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Genesis and Accumulation Period of CO_2 Gas Reservoir in Hailar Basin

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Abstract: Gas reservoirs with high CO_2 have been found in several wells in the Hailar Basin. In this paper, a composition analysis, stable carbon isotope analysis, and a rare gas helium isotope $^3He/^4He$ and argon isotope $^{40}Ar/^{36}Ar$ analysis were carried out. These comprehensive analyses show that the CO_2 in the Hailar Basin is inorganic-origin gas, which generally has the characteristics of crust–mantle-mixed CO_2, and the fraction of helium of mantle source can reach 15.12~18.76%. There are various types of CO_2 gas reservoirs. CO_2 gas mainly comes from deep crust. The distribution of gas reservoirs is mainly controlled by deep faults and volcanic rocks, as well as by reservoir properties and preservation conditions. Magmatic rocks provide gas source conditions for the formation of inorganic CO_2 reservoirs. Deep–large faults provide the main migration channels for CO_2 gas. The sandy conglomerate and bedrock weathering crust of the Nantun Formation and the Tongbomiao Formation provide favorable reservoir spaces for the formation of CO_2 gas reservoirs. The combination of volcanic rock mass and deep–large faults creates a favorable area for CO_2 gas accumulation. The age of magmatic intrusion and the homogenization temperature of oil–gas inclusions in Dawsonite-bearing sandstone indicate that 120 Ma in the Early Cretaceous was the initial gas generation period of the CO_2 reservoir and that oil and gas were injected into the reservoir in large quantities in 122~88 Ma. This period is the peak period of magmatic activity in Northeast China, as well as when the crust of Northeast China greatly changed. A large-scale CO_2 injection period occurred in 100~80 Ma, slightly later than the large-scale injection period of the oil and gas. Since the Cenozoic, the structure has been reversed, and the gas reservoir has been adjusted.

Keywords: Hailar Basin; CO_2 gas reservoir; genesis; controlling factors

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1. Introduction

CO_2 is an important mineral resource, and it has important practical value in petroleum, the chemical industry, agriculture, medicine, health and storage [1–4]. The study on the genesis of CO_2 gas reservoirs has always been one of the frontier and hot issues in the field of petroleum geology [5–15]. At present, the genesis of CO_2 is mainly divided into two categories: inorganic genesis and organic genesis [16–18]. CO_2 of organic origin is mainly formed through chemical actions, such as organic oxidation, organic thermal cracking, organic thermal degradation and organic microbial degradation [19,20]. Inorganic CO_2 is mainly formed by chemical processes, such as mantle degassing, crustal rock differentiation and carbonate thermal decomposition [21,22].

In recent years, inorganic CO_2 gas reservoirs have been found in the Songliao Basin, the Bohai Bay Basin, the Subei Basin, the Sanshui Basin and other basins in eastern China [23–27], with great exploration potential. Since the discovery of CO_2 gas in 1986, the Hailar Basin has obtained a high-content CO_2 gas flow in many wells, and the natural production capacity of a single well is generally more than 2000 m^3/d. Among these wells, 11 wells in the Wuerxun Sag have found CO_2 industrial gas reservoirs, with geological reserves of more than 10 billion cubic meters. The maximum daily gas production can reach 57,660 m^3, and the CO_2 content in the natural gas composition accounts for more than 80%, so it has great exploration potential. Other researchers have discussed the formation conditions, genesis and filling history of the CO_2 gas reservoirs in the Hailar Basin [28–33]. Based on the limitations of samples and test conditions, they failed to conduct a detailed and systematic analysis on the genesis, control factors and accumulation period of the CO_2 gas reservoirs, which restricted the understanding of oil and gas accumulation rules and the exploration of the CO_2 gas reservoirs. CO_2 gas reservoirs of different origins have obvious differences in CO_2 content, carbon isotope characteristics, and rare gas helium and argon isotope characteristics. With the support of key projects of Daqing Oilfield and the National Natural Science Foundation of China, new data were systematically supplemented. CO_2 gas samples from eight wells were collected, and the genesis of the CO_2 gas was systematically analyzed using various methods, such as a component analysis, a carbon isotope analysis, and a rare gas helium and argon isotope analysis. The control factors and the formation period of the CO_2 gas reservoirs were discussed. This is of great significance to the law of oil and gas accumulation and the exploration of CO_2 gas reservoirs in the basin.

2. Regional Geological Background

The Hailar Basin is an important replacement area for oil and gas exploration in Daqing Oilfield, located at 115°30 east longitude′~120°00′, 46°00 N′~49°20′. The basin covers a total area of 70,480 km^2. The basin is generally characterized as being high in the east and low in the west. Bounded by the Derbugan fault, it belongs to the Erguna fold system in the west and the Inner Mongolia Daxinganling fold system in the east. The Hailar Basin is located at the border of the two fold systems. It is a Meso–Cenozoic faulted basin superimposed on the Hercynian fold basement [34,35].

The evolution of the Hailar Basin has experienced two stages: fault depression (Tongbomiao period–Yimin period) and depression (Qingyuangang period–present). Before the deposition of the Nantun Formation, there was a strong subsidence period, and thick volcanic rock and the sandy-conglomerate formation were deposited. Tectonic movement occurred at the end of the Nantun period, resulting in the unconformity between the Damoguaihe Formation and the Nantun Formation, which is characterized as being strong in the southeast and weak in the northwest. The Damoguaihe stage has strong faulting and a large sedimentary thickness. The Yimin stage I settlement is strong, and the settlement occurs in the faulted area. The subsidence amplitude of Yimin phase II became smaller, but the sedimentary range expanded, and the uplift began to sink and transform into a depression. The structural change at the end of Yimin resulted in the emergence of thrust faults in some areas, and normal flower structures or up reverse and down normal faults in some areas. It was transformed into a depression in the Qingyuangang period.

At present, the basin has a structural pattern of two uplifts and three depressions, namely, the Zalainuoer depression, the Sagang uplift, the Beier lake depression, the Bayanshan uplift and the Huhehu depression, as shown in Figure 1, and these are further subdivided into 16 depressions and 4 bulges [36]. The basement of the basin is Hercynian–Indosinian granite and the strata of the Budate Group and Xing'anling group. The basin is filled with Jurassic, Cretaceous, Tertiary and Quaternary. The Cretaceous is the main deposit in the basin. From the bottom to the top, it is Tongbomiao Formation, Nantun Formation, Damoguaihe Formation, Yimin Formation and Qingyuangang Formation.

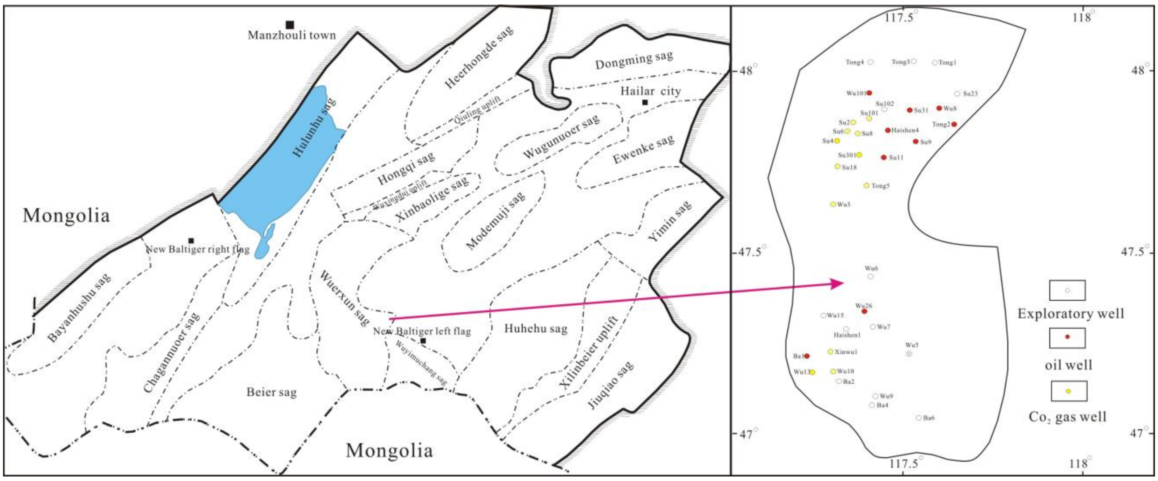

Figure 1. The location and drilling distribution map of Wuerxun depression.

3. Genetic Analysis of CO_2 Gas Reservoir

The study of CO_2 genesis is an important issue in the field of CO_2 research. CO_2 genesis is a key factor in controlling CO_2 distribution, and determining the genesis of CO_2 is the premise of mastering the law of CO_2 enrichment [37]. The identification of CO_2 genesis is mainly based on geochemical methods, such as rare gas abundance and the isotope ratio in natural gas, combined with the geological conditions of the natural gas reservoir's formation [38–41]. The gas samples of the Nantun Formation and the Tongbomiao Formation in different well sections of well Su 2, well Su 6, well Su 12, well Su 16, well Wu 10, well Wu 13, well Xin Wu 1 and well Hai can 3 were collected for gas testing, including gas component testing, carbon isotope testing, and rare gas helium and argon isotope testing.

3.1. CO_2 Content Analysis

More than 60% of carbon dioxide in natural gas is of inorganic origin, less than 20% is of organic origin, and the remainder is of mixed organic and inorganic origin [42]. Therefore, the genesis of natural gas reservoirs can be analyzed by measuring the content of CO_2 in the natural gas reservoir. According to the analysis results in Table 1, the content of CO_2 in the natural gas is greater than 60%, except for in well Wu 13, where the content of CO_2 is more than 90%, which is far greater than the limit of organic and inorganic dioxide gas reservoirs by 60%. It is a typical inorganic carbon dioxide gas reservoir [42].

Table 1. Characteristics of natural gas composition in Hailar Basin.

Well Number	Horizon	Well Section (m)	Gas Composition (%)				$\delta^{13}C_{PDB}$				Yield (m^3/d)
			CH_4	C_2H_6	CO_2	He	CH_4	C_2H_6	C_2H_8	CO_2	
Su 2	K_1n_1	1434.0–1449.0	0.40		96.2	0.019	−56.96	−41.19	−31.59	−11.35	22,191
Su 2	K_1n_1	1464.0–1490.8	0.471		96.2	0.198	−47.64	−41.19	−31.59	−8.2	2233
Wu 10	K_1t	1778.0–1921.6	2.16	0.18	97.6	0.003	−49.25	−31.57		−11.36	2000
Wu 13	Pz	1732.5–1747.0	20.22	1.49	78.25	0.04	−47.5	−37.59	−40.35	−8.78	32,487
Xin Wu 1	K_1n_1	1557.2–1579.0	5.92	0.59		0.18	−47.34	−36.12	−33.55		2300
Su 6	K_1n_1	2010.0–2024.0	1.65		98.8	0.008	−36.2			−10.2	57,660

3.2. Carbon Isotope Analysis

A carbon isotope analysis is an effective method for the identification of organic and inorganic carbon dioxide [43,44]. The organic genesis $\delta^{13}C_{CO2}$ value is less than −10‰, mainly in the range of −30~−10‰. The inorganic genesis $\delta^{13}C_{CO2}$ value > −8‰, mainly in the range of −8~3‰. Among the inorganic carbon dioxide, there are those with a carbonate-metamorphic-origin $\delta^{13}C_{CO2}$ value close to that of the carbonate rock $\delta^{13}C_{CO2}$ value, about 0 ± 3‰. Volcanic-magmatic-origin and mantle-origin $\delta^{13}C_{CO2}$ values are mostly in the range of −6 ± 2‰. Carbon dioxide in the range of −10~−8‰ is generally carbon dioxide of mixed organic and inorganic origins [42–45].

According to the data in Tables 1 and 2, the carbon isotope of the carbon dioxide $\delta^{13}C_{PDB}$‰ value is −13.6~−1.4‰, and according to the diagram of CO_2 $\delta^{13}C_{PDB}$‰ and CO_2 content by Dai Jinxing (1995), the CO_2 gas reservoir in the Hailar Basin belongs to magmatic volcanic inorganic gas, as shown in Figure 2 [46]. Regarding the CO_2 of the newly tested gas sample, the low value of $1\delta^{13}C_{PDB}$‰ may be caused by the mixing of deep magma in the middle and lower crust and then entering the sedimentary rock along the deep fault.

Table 2. The natural gas methane and series isotope test result in Hailar Basin.

Well Number	Horizon	Well Depth (m)	Carbon Isotope $\delta^{13}c_{pdb}$ C$_1$	CO$_2$	C$_2$	C$_3$	iC$_4$	nC$_5$
Haishen 3	t	2068–2094	−41.6	−1.4	−29.9	−27.4	−24.5	−26.4
Su 16	n_2	1771.4–1655.8	−51.5	−11.1	−42.1	−31.9		
Su 12	n_1	1491.8–1508.6	−52.4	−13.6	−43.5	−35.8		

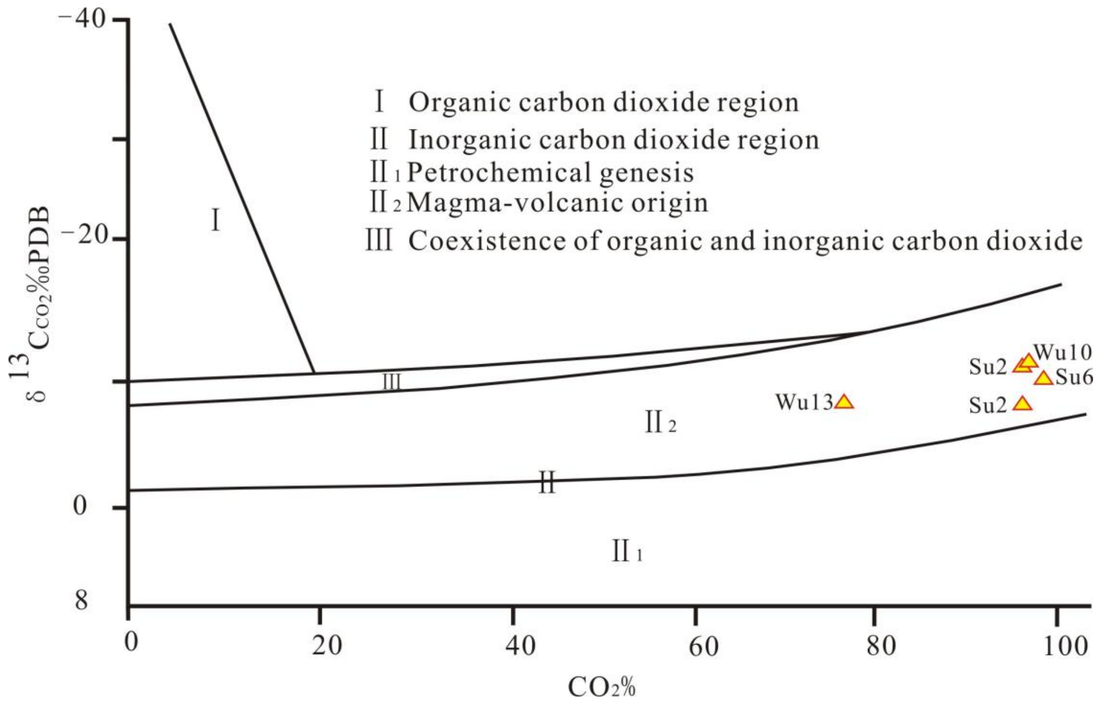

Figure 2. The discrimination map of CO_2 reservoir in Wuerxun depression of Hailar Basin.

3.3. Helium and Argon Isotope Analysis

In the isotopic composition of rare gases, ^{3}He and ^{36}Ar are generally considered to be the original components of the Earth, and there are few exogenous additives in the process of Earth evolution. However, ^{40}Ar and ^{4}He are the products of U, Th and K radioactive decay, and their yield is exponentially related to time; that is, ^{40}Ar formed by radiogenesis has an obvious chronological accumulation effect [47–49]. Helium and argon in natural gas come from the atmosphere, crust and mantle [49,50]. It is found that, compared with rare gases of crust origin, rare gases of mantle origin are relatively more enriched in ^{3}He and ^{40}Ar. The combination of a high $^3He/^4He$ value and a high $^{40}Ar/^{36}Ar$ value should be a typical characteristic of mantle-derived materials, while the combination of a low $^3He/^4He$ value and a low $^{40}Ar/^{36}Ar$ value should be a characteristic of typical shell-derived materials. $^3He/^4He$ and $^{40}Ar/^{36}Ar$ values can be used to identify the different sources of helium and argon.

The determination of helium isotope in natural gas associated with carbon dioxide is an indirect index used to identify the origin of carbon dioxide [50,51]. That is, atmospheric helium V(^{3}He)/V(^{4}He) is 1.4×10^{-6}, shell source helium V(^{3}He)/V(^{4}He) is 2×10^{-6}, and mantle-derived helium V(^{3}He)/V(^{4}He) is 1.1×10^{-5}. The ratio of sample helium isotope (R) to air helium isotope (Ra) is usually used to judge whether mantle-derived helium is mixed [45–50]. If the R/Ra value is greater than 1, it indicates the mixing of mantle-derived helium. If the R/Ra value is less than 1, it indicates shell-derived helium. When R/RA > 2, it is generally considered to be volcanic-mantle-derived helium, and the helium between them is helium mixed with crust and mantle [45–50].

According to the helium isotope analysis results, the R/RA values of wells Su 12, Su 16 and Su 6 are 1.26, 1.2 and 1.49, respectively, as shown in Table 3. It can be seen from the data on the discrimination map of helium isotope that it belongs to the origin of crust–mantle-mixed type, as shown in Figure 3. According to the helium isotope analysis and the judgment criteria of mantle-derived gas and crust-derived gas, the ^{3}He/^{4}He ratio of the Nantun Formation samples from wells Su 12, Su 16 and Su 6 is of the order of 10^{-6}, indicating that there is exchange and recombination between the volatiles of the crust and mantle. The end component values of the crust and mantle can be used to calculate their respective proportions according to the binary recombination model: $^3He/^4He_{mixing} = {}^3He/^4He_{mantle}X + {}^3He/^4He_{crust}(1 - X)$. The calculated fractions of mantle-derived helium in the natural gas of the Nantun Formation of wells Su 12, Su 16 and Su 6 are 15.85%, 15.12% and 18.76%, respectively. The calculation results show that the natural gas is of a shell source, the helium in the natural gas is mixed with mantle source helium to varying degrees, and the mixing proportion is 15.12–18.76%.

Table 3. The natural gas He and Ar isotope test result in Hailar Basin.

Well Number	Horizon	Well Depth (m)	Sampling Container	Sample's R = ^{3}He/^{4}He Value	Analysis Data		
					R/Ra	^{38}Ar/^{36}Ar	^{40}Ar/^{36}Ar
Su 12	n_1	1491.8–1508.6	steel cylinder	$(1.76 \pm 0.05) \times 10^{-6}$	1.26	0.1907(9)	996(6)
Su 16	n_2	1771.4–1655.8	steel cylinder	$(1.68 \pm 0.05) \times 10^{-6}$	1.2	0.1900(9)	916(5)
Su 6	n_1	2010.0–2024.0	steel cylinder	$(2.08 \pm 0.05) \times 10^{-6}$	1.49	0.1837(6)	289.6(5)

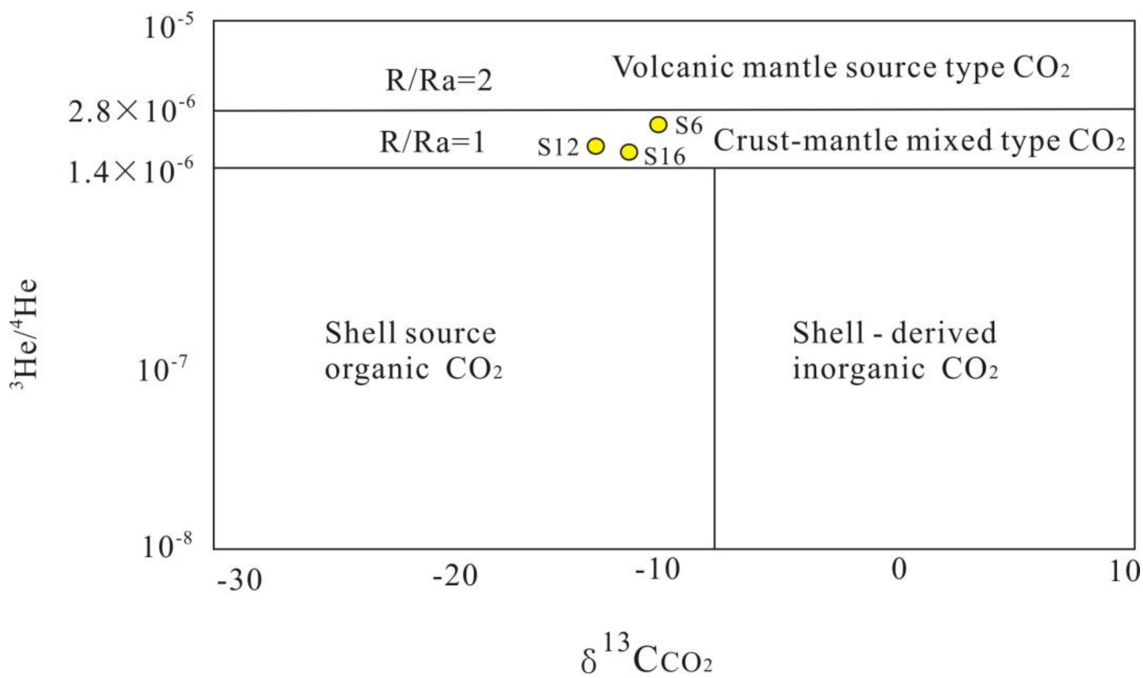

Figure 3. Helium isotope genetic discrimination map of Wuerxun depression of Hailar Basin.

In addition, the $^{40}Ar/^{36}Ar$ values of the three samples are 996, 916 and 289.6. Except for well Su 6, the first two values are far greater than the air argon isotope value of 295.5, indicating that they are inorganic gas reservoirs, which originate from deep crust and are related to deep faults and magmatic rock mass activities.

In addition, according to the $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ ratio projection points in Table 3, the isotopic values of helium and argon mixed into the gas reservoir fall at the upper part of the air isotopic ratio, and the $^{40}Ar/^{36}Ar$ values of wells Su 12 and Su 16 increase accordingly with the increase in the $^{3}He/^{4}He$ value, which has the characteristics of a crust–mantle-mixed gas reservoir, as shown in Figure 4.

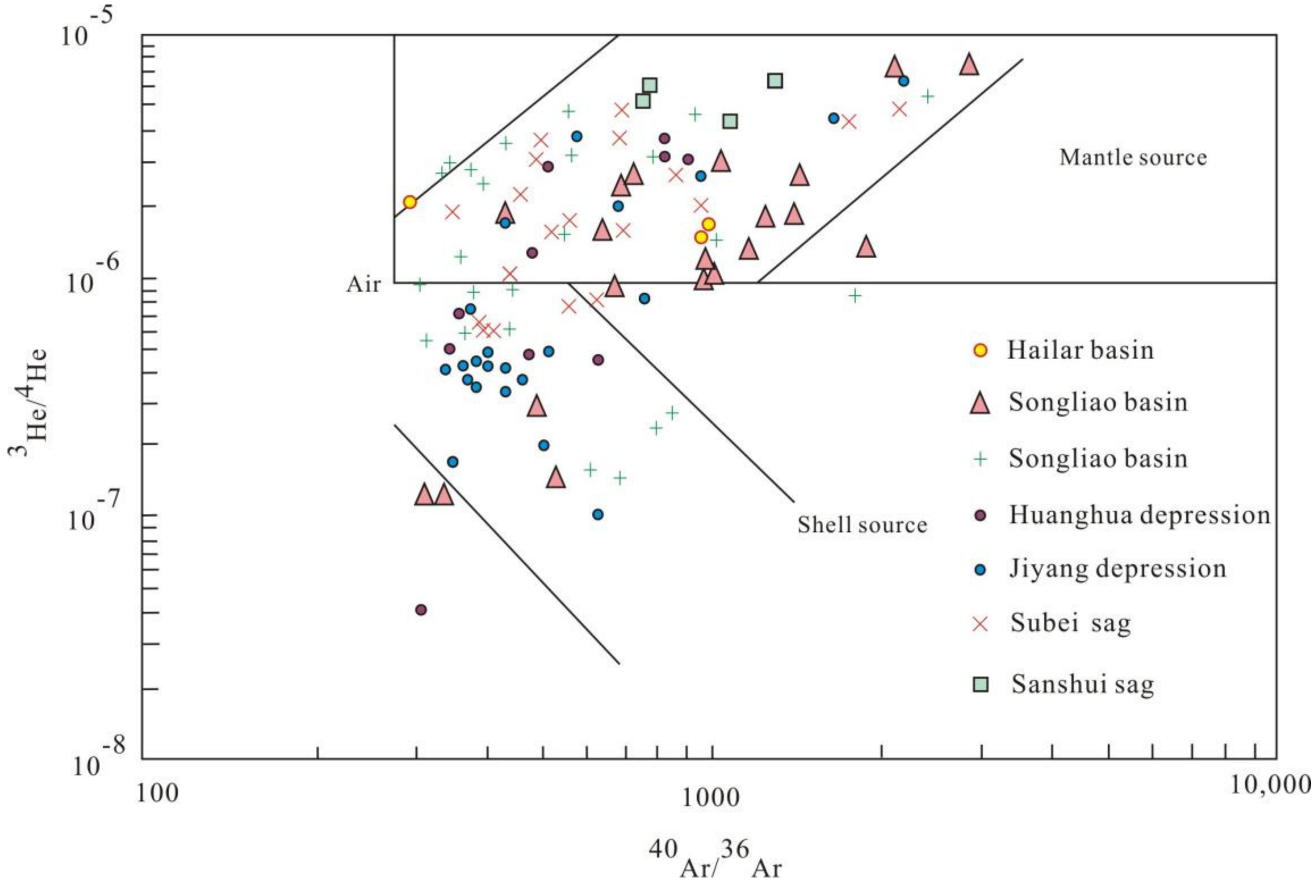

Figure 4. Diagram of 3He/4He and 40Ar/36Ar in Wuerxun depression of Hailar Basin (according to Xu Yongchang, 1996, modified).

4. Controlling Factors

The Hailar Basin is a faulted basin with deep basement faults and developed volcanic rocks [52]. The deep fault connects the gas source rock with the overlying sedimentary layer, which makes the deep source inorganic gas migrate to and accumulate in the uplift zone related to the deep fault and the overlying sandy conglomerate reservoir of the Nantun Formation. There are three main types of CO_2 gas reservoirs in the Hailar Basin: ① Fault anticline structural gas reservoirs: most of the discovered gas reservoirs are formed by fault shielding or by the combination of faults and structures, for example, the suliu-3 CO_2 gas reservoir revealed by well Su 2 and the Suwu-15-I CO_2 gas reservoir revealed by well Su 3. ② Fault block structural gas reservoirs: for example, the well Su 6 gas reservoir is obviously blocked by faults, which is a fault-block structural gas reservoir. ③ Buried hill gas reservoirs: this type of CO_2 gas reservoir, such as the Paleozoic buried hill gas reservoir revealed by the Wu 13 well, is mainly composed of bedrock weathering crust.

There are various types of CO_2 gas reservoirs in the Hailar Basin, the reservoir-forming mechanism is complex, and the gas reservoir distribution is affected by many factors. CO_2

gas reservoirs are mainly controlled by the distribution of deep and large faults and volcanic rocks, as well as reservoir, caprock and preservation conditions [28,29]. According to the analysis of the CO_2-gas-reservoir-forming system in the Hailar Basin, the activities of magma and deep faults provide the material basis of CO_2 gas reservoir formation. Deep faults provide the channels of CO_2 gas transportation, and the sandstone of the Nantun Formation, the sandy conglomerate of the Tongbomiao Formation and bedrock weathering crust are favorable reservoirs of CO_2 gas. The mudstone of the Nantun Formation is a good local caprock, and the mudstone of the first member of the Damoguaihe Formation is a good regional caprock.

(1) Magmatic rock mass provides gas source conditions for the formation of inorganic CO_2 gas

Magma is the carrier of the occurrence and migration of deep gas sources. Tectonic activities, especially fault activities, provide favorable conditions for the upward movement and eruption of magma. At present, most of the CO_2 gas reservoirs discovered in the world are distributed in geological history or modern volcanic activity zones [1,2]. The well-known high-CO_2 gas reservoirs found in Tampico, Mexico, the eastern foothills of the Rocky Mountains in the United States, Sicily, Italy and the eastern basins of China are all in magmatic areas [1,12,33]. The gas ejected from volcanos is rich in CO_2, and the discovered CO_2 gas reservoir is very close to the ancient crater or magmatic intrusion. There are three stages of Mesozoic volcanism in the Hailar Basin, and the volcanic activity lasted from the Late Jurassic to the Early Cretaceous [52]. During the volcanic activity, the deep fault had strong tension, the magma upwelled along the deep fault, and the CO_2 gas released by the exothermic and depressurization of the intrusive rock mass provided the material basis for the formation of the CO_2 gas reservoir. CO_2 gas reservoirs with industrial value have been found successively in the surennor and Bayantala areas of the Wuerxun Sag in the Hailar Basin, and the distribution of gas reservoirs is closely related to magmatic rock mass, as shown in Figure 5. No carbonate strata have been found in the deep wells of the basin. CO_2 gas belongs to magmatism; that is, it is controlled by Yanshanian magmatism.

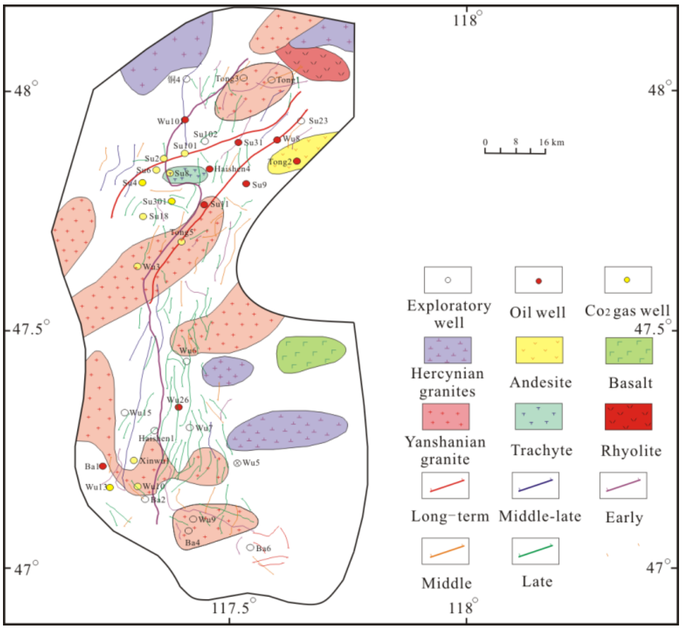

Figure 5. Distribution map of CO_2 gas reservoir and rocks of Wuerxun depression in Hailar Basin (according to Liu Qun, 2007, modified).

(2) Deep faults provide the main channels of CO_2 gas migration

The distribution of faults has a strong control over the formation of carbon dioxide gas reservoirs. Faults provide migration channels and reservoir space for the formation of CO_2 gas reservoirs [53]. In the Early Mesozoic, the Hailar Basin was affected by the high-temperature field, which caused the uplift of upper mantle materials to produce faults. In the Early–Middle Jurassic, affected by the Yanshan movement, the fault activity in the region intensified, forming a complex fault system and becoming a vertical channel for CO_2 gas migration. At the same time, the energy released by the upwelling of high-temperature and high-pressure thermal materials in the mantle could also provide power for the migration of CO_2. Although the production horizon and reservoir lithology of the Hailar Basin are different, CO_2 gas is distributed near deep faults and Yanshanian granite intrusions, as shown in Figure 5, reflecting the genetic relationship between CO_2 gas and deep faults [53]. The faults in the Hailar Basin are relatively developed. According to the fault activity period, the faults are divided into early, middle, late and long-term inherited faults. The early fault formed before the deposition of the Tongbomiao Formation, the middle fault is the deposition period of the Nantun Formation–Damoguaihe Formation, the late fault is the deposition period of the Nantun Formation–Yimin Formation, and the long-term fault is the deposition period of the Tongbomiao Formation up to now①. Well Su 2, well Su 101 and well Su 6, with a high CO_2 content, are distributed near deep and large faults, as shown in Figures 5 and 6. Volcanic channels have been found in line 381 of the Wuerxun Sag, line 5 of the Beier Sag, and lines 545 and 992 of the Huhehu Sag in the Hailar Basin. These volcanic channels are connected to faults, providing favorable migration channels for deep source inorganic genetic gas.

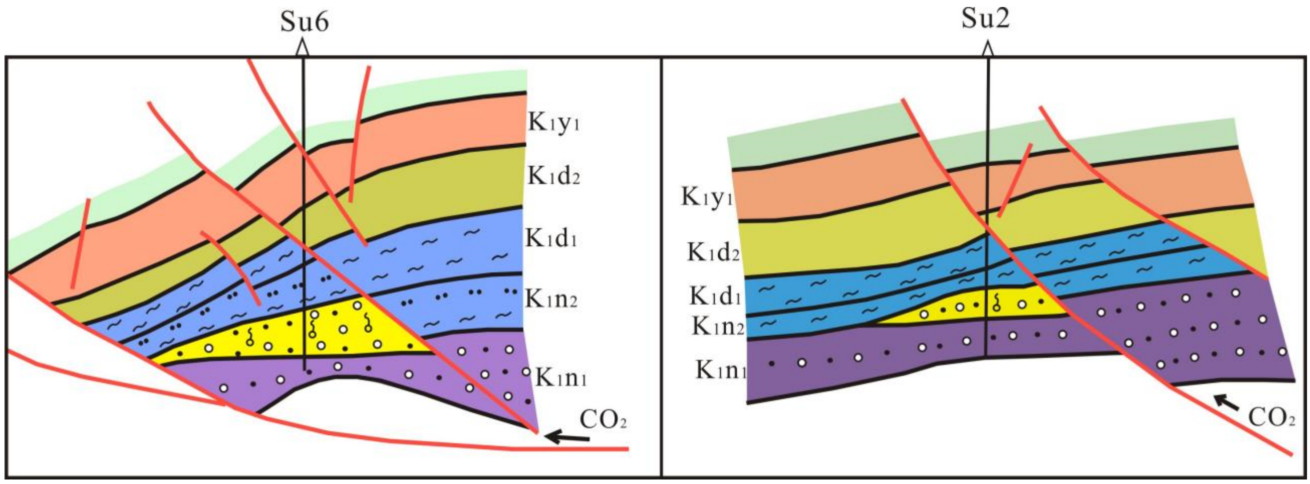

Figure 6. Relationship between CO_2 reservoir and deep faults in Wuerxun depression of Hailar Basin.

The distribution of faults has a strong control over the formation of carbon dioxide gas reservoirs. Not only do faults provide channels and storage space for carbon dioxide migration, but the whole basin is also dominated by extensional faults in the early stage and compressional faults in the late stage. This feature can block the carbon dioxide gas reservoir formed in the early stage and form good traps, which are conducive to carbon dioxide storage. However, not all faults can be used as transport channels or storage spaces for carbon dioxide gas, and only those faults connected to deep magmatic rocks carrying carbon dioxide gas can be used as effective gas source faults.

(3) Reservoir physical properties and caprock have a certain control over the enrichment of CO_2 gas

CO_2 gas reservoirs in the surennor area of the Hailar Basin are mainly distributed in the sandy conglomerate of the first member of the south. The porosity is generally 4.7~17.41%, up to 17.41%, and the average permeability is 0.3~6.2 × 10^{-3} μm^2, as shown in Table 4. The pore types are mainly intergranular pores and secondary pores. The cumulative thickness of the gas-bearing sandstone in well Su 2 in this area is 40–200 m, up to 267.8 m. At the same time, the surennor area is close to the huangde zagen hure fault. Controlled by the deep fault, fractures are developed, which improves the physical conditions and easily forms an enrichment area of CO_2 gas. The stably distributed mudstone caprock is very important for the formation and preservation of oil and gas reservoirs in complex fault-block areas. Not only can the mudstone, with a large thickness and stable distribution, seal oil and gas in a large area horizontally, but it can also cooperate with faults to form important lateral lithologic plugging conditions. Argillaceous rocks are developed in the first member of the Damoguaihe Formation in the Hailar Basin, with a thickness of 201–326 m, covering about 90% of the development thickness of the layer, and a single layer thickness of 35–70 m. It is a stable lacustrine deposit and a good regional caprock. A good reservoir cap combination provides favorable reservoir space and sealing conditions for CO_2 gas accumulation.

Table 4. Reservoir physical property statistics of CO_2 gas well in Hailar Basin.

Well Number		Tong5	Su 2	Su 3	Su 4	Su 6	Su 8	Su 101
Naner section	porosity (%)	10.0–16.5 13.4/57	3.51–10.12 6.8/19	6.54–16.87 9.4/44	3.13–18.93 10.3/60	4.8–13.5 10.1/54	10.1–12.8 11.5/2	2.81–20.82 10.7/114
	permeability (10^{-3} μm^2)	/	/	0.03–15.9 6.2/44	0.05–26.4 1.0/60	0.03–6.04 0.3/54	/	0.02–25.2 5/114
Nanyi section	porosity (%)	4.7–16.1 11.3/19	8.37–17.02 12.2/28	/	8.57–15.58 12.1/15	/	8.3–17.4 12.9/67	8.21–17.41 10.7/114
	permeability (10^{-3} μm^2)	/	0.05–12.5 1.1/28	/	0.19–5.31 2.0/15	/	/	0.24–14.9 6.4/114

5. Discussion

The Hailar Basin is located at the eastern end of the Inner Mongolia Xing'an Paleozoic geosynclinal fold system. In the Early Mesozoic, due to the influence of Variscan movement and the high-temperature field, the upper mantle material uplifted and faulted. The uplift of the mantle and the upwelling of the mantle plume made the upper rocks stretch and crack, and the deep magmatic melt erupted into the crust or invaded the shallow rock mass, accompanied by the release of a large number of mantle-derived magmatic fluids. The mantle-derived fluids released during the magmatic period were stored in the shallow rocks, creating conditions for the migration and accumulation of CO_2 gas [11]. The helium isotope analysis, and the judgment standard of mantle source gas and crust source gas confirm that the CO_2 gas reservoir in the Hailar Basin is a crust–mantle-mixed inorganic gas reservoir, indicating that there is exchange and recombination between crust and mantle volatiles, and the fraction of mantle source mixing can reach more than 15%.

The magmatic activity in the Hailar Basin can be divided into the Hercynian and Yanshanian periods. The Hercynian period is mainly distributed in the Bayan mountain in the middle, and cuogang and the east of Yimin River in the east. The Yanshanian period is sporadically exposed in the basin and intruded into Hercynian and Mesozoic strata in the form of rock strains and dikes (for example, Yanshanian granite can be seen in 2031.5 m of well Tong1). The intruded horizon is argon formation–Damoguaihe Formation. Volcanic intrusions can be seen on the sections of the argongxi fault, Beier Sag, Huhehu sag, Tongbomiao South and helhongde sag. CO_2 gas in different production horizons in the Hailar Basin is distributed near Yanshanian granite and trachyte, indicating that the CO_2 gas reservoir is closely related to Yanshanian magmatic intrusion [17]. According to the genetic relationship between CO_2 and magmatism, the lower limit of the CO_2 formation time can be defined by using the magmatic rock age [14]. Yanshanian granite intrusions were encountered in well Tong3, well Tong5 and well Wu 13 in the Hailar Basin. The isotopic dating result is 120 Ma, which is equivalent to the late Early Cretaceous, corresponding to the third stage of Mesozoic volcanism, Early Cretaceous Aptian (117–125 Ma) [52]. Well Su 3, well Su 6 and well Su 8 in the surennol area have drilled a set of trachyte in the Nantun Formation, which is characterized by neutral rock and belongs to the shoshonite series. The distribution area of trachyte is only in the distribution area of the CO_2 gas reservoir, as shown in Figure 5. A regional correlation of the stratigraphic age of this set is the late Early Cretaceous [54]. The intrusion and eruption of magma is actually a gas generation period or gas generation peak of inorganic gas. Therefore, 120 Ma of the magma intrusion period in the late Early Cretaceous can be regarded as the initial degassing period of CO_2 gas in the basin [30].

The earliest stage of CO_2 gas released from mantle-derived magma can be constrained by the isotopic age of igneous rocks. The homogenization temperature method of saline inclusions at the same time in CO_2 gas reservoirs is used to estimate the age of CO_2 charging [14]. The authigenic mineral assemblages formed before CO_2 gas injection are mainly secondary enlarged quartz and kaolinite. After CO_2 gas injection, in addition to some gas reservoirs, carbonate minerals, such as allite and andolomite, can form. Dawsonite is a "tracer mineral" for CO_2 migration and accumulation, and it records the period of CO_2 migration and accumulation [54,55]. According to the homogenization temperature of primary hydrocarbon-containing saline inclusions on lamalite and andolomite in the samples of the second member of the Nantun Formation in wells Haichan 4, Su 16, Su 12, Su 101 and Su 302 tested by Gao Yuqiao (2007), the low-temperature group was 87~96 °C, indicating that the injection period of the CO_2 gas reservoir was 100~80 Ma, as shown in Figure 7 [31]. This period is also the main accumulation period of the mantle-derived CO_2 gas reservoirs in the Songliao Basin [55].

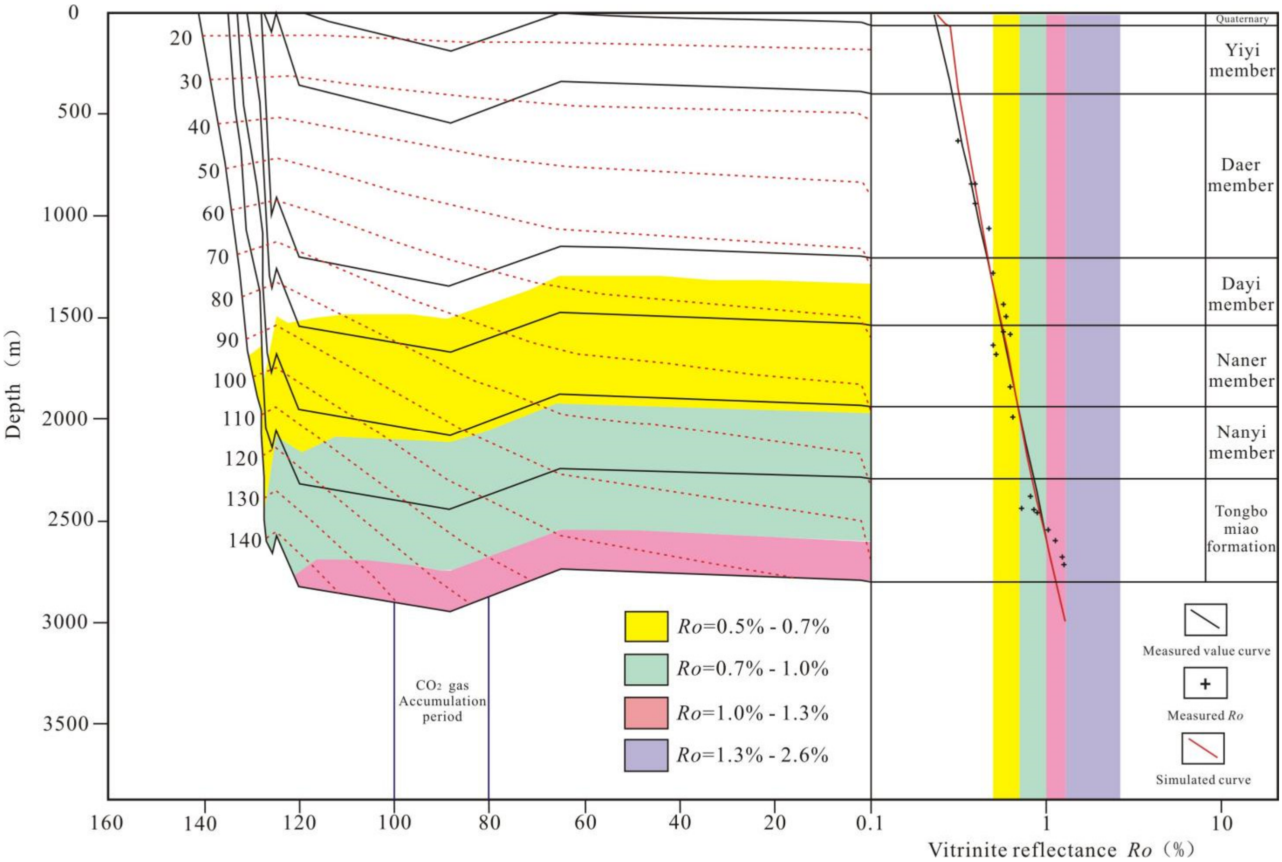

Figure 7. Thermal history of Haishen 4 in Wuerxun depression and accumulation period of CO_2 reservoir in Hailar Basin.

CO_2 migration and accumulation generally go through four stages: the mantle-derived magma rising stage, the primary degassing stage, the secondary gas release stage and the CO_2 trap accumulation stage of CO_2 gas [14]. During the Aptian period of the Early Cretaceous, the Pacific plate subducted in the SW direction, and strong tension occurred in the northeast, resulting in the uplift of upper mantle material and fractures [15]. The uplift of the mantle and the upwelling of the mantle plume made the upper rocks stretch and crack, and the deep magmatic melt erupted into the crust or invaded the shallow rock mass, accompanied by the release of a large amount of mantle-derived magmatic fluids. The released mantle-derived fluids were stored in the shallow rocks and are the source of inorganic CO_2. At the same time, the deep fault activity provided a channel for CO_2 upwelling, as shown in Figure 8. The isotopic age of the Yanshanian granite in the Hailar Basin is 120 Ma, which should be the initial degassing period of CO_2 gas in the basin. This period corresponds to the 130~120 Ma period of strong magmatism in Northeast China, which is the peak of magmatic activity in Northeast China. This period is the time of major changes in the crust in Northeast China [56]. The Hailar Basin was in the stage of faulted depression in the Early Cretaceous, which was dominated by large and rapid subsidence and deposition, accompanied by strong volcanic eruptions, forming a high geothermal field and accelerating the maturation and evolution of source rocks. A thermal history simulation shows that this period is also the period of the formation of the maximum paleotemperature and the period of large-scale oil and gas injection. According to the homogenization temperature of fluid inclusions and the thermal history simulation, the large-scale CO_2 injection and reservoir-forming period occurred in 100~80 Ma, slightly later than the peak of magmatic activity in Northeast China. Since the Late Cretaceous, the Hailar Basin has entered the depression development stage. Due to uplift, the lake basin shrinks, the subsidence amplitude decreases, the formation temperature decreases, and the oil and gas redistribution and recombination in the early formed oil and gas reservoirs form new oil and gas reservoirs.

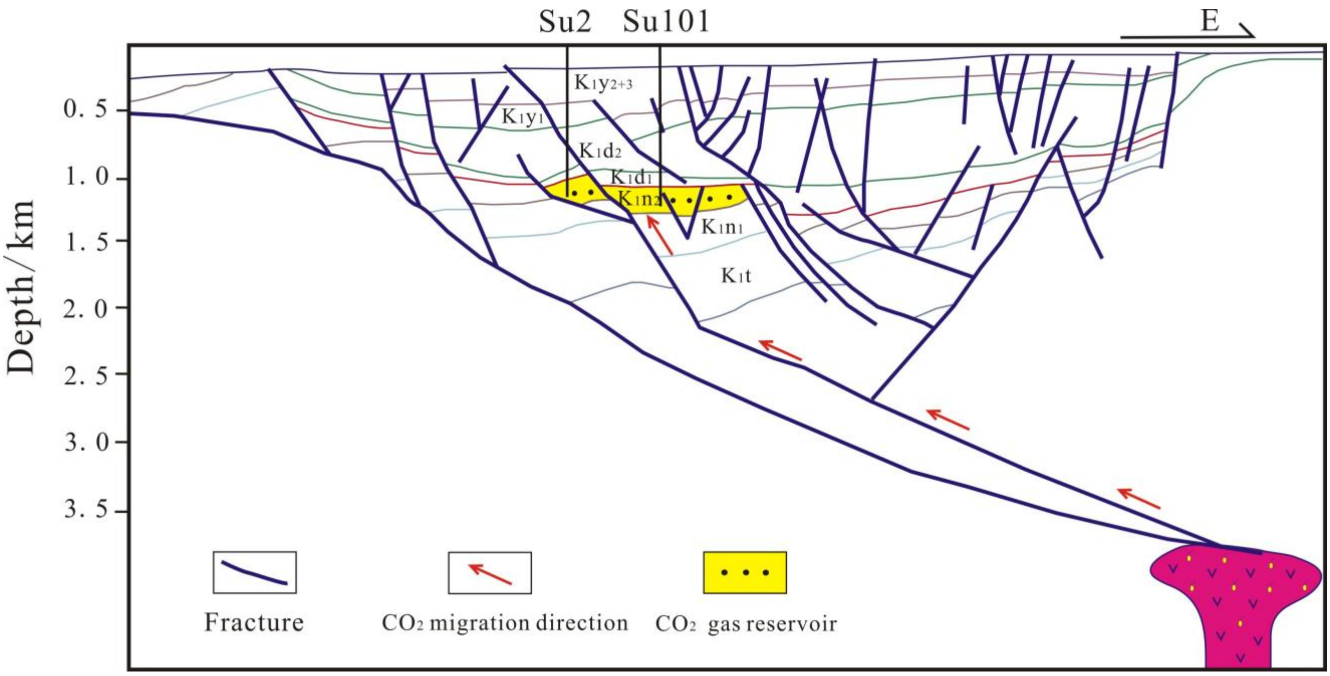

Figure 8. Forming mode of CO_2 reservoir in Wuerxun depression of Hailar Basin.

6. Conclusions

1. Natural gas reservoirs with a high CO_2 content have been found in many wells in the Hailar Basin. The CO_2 content is more than 90%, except for in Wu 13. The stable carbon isotope is distributed in the range of -13.6~-1.4‰, and the $^3He/^4He$ value of rare gas helium isotope is 1.68×10^{-6}~2.08×10^{-6}. The R/Ra value is 1.2~1.49; the $^{40}Ar/^{36}Ar$ values of noble gas argon isotopes are 289~996. The above comprehensive analysis shows that the CO_2 gas in the Hailar Basin is inorganic gas, which generally has the characteristics of crust–mantle-mixed CO_2 gas, and the fraction of mantle-derived helium can reach 15.12–18.76%. CO_2 gas mainly comes from the deep crust and is related to deep faults and magmatic rock mass activities.

2. The distribution of CO_2 gas reservoirs in the Hailar Basin is mainly controlled by the distribution of deep faults and volcanic rocks, as well as the reservoirs' physical properties and preservation conditions. Magmatic rock mass provides gas source conditions for the formation of inorganic CO_2 gas reservoirs. Deep faults provide the main channels of CO_2 gas migration. The sandy conglomerate of the Nantun Formation and Tongbomiao Formation provides favorable reservoir space for the formation of CO_2 gas reservoirs. The overlying mudstone of the Nantun Formation and Damoguaihe Formation has a good regional caprock. The composite part of the volcanic rock mass and deep fault is a favorable CO_2 gas accumulation area.
3. The age of magmatic intrusion and the homogenization temperature of oil–gas inclusions in the oil-bearing sandstones indicate that the initial degassing period of CO_2 gas was 120 Ma in the Early Cretaceous, which was the peak of magmatic activity in Northeast China and the period of great crustal changes in Northeast China. The CO_2 large-scale injection occurred at 100–80 Ma, slightly later than the oil and gas large-scale injection. The adjustment period of the oil and gas reservoir is from the Late Cretaceous.

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Data Availability Statement: All data related to this manuscript, including natural gas composition, stable carbon isotope, rare gas helium isotope $^{3}He/^{4}He$ and argon isotope $^{40}Ar/^{36}Ar$, have been fully submitted to and are available from the editorial board.

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References

1. Zhu, Y. Significance of studying CO_2 geology and the global distributive features of high CO_2-bearing gas. *Adv. Earth Sci.* **1997**, *12*, 26–31.
2. Du, L. Progress in the studies of inorganic-genetic CO_2 gas reservoirs. *Pet. Geol. Oilfield Dev. Daqing.* **2005**, *24*, 1–4.
3. Liang, C.B.; Zhong, J.H.; Qu, F.; Zhang, J.T.; Yang, Y.F. An overview of origin and accumulation of CO_2. *Spec. Oil Gas Reserv.* **2007**, *14*, 7–12.
4. Li, Z.S.; Tian, X.L.; Liu, D.L. Geological research progress of carbon dioxide in non-hydrocarbon natural gas. *Adv. Earth Sci.* **2012**, *27*, 76–81.
5. Wycherley, H.; Fleet, A.; Shaw, H. Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins. *Mar. Pet. Geol.* **1999**, *16*, 489–494. [CrossRef]
6. Zhang, T.; Zhang, M.; Bai, B.; Wang, X.; Li, L. Origin and accumulation of carbon dioxide in the Huanghua depression, Bohai Bay Basin, China. *AAPG Bull.* **2008**, *92*, 341–358. [CrossRef]
7. Dai, J.X.; Song, Y.; Hong, F.; Dai, C.S. Inorganic Genetic Carbon Dioxide Gas Accumulations and Their Characteristics In East Part Of China. *China Offshore Oil Gas* **1994**, *8*, 215–222.
8. Dai, J. Inorganic genesis of gas-bearing basins in China and their gas reservoirs. *Nat. Gas Ind.* **1995**, *15*, 22–27.
9. Dai, J.; Shi, X.; Wei, Y.Z. Inorganic petroleum theory and the Summary of Abiogenic gas deposits (fields). *Acta Pet. Sin.* **2001**, *22*, 5–10.
10. Tu, G. The discussion on some CO_2 problems. *Earth Sci. Front.* **1996**, *3*, 53–62.
11. Cheng, Y. Origins of carbon dioxide in petroliferous basins. *Adv. Earth Sci.* **2000**, *15*, 684–687.
12. He, J.X.; Xia, B.; Liu, B.M.; Zhang, S.L. Origin, migration and accumulation of CO_2 in east China and offshore shelf basins. *Pet. Explor. Dev.* **2005**, *32*, 42–49.
13. Lu, X.S.; Song, Y.; Liu, S.B.; Hong, F.; Fu, X.F. Progress in the studies of mantle-derived CO_2 degassing mechanism, degassing model and pool-forming mechanism. *Earth Sci. Front.* **2008**, *15*, 293–302.

14. Chen, H.H.; Mi, L.J.; Liu, Y.H.; Han, J.Y.; Kong, L.T. Genesis, distribution and risk belt prediction of CO_2 in deep-water area in the pearl river mouth basin. *Acta Pet. Sin.* **2017**, *38*, 119–134.
15. Zhao, F.Y.; Jiang, S.H.; Li, S.Z.; Cao, W.; Wang, G.; Zhang, H.X.; Gao, S. Abiogenic CO_2 gas reservoirs in eastern China and subduction of (paleo) pacific plate. *Earth Sci. Front.* **2017**, *24*, 370–384.
16. Schoell, M. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* **1980**, *44*, 649–661. [CrossRef]
17. Xu, Y.B.; Feng, Z.H.; Yao, D. Generation of coz gas reservoir in liangs basin. *Pet. Geol. Oilfield Dev. Daqing* **1995**, *14*, 9–11.
18. Yang, X.Y.; Liu, D.L.; Wang, B.C.; Li, Z.S.; Tan, Y.; Yang, Q. Study on formation of inorganic carson dioxide gas reservoirs. *Pet. Geol. Exp.* **2007**, *29*, 154–161.
19. Pankina, R.G. Origin of CO_2 in petroleum gases (from the isotopic composition of carbon). *Int. Geol. Rev.* **1979**, *21*, 535–539. [CrossRef]
20. Barker, C.; Takach, N.E. Prediction of natural gas composition in ultradeep reservoir. *AAPG Bull.* **1992**, *76*, 1859–1873.
21. Kennedy, B.M.; Kharaka, Y.K.; Evans, W.C.; Ellwood, A.; DePaolo, D.J.; Thordsen, J.; Ambats, G.; Mariner, R.H. Mantle Fluids in the San Andreas Fault System, California. *Science* **1997**, *278*, 1278–1280. [CrossRef]
22. Lowenstern, J.B. Carbon dioxide in magmas and implications for hydrothermal systems. *Miner. Depos.* **2001**, *36*, 490–502. [CrossRef]
23. Fu, X.F.; Song, Y. Inorganic gas and its resource in Songliao basin. *Acta Pet. Sin.* **2005**, *26*, 23–28.
24. Tan, Y.; Liu, D.L.; Li, Z.S. Geochemical characteristic of changdedong CO_2 gas reservoir in the northern Songliao basin. *Pet. Geol. Exp.* **2006**, *28*, 480–483.
25. Hu, A.P.; Dai, J.X.; Yang, C.; Zhou, Q.H.; Ni, Y.Y. Geochemical characteristics and distribution of CO_2 gas fieldsin Bohai Bay Basin. *Pet. Explor. Dev.* **2009**, *36*, 181–189.
26. Wang, J.; Liu, W.H.; Qin, J.Z.; Zhang, J.; Shen, B.J. Reservoir forming mechanism and origin characteristics in Huangqiao carbon dioxide gas field, north Jiangsu basin. *Nat. Gas Geosci.* **2008**, *19*, 826–834.
27. Yang, C.Q.; Yao, J.X. Modes of CO_2 gas reservoir formation in sanshui basin. *Nat. Gas Ind.* **2004**, *24*, 36–39.
28. Wang, J.; Zhang, H.; Lin, D.C. Exploration prospect of helium-bearing CO_2 gas reservoir in urson, Hailar Basin. *Nat. Gas Ind.* **2002**, *22*, 109–111.
29. Wang, P.Z.; Li, M.S.; Wang, J. Petroleum geology and exploration potential of Wuerxun helium-bearing CO_2 Gas reservoir in Hailaer Basin. *Spec. Oil Gas Reserv.* **2003**, *10*, 9–12.
30. Liu, L.; Gao, Y.Q.; Qu, X.Y.; Meng, Q.A.; Gao, F.H.; Ren, Y.G.; Zhu, D.F. Petrology and carbon-oxygen isotope of inorganic CO_2 gas reservoir in Wuerxun depression, Hailaer basin. *Acta Petrol. Sin.* **2006**, *22*, 2229–2236.
31. Gao, Y.Q.; Liu, L. Time Recording of Inorganic CO_2 and Petroleum Infilling in Wuerxun Depression, Hailaer Basin. *Acta Petrol. Sin.* **2007**, *25*, 574–582.
32. Gao, Y.Q.; Liu, L.; Hu, W.X.; Qu, X.Y. Petroleum displacement by inorganic CO_2 in Wuerxun depression, Hailaer basin: Evidence from fluid inclusions. *Bull. Mineral. Petrol. Geochem.* **2009**, *28*, 80–91.
33. Zhang, T.L.; Chen, J.F.; Zhu, D.F.; Zhao, X.Q. Genetic analysis of CO_2 in CO_2 gas reservoirs of middle fault zone of Hailaer-Tamtsag Basin. *J. China Univ. Pet.* **2012**, *36*, 68–75.
34. Zhang, X.D.; Liu, G.D.; Wang, J.L. Tectonic characteristics and evolution of hailaer basin. *Pet. Geol. Exp.* **1994**, *16*, 119–127.
35. Zhang, Y.Q.; Zhao, Y.; Dong, S.W.; Yang, N. Tectonic evolution stages of the Early Cretaceous rift basins in Eastern China and adjacent areas and their geodynamic background. *Earth Sci. Front.* **2004**, *11*, 123–133.
36. Chen, J.L.; Wu, H.Y.; Zhu, D.F.; Lin, C.H.; Yu, D.S. Tectonic evolution of the hailar basin and itspotentials of oil-gas exploration. *Chin. J. Geol.* **2007**, *42*, 147–159.
37. Guo, D.; Wang, X.M. Comprehensive exploration technology and exploration example of CO_2 gas reservoir. *Pet. Geophys.* **2004**, *2*, 30–36.
38. Pang, Q.S.; Wang, L.; Zhao, R.; Wang, F.G. Origin and mechanism of the forming of carbonate dioxide gas pool in Changde. *J. Daqing Pet. Inst.* **2002**, *26*, 89–91.
39. Yang, C. Study on the genesis of CO_2 in huanghua depression. *Nat. Gas Geosci.* **2004**, *15*, 7–11.
40. Du, L.T.; Lv, X.B.; Chen, H.H. Origin Discr imination of CO_2 Gas Pools in Jiyang Depression. *Xinjiang Pet. Geol.* **2006**, *27*, 629–632.
41. Yun, J.B.; Wu, H.Y.; Feng, Z.H.; Mei, H.N. CO_2 gas emplacement age in the Songliao Basin: Insight from volcanic quartz 40Ar-39Ar stepwise crushing. *Chin. Sci. Bull.* **2010**, *55*, 1795–1799. [CrossRef]
42. Dai, J.X. Identification of various genetic natural gases. *China Offshore Oil Gas* **1992**, *6*, 11–19.
43. Gould, K.W.; Smith, J.W. The genesis and isotopic composition of carbonates associated with some Permian Australian coals. *Chem. Geol.* **1979**, *24*, 137–150. [CrossRef]
44. Shen, P.; Xu, Y.C. The isotopic composition of natural gases from continental sediments in China. *Geochemical* **1991**, *2*, 144–152.
45. Song, Y.; Xu, Y.C. Origin and identification of natural gases. *Pet. Explor. Dev.* **2005**, *32*, 24–29.
46. Dai, J.X.; Song, Y.; Dai, C.S.; Chen, A.F. *Inorganic Genetic Gas and Gas Reservoir Forming Conditions in Eastern China*; Science Press: Beijing, China, 1995; pp. 80–186.
47. Xu, Y.C.; Wang, X.B.; Wu, R.M.; Shen, P.; Wang, Y.X.; He, Y.P. Rare gas isotopic composition of natural gases. *Geochemical* **1979**, *4*, 271–282. [CrossRef]
48. Liu, W.H.; Xu, Y.C. Research status of argon isotopes in natural gas. *Nat. Gas Geosci.* **1990**, *2*, 9–13.

49. Liu, W.H.; Xu, Y.C. The significance of helium-argon isotope composition in natural gas. *Chin. Sci. Bull.* **1993**, *2*, 818–821.
50. Xu, Y.C. The mantle noble gas of natural gases. *Earth Sci. Front.* **1996**, *3*, 63–71.
51. Dai, J.X. Carbon dioxide gas fields (reservoirs) and their gas types in eastern China and continental shelf. *Explor. Nat.* **1996**, *4*, 18–20.
52. Li, P.; Ge, W.C.; Zhang, Y.L. Division of volcanic strata in the northwestern part of Hailar basin: Evidence fromzircon U-Pb dating. *Acta Petrol. Sin.* **2010**, *26*, 2482–2494.
53. Li, L.; Zhong, D.L.; Yang, C.C.; Zhao, L. Faults role in formation and distribution of the mantle derived carbon dioxidegas pools: Case study of the Jiyang Depression in Bohai Bay Basin, China. *Acta Petrol. Sin.* **2016**, *32*, 2209–2216.
54. Qu, X.Y.; Liu, L.; Gao, Y.Q.; Liu, N.; Li, F.L.; Liu, Y.H. Geology record of mantle-derived magmatogenetic CO_2 gas in the northeastern China. *Acta Pet. Sin.* **2010**, *31*, 61–67.
55. Fu, X.F.; Sha, W.; Wang, L.; Liu, X.B. Distribution Law of Mantle-Origin CO_2 Gas Reservoirs and Its Controlling Factors in Songliao Basin. *J. Jilin Univ.* **2010**, *40*, 253–263.
56. Zhang, C.H.; Kang, Z.; Zhang, G.Y.; Liu, Y.C. Corresponding chronogenesis between the Mesozoic metallogeny and magmatic activity in northeast China. *Geol. Resour.* **2009**, *18*, 87–90.