

Interactions between basalts and oil source rocks in rift basins: CO₂ generation

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Abstract Basalts interbedded with oil source rocks are discovered frequently in rift basins of eastern China, where CO₂ is found in reservoirs around or within basalts, for example in the Binnan reservoir of the Dongying Depression. In the reservoirs, CO₂ with heavy carbon isotopic composition ($\delta^{13}\text{C} > -10\text{‰}$ PDB) is in most cases accounts for 40% of the total gas reserve, and is believed to have resulted from degassing of basaltic magma from the mantle. In their investigations of the Binnan reservoir, the authors suggested that the CO₂ would result from interactions between the source rocks and basalts. As the source rocks around basalts are rich in carbonate minerals, volcanic minerals, transition metals and organic matter, during their burial history some of the transition metals were catalyzed on the thermal degradation of organic matter into hydrocarbons and on the decomposition of carbonate minerals into CO₂, which was reproduced in thermal simulations of the source rocks with the transition metals (Ni and Co). This kind of CO₂ accounts for 55%–85% of the total gas reserve generated in the process of thermal simulation, and its $\delta^{13}\text{C}$ values range from -11‰– -7.2‰ PDB, which are very similar to those of CO₂ found in the Binnan reservoir. The co-generation of CO₂ and hydrocarbon gases makes it possible their accumulation together in one trap. In other words, if the CO₂ resulted directly from degassing of basaltic magma or was derived from the mantle, it could not be accumulated with hydrocarbon gases because it came into the basin much earlier than hydrocarbon generation and much earlier than trap formation. Therefore, the source rocks around basalts generated hydrocarbons and CO₂ simultaneously through catalysis of Co and Ni transition metals, which is useful for the explanation of co-accumulation of hydrocarbon gases and CO₂ in rift basins in eastern China.

Key words basalt; source rock; interaction; CO₂; hydrocarbon gas

1 Introduction

Volcanic rocks, especially basalts, are often distributed within oil source rocks in rift basins including the Songliao Basin, the Baihai Bay Basin, the North Jiangsu Basin and so on (Jin Qiang, 1998a; Zhang Shungan, 1998; Du Xianyue, 1998; Xiong Shousheng and Lu Peide, 1996; Zhai Qinglong et al., 2004). Around the basalts, hydrocarbon gases and CO₂ are accumulated together. In the accumulations, the CO₂ is often over 40% with heavy stable isotopic composition ($\delta^{13}\text{C}$ is generally greater than -10‰), and it is believed to come either from degassing of basaltic magma or from the mantle (e.g. Dai Jinxing et al., 1994; Jeffery and Kaplan, 1988; Berner et al., 1983; Dai Jinxing et al., 2002). In fact, the $\delta^{13}\text{C}$ values of CO₂ discovered in the Binnan reservoir range from -10‰– -7‰ (Dai Jinxing et al., 2002), and hydrocarbons associated with CO₂ are characterized as being of organic origin, because of the $\delta^{13}\text{C}$ values of

methane being lighter than -46‰ or even lighter than -55‰ PDB (Jin Qiang et al., 1999a; Patrick et al., 2004).

Some of the authors of this paper conducted a series of experiments and observed that olivine and zeolite in the basalts interacted with organic matter in the source rocks to generate more hydrocarbons during thermal degradation of kerogens (Jin Qiang et al., 1999b). Such interactions are applied to explanation of the origin of immature or low-mature oil and gas found in the rift basins (Wan Congli et al., 2001; Wan Congli and Jin Qiang, 2001; Jin Qiang, 2001). In recent thermal simulations, the transition elements were added in the source rock samples which contain high carbonate minerals, and much CO₂ was produced in addition to hydrocarbons generated in the simulations. The $\delta^{13}\text{C}$ values of the CO₂ range from -11‰ to -7‰. So the authors believe that the CO₂ was really derived from interactions between the transition metals and the source rocks. In fact, CO₂ also results from the thermal degradation of kerogens,

but its $\delta^{13}\text{C}$ is less than -14‰ (PDB) (Dai Jinxing et al., 2002). This paper introduces the thermal simulations to illustrate how much CO_2 was generated in the process of interaction between basalts and organic matter.

2 Geological setting and research background

The basalts and source rocks were discovered in the Binnan area in northwestern Dongying Depression (Fig. 1; Wang Binhai and Qian Kai, 1992), where a listric fault cuts as deeply as 15 km and serves as a passage for basaltic magma (He Yuan et al., 2001). During the source rock deposition (Late Oligocene, Member 3 of the Shahejie Formation) basaltic magma erupted at least 5 or 6 times, but its distribution was limited just in the Binnan area (no more than 80 km^2). Each eruption event resulted in a circle of rocks from the bottom to the top: black-colored basalt, light gray-colored tuff, dark gray-colored muddy lacustrine carbonate rock, and dark gray-colored calcareous shale (Fig. 2), in which the tuff and carbonate rock occurred as thin layers ($<1.5\text{ m}$), and the carbonate rock and shale were defined as the source rocks (Table 1). Inside and outside the rock circle, oil and gas reserves have been found, including natural gases, immature and mature oils, and CO_2 -high gas (CO_2 up

to 40%–90%, its $\delta^{13}\text{C}$ values -7.5‰ – -10.4‰).

Persisting volcanic eruptions provided large volumes of materials to the surrounding environments, including CO_2 , H_2 and volcanic minerals (Avila et al., 2005; Simoneit, 1988; Coveney et al., 1987). This kind of CO_2 is hard to preserve in any gas reservoir, because there is no seal or trap formed before volcanic eruption. However, it is possible that the CO_2 was dissolved in the lake water when volcanic eruption took place in a lake for the deposition of Member 3 of the Shahejie Formation in the Binnan area, leading to the formation of carbonate rocks or carbonate minerals (such as calcite and dolomite) in the lacustrine shale sequence. Meanwhile, some volcanic materials served as nutrients to hydrophytes and aquatic livings, so that the livings were in bloom in the environments (Simoneit, 1992; Jin Qiang, 1998b). Therefore, after an event of basalt eruption, shale would become either rich in organic matter or rich in carbonate minerals, with the contents of calcite being over 20% in most cases.

We conducted $\delta^{13}\text{C}$ measurements on carbonate minerals contained both in basalt and shale from the Binnan area. Air bubbles are a common structure of the basalts in the Binnan area, they are filled mostly by white-colored calcite, and the $\delta^{13}\text{C}$ values of the calcite vary between 5‰ and 7‰. The $\delta^{13}\text{C}$ values of the carbonate minerals in the shale are within the same

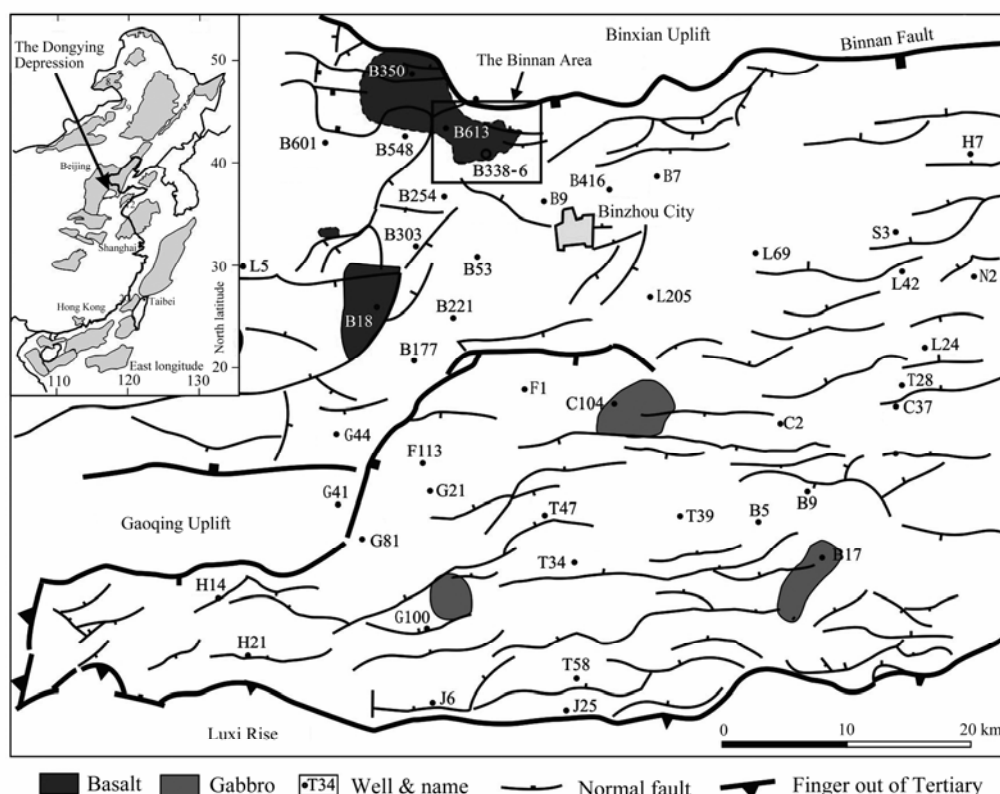


Fig. 1. Geological sketch map of the Binnan area in the Dongying Depression, eastern China.

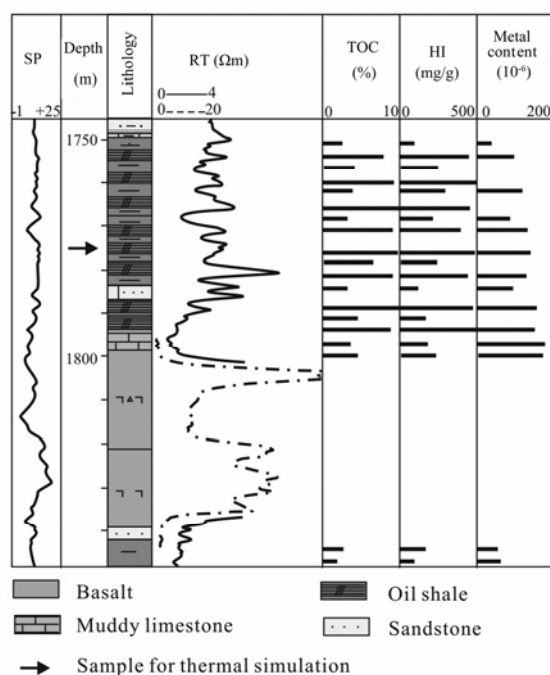


Fig. 2. A column of the basalt-source rock assemblage of well B338-6 in the Binnan area in the Dongying Depression.

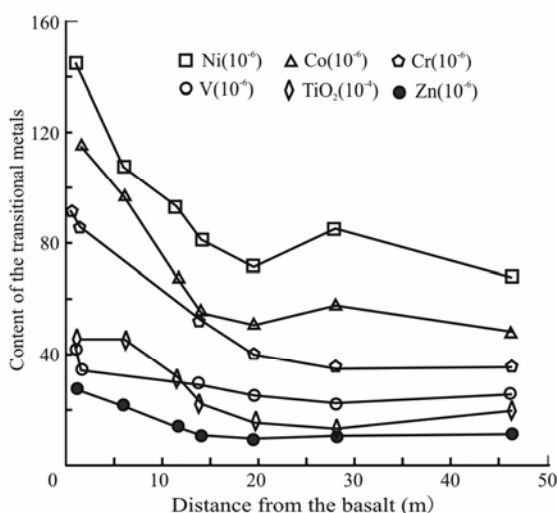


Fig. 3. Plot showing migration of the transition metal elements from the basalt to the source rocks in the Binnan area.

range as those of air-bubble calcite in the basalts. In contrast, the $\delta^{13}\text{C}$ values of ordinary lacustrine carbonate rocks range from -2‰ to $+3\text{‰}$ (Yin et al., 1994; Cartwright et al., 2004). Therefore, carbonate minerals in the shales are genetically connected with basalt eruption. During a long-term burial history, some calcite in the basalt air-bubbles was dissolved. What relationship would there be between the calcite and CO_2 ? This is a focus of discussion in this paper.

No evidence shows that the shales were baked by the basalts in the Binnan area so that the interaction between volcanic materials and organic matter did not

occur during deposition of the shales. But the shales contain many volcanic minerals, such as zeolite, olivine and pyrite (Coveney et al., 1987; Jin Qiang, 2001; Xiao Jiafei and Hu Ruizhong, 2005), and the rocks contain many kinds of transition metal elements, including Co, Ni, Cr, V, Ti, etc. (Fig. 3). Volcanic minerals were distributed in the shales during volcano eruption, but the transition metals could be derived from thermal fluids in and after volcanic eruption. The authors found that the contents of transition metals in the shales near the basalts were as twice as those in the shale 15 m away from the basalt (Fig. 3), for example, Ni in the shale is 146×10^{-6} about 0.3 m apart from the basalt, and is reduced to 76×10^{-6} about 15 m away to the basalt. In the burial history, the volcanic materials in the shales could probably interact with organic matter to generate more hydrocarbons (Wan Congli and Jin Qiang, 2001), and the transition metals (especially Co and Ni) were of strong catalysis on hydrocarbon generation from organic matter (Mango and Hightower, 1994).

Recently, we made a series of thermal simulation experiments on hydrocarbon generation from shale samples with transition metals, and found that not only hydrocarbon generation intensified greatly, but also CO_2 increased obviously. As the CO_2 and hydrocarbons were generated at the same time, it is possible for them to be accumulated together. Meanwhile, the carbon isotopic composition of the CO_2 is similar to that reported from the Binnan Reservoir. Therefore, this kind of CO_2 is useful for explanation of the CO_2 distribution in the rift basins of eastern China.

Table 1. Basic data of the source rocks in the basalt-source rock assemblage in Member 3 of the Shahejie Formation in the Binnan area

Lithology	TOC (wt%)	HI (mg/g TOC)	T_{max} ($^{\circ}\text{C}$)	Kerogen type	Carbonate content (wt%)
Oil shale	8.38(34)	627(28)	331(28)	I (19)	18.6(25)
Lime mudstone	1.75(26)	469(21)	334(21)	II ₁ (11)	26.4(18)
Muddy limestone	1.29(17)	417(15)	332(15)	II ₁ (10)	52.7(9)

Note: The data in the table are average values, and those in the brackets are the numbers of samples.

3 Materials and methods

One shale sample was selected from well B338-6 in the Binnan area for thermal simulation experiment, and its fundamental geochemical characteristics are listed in Table 2. The sample is either rich in organic matter or in carbonate minerals, and is considered as a potential source rock in the Binnan area.

Table 2. Geochemical data of the shale sample from well B338-6

Lithology	TOC (wt%)	Kerogen type	Carbonate content (wt%)	$\delta^{13}\text{C}$ of organic matter (PDB‰)	$\delta^{13}\text{C}$ of carbonate (PDB‰)
Oil shale	7.26	I	21.3	-25.65	4.63

As Ni and Co are two major transition metals derived from the basalts, we chose them as catalysts for the thermal degradation of organic matter and carbonate. The catalysts were prepared in two ways, according to their natural states in the shale, i.e., adsorbed state or ionic state. In the first situation, NiS and CoS were prepared, so that the solid powders were easily adsorbed by organic matter in the shale. In the second situation, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared, they were easy to dissolve in water, so that Ni and Co turned into ions again and were in close contact with clay and organic matter in the shale. The detailed steps of simulation experiment are described as follows:

(1) To crush the shale sample as fine as 80 mesh, and to extract soluble organic matter with CH_2Cl_2 ;

(2) To put 50 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ into two beakers separately, and add 51 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ separately, then get them agitate with water until there are mixed completely;

(3) To dry the mixed material with a spin-drier for three times to eliminate NaCl from the mixed material completely so that pasty NiS and CoS are prepared. Then to put the pasty NiS and CoS into desiccators below 50°C temperature, and obtain black powder of NiS and CoS;

(4) To take 0.4 g NiS and CoS, and 1.04 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, respectively (in which the transition metal is 0.26 g) and let them to mix with 200 g shale powder (the mass ratio of the shale and transition metal is 1 : 0.0013);

(5) To put the shale, the mixture of shale and NiS, the mixture of shale and CoS, the mixture of shale and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and the mixture of shale and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ into different autoclaves, and add 1 g water. To seal the autoclaves under inert gas and keep temperature at 50°C constantly for 24 hours to make the shale and catalyst mix completely;

(6) To heat the autoclaves at varying temperatures (e.g. 120, 160, 200°C and so on) for 8 hours to let interaction and reaction to occur among organic matter, transition metal, and carbonate in the autoclaves; then to cool the autoclaves and conduct analysis of the gas products by gas chromatography, and measurement of the $\delta^{13}\text{C}$ values of CH_4 and CO_2 ;

(7) To extract soluble organic matter from the solid residuals with chloroform, and to measure carbonate contents in the solid residuals.

The gaseous products were analyzed for their compositions on an Agilent 6890 Gas Chromatograph, in which there are two chromatographic columns: one is a purged-packed stainless steel column connected with TCD for CO_2 detection, and the other is a DB-5 capillary column (30 m, 0.25 mm, 0.25 μm) connected with FID for hydrocarbon detection.

The stable carbon isotopes were measured on a Finnigan MAT252 Mass Spectrometer (Finnigan MAT, Bremen, Germany) for CO_2 and CH_4 , using the standard procedure (Zhang Chanlin et al., 2003). The results are all given in PDB standard.

4 Results and discussion

Hydrocarbon generation from the thermal degradation of organic matter under catalysis of volcanic minerals in simulation experiments has been reported (Jin Qiang, 1998a; Ceron et al., 1998). This thermal simulation experiment revealed the co-generation of CO_2 and hydrocarbons from the source rock sample with transition metals under 240°C.

In an ordinary thermal simulation experiment on the source rocks, only a little amount of CO_2 will be generated under the temperature of 300°C (Lewan et al., 1995; Wan Congli, 2002). In our simulation experiments, if no Co and Ni catalysts were put into the samples, only small amounts of CO_2 and other hydrocarbon gases were detected in the gas products under the temperatures of lower than 280°C. While with Co and/or Ni catalysts, the gas products will increase greatly (Fig. 4), from 120°C the total gas productivity is at least two or three times higher than that from the shale alone, which indicates that Co and Ni play a significant role as catalysts in the generation of CO_2 and hydrocarbon gases. Among the gases produced from thermal simulation, CO_2 accounts for two-thirds. When the temperature is over 120°C, the CO_2 tends to increase very rapidly from the mixtures of shale and Co and/or Ni catalysts (Fig. 5). At 200°C, the generated CO_2 from the mixtures of shale and catalysts is about 80 times higher than that from the shale alone. At 240°C, the generated CO_2 and other gases all decrease a little (Fig. 5), implicating that the catalysis of Co and Ni on the generation of gases including CO_2 is abated. Therefore, the efficient catalysis of Co and Ni on the generation of CO_2 and hydrocarbon gases is available at temperatures between 120°C and 240°C under the simulation conditions.

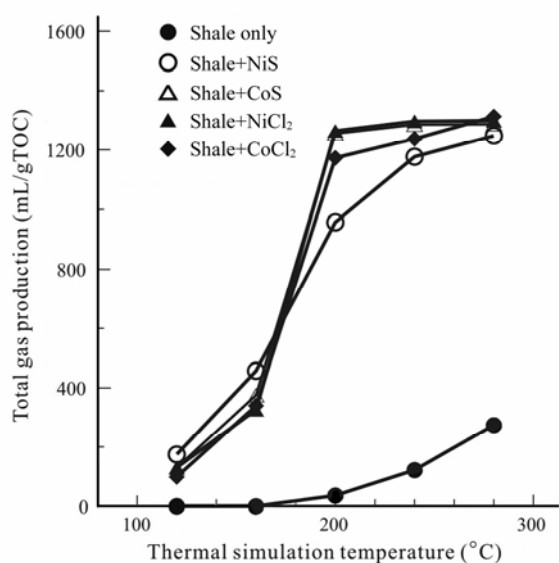


Fig. 4. Plot of total gas production vs. thermal simulation temperature.

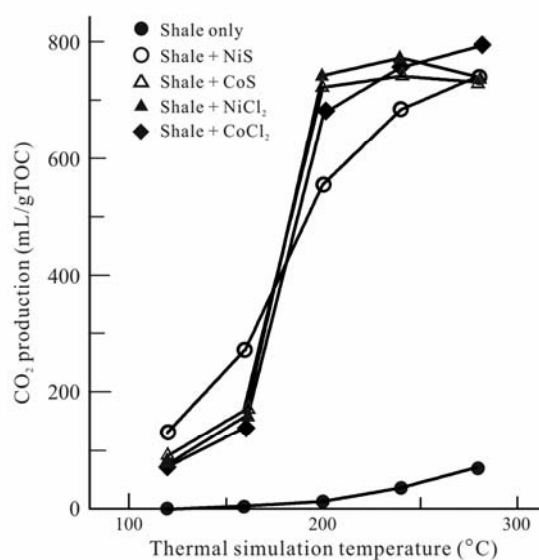


Fig. 5. Plot of CO₂ production vs. thermal simulation temperature.

From the previous discussion, it is seen that CO₂ and hydrocarbon gases are generated at the same time. However, it is not clear whether the CO₂ is generated from the thermal degradation of organic matter in the shale or from the decomposition of carbonate minerals in the shale. Before thermal simulation experiments, carbonate contents in the shale sample were measured. After the simulation experiments, the carbonate contents of solid residuals were also measured, which showed that carbonate contents in the solid residuals decreased obviously at the temperatures between 120°C and 240°C (Fig. 6). The decrease of carbonate contents in the shale sample is just corresponding to an increase in CO₂ in the produced gases, therefore, the CO₂ is possibly generated from the decomposition

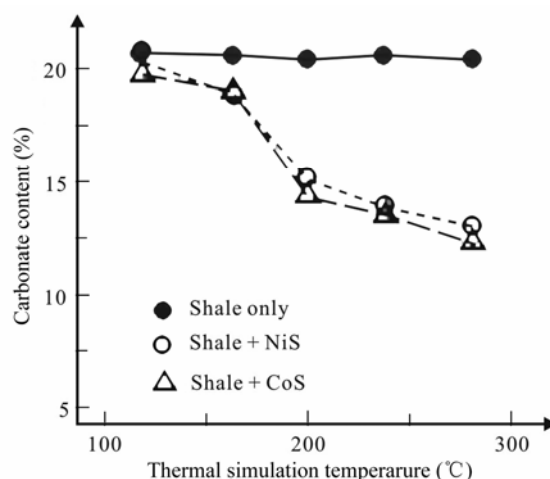


Fig. 6. Relationship between carbonate contents in the solid residues and simulation temperature.

of carbonate minerals in the shale.

The $\delta^{13}\text{C}$ of CO₂ is a good indicator of its origin (Dai Jinxing, 1992). At low simulation temperature (e.g. 120°C), the CO₂ production from the mixtures of shale and Co and/or Ni catalysts is very few, its $\delta^{13}\text{C}$ values are about or less than -10‰ (Table 3), which indicates that the CO₂ is generated either from carbonate or from organic matter (Yoshimura et al., 2004). When simulation temperatures are over 160°C, all the $\delta^{13}\text{C}$ values of CO₂ are greater than -10‰ (Table 3), similar to those of the CO₂ discovered in the Binnan area, and also coincide with those of the CO₂ derived from degassing of magma (Fiebig et al., 2004; Wei Qirong and Wang Jianghai, 2004). Because the carbonate contents in the residues decreased dramatically at simulation temperatures 160–240°C and the $\delta^{13}\text{C}$ of carbonate minerals in the shale is as high as 4.63‰, it is believed that the CO₂ generated in the simulation experiments is mostly resultant from the decomposition of carbonate in the shale, and a minor amount from the degradation of organic matter under the action of Co and/or Ni catalysts.

It is important that CO₂ generation occurs under 300°C (actually 280°C is the maximum temperature) in the simulation experiments, which is avoided of carbonate decomposition at temperature over 350°C

Table 3. $\delta^{13}\text{C}$ (PDB‰) of CO₂ in the gaseous products generated in the thermal simulation experiments

Simulation temperature (°C)		120	160	200	240	280
Reactants	Shale only				-15.69	-14.42
	Shale and NiS		-10.46	-8.72	-7.75	-7.38
	Shale and NiCl		-9.35	-8.29	-7.21	-6.89
	Shale and CoS	-10.72	-9.61	-9.25	-8.27	-7.65
	Shale and CoCl	-11.19	-9.73	-9.65	-8.93	-7.21

(Jin Zhijun et al., 2002; Cody et al., 2004) In our simulation experiments, the total gases including CO₂ generated from the shale alone are low in amounts as compared with those generated from the mixtures of shale and Co and/or Ni catalysts, which indicates that the transition metals played a key role in carbonate decomposition. The co-generation of CO₂ and oil and gas is very useful to understand why CO₂ and hydrocarbons are co-accumulated in traps within or around the basalt-source rock assemblages in the rift basins of eastern China. If CO₂ comes directly from magma degassing or the mantle, it is difficult to accumulate together with oil and gas generated from organic matter in the source rocks. For example, in the study area, volcanic eruptions took place during the deposition of source rocks of Member 3 of the Shahejie Formation (Jin Qiang, 1998a), it is impossible for CO₂ to accumulate in the overlying reservoirs (in the upper part of the Shahejie Formation and younger strata). The source rocks of Member 3 of the Shahejie Formation did not generate any oil and gas, or CO₂ either, until Miocene (deposition of the Minghuazhen Formation). Meanwhile, many traps in the Shahejie Formation and younger formations were formed, and then charged with hydrocarbons and CO₂ together in the Miocene (Duan Zhibin, 1990).

What is noteworthy is that Ni and Co contents in the muddy limestone in close contact with the basalt reach peak values in the source rock sequence in well B338-6 (i.e., 146×10^{-6} and 118×10^{-6} , respectively, Fig. 3). But Ni and Co contents in the mixtures obtained in the thermal simulation experiments are 975×10^{-6} , and 6 or 8 times higher than those in the muddy limestone. Is it artificially enhancing the catalysis of Ni and Co on the decomposition of carbonate minerals and on the thermal degradation of organic matter? The answer is "Yes". Because we also conducted three thermal simulation experiments on the mixture of Ni, Co and the shale at 160, 200 and 240°C, respectively, in which the Ni and Co contents were reduced to one-third (i.e., 325×10^{-6}), we observed that the products of hydrocarbon gases and CO₂ were about 50%–70% higher than those from the shale sample alone. However, Ni and Co added in the reactants in our thermal simulation experiments were much less than those in previous thermal experiments (e.g. Mango and Hightower, 1994). Therefore, the transition metals Ni and Co are of significant catalysis on the decomposition of carbonate minerals as well as on the thermal degradation of organic matter in the source rocks. It is evidenced that the more the transition metals are, the more the CO₂ and hydrocarbons will be generated.

5 Conclusions

In the rift basins of eastern China, basaltic volcanic rocks and thermal fluids occur frequently in oil source rocks (such as shale and muddy limestone), meanwhile hydrocarbons and CO₂ are accumulated around the basalts. Previously, it was believed that the CO₂ was derived directly from volcanic rocks or thermal fluids, because its δ¹³C was heavier than -10‰. Having conducted a series of thermal simulation experiments on the source rock sample with Co and Ni catalysts, we recognized that the CO₂ resulted from interaction between transition metals and carbonate in the shale during thermal degradation of organic matter to hydrocarbons, so that the CO₂ and hydrocarbons were generated together. This kind of CO₂ appears to be accumulated in one trap with hydrocarbons, though it has the same stable isotopic composition as that resultant from current volcanic degassing (Chiodini and Frondini, 2001; Dai Jinxing et al., 1994).

The case study in the Binnan area in the Dongying Depression showed that the basaltic volcanic eruption provides the transition metals to the shale, and the transition metals act as catalysts on the decomposition of carbonate into CO₂. At temperatures ranging from 120°C to 240°C in the simulation experiments, carbonate contents in the shale sample mixed with Co or Ni catalysts decreased significantly, hydrocarbon gases and CO₂ increased rapidly, and the CO₂ accounts for up to 2/3 of the gaseous products. Although CO₂ could be generated from degassing of basaltic magma in the area, it was not possible for it to be accumulated in the traps with hydrocarbons at the same time because volcanic eruption was much earlier than that trap formation in the Binnan area. Therefore, CO₂ generation from the decomposition of carbonate minerals in the source rocks under catalysis of the transition metals is of great significance in a better understanding of CO₂ distribution in the rift basins of eastern China.

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