Natural gas generation model and its response in accumulated fluids in the Yinggehai basin

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Abstract The natural gases found in the Yinggehai basin have nitrogen gas content ranging from 3.5% to 35%, and carbon dioxide content ranging from 0.1% to 93%. The nitrogen and CO_2 contents show a wide variation even in the same gas field. The natural gas generation and evolution model has been established based on the relationship among the contents of nitrogen, carbon dioxide and hydrocarbon gases in the discovered gas fields, and the results of simulation experiments. The thickness of the Tertiary and Quaternary in the Yinggehai basin is over 17 km, and gas generation stages from diagenesis (microbial methane) to metamorphism have been developed. Nitrogen in this basin is organic in origin, and has been generated mainly in the catagenetic stage, roughly synchronous with hydrocarbon gases. Carbon dioxide is mainly inorganic in origin, and has been generated from high-temperature decomposition of carbonates in the metamorphic stage. The Dongfang gas field shows strong inter-reservoir compositional heterogeneities, and different gas reservoirs have recorded the products of gas generation at different stages. It has been confirmed that the complexity in natural gas composition in the Yinggehai basin is the combined results of multi-stage natural gas generation and multi-stage gas injection and accumulation.

Keywords: Yinggehai basin, non-hydrocarbon gases, gas generation, reservoir fluids.

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The generation of natural gases is much more complicated in comparison with liquid petroleum in that natural gases could be generated from both humic and sapropelic organic matter at different stages and that natural gases could be organic and inorganic in origin. Carbon dioxide and nitrogen are non-hydrocarbon gases commonly found in natural gases. The origins of CO_2 has been widely studied[1,2], and effective parameters for distinguishing CO_2 of different origins have been established. Because of the wide variation of isotopic composition for nitrogen of the same origin[3—5], the origin and genesis of nitrogen, and parameters for distinguishing nitrogen of different origins have remained the most vulnerable spot in natural gas generation studies. Natural gases found in the Yinggehai basin display a wide variation in the contents of hydrocarbon gases (7%—85%), nitrogen (3.5%—35%) and carbon dioxide (0.1%—93%), which provides an ideal case for studying the origin and genesis of nitrogen, and for establishing a combined generation model of natural gases of both organic and inorganic origins. The purpose of this paper is to establish the natural gas generation model and its response in the accumulated fluids in the Yinggehai basin by combined geological and geochemical studies as well as simulation experiments.

1 Geological setting

The Yinggehai and Qiongdongnan basins, which are separated by the No. 1 Fault, are important Cenozoic, petroleum-bearing basins developed in the northern continental shelf of the South China Sea. The Qiongdongnan basin trends east to northeast and is a rift basin with characteristics of multi-stage rifting. The Yinggehai basin trends northwest. It is a transform-extensional basin whose development was controlled by the combination of the lithosphere extension and the strike-slip movement along the Red River fault zone[6].

The Yinggehai basin is characterized by high subsidence rates (500—1400 m/Ma), and the maximum thickness of Tertiary-Quaternary is over 17 km. The Neogene-Quaternary is dominated by fine-grain sediments, and no faults except small-throw faults associated with diapirs have developed. The thermal gradient of the Yinggehai basin is about 46℃/km, obviously higher than the average thermal gradients (30℃/km) of sedimentary basins of all ages in the world[7].

As a result of rapid loading and the resulting undercompaction, as well as hydrocarbon generation and thermal expansion of pore fluids, strong overpressures developed over a large part of the basin[6,8,9]. The maximum pressure coefficient (fluid pressure/hydrostatic pressure ratio) so far measured is up to 1.9, and pressure prediction from geophysical data indicates that the pressure coefficients of deep-buried rocks are even higher.

The Miocene Sanya and Meishan formations are the most important source rocks in the Yinggehai basin[6,10]. The richness of organic matter of each interval in the Yinggehai basin is usually low, with average total organic carbon (TOC) content less than 0.6%. Most stratigraphic intervals of the Yinggehai Basin are dominated by Type III kerogen, with atomic H/C ratio less than 1.0, and Rock-Eval hydrogen index (HI) less than 200 mg/g TOC. The Meishan and Sanya formations contain inorganic carbonate, with maximum inorganic carbonate content up to 15%.

2 Association of hydrocarbon gases, N_2 and CO_2 and their origin

The hydrocarbon gas content in the Yinggehai basin ranges from 7.0% to 85%. All the gases have low heavy hydrocarbon gas (C^{2+}) contents, with $C_1/\Sigma C_n$ ratios higher than 0.95. The ethane $\delta^{13}C$ values vary between −21.8‰ and −26.9‰, reflecting an origin of higher plants[11]. Therefore, these gases should be classified as “coal-type gases”, which is consistent with the fact that the source rocks in this basin are dominated by humic kerogen. Most gases display methane $\delta^{13}C$ values ranging from −40‰ to −29‰. These gases are the thermal degradation products of humic organic matter in the catagenetic stage, especially within the condensate/wet gas window [source rock vitrinite reflectance (R_o) between 1.3% and 2.0%][11,12].

The CO_2 content of the Yinggehai basin gases ranges from 0.1% to 93%, and CO_2 content decreases with methane content (fig. 1(a)). CO_2 $\delta^{13}C$ values are effective parameters of the origin and genesis of CO_2. In the Yinggehai basin, CO_2 in gases with its content lower than 10% has $\delta^{13}C$ values lighter than −10‰, and is mainly organic in origin; whereas in the gases with CO_2 content higher than 10%, CO_2 has $\delta^{13}C$ values larger than −10‰, and therefore is mainly inorganic in origin (fig. 1(b)).

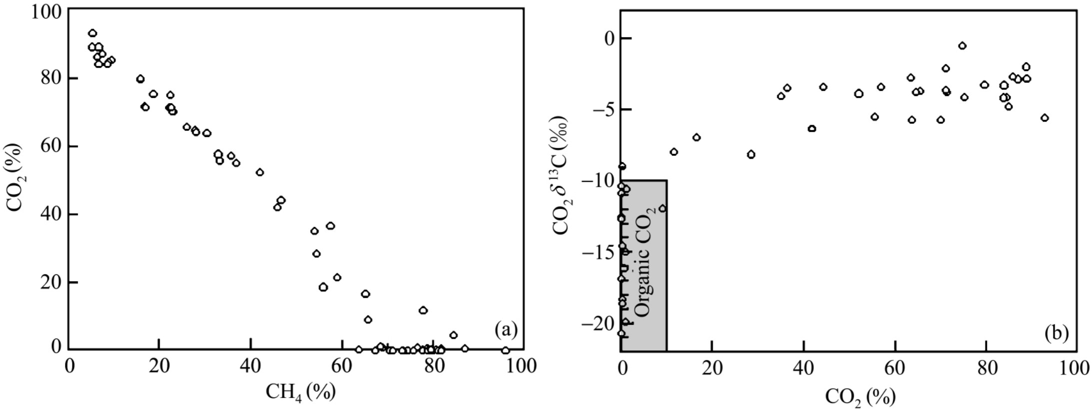

Fig. 1. Variation of carbon dioxide content with methane content (a), and variation of carbon dioxide $\delta^{13}C$ values with carbon dioxide contents for natural gases from the Yinggehai basin (b).

The content and isotopic composition of helium are sensitive indicators of mantle gases. Natural gases from the Yinggehai basin have very low helium content. The $^3He/^4He$ ratios range from 0.049×10^{-6} to 0.679×10^{-6}, and the valaes of the ratio of $^3He/^4He$ for gas samples from the Yinggehai basin to that for the atmosphere ($R_A=1.4\times10^{-6}$) range from 0.035 to 0.485 (fig. 2). Such a helium isotopic composition indicates that the carbon dioxide is mainly of crustal origin and is the product of high-temperature decomposition of inorganic carbonate.

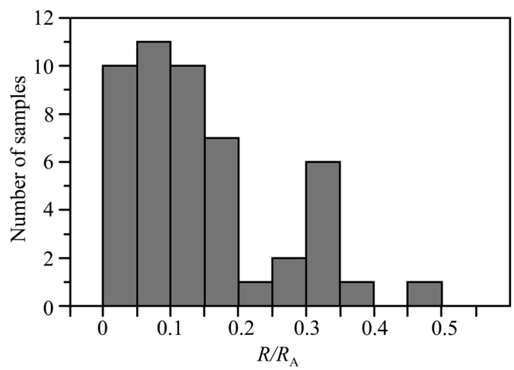

Fig. 2. Helium isotope distribution for natural gases from the Yinggehai basin. R/R_A = Ratios of $^3He/^4He$ for gas samples to $^3He/^4He$ for atmosphere (R_A = 1.4×10^{-6}).

The commercial gas reservoirs in the Yinggehai basin have a nitrogen content ranging from 3.5% to 35%, and the non-commercial gas shows a nitrogen content up to 58.31%. On the whole, the nitrogen content decreases as CO_2 content increases (fig. 3(a)) and increases as methane content increases (fig. 3(b)). There are many possible sources for nitrogen-rich gases, including atmospheric nitrogen[13], mantle degassing[14], metamorphism[3] and thermal degradation of organic matter[15]. Because of the wide variation of isotopic composition for nitrogen of the same origin[3—5], there are yet no effective parameters for classifying the origin and genesis of nitrogen[14,15]. Nitrogen in the Yinggehai basin has $\delta^{15}N$ values ranging from −15‰

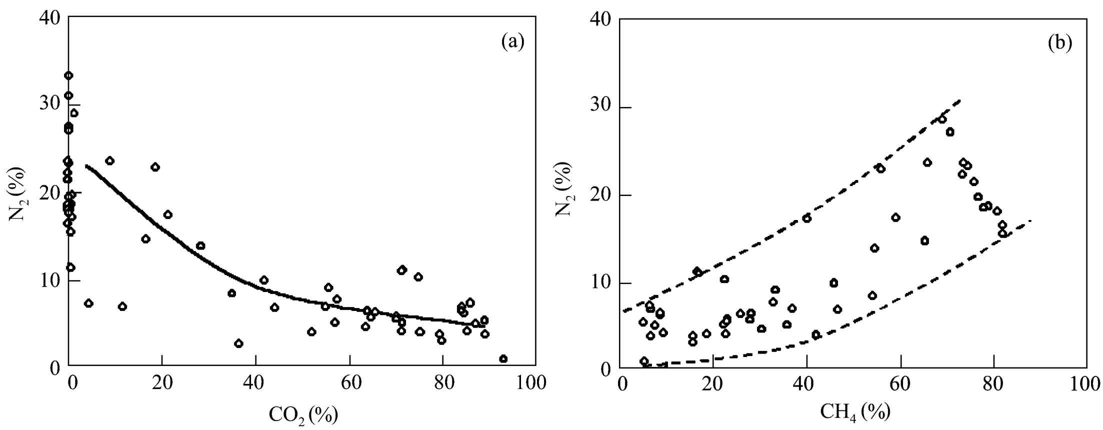

Fig. 3. Relationship between nitrogen content and carbon dioxide content (a) and methane content (b) for natural gases from the Yinggehai basin.

to +10‰ (fig. 4), which do not permit a satisfactory distinction among different nitrogen sources. The association among hydrocarbon gases, nitrogen and carbon dioxide, however, provides important information about the sources of the nitrogen. Firstly, the molar ratio of molecular nitrogen to argon is about 80 in the atmosphere. The measured molar N_2/Ar ratios for gases from the Yinggehai basin range from less than 200 to 3600, which excludes the atmospheric origin. Secondly, nitrogen-rich gases derived from mantle degassing are usually characterized by high helium concentrations[16] and high ^{3}He/^{4}He ratios[14]. As discussed above, natural gases from the Yinggehai basin display low helium concentration with ^{3}He/^{4}He ratios considerably smaller than that of the air, indicating that nitrogen could not have derived from mantle degassing.

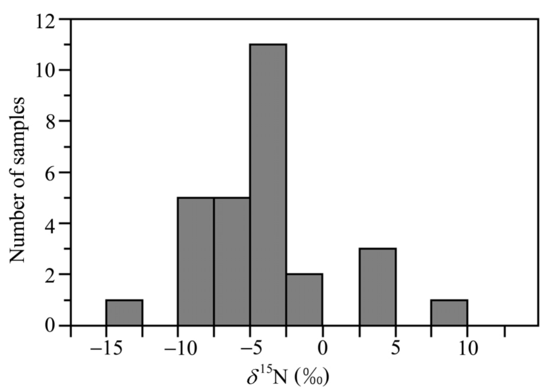

Fig. 4. δ^{15}N values for gases from the Yinggehai basin.

As discussed above, in the Yinggehai basin the nitrogen content decreases as CO_2 content increases (fig. 3(a)), which indicates that nitrogen and CO_2 have different sources. All gases with nitrogen content higher than 15% have CO_2 δ^{13}C values lighter than –10‰ (fig. 5(a)), which suggests that nitrogen co-exists with organic CO_2. The positive correlation of nitrogen content with hydrocarbon gas content (fig. 3(b)) and the co-existence of nitrogen with organic CO_2 indicate that nitrogen in the Yinggehai basin is mainly organic in origin.

It is widely believed that, during thermal evolution of organic matter, nitrogen-rich gases are mainly generated in the over-mature stage (with source rock vitrinite reflectance higher than 3.0%) when hydrocarbon gas generation almost ends and sedimentary rocks turn into metamorphic rocks[15]. For the gases generated under such conditions, nitrogen content would have reversed correlation with hydrocarbon gas content, and with increasing maturity of hydrocarbon gases (isotopic composition becoming heavier), nitrogen content would increase. Yet, exactly the opposite is observed in the Yinggehai basin: nitrogen content displays positive correlation with hydrocarbon gas content (fig. 3(b)) and, as methane becomes more mature (δ^{13}C becomes heavier), nitrogen content decreases (fig. 5(b)). Moreover, almost all the gases with nitrogen content higher than 15% have methane δ^{13}C values smaller than −35‰ (fig. 5(b)). Obviously, nitrogen-rich gases in the Yinggehai basin could not have been generated in the metamorphic stage. Instead, the nitrogen-rich gases have been generated from organic matter within the catagenetic stage (vitrinite reflectance <2.0%). Most nitrogen-rich gases co-exist with a small amount of condensates, which further confirms that the nitrogen-rich gases in the Yinggehai basin have been generated within catagenetic stage.

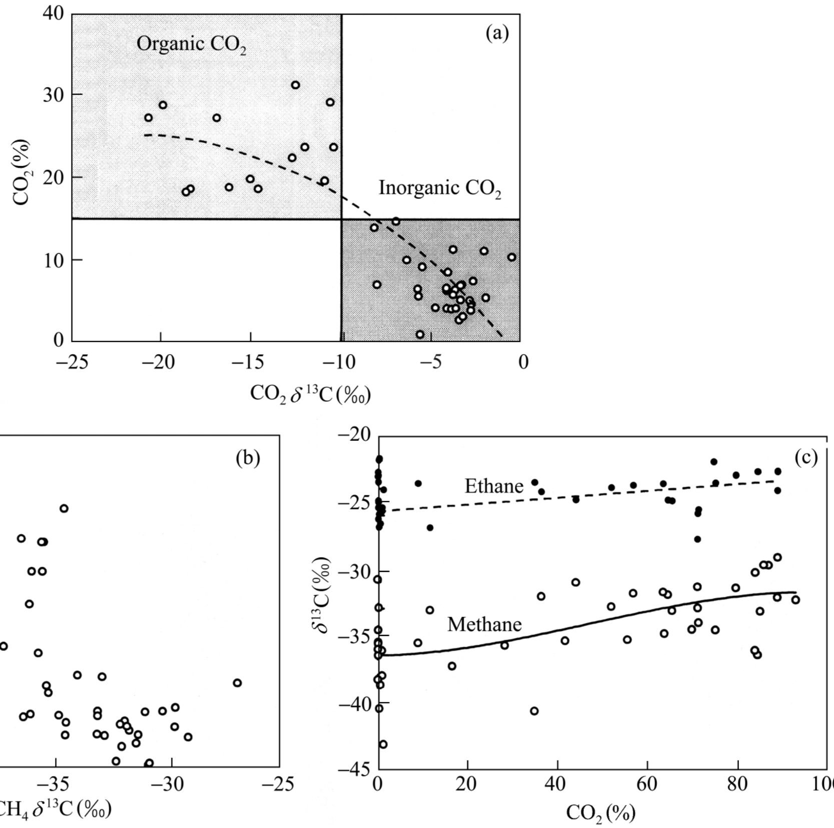

Fig. 5. Variations of nitrogen content with CO_2 δ^{13}C values (a) and methane δ^{13}C values (b), and variations of methane and ethane δ^{13}C values with CO_2 content for natural gases (c) from the Yinggehai basin.

As CO_2 content increases, δ^{13}C values of methane and ethane become larger (fig. 4(d)), which is contrary to the correlation of nitrogen content with methane δ^{13}C values, reflecting that inorganic CO_2 was generated at an even higher temperature/maturity level and that hydrocarbon gases and nitrogen were generated earlier than inorganic CO_2.

3 Simulation experiments on non-hydrocarbon gas generation

Simulation experiments on hydrocarbon gas generation have been carried out by many investigators. Simulation experiments on the generation of non-hydrocarbon gases, however, have been rarely reported. In order to determine the source and genesis of the nitrogen and carbon dioxide in the Yinggehai basin and establish a combined generation model of both hydrocarbon gases and nonhydrocarbon gases, simulation experiments were carried out using shale samples from Meishan and Yinggehai formations. The variation of the composition of the experiment products is shown in fig. 6. It can be seen from fig. 6 (i) that most nitrogen was generated at temperatures between 300℃ and 600℃, with peak generation temperature for the sample from the Yinggehai formation being at 450℃, slightly higher than that for the sample from the Meishan formation (fig. 6(b)); (ii) that the significant carbon dioxide generation began at temperatures higher than 450℃, with peak generation temperature between 600℃ and 700℃; (iii) and that the range of temperature for CO_2 generation was wider than that for nitrogen, and the peak generation temperature for CO_2 generation was higher than that for nitrogen generation. As a result, nitrogen generation should be earlier than CO_2 generation for the same source rock.

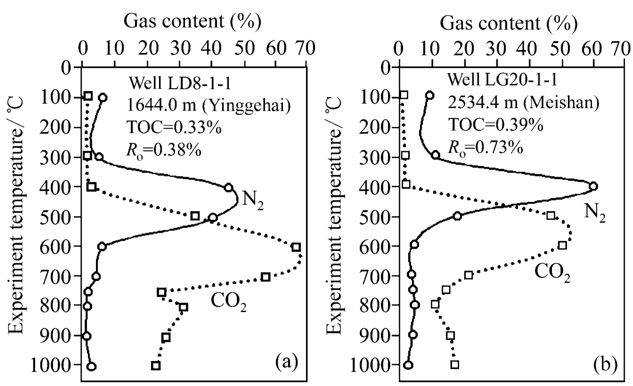

Fig. 6. Variation of the product composition of the experiments on marine shales from the Yinggehai basin with temperatures.

No reliable nitrogen isotopic measurement on the experiment products was obtained in this study. CO_2 generated in the experiments had a measured $\delta^{13}C$ value of –4.6‰, similar to the $\delta^{13}C$ values for the inorganic CO_2 from the Yinggehai basin gases (cf. fig. 1(b)). The measured CO_2 $\delta^{13}C$ value confirms that the carbon dioxide was the product of high-temperature decomposition of inorganic carbonate. The experimental result also confirms that shales with average inorganic carbonate content of about 10% could generated a large amount of CO_2, which indirectly suggests that the inorganic CO_2 in gases in the Yinggehai basin could have been generated from high-temperature decomposition of inorganic carbonates in the Sanya and Meishan formations.

4 Natural gas generation and evolution model in the Yinggehai basin

Simulation experiments confirm that the potential source rocks in the Yinggehai basin could generate large amounts of nitrogen and carbon dioxide (fig. 6). What is more important is that, the simulation experiments confirm that nitrogen was generated earlier than CO_2, which is consistent with the association among hydrocarbon gases, nitrogen and CO_2, i.e. nitrogen content has a positive correlation with hydrocarbon gas content (fig. 3(b)) and nitrogen co-exists with organic CO_2. Therefore, both simulation experiments and analysis of natural gas origin in the Yinggehai basin confirm that organic, nitrogen-rich gases could be generated not only in the metamorphic stage (source rock R_o>3.0%)[15], but also within the catagenetic stage (source rock R_o >2.0%). This new mechanism of nitrogen-rich gas generation is a key to understanding non-hydrocarbon gas distribution in the Yinggehai basin. On the basis of combined analysis of the origin of the natural gases and the results of simulation experiments, the natural gas generation and evolution model in the Yinggehai basin can be established (fig. 7).

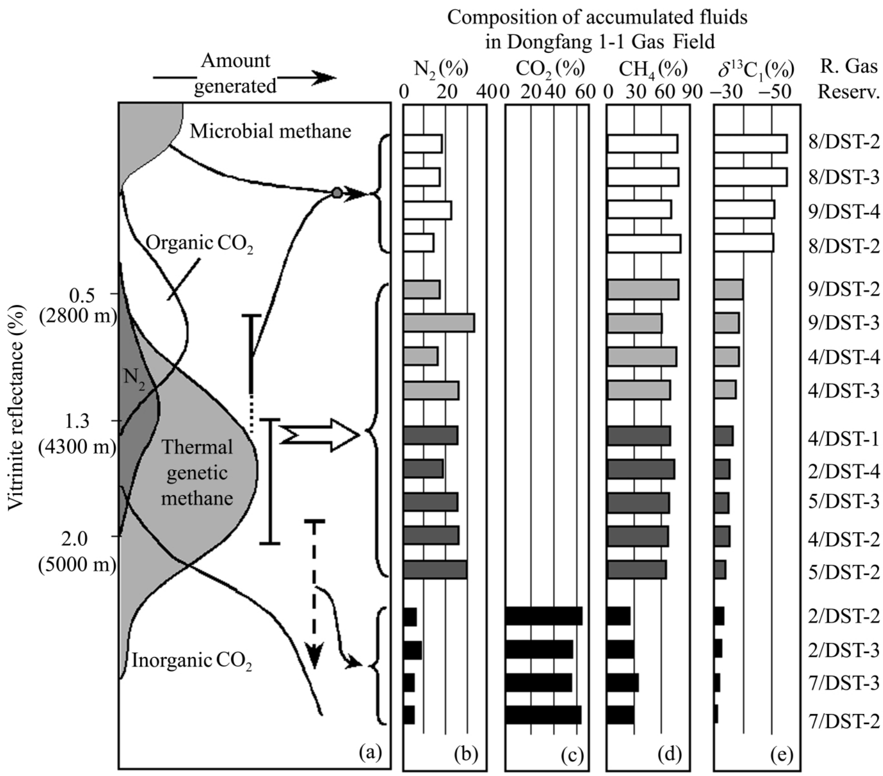

Fig. 7. Natural gas generation model in the Yinggehai basin and its responses in the accumulated fluids of different injection stages in the Dongfang 1-1 gas field. R. Gas Reserv. = representative gas reservoirs.

(i) Diagenetic stage (R_o<0.5%, burial depth<2800 m). The main product of the early diagenetic stage was microbial methane. The depth for microbial methane generation was no deeper than 2000 m. Each stratigraphic interval was dominated by Type III kerogen, and therefore had relatively high biogenetic gas potential. Strong gas shown in the shallow part of Well Ld3011A was biogenetic methane. The main product in the late diagenetic stage was organic CO_2, which was the result of organic matter decarboxylation. The generation of organic CO_2 sustained until vitrinite reflectance reached about 1.3% (fig. 7). However, most organic CO_2 could not accumulate because of its high solubility in water and large amount of formation water in the generation stage of organic CO_2.

(ii) Early catagenetic stage (R_o= 0.5% to 1.3%, burial depth from 2800 m to 4300 m). The main products of this stage were thermal genetic hydrocarbon gases, nitrogen and a small amount of liquid hydrocarbons, with the generation of organic CO_2 still ongoing. Because no major faults developed plus rapid sedimentation of fine-grained sediments, the overpressured source rocks long remained a closed or semi-closed fluid system[10,17]. As a result, the products of the major gas source rocks (the Maishan and Sanya formations) at the early catagenetic stage had long been retained, and were expelled along with natural gases generated later[10].

(iii) Late catagenetic stage (R_o = 1.3% to 2.0%, burial depth from 4300 m to 5000 m). The major products of this stage were hydrocarbon gases dominated by methane and nitrogen. Late at this stage, inorganic carbonate decomposition began and a considerable amount of inorganic CO_2 was generated.

(iv) Metamorphic stage (R_o>2.0%, burial depth >5000 m). The major product of this stage was CO_2 generated from the decomposition of inorganic carbonates and methane from high-temperature cracking of kerogen and/or liquid hydrocarbons.

5 Response of the natural gas generation and evolution model in the accumulated fluids

There are considerable compositional variations among different reservoirs in the same gas field in the Yinggehai basin. We call these variations inter-reservoir heterogeneities. Compared with the lateral compositional variations in the same reservoir or in-reservoir heterogeneities, inter-reservoir heterogeneities have the advantage of being unaffected by in-reservoir mixing processes after accumulation, and therefore “record” the original differences in the composition of petroleum that filled the reservoir in different periods. The Dongfang gas field is the largest gas field found in the Yinggehai basin. The composition and characteristics of the natural gases in different fault blocks and different reservoirs reflect the products of different gas generation stages, and therefore provide a basis for examining the established natural gas generation model.

Gases from DST2 and DST3 in Well DF118 and those from DST2 and DST4 in Well DF119 are dominated by methane, with nitrogen content of 15%—23% and methane $\delta^{13}C$ values smaller than −50‰ (fig. 7). These gases represent the mixture of biogenetic gas with a small amount of thermal genetic gas generated within catagenetic stage (fig. 7).

Gases from DST2 and DST3 in Well DF119 and those from DST3 and DST4 in Well DF114 are dominated by methane, with nitrogen content of 18%—33%. These gases have very low CO_2 content with CO_2 $\delta^{13}C$ values ranging from −12.5‰ to −19.9‰ (fig. 7), suggesting organic origin. The methane $\delta^{13}C$ values range from −38‰ to −40‰. These gases represent gases generated in early catagenetic stage.

Gases from DST1 and DST2 in Well DF114, those from DST4 in Well DF112 and those from DST2 and DST3 in Well DF115 have relatively larger methane $\delta^{13}C$ values (−33.0‰ to −37.0‰), and the hydrocarbon gases display a higher level of maturity. These gases represent the gases generated in late catagenetic stage.

Gases from DST2 and DST3 in Well DF112 and those from DST3 and DST2 in Well DF117 are dominated by carbon dioxide, with nitrogen content lower than 10%. The carbon dioxide has $\delta^{13}C$ values larger than –10‰, and is mainly inorganic in origin. The methane $\delta^{13}C$ values become larger (>–32.0‰), suggesting a higher maturity level. These gases represent products of the metamorphic stage.

6 Conclusions

Based on the analysis on the origin and genesis of the natural gases in the Yinggehai basin and simulation experiments on potential source rocks, the following conclusions have been drawn: (1) Because of the huge thicknesses of the Tertiary and Quaternary, natural gas generation stages from diagenesis to metamorphism have been developed in the Yinggehai basin. (2) Organic nitrogen-rich gases can be generated from organic matter not only at metamorphic stage (source rock R_o>3.0%), but also within the catagenetic stage (source rock R_o<2.0%). Such a mechanism of nitrogen-rich gas generation is a key to understanding and predicting the distribution of non-hydrocarbon gases in the Yinggehai basin. (3) The inter-reservoir compositional heterogeneities of the gas fields found in the Yinggehai basin have recorded the products generated at different gas generation stages, and the complexities in the composition of the natural gases in the Yinggehai basin are a combined result of multi-stage gas generation and multi-period natural gas migration and accumulation.

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