, but the $\delta^{13}C_1$ values are generally similar to that of the precursor coals (Andresen et al, 1995; Jiang et al., 2000) and far more positive than those of biogenic methane in coal beds (< −50‰; Tang et al., 1988; Rowe and Muehlenbachs, 1999). In contrast, the $\delta^{13}C$ values of propane and butane are similar to those of thermogenic gases (Prinzhofer and Huc, 1995; Dai et al., 1997).

The $\delta^{13}C$ values of C_{2+} gaseous hydrocarbons produced from the HPT pyrolysis are more negative than those of methane, exhibiting a "reversed" isotope distribution pattern (Fig. 4). This situation is in contrast to those produced from low pressure pyrolysis and from most of the biogenic gases (e.g., Fig. 3), but is similar to those of the gases from meteorites (Yuen et al., 1984) and igneous rocks (Galimov, 1975). Gases from the Daqing Oilfield of the Songliao Basin in northeastern China also show a "reversed" isotope distribution pattern that was thought to indicate an abiogenic origin (Fig. 5; Guo and Wang, 1994).

The difference between the "normal" and "reversed" distributions is shown clearly in Fig. 5, when the isotopic compositions of C_{2+} gaseous hydrocarbons were compared with that of methane using the $\Delta\delta^{13}C$ values (defined as the difference of $\delta^{13}C_1$–$\delta^{13}C_i$, where i is equal
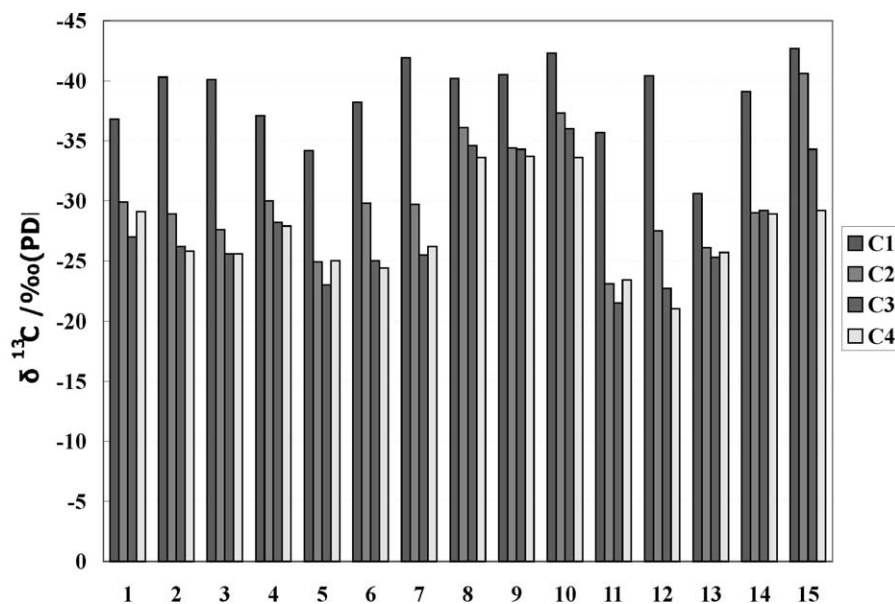
Fig. 3. Stable carbon isotope data of methane (C_1), ethane (C_2), propane (C_3), and butane (C_4) in selected natural gas samples around the world. Sample Nos. 1–7 from Angola (Prinzhofer and Huc, 1995), Nos. 8–10 from North Sea (Andresen et al., 1995), and Nos. 11–15 from northwestern China (Dai et al., 1997). All the gases show a "normal" distribution with $\delta^{13}C$ values decreasing with increasing molecular weight. Some of the gases show $\delta^{13}C_3$ values that are more positive than the $\delta^{13}C_4$, but none has the $\delta^{13}C_1$ values more positive than the $\delta^{13}C_{2+}$.

to 2, 3 and 4). The abiogenic gases usually give positive $\Delta\delta^{13}C$ values, whereas the opposite is true for the biogenic gases. Gases from the HPT pyrolysis would be considered to be biogenic because they are derived from organic matter in the coal. However, the similarity in the carbon isotope distributions between these gases and abiogenic gases (Fig. 5) suggests that the mechanisms of gas generation under HPT conditions may be significantly different from those under low temperature and low-pressure conditions.
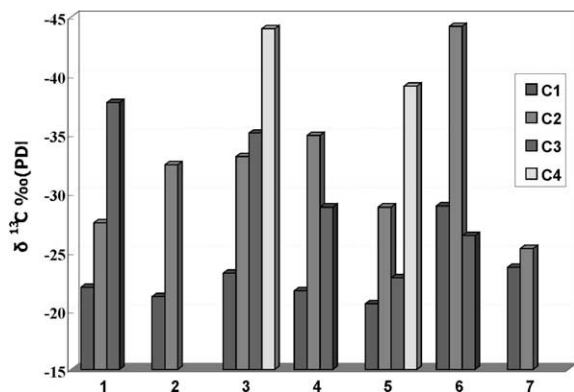

Fig. 4. Stable carbon isotope compositions of the generated gaseous hydrocarbons in the HPT pyrolysis experiments. The sequence number on the *x*-axis corresponds to that in the first column of Table 1.

3.2. Mechanism of gas generation

It is widely believed that the factors affecting molecular and isotopic compositions of gases are the sources of organic matter, thermal maturation, fluid migration,
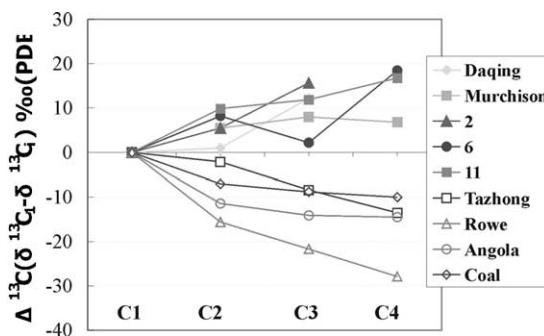

Fig. 5. Differences between $\delta^{13}C_{2+}$ and $\delta^{13}C_1$ in various gases thought to have biogenic and abiogenic origins. Sources of the data: Daqing—gas produced from the Daqing oil and gas field (Guo and Wang, 1994); Murchison–Murchison meteorite (Yuen et al., 1984); Sample Nos. 2, 6 and 11—HPT pyrolysis at pressures of 1, 2, 3 GPas (this study; Table 1); Tazhong—Natural gas produced from the Tazhong-1 well in the Tarim Basin, NW China (Dai et al., 1997); Rowe—Gas from the drilling mud in the Wildmere field (Rowe and Muehlenbachs, 1999); Angola—Natural gas from Angola (Prinzhofer and Huc, 1995); Coal- Gases produce by low pressure pyrolysis of brown coal at 365 °C (Andresen et al., 1995).

and in-reservoir alteration (Curiale and Bromley, 1996; Xu, 1994). Natural gases of different origins have significantly different molecular and isotope compositions. Bacterial gases are characterized by $\delta^{13}C_1$ values of lower than −60‰ (Tang et al., 1988; Rowe and Muehlenbachs, 1999; Ahmed and Smith, 2001). Thermogenic gases usually have $\delta^{13}C_1$ values between −60 and −20‰ with a "normal" carbon isotope distribution as shown in Fig. 3.

The "normal" isotope distribution (i.e. $\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$) of thermogenic gases are explained by a kinetic isotope fractionation where ^{12}C–^{12}C bonds of source organic matter are preferentially cracked, leading to the formation of ^{13}C-depleted gas hydrocarbons with methane being the isotopically lightest compound. This hypothesis is supported by molecular and isotopic evidences from laboratory pyrolysis of various organic material at different temperatures with generated gaseous hydrocarbons all depleted in ^{13}C relative to source organic matter, and the carbon isotope compositions exhibit the "normal" distribution (Andresen et al, 1995; Berner and Faber, 1997; Behar et al., 1997; Tang et al., 2000). However, most of the pyrolysis experiments were conducted at low pressure with the assumption that pressure does not affect isotope fractionation and hydrocarbon generation. Results of this study at high pressure suggest that pressure is playing an important role during gas generation and the carbon isotope compositions of the gases generated under high-pressure conditions are completely different from those from the low-pressure regime.

Although it is not clear how pressure affects the isotope compositions of individual hydrocarbons, it is likely that some of the processes similar to that in the formation of abiogenic gases might be present during the HPT pyrolysis. The carbon isotope compositions of abiogenic gases in meteorites (Yuen et al., 1984) and igneous rock (Galimov, 1975) as well as in the products of methane polymerization (Des Marais et al., 1981) have a "reversed" distribution. It was possible that condensation and polymerization of small fragments of molecules and atoms can result in the "reversed" isotope distribution pattern in meteorites and in igneous rocks.

Theoretically, gas-generating reactions are favored at low-pressure conditions because of increased molar volumes of the products. Condensation and polymerization are favored at high pressure instead. Temperature, on the contrary, generally increases reaction rates and decreases the stability of chemicals. At high temperature, organic material in coals and sediments are cracked and decomposed to form light hydrocarbons and other compounds. Supercritical water can reduce the free energy of carbon and hydrogen and form transient "ghost" molecules, thus facilitating polymerization in the substrates (Shaw et al. 1991; Alfrons, 1999).

Water at high temperature and high pressure under the experimental conditions we used is likely present in the supercritical state and in the forms of H^+, OH^- and O^-. Thus, the reactivity of organic components in the system can be enhanced by providing reaction media and participating in reactions. One possible way to form gaseous hydrocarbons would be that H^+ combines with unsaturated free radical groups to form preferentially bigger carbon-numbered, saturated hydrocarbon gases relatively enriched in ^{12}C. In contrast, oxygen anions (o^-) combine oxygen-bearing radical groups (such as carboxyl groups enriched in ^{13}C) to form CO_2 (Galimov, 1980). Therefore, the end products would be a reversal in the carbon isotope distribution of gaseous hydrocarbons and a ^{13}C-enriched carbon dioxide.

Formation of gaseous hydrocarbons in the HPT closed system may, therefore, be the combined results of both kinetic cracking and decomposition of lignite organic matter and condensation and recombination of intermediates. Consequently, methane, ethane, propane, and butane are not produced by the relatively simple kinetic model of low-pressure pyrolysis. Decomposition of organic matter at high temperature produces many types of free radicals, such as $-CH_2-CH_2-$, $-CH_2-CH_2-O-$, $-O-$, $-OH$, $=C=O$, $-C-OH$, CH_3-, C_2H_5-, and C_3H_7-. High pressure reduces the stability of these free radical groups, and favors condensation and polymerization. Because of the differences in bond energy and strength, a ^{12}C–^{12}C bond is weaker than a ^{12}C–^{13}C bond and a ^{12}C–^{12}C bond is preferentially broken over a ^{12}C–^{13}C bond during organic matter decomposition and organic fragment hydrogenization to form saturated hydrocarbons. However, during condensation and recombination reactions, a ^{12}C–^{12}C bond is formed in preference to a ^{12}C–^{13}C bond, leading to the formation of ^{13}C-depleted condensation products (Qian et al., 1992). If some of the gaseous hydrocarbons were formed by recombination processes, the "normal" distribution pattern of carbon isotope compositions resulted from cracking of organic matter will be changed. These possible recombination and condensation reactions favored at high pressure could lead to the formation of gases with the "reversed" isotope distribution pattern.

For the formation of relatively ^{13}C-enriched methane, another mechanism was possibly present. Results from an earlier experiment at extremely high pressure suggest that methane could decompose and form a mixture of hydrocarbons at pressures below 100 GPas (Ancilotto et al., 1997). It is also known that methane could be broken down to form diamond at pressures between 10 and 50 GPas and about 2000–3000 K (Benedetti et al., 1999). These studies indicate that methane might be partially decomposed and polymerized to larger carbon-numbered compounds under the HPT pyrolysis conditions, which would result in ^{13}C-enriched methane and ^{13}C-depleted heavier alkanes. As a result, the dependence

of some isotopic equilibrium fractionation on pressure may not be negligible (Sheppard, 1997), particularly in thermal fluid-bearing systems (Driesner, 1997). Data obtained from eclogitic diamonds suggests that the wide range of the stable carbon isotope ratios may result from fractionation process at HPT conditions (Cartigny et al., 1998). The results presented in this study support the idea that pressure can be an important factor controlling the gas formation and isotope fractionation under conditions simulating those of the deep subsurface. Thus, sedimentary organic matter that is under anomalously high pressure in the crust (e.g., in high pressure-induced volcanic explosions), or is carried into the mantle by a subducting plate can generate natural gas. Some of the gases discovered in the Songliao Basin of northeastern China may have been formed in this way, where they frequently occur adjacent to the Quaternary volcanoes (Guo and Wang, 1994).

4. Conclusions

Laboratory high temperature (500–700 °C) and high pressure (1–3 GPas) pyrolysis experiments conducted in a closed system on a low-maturity lignite (with only 0.45–0.48% R_0) revealed that the produced gaseous hydrocarbons are characterized by a "reversed" distribution in the stable carbon isotopes, with $\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$. The $\delta^{13}C_1$ values of the gaseous products ranged from -28.9 to -20.6‰, with the $\delta^{13}C_2$ from -34.9 to -25.3‰, the $\delta^{13}C_3$ from -22.8 to -37.7‰, and the $\delta^{13}C_4$ from -44.0 to -39.1‰. The $\delta^{13}C$ values of carbon dioxide produced in the experiments (-18.6 to -22.3‰) are more positive than that of the starting lignite (-26.8‰), and appear to increase with increasing temperature from 500 to 700 °C at 3 GPas and with increasing pressure from 1 to 3 GPas at high temperatures. The large isotope fractionation at high temperature and pressure was likely caused by a combination of decompositions and recombinations in the closed system.

Results of this study suggest that pressure is not a negligible factor in gas generation at HPT conditions. As isotope compositions of gaseous hydrocarbons can be significantly altered at high pressures, a reversal in the carbon isotope distribution of C_1–C_4 alkanes may be a necessary but not sufficient criterion for the identification of abiogenic gases. Clearly, organic derived gases can also display a reversed carbon isotope distribution if they were formed at high pressures. Suitable geological settings with high-pressure regimes developing to produce this type of gases are commonly found in basins near the continental margins, where sedimentary organic matter can be re-injected into the mantle at the subduction zone or near the magmatic intrusions.

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