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Geochemistry and episodic accumulation of natural gases from the Ledong gas field in the Yinggehai Basin, offshore South China Sea

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Abstract

The Ledong gas field, consisting of three gas pools in a shale diapir structure zone, is the largest gas discovery in the Yinggehai Basin. The gases produced from the Pliocene and Quaternary marine sandstone reservoirs show a considerable variation in chemical composition, with 5.4–88% CH_4, 0–93% CO_2, and 1–23.7% N_2. The CO_2-enriched gases often display heavier methane $\delta^{13}C$ values than those with low CO_2 contents. The $\delta^{15}N$ values of the gases range from -8 to $-2‰$, and the N_2 content correlates negatively with the CO_2 content. The high geothermal gradient associated with a relatively great burial depth in this area has led to the generation of hydrocarbon and nitrogen gases from the Lower–Middle Miocene source rocks and the formation of abundant CO_2 from the Tertiary calcareous-shales and pre-Tertiary carbonates. The compositional heterogeneities and stable carbon isotope data of the produced gases indicate that the formation of the LD221 gas field is attributed to three phases of gas migration: initially biogenic gas, followed by thermogenic hydrocarbon gas, and then CO_2-rich gas. The filling processes occurred within a short period approximately from 1.2 to 0.1 Ma based on the results of the kinetics modeling. Geophysical and geochemical data show that the diapiric faults that cut through Miocene sediments act as the main pathways for upward gas migration from the deep overpressured system into the shallow normal pressure reservoirs, and that the deep overpressure is the main driving force for vertical and lateral migration of the gases. This gas migration pattern implies that the transitional pressure zone around the shale diapir structures was on the pathway of upward migrating gases, and is also a favorable place for gas accumulation. The proposed multiple sources and multiple phases of gas migration and accumulation model for the Ledong gas field potentially provide useful information for the future exploration efforts in this area.

1. Introduction

The Yinggehai Basin, offshore South China Sea, is one of the most gas-rich Cenozoic rift basins in China (Gong, 1997; Huang et al., 2003). Great

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attention has been paid to the basin in recent years because of its huge thickness (>16 km) of Paleogene-Quaternary sediments, rapid sedimentation rates, high geothermal gradients, deep overpressure system, and regional diapir activities. Since 1990, two gas fields (Ledong and DF1-1) and a number of gas-bearing structures have been discovered (Fig. 1). The Ledong gas field, consisting of three gas pools (L22-1, L15-1 and L8-1), has larger gas reserves than the DF1-1 field. There have been several recent publications documenting the characteristics and origin of the DF1-1 gas field (e.g. Dong and Huang, 1999; Hao et al., 2000; Huang et al., 2002b). However, little information on the origin and migration and accumulation models of the gases in the Ledong gas field is available in the public domain. Gas produced from the Ledong field is rich in non-hydrocarbon components, with

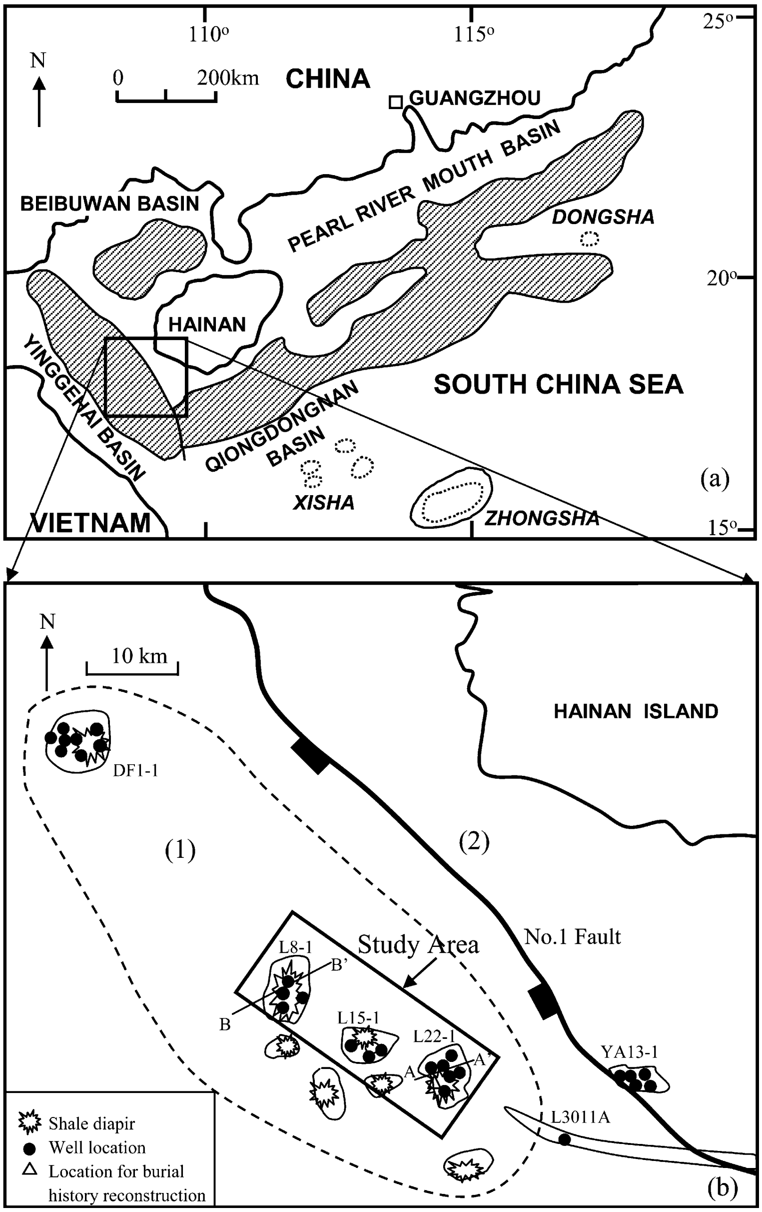

Fig. 1. Maps showing the location of the Ledong gas field in the Yinggehai Basin, offshore South China Sea: (1) Diapir belt and (2) Yingdong slope.

0–93.05% CO_2 and 1–23.7% N_2, thus the risk of encountering CO_2 has become one of the major concerns for further exploration in this area. A detailed investigation of the geochemistry of different gas components and a clear understanding of migration and accumulation history of the gas field hold the key for predicting gas distribution and finding satellite gas pools around the Ledong field. The purpose of this paper is to investigate the characteristics and origin of the gases, to demonstrate the relationship between the gas pool formation and the diapiric faults and overpressures, and to determine the timing of gas migration and accumulation in the Ledong field. This work will help to better define favorable targeting areas and reduce risk associated with the future exploration in this basin.

2. Geological setting

The Yinggehai Basin is a relatively young, hot, trans-extensional basin. The tectonic evolution of the basin can be divided into two stages: a Paleogene extensional rifting event and a Neogene post-rift thermal subsidence (Gong, 1997). The basin is filled with thick Tertiary clastic deposits on Paleozoic and Mesozoic basement rocks (Gong, 1997). It is estimated that the maximum thickness of the Cenozoic sediments reaches 16 km at the basin center (Gong, 1997). Figure 2 shows the stratigraphic section of the Yinggehai Basin. Based on seismic data, about 5000–7000 m of Eocene–Oligocene rift stage sediments occur in the central depression (Gong, 1997). The major portion of the sedimentary rocks is Miocene–Pliocene age. The post-rift marine sediments have a thickness up to 9000 m (Fig. 2). These sediments have not been structurally disrupted except where shale diapiric structures developed.

The basin is characterized by a rapid subsidence with the maximum sedimentation rate up to 1.2 mm/year and a high geothermal gradient (42.5–45.6 °C/km) during the Tertiary (Huang et al., 2002a, 2003). As a result of the rapid loading and under-compaction of the sediments, overpressure developed throughout most of the basin. The maximum pressure coefficient (pressure coefficient C_p = pore pressure/hydrostatic pressure ratio) is as high as 2.3 (Zhang et al., 1996; Huang et al., 2003). The combination of overpressure and high paleo-geothermal gradient, together with the diapirism, had an important influence on the generation, migration and accumulation of the natural gases in the basin. Available geological and geochemical data have indicated that the Miocene strata, especially the Meishan and Sanya formations (Fig. 2), are composed mainly of neritic and deltaic dark calcareous mudstones (Huang et al., 2002a), which have been believed to be the main hydrocarbon source rocks in the Yinggehai Basin (Dong and Huang, 1999; Hao et al., 2000; Huang et al., 2003). These source rocks are enriched in higher plant-derived type III organic matter (Huang et al., 2002a, 2003).

3. Samples and experimental conditions

All gas samples used in this study (Table 1) were collected during drill stem tests and module formation tests. These samples were analyzed for their composition using a Hewlett Packard 5890 II gas chromatograph, equipped with a thermal conductivity detector. Methane, C_{2+} gaseous hydrocarbons and CO_2 were prepared for $\delta^{13}C$ measurements following the procedures similar to those described by Schoell (1980) on a Finnigan-MAT gas chromatograph combustion system. The isotope analyses were conducted using a Finnigan-MAT251 mass spectrometer. The $\delta^{13}C$ values are reported relative to the PDB standard, with an analytical precision of ±0.02‰. Nitrogen isotope analyses were carried out following the procedure described by Sweeney et al. (1978), using atmospheric nitrogen as the reference standard.

The $^3He/^4He$ measurements were carried out using a VG-5400 static-vacuum noble gas mass spectrometer, with the sensitivity remaining stable at 10^{-4} A/cm^3 standard temperature and pressure (STP) He.

Pyrolysis experiments were conducted in gold tube reactors. Kerogen samples were isolated from a typical immature source rock (Table 2) collected from the Meishan Formation in the Yinggehai Basin, and were then loaded into the gold tubes (9 mm o.d. × 60 mm length). After loading into stainless steel cells next to a thermocouple providing control of the temperature to ±1 °C, the samples were placed into the pyrolysis furnace and kept at a pressure of 50 MPa during the entire course of the experiment. The samples were heated to the required (isothermal) temperatures ranging from 250 to 600 °C at either 2 °C/h or 20 °C/h. Methane, ethane and propane were trapped from the pyrolysates using a GC analyzer, and then transferred into a

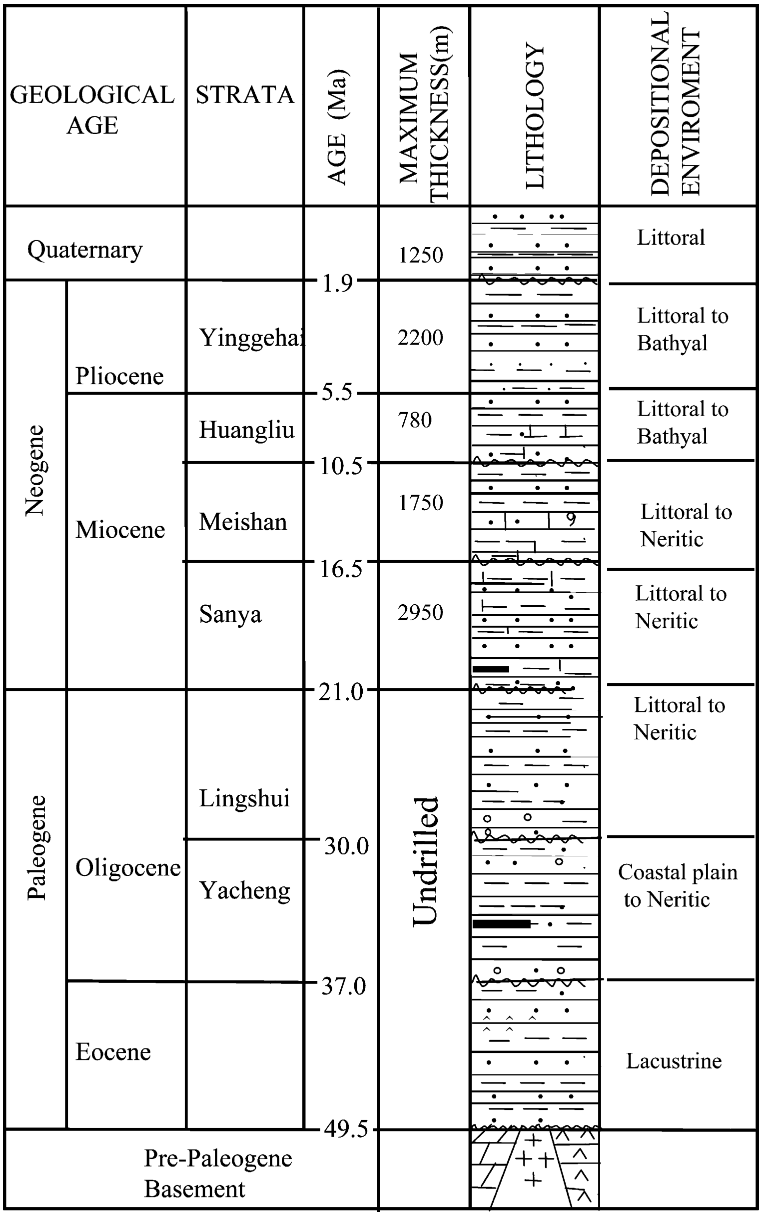

Fig. 2. Schematic stratigraphic column of the Yinggehai Basin (modified after Huang et al., 2003).

Finnigan-MAT251 mass spectrometer to measure their carbon isotope values. On the basis of the experimental data, reaction kinetic parameters (Table 2) were calculated using methods similar to those described by Tang et al. (2000) and Cramer et al. (2001). For reaction kinetic modelling of gas generation and carbon isotope fractionation, the software called "GOR-kinetics" developed by Tang et al. (2000) was used. The geological inputs used in the modeling will be described below.

4. Results and discussion

4.1. Geochemical characteristics of the natural gases in the Ledong field

The Ledong gas field is situated in the shale diapiric structure zone of the Yinggehai Basin (Fig. 1). The gas payzones are Pliocene – Quaternary marine sandstones with a burial depth of 390–2000 m, being normally pressured. The gases are mainly

Table 1
Chemical and carbon isotopic compositions of natural gases produced from the Ledong gas field

Sample no.	Depth (m)	Reservoir age	Composition (%)				C_1/C_{1-5}	$\delta^{13}C$(‰)			$^3He/^4He$ ($\times 10^{-7}$)	$\delta^{13}N$ (‰)
			C_1	C_{2+}	CO_2	N_2		C_1	C_2	CO_2		
L2211-5	854.5	Q	83.47	1.11	0.17	15.24	0.99	−54.30	−23.52	−14.00	0.97	−6
L2211-4	978.5	Q	81.68	2.16	0.10	16.06	0.97	−38.29	−23.18	−12.73	0.98	−15
L2211-3	1048	Q	75.53	2.18	0.11	22.18	0.97	−36.04	−21.72	−10.44	0.89	−7
L2211-2	1368.5	Q	65.28	1.94	0.32	32.46	0.97	−32.93		−8.99	0.89	−8
L2211-1	1498	Pliocene	13.44	0.85	80.42	5.29	0.94	−26.92		−0.56	0.55	−4
L2212-6	396	Q	81.10	0.60	0.10	18.20	0.99	−40.62			0.60	−5
L2212-5	525	Q	80.10	1.10	0.10	18.70	0.99	−36.36	−19.77		0.56	−4
L2212-4	586	Q	80.10	1.40	0.00	18.50	0.98	−37.64	−20.63		0.60	−3
L2212-3	916.5	Q	79.00	2.20	0.10	18.70	0.97	−34.01	−23.36		0.56	−3
L2212-2	974	Q	79.20	2.20	0.10	18.50	0.97	−34.14	−23.30		0.79	−4
L2213-5	403	Q	87.09	0.70	0.73	11.48	0.99	−63.14			0.62	−6
L2213-4	584.5	Q	81.93	1.33	0.07	16.67	0.98	−40.15	−21.41		0.62	−5
L2213-3	913	Q	75.81	2.48	0.07	21.64	0.97	−39.56	−23.72		0.72	−6
L2213-2	970.5	Q	79.55	2.42	0.27	17.76	0.97	−35.82	−23.06		0.63	−5
L2213-1	1491	Q	58.97	2.08	21.46	17.49	0.97	−29.08	−22.82	−5.74	0.61	−4
L2214-4	585	Q	88.14	2.08	0.08	9.70	0.98	−55.72	−22.29			
L2214-2	985	Q	81.01	2.14	0.09	16.76	0.97	−35.39	−23.60			
L2214-1	1275	Q	79.12	1.98	0.12	18.79	0.98	−34.09	−23.35		0.73	−6
L2215-3	965	Q	84.27	1.70	0.71	13.32	0.98	−49.30	−23.52			
L2215-2	1185	Q	77.80	2.03	0.10	20.07	0.97	−32.50	−23.18		0.57	−9
L2215-1	1597.5	Pliocene	81.00	2.32	0.11	16.57	0.97	−28.78	−21.72		0.43	−6
L2216-4	590	Q	79.31	1.25	0.20	19.24	0.98	−36.28	−20.29		0.68	−7
L2216-3	836.5	Q	78.63	1.58	0.12	19.67	0.98	−35.99	23.10			
L2216−2	1475	Q	50.11	1.32	34.82	13.75	0.97	−31.21	−22.86	−2.15	0.51	−7
L815-1	1254.5	Pliocene	35.22	1.12	59.74	3.92	0.97	−28.59		−3.33	20.40	−7
L812-3	1199.5	Q	56.03	2.00	37.46	4.51	0.97	−32.87	−23.35	−4.50	21.30	−4
L812-1	1343.5	Pliocene	75.95	2.30	19.52	2.22	0.97	−30.60	−23.50	−4.63	14.70	−6
L811-2	1537.5	Pliocene	24.64	2.25	69.33	3.78	0.92	−31.32	−27.74	−3.65	21.90	
L811-1	1915.5	Pliocene	16.00	1.28	79.74	2.98	0.93	−31.39	−22.95	−3.26		
L1511-3	1487	Q	65.46	3.08	16.73	14.73	0.95	−37.28	−20.08	−6.96	2.48	
L1511-2	2337.5	Pliocene	5.57	0.46	93.02	0.95	0.92	−32.28		−5.63	4.20	
L1512-1	1377.75	Pliocene	34.01	1.41	56.63	7.96	0.96	−35.28	−19.49	−5.52		
L1514-4	1436.5	Q	28.27	1.34	64.20	6.19	0.95	−34.82	−17.88	−5.76		
L1514-3	1465	Q	23.15	1.19	70.52	5.15	0.95	−34.50	−19.13	−5.72		
L1514-2	1596.25	Pliocene	46.02	2.14	42.04	9.80	0.96	−35.38	−19.12	−6.37		
L1514-1	1864	Pliocene	9.83	0.50	87.62	2.05	0.96	−33.12	−19.40	−4.78		

Table 2
Basic data, methane generation and carbon isotopic fraction kinetics parameters from the pyrolysis sample

Sample	Fm.	Depth (m)	TOC (%)	Ro (%)	Methane generation kinetics parameters		Methane carbon isotopic fraction kinetics parameters	
					Activation energy distribution (Kcal/mol)	Frequency factor	E_o (Kcal/mol)	γ (Kcal/mol)
Y741 Mudstone	MS	2347	0.65	0.40	$46 \sim 71$	3.84×10^{12}/s	50.98	0.01096

Fm. = Formation; MS = Meishan; Eo = average activation energy; γ = activation energy threshold (Tang et al., 2000).

composed of CH_4, CO_2 and N_2, with variable chemical compositions in different reservoirs (Fig. 3).

4.1.1. Hydrocarbon gases

The gases from the Ledong gas field contain variable amounts of CH_4 relative to CO_2 and N_2 (Table 1). Regardless of their contents of non-hydrocarbon components, these gases display high C_1/C_{1-5} ratios (0.92–0.99).

The $\delta^{13}C_1$ values of the gases vary from −63‰ to −27‰, indicating a variable origin. Except for a small amount of biogenic gases, most of the gases in the Ledong field display a $\delta^{13}C_1$ range of

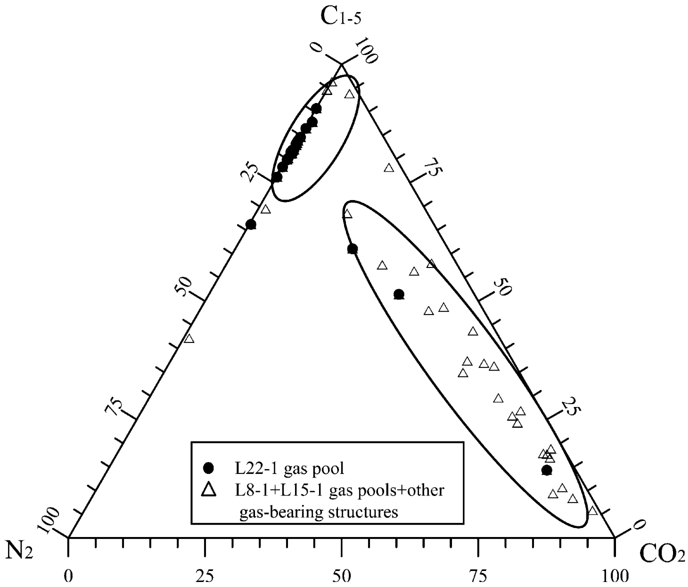

Fig. 3. Plot showing the compositions of natural gases from the Ledong gas field.

−40.62‰ to −26.92‰, indicating a moderate to high thermal maturity of the gases.

$\delta^{13}C_2$ values of the gases range from −18‰ to −23.6‰, about 2–8‰ less negative than those of the gases from the Yacheng 13-1 gas field in the adjacent Qiongdongnan Basin where the gases are believed to have been derived from the Oligocene coal-bearing source rocks (Huang et al., 2003). These $\delta^{13}C_2$ data are within the empirical range of values (>−28‰) derived from humic organic matter or coal-bearing strata suggested by Xu (1994), based on data from Chinese petroleum basins. This idea is also supported by the relatively high contents of benzene and toluene (15–50%) in the $C_{6\text{-}7}$ hydrocarbons (Huang et al., 2003). Available geological and geochemical data indicate that, with the exception of biogenic gases, the hydrocarbon components and associated organic CO_2 and N_2 in the gases from the Yinggehai Basin were derived mainly from the source rocks in the Sanya and Meishan formations (Schoell et al., 1996; Hao et al., 2000; Huang et al., 2003). These source rocks occur mainly in the Central Yinggehai Depression and are composed of deltaic to neritic deposits. The Miocene shales collected from the wells LD3011A and LD2217 have TOC contents of 0.4–2.97%, with type II_2–III kerogens (Huang et al., 2002a, 2003).

4.1.2. Carbon dioxide

Based on the content and stable carbon isotope values, the CO_2 in the gases from the Ledong field can be divided into two genetic types (Fig. 4). Those with an organic source mainly display a $\delta^{13}C_{CO_2}$ range of −14‰ to −8.99‰, usually with less than 1% CO_2. Those with an inorganic origin occur in deeper reservoirs connected with diapiric faults, with 21–93% CO_2. The $\delta^{13}C_{CO_2}$ values of these gases range from −6.96‰ to −0.56‰ (Table 1), within

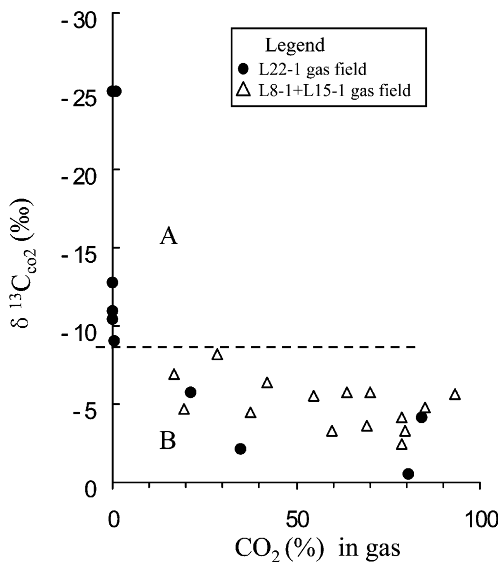

Fig. 4. Classification of CO_2 in the Ledong gas field, the Yinggehai Basin: (A) CO_2 generated from organic matter and (B) CO_2 generated from thermal decomposition of calcareous shale/carbonate and mantle.

the empirical range of inorganic CO_2 suggested by Dai et al. (1996).

The helium contents in the gases with inorganic CO_2 are only 5–45 mg/l. Their $^3He/^4He$ ratios range from 0.51×10^{-7} to 4.4×10^{-7} (Table 1), and are much lower than that of air (1.4×10^{-6}). The fact that the $^3He/^4He$ ratios are significantly different from those of the mantle and magmatic derived CO_2 gases (3.19×10^{-6} to 6×10^{-6}, Dai et al., 1996) found in eastern China and the R/R_a ratios (the R and R_a are the $^3He/^4He$ ratio of the gas sample and the $^3He/^4He$ ratio of the atmosphere, respectively) are much less than 1 indicates it has a crustal origin. Only four CO_2-rich gas samples collected from the L8-1 gas pool have higher $^3He/^4He$ ratios (1.47×10^{-6}–2.19×10^{-6}) (Table 1) and R/R_a ratios (1.05–1.56), possibly indicating some contribution from magmatic activities. Therefore, the abundant carbon dioxide in the Ledong gas field is mainly of inorganic origin, probably from thermal decomposition of carbonate minerals in the Cenozoic and pre-Cenozoic sediments.

4.1.3. Nitrogen

Nitrogen accounts for 1.05–23.87% of the gases in the Ledong gas field, and the gases with more than 15% nitrogen almost always contain organic-derived carbon dioxide (Fig. 5). The $\delta^{15}N$ values of these gases vary from −8‰ to −2‰ (Fig. 6). Although $\delta^{15}N$ values are controlled by multiple factors, more negative $\delta^{15}N$ values (−15‰ to −2‰) are usually associated with organic-derived gases (Hoering and Moore, 1958; Stahl, 1977). Stahl (1977) reported that a type of carboniferous gas in the northern Germany had δN values between −15‰ and −5‰. The similar range in the $\delta^{15}N$ values of the Ledong field gases to those of the carboniferous gases in northern Germany is clear evidence for an organic origin.

According to the published models, nitrogen can be generated from humic organic matter in the main stage of hydrocarbon generation (Hunt, 1996), or after the peak methane stage when source rocks are matured to more than 3.0 %Ro (Littke et al., 1995). The nitrogen in the high-N_2 gases from the Ledong gas field is isotopically different from that of the Rotligend Basin in Europe where the nitrogen was believed to have originated from the post-mature Carboniferous-Permian coal (Schoell et al., 1996). On the other hand, the nitrogen content in the Ledong gas decreases with increasing CO_2 content and $\delta^{13}C_1$ value (Fig. 5a; Table 1).

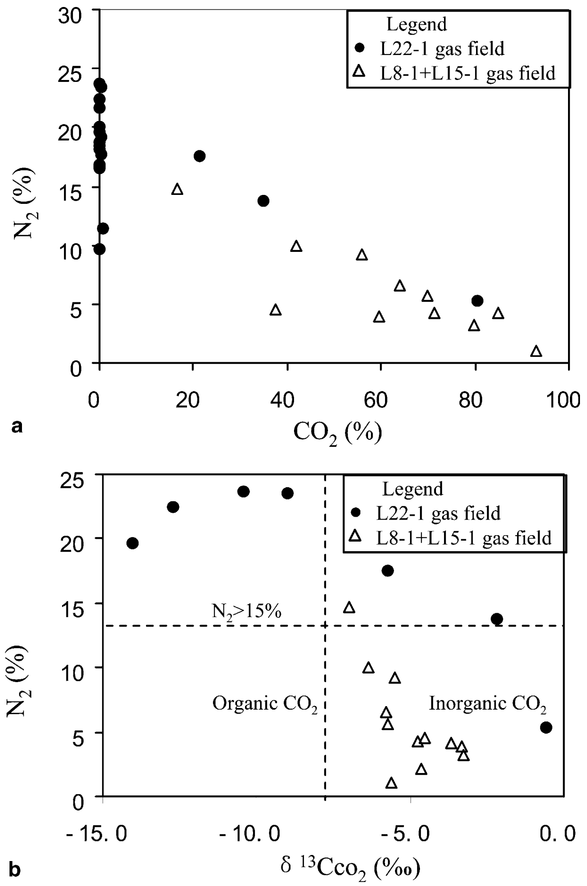

Fig. 5. Variation of nitrogen content with carbon dioxide content (a), and carbon dioxide $\delta^{13}C$ values (b) for the studied gas samples, indicating compositional interplays for the gases from the Ledong gas field.

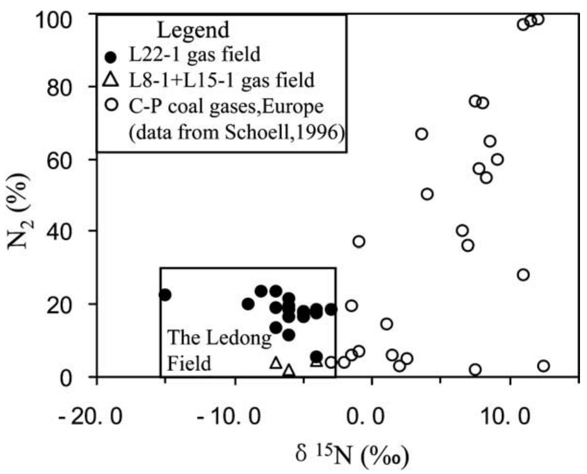

Fig. 6. Comparison of nitrogen characteristics of the gases from the Ledong gas field with those from overmatured Carboniferous-Permian coals of the European Rotliegend Basin.

This result is in contrast to that expected for terrestrial organic matter derived nitrogen at extremely high temperature (>3.0 %Ro, Littke et al., 1995), suggesting that most of the nitrogen in the Ledong field was generated from humic organic matter at moderate maturity (<2.0 %Ro, Hunt, 1996). This is consistent with a source in the Meishan – Sanya formations (with 1.3–2.8 %Ro and type II_2-III kerogens, Fig. 7). In fact, if the CO_2 content was subtracted from the total gas composition, the nitrogen content of the gases would be around 15–25%. This indicates that there would be co-generation and the same migration history for both the thermogenic hydrocarbon gases and nitrogen in the Ledong gas field.

4.2. Gas pool-filling events

Because diapir-related gas payzones in the Ledong field are usually separated by faults, shale seams or other non-permeable zones, episodic expulsion of natural gases during different stages of subsidence, diapiric activity and source rock maturation likely results in compositionally different gases in the reservoirs. Reconstruction of the gas pool filling history will help to understand the process of gas migration into the reservoirs (Dong and Huang, 1999; Huang et al., 2002b). An integration of the gas compositional heterogeneities and stable carbon isotopic data with geological data can be used to trace the migration and accumulation of the hydrocarbon and CO_2 gases (Schoell, 1993). Taking the L221 gas pool as a case, three different phases are recognized (Fig. 8, Table 3).

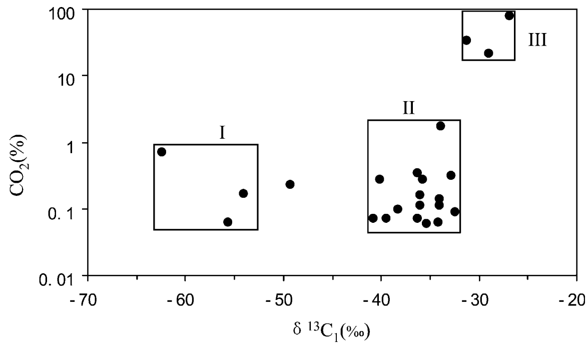

Fig. 8. Relationship between the $\delta^{13}C_1$ value and CO_2 content of the studied gas samples collected from the L22-1 gas pool. Note the three phases of gas generation, migration and accumulation.

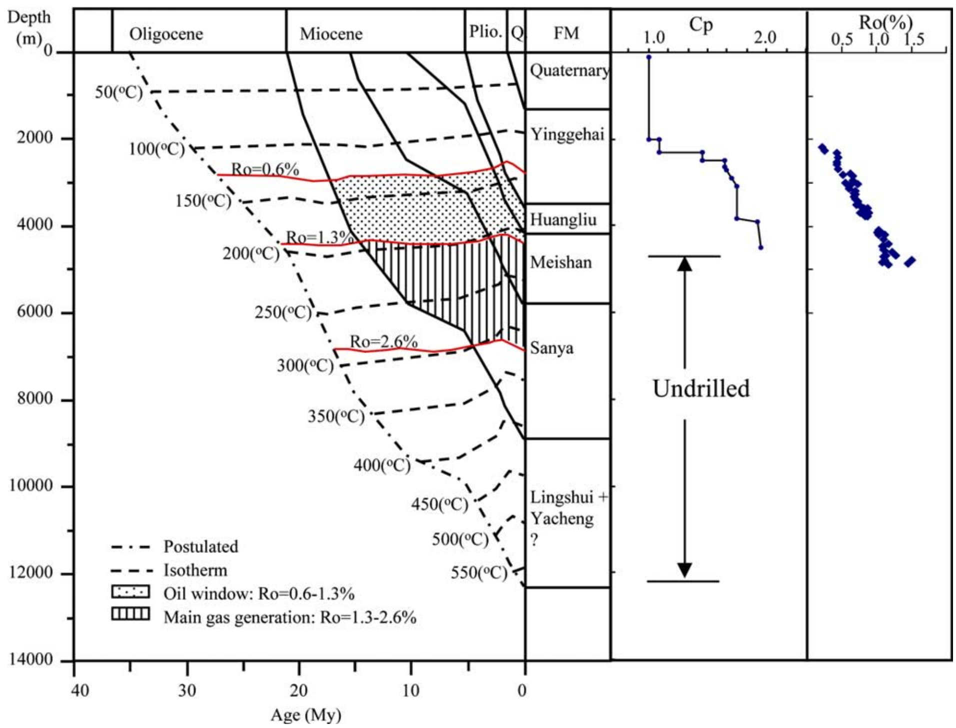

Fig. 7. Burial history, thermal maturation evolution, pressure coefficients and vitrinite reflectance of the Tertiary strata in the well L221S. Plio. = Pliocene, Q = Quaternary. C_p: pressure coefficient = pore pressure/ hydrostatic pressure.

Table 3
Geological and geochemical constraints of three filling events in the L22-1 gas pool

Phase	I	II	III
Geological setting	Shallow-trap forming above the diapir	Diapir uplifting and piercing	Reactivation of diapiric faults and deep resting faults
Reservoir			
Age	Q	Q-Pliocene	Pliocene
Depth (m)	400–850	400–1600	400–1600
Pressure	Normal	Normal	Normal
Natural gas	Biogas	Thermo-genetic gas	Rich-inorganic CO_2 gas
C_{1-5} (%)	87.09–88.14	65.7–83.1	14.3–61
CO_2 (%)	0.1–0.7	0.1–3	21.46–80.4
$\delta^{13}C_1$(%)	−63.14 to −54.3	−40.62 to −32.5	−29.08 to −26.92
T_H (°C)	<90	120–170	180–200
Timing of M&A	−2.5 Ma–Present day (−2.5 to −1.2 Ma)	−1.2 to −0.3 Ma	After −0.3 Ma (−0.3 to −0.1 Ma)
Source-rock			
Age	Q-Pliocene	Meishan and Sanya Formations	Meishan and Sanya Formations /basement carbonate
Maturity	Immature	Main gas window	Over-mature
Pressure	Normal	Overpressure	Overpressure

T_H = Homogenization temperature of inclusion M&A = Migration and accumulation.

Phase I: Injection of biogenic gas. Biogenic gases derived from immature mudstones migrated into adjacent reservoirs during 2.5–1.2 Ma. This phase is exemplified by the gases produced from the wells L2211, L2214 and L2215 (Table 1). The gases are characterized by a high CH_4 content (87.09–88.14%), with low $\delta^{13}C_1$ values (−63.14% to −54.3%) and high C_1/C_{1-5} ratios (0.98–0.99). A close analogue of these gases is the biogenic gases in the Caidam Basin, northwestern China (Huang et al., 2003).

Phase II: Injection of thermogenic gas. These gases account for the overwhelming majority of the discovered gas reserves in the L221 gas pool (Table 1; Fig. 8). They are dominated by hydrocarbon gases with about 75% methane, 3–5% C_{2+} hydrocarbons, 13.3–23.7% N_2, and a minor amount of CO_2 (0.1–3%). The $\delta^{13}C_1$ values of these gases range from −40.62% to −32.5%, indicating moderate to high maturity. Because the reservoir depth was less than 1600 m and thermally immature at the time of being charged, most of the thermogenic gas present in the reservoir must have undergone a long distance vertical migration from deeper sources and was probably redistributed in a first phase of shale movement with not so deep reaching faults.

Phase III: Injection of CO_2-rich gases. These gases, generated from much deeper sources, consist of 21–80% CO_2, less than 15% N_2, and 14–61% hydrocarbon gases. The reservoirs are typically connected to diapiric faults. The gases have $\delta^{13}C_{CO_2}$ values in the range of −5.74‰ to −0.56‰, $^3He/^4He$ ratios 0.20×10^{-7} to 0.98×10^{-7}, and less negative $\delta^{13}C_1$ values (−29.08‰ to −26.92‰) (Fig. 8). This indicates that most of the CO_2 gases were of inorganic origin, and the associated hydrocarbon gases originated from source rocks with high thermal maturity. It is likely that the CO_2-rich gases were trapped in fault-connected reservoirs after the emplacement of the thermogenic gases during the Phase II. During Phase III, most of the gaseous hydrocarbons and CO_2 were likely to have been generated from the deeply buried the Sanya and Meishan formations where the temperatures were high enough for carbonate minerals to be decomposed.

Stratigraphically, the biogenic gas normally occurs in shallow reservoirs, whereas the CO_2 rich gases are in reservoirs with a greater depth (Fig. 9). In the well L2213, for example, the shallowest reservoir contains only biogenic gases with a low CO_2 content (1.01%); the upper and middle reservoirs produce hydrocarbon-rich gases with less than 1% CO_2; and the deepest reservoir contains 21–80% CO_2. The gas sample with a $\delta^{13}C_1$ value of −49.3‰ in Fig. 8 could be interpreted as the mixing of dominantly biogenic gas with a small amount of thermogenic gas, and likely as the result of diapiric activity that led to deep source thermogenic gases migrating into the shallow biogenic gas reservoir.

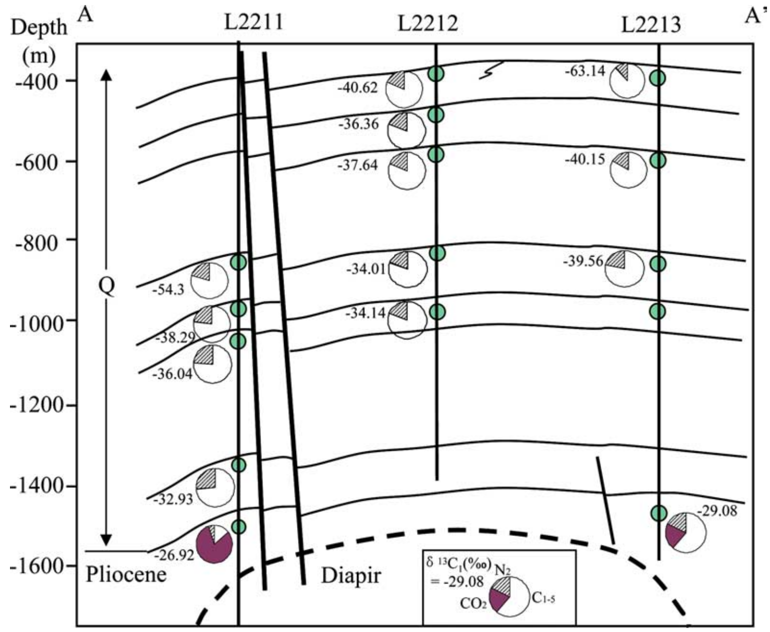

Fig. 9. A cross section through the L221 gas pool, showing the gas compositional heterogeneities in different reservoir units. The location of the section is shown in Fig. 1.

4.3. Timing of gas migration and accumulation

Dating petroleum migration and accumulation is a challenging scientific exercise. The combination of homogenization temperatures of reservoir fluid inclusions with their burial history is widely used to investigate the timing of petroleum charging (Karlsen et al., 1993; Shi et al., 1987; Xiao et al., 2002). The age of the K-feldspar or illite formation in a reservoir rock (measured by K–Ar method) can also be used to constrain the timing of water–rock reactions and investigate the timing of petroleum filling reservoirs (Liewing et al., 1987). However, the application of these methods is dependent on the geological setting of a basin. Due to the strong effects of hot fluids on both reservoir diagenesis and fluid-inclusion homogenization temperatures in the study area (Xie and Li, 1999), it is impossible to determine the absolute ages of fluid events by K–Ar dating or the combined Th-burial history. Recently, the combination of isotope-specific reaction kinetics with the burial history has proved to be a useful tool to dating gas migration and accumulation (Tang et al., 2000; Cramer et al., 2001). On the basis of the programmed-heating experimental data (including the pyrolysis yields and $\delta^{13}C$ values of methane) from an immature source rock taken from the Meishan Formation in the Yinggehai Basin, reaction kinetic parameters (Table 2) have been derived for methane carbon isotopes using the software “GOR-kinetics” developed by Tang (2000). The resulting kinetic parameters were then applied to geologic conditions to model the methane generation and carbon isotope fractionation of natural gases generated and accumulated in the reservoirs based on the burial history of the source rock occurring underneath the L221 gas field. The well L211S was selected as the model point, as it is presumably located near the center of the source kitchen. The sedimentary sequences used were based on both seismic interpretations and well data. The sequence boundaries used in the modeling were determined by the CNOOC Nanhai West Research Institute (Fig. 7). Paleogeothermal gradients of 36.5–41.0 °C/km were used (Gong, 1997). The modeled maturities were calibrated using measured vitrinite reflectance data.

The modeling results are presented in Fig. 10. Because the gas injection into the gas pool was interpreted to be episodic, the measured $\delta^{13}C_1$ values (−40.15% to −26.92%) from the gas pool correspond to the cumulative generation curve between 1.2 and 0.1 Ma (Fig. 10). This means that the gas field is young, likely formed after 1.2 Ma. This interpretation is consistent with the timing for the trap formation. The gas reservoirs are late Pliocene and

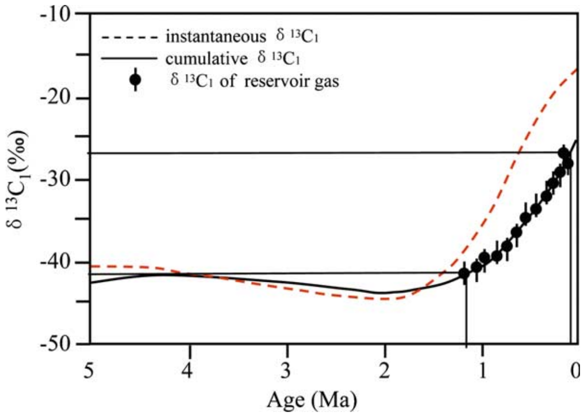

Fig. 10. Comparison of the methane stable carbon isotope trends between the modeling result from a typical Meishan shale and the measured data for gases from the L221 gas pool that are believed to have been derived from a deeper source in the Meishan Formation. The measured gas $\delta^{13}C_1$ values correlate well with the cumulative $\delta^{13}C_1$ during the past 1.2–0.1 Ma.

Quaternary in age, and the effective cap rocks developed after 2 Ma (Gong, 1997; Huang et al., 2002a).

4.4. The role of overpressure and diapiric faults in gas migration

As mentioned before, about 8000 m of Neogene marine sediments were deposited in the Ledong field area, with a sedimentation rate of 400–780 m/Ma. This rapid loading, together with a higher paleotemperature gradient (about 43.5 °C/km), led to a rapid gas generation and thermal expansion of pore fluids, causing the build up of overpressure in the source rocks in the central depression. Rock fractures when the pore pressure overcomes the effective stress and tensile strength of the rock (Hunt, 1990). Previous studies indicate that fracturing occurs when the local pore fluid pressure is greater than 85% of the lithostatic pressure due to lithostatic overburden, i.e. with a pressure coefficient (C_p) > 1.85 (Roberts and Nunn, 1995). Significant overpressure was encountered in the well L221S. The sandstone and siltstone reservoirs at a depth less than 2000 m are normally pressured with $C_p < 1.15$. The strong overpressure zone ($C_p > 1.85$) is encountered at a depth of about 2900 m, including the Huangliu (N_1h), Meishan (N_1m) and Sanya (N_1s) formations where the source rocks have C_p values up to 2.10 (Fig. 7). Overpressure developed in the shales in the basin center appears to be the main driving-force for the formation of the diapir structures and overpressured fluid migration.

The two most common forces influencing gas migration are buoyancy and pressure differential in the Ledong area. Migration driven by buoyancy is mostly restricted to shallower normal pressure reservoirs. In overpressured intervals, gas usually cannot migrate only by buoyancy force. Commercial quantities of gas in such an environment migrate most likely due to high pressure differential (Clayton et al., 1990). In the study area, we suspect that gases generated from the overpressured source rocks beneath the Ledong field are in aqueous phase and/or in mixed phase, and migrate upward to the shallow normal pressure or near normal-pressure reservoirs by the drive of the abnormal pressure. However, once the gases are pumped out of the overpressured source rocks through the diapiric faults and fractures, and enter into the nearby normal pressure reservoirs with good permeability, the upward migration to a lower pressure environment could take place by buoyancy, perhaps together with pressure differential.

Seismic reflection data (Fig. 11) show that the diapirs are separated by high angled fracture and contemporaneous faults caused by overpressure discharge. These fractures and faults vertically extend from several meters to two kilometers, and can cut through the Miocene sediments (Fig. 11). The deep source rocks in the Meishan and Sanya formations were cut through by the faults along which the gases migrate vertically to Pliocene and Quaternary reservoirs. Overpressured fluids and gases migrated up along these faults and fractures to cause the pressure to drop rapidly in the system, and then the fractures and faults closed until the next diapiric episode, reactivated by the next build-up of overpressure within the system. This process probably occurs in an interval of thousands of years (Hunt, 1990; Xie and Li, 1999). Although the Ledong field is young, the focused and episodic gas migration with high hydrocarbon expulsion efficiency can be responsible for a large scale of gas accumulation within very short time spans.

4.5. Episodic accumulation model of gas pools

Based on the above discussion, the following multi-source and episodic model has been proposed for the gas accumulation in the Ledong gas field (Fig. 12; Table 3).

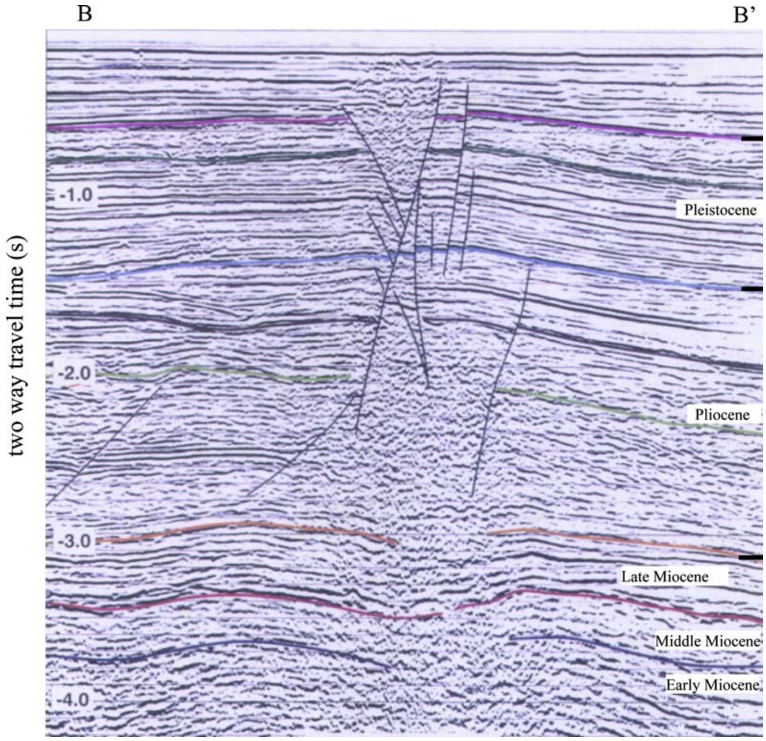

Fig. 11. Seismic profile through the L81 diapiric structure, showing the diapir piercing zone and associated faults. The diapir is separated by high angled faults. The location of seismic section is shown in Fig. 1.

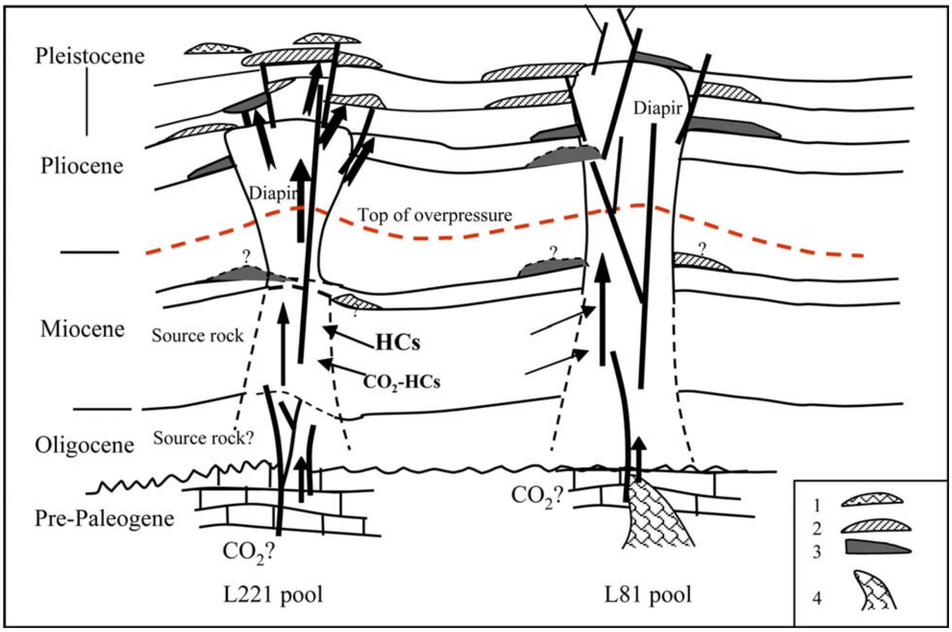

Fig. 12. Gas migration pathways and accumulation model of the Ledong diapir zone, Yinggehai Basin. (1) In situ biogenic gas; (2) Thermogenic hydrocarbon-rich gas; (3) CO_2 rich gas; (4) Igneous intrusion.

When the early shallow traps were formed above the Ledong diapirs, a small amount of biogenic gas generated from the shallow Pliocene and Quaternary source rocks could migrate into adjacent reservoirs within the same stratigraphic intervals. During this period, the Miocene source rocks in the overpressured compartment reached the main stage of gas generation, but the generated gases were difficult to move out of the source rocks into shallow reservoirs due to the lack of efficient migration channels. Accompanying diapir development, abundant hydrocarbon gases and some amounts of nitrogen and organic derived CO_2 were spilled into the shallow reservoirs along the forming diapir structures and associated faults.

With the continued basin subsidence, the calcareous shales in the lower Miocene strata eventually reached the threshold temperature for thermal decomposition (about 300 °C – Cathles et al., 1990) to release a large amount of CO_2. At the same time, reactivation of diapiric faults and deep seated faults induced by the trans-extensional movement of the basin provided pathways for upward CO_2 migration. An earlier study (Huang et al., 2003) suggested that some of the CO_2 came from the possible magmatic degassing. Gases introduced into the reservoirs during the late stage injection included abundant CO_2 and a little hydrocarbon with relatively high $\delta^{13}C_1$ values. The L81 gas pool, with more abundant CO_2 than the L221 Gas Pool (Table 1), clearly shows a stronger piercing intensity, as indicated from seabed pockmarks and seepages over the pool (Xie and Li, 1999; Huang and Zhang, 1992).

Clearly, in a diapir-related petroleum system, faults associated with diapir activities act as main pathways, and the deep overpressures provide an excellent driving force for the migration of deeply sourced gases. Consequently, the transitional pressure zone in/around the diapir structures should be an ideal location for gas accumulation, in addition to the shallow diapir structures in the Yinggehai Basin.

5. Conclusions

This study demonstrated that the natural gases from the Ledong gas field in the Yinggehai Basin, offshore South China Sea have complex origins. The major sources for the thermogenic gaseous alkanes and associated organic CO_2 and N_2 are the Sanya and Meishan formations in the central depression of the Yinggehai Basin. Abundant inorganic CO_2 is mostly derived from thermal decomposition of carbonate minerals in deep Cenozoic and pre-Cenozoic carbonates, with a possible minor contribution from the mantle. As indicated from the chemical and isotopic compositions of gases, multiple filling phases occurred as the result of the focused, episodic, and rapid upward migration of deeply sourced gases. The episodic gas migration with high hydrocarbon expulsion efficiencies from several excellent source rocks was responsible for a large gas accumulation in the Ledong gas fields during a short period of 1.2 to 0.1 Ma. Because faults associated with diapiric activities controlled gas migration and occurrence, future exploration should focus on both the shallower payzones and the transitional pressure zones in and around the diapir structures of the basin.

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