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The origin and formation of CO_2 gas pools in the coal seam of the Yaojie coalfield in China

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ABSTRACT

High concentrations of CO_2 have been observed in the No. 2 coal seam in the Yaojie coalfield. A number of instantaneous CO_2 outbursts occurred during coal mining. The CO_2 concentration range in the eastern coalfield is 18.79 to 96.6%. The $\delta^{13}C_{CO_2}$ values are mainly in the range of −5.0‰ to +1.0‰ (PDB), suggesting an inorganic origin of CO_2. The $^3He/^4He$ ratios are $(0.6–25.9)\times10^{-8}$, and the R/Ra is 0.0042–0.185, which is a characteristic of crust-derived CO_2 gas. The dynamic-thermal metamorphism of the F19 ductile-brittle shear zone is believed to result in the release of CO_2 from basement marble formations, which show an inorganic source of CO_2 in the Yaojie coalfield. The regional geological evolution and multi-periodical F19 fault movement control the formation, migration, and accumulation of the CO_2, in addition to the development of CO_2 gas pools in the Yaojie coalfield. The F19 fault played multiple roles in the generation, transport, and sequestration of gas during the CO_2 formation. The displacement of CH_4, carbonate generation, and pore structure transformation of coal due to a series of physical and chemical effects occurred after CO_2 flux into the coal seams.

1. Introduction

The No. 2 coal seam in the Yaojie coalfield, located in northwestern China, is characterized by extensive CO_2 distributions. A number of instantaneous CO_2 outbursts have occurred during coal mining since 1977. There are various potential sources of CO_2 in the Yaojie Coalfield, such as magmatic origin, mantle degassing, and the spontaneous combustion of coal (Tao, 1993; Wei et al., 2007). Locations that are associated with rock and CO_2 outbursts include the Yanbian and Helong Mines in China (Yu, 1992), the Cevennes Basin in France, the Lower Silesia in Poland, and the Sydney and Bowen Basins in Australia (Lama and Bodziony, 1998; Beamish and Crosdale,1998; Faiz et al., 2007). While volcanic and magma activities are the typical sources of CO_2 outbursts, CO_2 penetrates the coal seams through deep faults and attenuated coal formation. However, few studies have been conducted on CO_2 migration and accumulation in coal strata.

The volcanic or geothermal areas and the magma degassing or thermo-metamorphic alteration of carbonates result in the production of large amounts of CO_2 (Clayton, 1998; Pearce et al., 2004; Annunziatellis et al., 2008). Fault zones can act as barriers, conduits, or mixed conduit–barrier systems. Deep faults in the reservoir play an important role in the process of CO_2 accumulation, which is controlled by regional tectonic movements in the forms of generation, migration, accumulation or dispersion and preservation (Antonellini et al., 1994; Evans et al., 1997; Sibson, 2000).

In this study, CO_2 concentrations coupled to carbon and helium isotopes are analyzed to evaluate the origins of CO_2 in the Yaojie coal seam. The ida-scale regional tectonic features and evolutionary activities of the F19 fault are also employed in the derivations. Migration and accumulation processes are analyzed based on a geological survey of CO_2 characteristics in the coal seam. The research presented in this work can unveil occurrence CO_2 in the coal seam, based on which some precautionary steps can be taken on CO_2 drainage to prevent and treat the coal and CO_2 outburst. These results also may provide a natural analog for assessing the deep storage of CO_2 in coal seams.

2. Regional geological evolutions

The Yaojie coalfield is located in the western margin of Minhe and extends across the Gansu and Qinghai provinces, consisting of the Yaojie No. III mine and Haishiwan coalfield (shown in Fig. 1). The Minhe basin is a mountain depression basin that developed during the Mesozoic–Cenozoic on the Qilian orogenic belt. The current structural layer of the basement lies mainly in the NW direction. The main source of significant deformation occurred in the early Yanshan tectonic (208–135 Ma) when the primary tectonic stress was in the NE direction. The primary regional tectonic compression stress of the middle and late Yanshan tectonic (135–65 Ma) was primarily in the NW-NNE direction. The principal compression stress of the Himalayan tectonic (23.5–0.78 Ma) was in the NW direction. The analysis above

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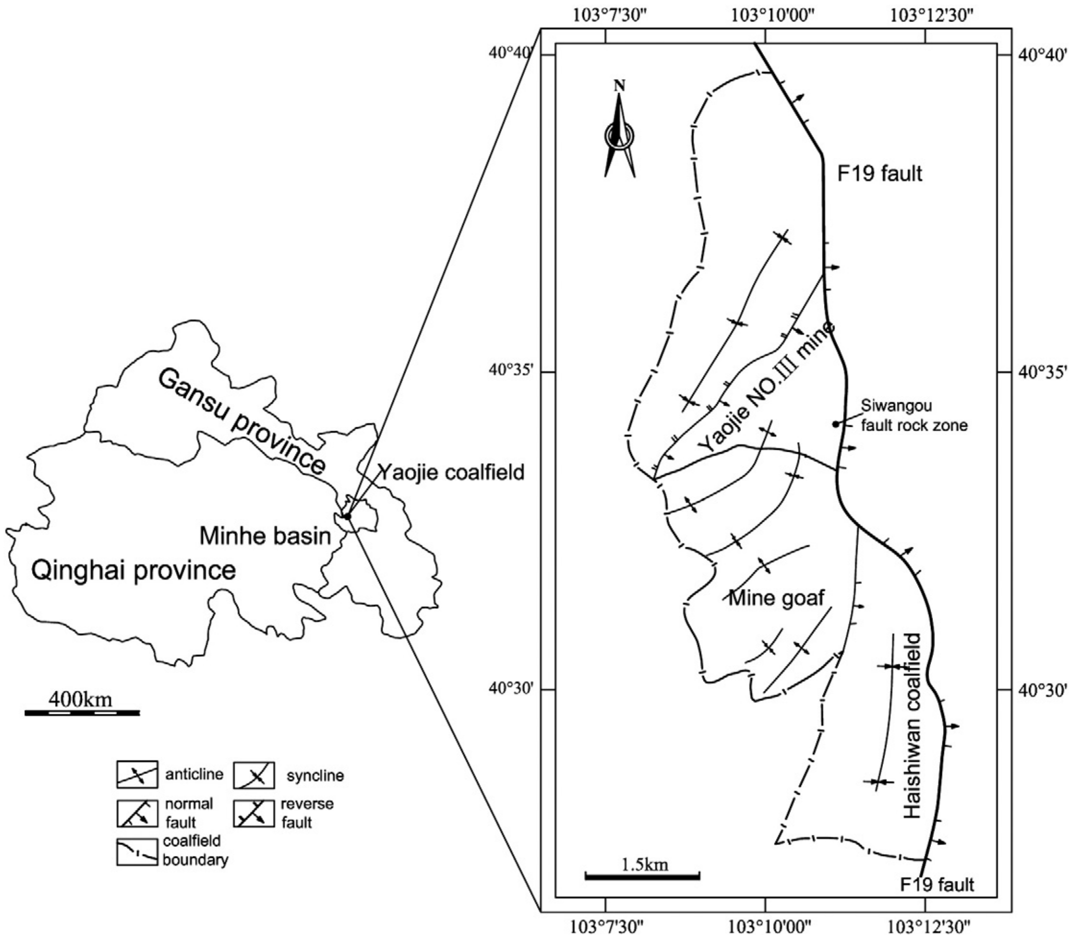

Fig. 1. Map showing the study area and data locations for gas volume, composition, and geochemical characteristics.

indicates that the structure is well developed with multiple stages and tectonic movements (Cao, 1997; Zhao et al., 2000). The current principal compression stress of the tectonic stress field is in the NE direction. The basin stratum is Mesozoic–Cenozoic sedimentary, which generally lacks Paleozoic and Mesozoic sedimentary Triassic deposits, and the basement is Proterozoic metamorphic sedimentary (Tao et al., 1995).

The Proterozoic basement mainly composes of marble, gneiss, quartz schist, and siliceous limestone, making up a cluster of metamorphic rocks with a thickness greater than 6000 m and outcropped in surrounding of Yaojie coalfield (Wei et al., 2007). The coal-bearing strata of the Yaojie coalfield is part of the Yaojie series in the Jurassic system middle stratum. The Yaojie coalfield lies roughly on a NNW direction with the F19 fault zone located to the east of it. The coal basin is directly integrated at the top of the Huangyuan Group. The total average thickness is 163 m with the coal seam at approximately 30 m. Coal seams are located primarily in the lower second petrofabric. Two of the three coal seams are suitable for mining. The No. 2 coal seam is a primary coal bed suitable for mining with hazards of coal and CO_2 outbursts (Fig. 2). The No. 1 coal seam, the other minable coal seam, produces sapropelic coal with maximum vitrinite reflectance (VR) values ranging from approximately 0.511 to 0.584%. Coal from the No. 2 coal seam is high volatile bituminous with maximum vitrinite reflectance (VR) values ranging from approximately 0.690 to 1.056%.

3. Materials and methods

The current study was conducted by compiling information from published and unpublished data on exploration boreholes and underground coal mines. This information has been supplemented with new data obtained from the sample measurements of selected locations.

The carbon isotopic composition of gas was determined on a DeltaPlusXP isotopic mass spectrometer equipped with an Agilent 5890 NGC at the Lanzhou Institute of Geology of the Chinese Academy of Science. Hydrocarbon gas compounds were separated individually using a capillary column (30 m × 0.32 mm × 0.53 mm C2000). The inlet temperature was 30 °C, the oxidation oven temperature was 840°, and the gas chromatograph temperature began at 30 °C for 5 min followed by an increase from 30 °C to 200 °C at a rate of 15 °C/min. The analytical precisions for the measured $\delta^{13}C_{CO_2}$ values for CO_2 are within ±0.02‰ based on the PDB standard.

The helium isotope compositions were performed using a noble gas mass spectrometer (VG5400 VG Isotopes) at the Lanzhou Institute of Geology of the Chinese Academy of Science. An inlet system with high vacuum purification line, low leakage, and low background levels was used. Based on multiple analyses on laboratory standards, reproducibility of $^3He/^4He$ measurements are better than ±2%.

The detailed analytical conditions are described by Ye et al. (2001, 2007).

The maceral group composition and minerals was determined using a reflection polarizing microscope (DTACX-P01) at the Institute of Coalfield Geology of the Gansu Coal Geological Bureau. Through bonding, molding, and polishing, the air-dried coal samples with particle sizes less than 1 mm were obtained in polished sections. The polished section of powder coal was visualized underneath the reflection of a polarizing microscope with white incident light. With a cross polarizer or monopolarizer and clear identification, the maceral group composition and minerals were determined using a point

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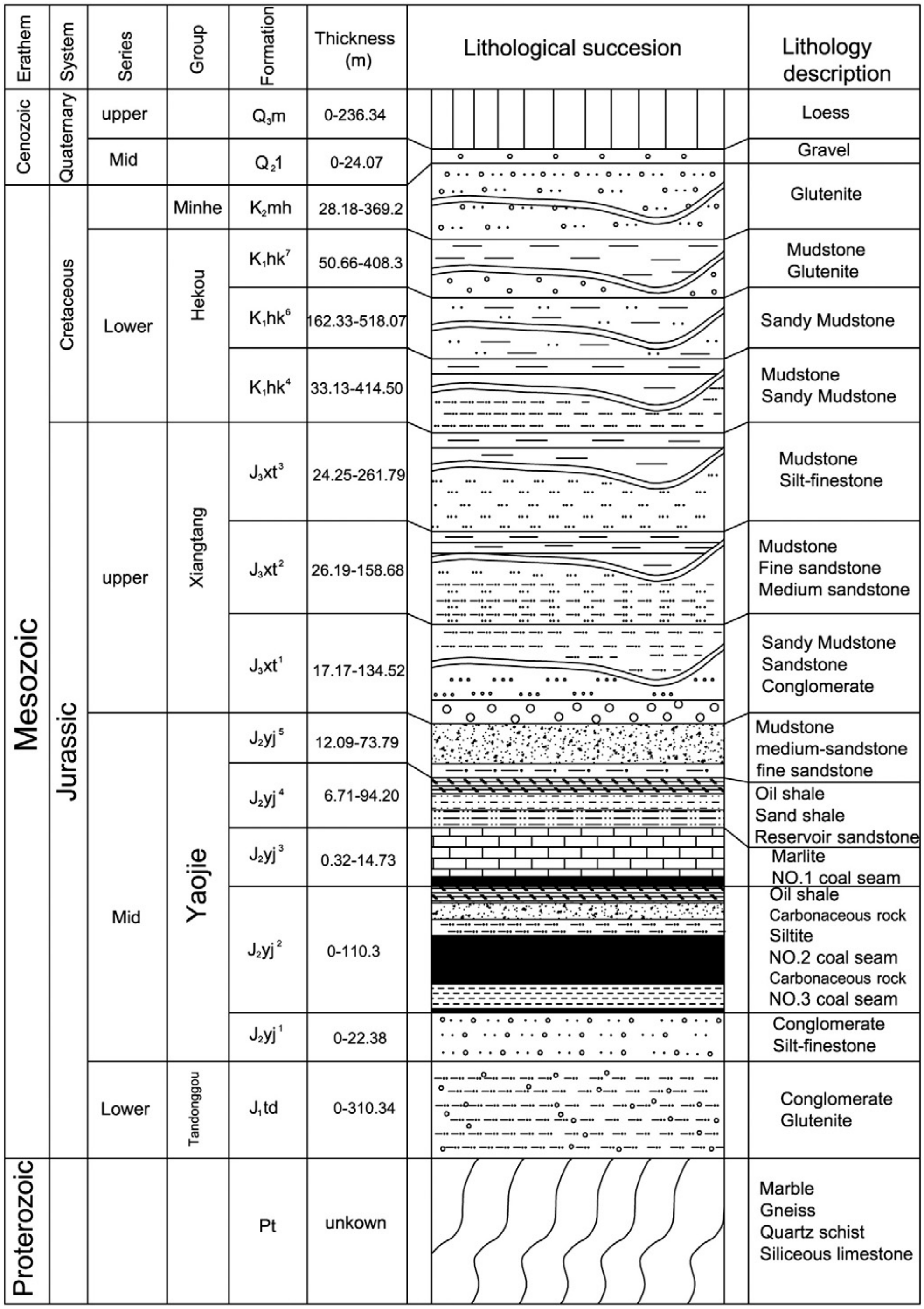

Fig. 2. Generalized stratigraphy and tectonic events of the Yaojie coalfield.

counting method. The detailed experimental procedure was performed according to the requirements of the National Standards of the People's Republic of China (GB/T 8899-1998, GB/T16733-1997).

Coalbed gas content were determined using the desorption method during the geological exploration in accordance with the China Safety Industry Standards (AQ1066-2008; MT/T77-1994). In situ gas contents were determined according to the formula (1):

$$X_0 = \frac{V_1 + V_2 + V_3 + V_4}{Q} \quad (1)$$

where X_0 is the total in situ gas contents (ml/g), V_1 is the desorption gas content in the mine (ml), V_2 is the gas loss content (ml), V_3 is the negative pressure desorption gas content before comminution (ml), V_4 is the negative pressure desorption gas content during comminution (ml), and Q is the coal sample quality (g). V_2 was obtained from the empirical formula, while V_3 and V_4were determined in the laboratory. Gas volume was converted to standard conditions (0 °C, 101.3 kPa).

4. Results and discussions

4.1. Geochemical characteristics of natural gas

The molecular composition of CO_2 from the Yaojie coalfield is determined from gas samples of the geological surface and mine borehole of the No. 2 coal seam, as shown in Table 1 (data from Tao

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Table 1
Composition and geochemical characteristics of CO_2 in the eastern Yaojie coalfield (data from Tao et al., 1991; Tao, 1993 and new experimental determination).

Region	CO_2 (%)	$\delta^{13}C_{CO_2}$ (‰, PDB)	$^3He/^4He$ ($\times10^{-8}$)	R/Ra	$\delta^{18}O_{CO_2}$ (‰, SMOW)	Data sources
	84.39	−3.6	20.3	0.1450	23.43	This paper
	81.53	−4.6	5.07	0.0362		
	89.65	−0.35				
	74.25	−3.66			21.93	
	76.62	−4.11			22.23	
	58.85	−3.79			21.81	
Haishiwan coalfield	18.79	−4.79				
	68.82	+1.12				
	96.20	−4.94			19.88	Tao, 1993
	85.07	−1.27	3.92	0.0280	24.22	
	89.39	−1.38	3.49	0.0250	24.07	
	89.30	−9.41			18.65	
	89.67	−9.94			16.29	
	88.32	−8.00				
	95.40	−0.55	10.1	0.0720	22.17	Tao, 1991; Tao, 1993
Yaojie NO. III coal mine	96.60	−4.06	25.9	0.1850	19.89	
	96.60	−4.64	3.8	0.0270	20.47	
	88.10	−2.98	0.6	0.0042	20.78	
	87.38	−3.65	2.2	0.0150	21.90	

et al., 1991; Tao, 1993 and new experimental determination). The CO_2 concentration ranges from 18.79 to 96.60% of the total gas content with an average of 81.83% in the eastern coalfield. Other species are methane, nitrogen, and hydrocarbon. The highest CO_2 contents are distributed in the eastern Yaojie coalfield. According to the literature, the CO_2 is inorganic if the CO_2 composition accounts for more than 60% in gas pools. Therefore, CO_2 derived from coal spontaneous combustion is excluded.

The measured $\delta^{13}C_{CO_2}$ values range from +1.12‰ and −20.00‰ (Fig. 3; Table 3), and most of them are in the range of −5.0‰ to +1.0‰. $^3He/^4He$ values ranges from $(0.6\pm0.6)\times10^{-8}$ to $(25.9\pm0.3)\times10^{-8}$, and R/Ra value ranges from 0.0042 to 0.185 (where Ra is the atmospheric value of $^3He/^4He$ and R the sample value of $^3He/^4He$). These results indicate that He is derived from the crust and implies that CO_2 in the Yaojie coalfield is of crustal origin. The $\delta^{13}C_{CH_4}$ of the No. 2 coal seam gas ranges from −32.76‰ to −44.08‰ (Wei et al., 2007), indicating that the methane is of organic origin and not related to inorganic CO_2.

The present CO_2 in coalbeds can be the result from several processes that are not related to coalification, including recent microbiological activities, the thermal degradation of carbonates, and the migration from magma chambers or the upper mantle (Smith and Pallasser, 1996; Clayton, 1998). The $\delta^{13}C$ values of metamorphic CO_2 derived from carbonate thermal decomposition are close to the mean $\delta^{13}C$ values of carbonate rocks (0±3‰). CO_2 with $\delta^{13}C_{CO_2}$ values in the range of −4‰ to −7‰ is considered mantle-derived. (Clayton et al., 1990; Thrasher and Fleet, 1995). Carbon isotopic fractionation and organogenic CO_2 mixes result in reduced $\delta^{13}C$ values of CO_2 from decarbonization. There is a significantly positive correlation between CO_2 contents and $\delta^{13}C_{CO_2}$ values of CO_2 from the Yaojie coalfield (Fig. 3).

Tao (1993) measured the $\delta^{13}C$ and $\delta^{18}O$ of calcite veins and CO_2 from the No. 2 coal seam and the Yaojie coalfield roof and floor. Most $\delta^{13}C$ and $\delta^{18}O$ values for CO_2 and calcite do not fall within the interval of carbonate (Fig. 4). The O and C isotope interaction between calcite and fluid primarily reflects the calcite-water fractionation and calcite − H_2CO_3 or HCO_3^- fractionation, respectively. The C and O isotope of calcite tends to display much smaller variation in the $\delta^{13}C$ values than the $\delta^{18}O$ values due to the precipitation of calcite in a HCO_3^- dominant fluid. A positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values for CO_2 may be due to a progressive decrease in temperature during CO_2 degassing (Zheng, 1990). The dissolving and degassing of CO_2 accompanied by the C and O isotope fractionation generates the trace calcite veins of the Yaojie coalfield. Moreover, the isotope fractionation of multi-source CO_2 occurs because of the co-existence of inorganic and organic CO_2 in the coal seam. When different isotopic composition of CO_2 are mixed, their equilibrium conditions depend on the chemical and physical conditions in the process, e.g. temperature, adsorption/desorption process (Valkiers et al., 2007).

4.2. Crustal sources of CO_2

Crustal sources of CO_2 can be divided into contact metamorphism of carbonates and dynamic metamorphism of fault activities. The pyroxenite, serpentinized peridotite, and serpentinite form a basic-ultrabasic rock band that is distributed along the F19 fault discontinuously. The amphibole isotopic age (K-Ar method) is 323–366 Ma, and the geological age of Hercynian magmatic activities is earlier than that for Jurassic coal (Wei et al., 2007). No magmatic activities have occurred in the region since the Paleozoic (GanSu Province Geology and Mining Bureau, 1989; Tao, 1993). Magmatic rock was not found during the geological exploration of the Haishiwan coalfield. Therefore, there is little possibility that CO_2 is derived from contact metamorphism of carbonates.

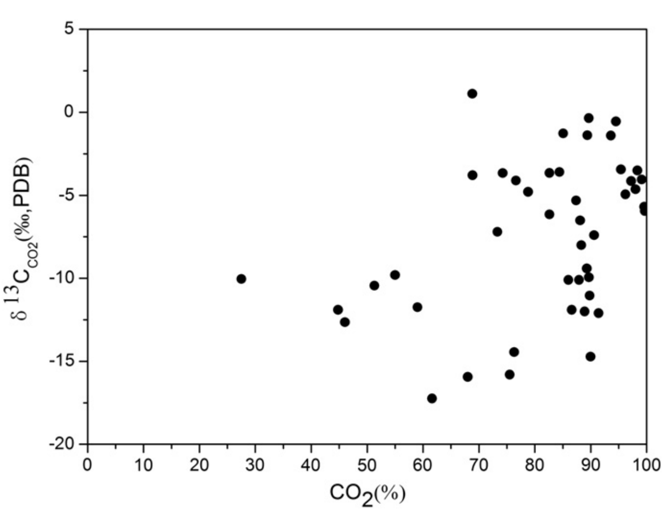

Fig. 3. CO_2 concentrations and $\delta^{13}C_{CO_2}$(PDB) values for CO_2 from the No. 2 coal seam in the Yaojie coalfield.

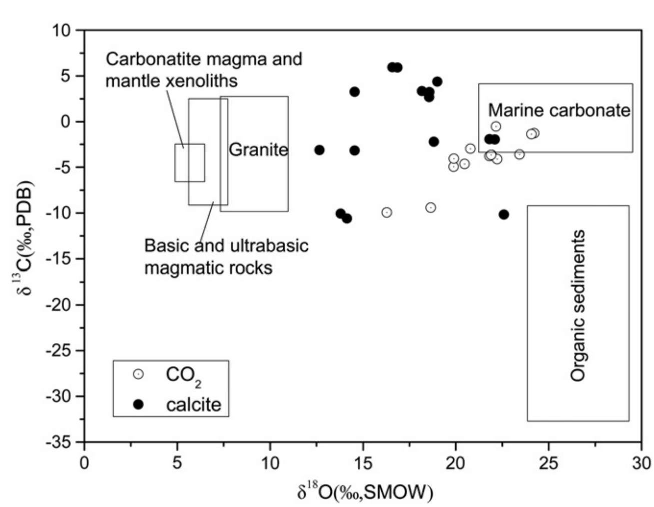

Fig. 4. Carbon and oxygen isotope compositions of CO_2 and calcite in the Yaojie coalfield (in ‰ relative to PDB and SMOW, respectively, and modified according to Liu et al., 1997).

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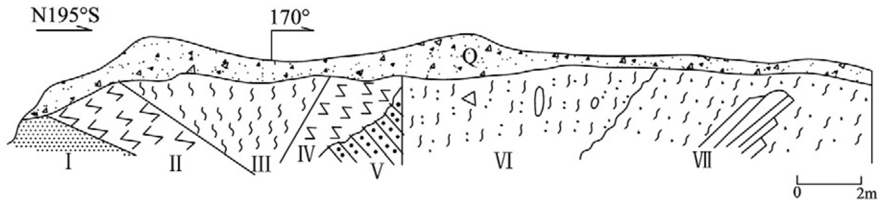

Fig. 5. Geological survey profile of the F19 fault belt tectonite in Siwangou, *Q*(Quaternary strata) (Tao et al., 1995).

Dynamic metamorphism is the only source of CO_2 in the Yaojie coalfield as determined by the exclusion approach. Proof of dynamic metamorphism is important to verify our hypotheses. The fracture zone of the F19 fault outcrops for 30 m in the southern foothills of Siwangou (Fig. 5). Many types of tectonic filling fault fracture zones with mixed characteristics have appeared featured with sequence in the cross-section and assembly characteristics of the tectonite belt, as shown in Table 2.

The altered rock belt is influenced by both fracture force and hydrothermal activities with diverse structural and tectonic features. The stress generation of minerals and dynamic metamorphism of the tectonic belt is obvious, e.g. epidote, cataclasite, wavy extinction, and crackle. Mylonite formed by extruded rub reflects typical ductile-brittle shearing. The process was accompanied by chloritization, strong silicification and calcite disappearance. These phenomena indicate strong structural-hydrothermal activities (Wang and Zhu, 1995; He et al., 1996). These activities of brittle-ductile shear zone result in the development of significant decarbonization of carbonatite, element differentiation, migration, and CO_2 formation in the fault zone (O'Hara and William, 1989; O'Hara, 1994). This is the main source of inorganic CO_2 formed with the dynamic metamorphism of the fault zone. The amount of CO_2 generated is closely related to fluid interaction, rheological behavior of rocks, and rock volume loss. Theoretical studies demonstrate that every 100 g of carbonate rock mass generates 22.90–33.90 g of CO_2 during the structural dynamic metamorphism (Tao et al., 2000; Yang et al., 1997, 2002). During the Yanshan movement and Himalayan movement from the late Jurassic to the early Neogene, the structural thermal-dynamic and action of the brittle-ductile shear zone of the F19 fault caused the marble at the basement to decompose into CO_2.

Therefore, a general downwards progression in dominant fault-rocks (gouge–breccia–cataclasite–phyllonite–mylonite–mylonitic gneiss) is inferred for a normal fault zone developed in the quartzo-feldspathic crust, as shown in Fig. 6. The fault rock distribution of Siwangou horizontal zoning quarry suggests that ductile-brittle shear and fault rock zoning of the F19 fault occur in the vertical direction. Stable mineral assemblages of the F19 fault are quartz–feldspar–sericite–chlorite. Therefore, the isotherm defining the onset of stable mineral assemblage conditions is estimated in the range of 350–500 °C. For normal geothermal gradients of 30 °C/km, the 350–500 °C hydrotherm is within the 11–16 km interval. The estimated 11 km (350 °C) depth is the cataclasite–phyllonite transition of the normal fault. In the regions deficient in water, the transition may occur at greater temperatures and depth (Sibson, 2000). Under water participation, the reactive dissolution of carbonatite could product large quantities of CO_2 at temperatures between 70 and 220 °C (Hutcheon et al., 1990).

Table 2
Features of tectonite divisions and fault rock distribution in the Siwangou geological survey profile.

Tectonite divisions	Rock belt names	Main mineral	Main features
I	Fault gouge	Sericite Chlorite plagioclase quartz	Polysynthetic twin developed
II	Mylonite	Quartz Epidote chlorite	Obvious plastic rheological phenomenon of rock
III	Cataclasite	Chlorite schist	Fragment rock and fractures filled with carbonatite dyke
IV	Sallow mylonite	Quartz	Polysynthetic twin developed
V	Cataclasite (sandstone)	Feldspar	Tartan twinning and polysynthetic twin developed; undulatory extinction
VI	Scaly mudstone hybrid zone	Calcite	Mudstones schistosity developed; calcites vein nearly vertically developed
VII	Cataclasite	Chlorite quartz Oil sands	Rock fragmentation with oil sand rock block

4.3. The characteristics of CO_2 transport in the No. 2 coal seam

Contents and gas compositions of CO_2 and CH_4 were determined from 27 surface borehole samples for the No. 2 coal seam of the Haishiwan coalfield (Fig. 7; Table 3). In situ CO_2 gas contents of coal in No. 2 ranges from 0.3 to 10 m^3/t, and CH_4 gas contents ranges from 0.05 to 6.22 m^3/t. Gas composition for CO_2 from coal seams of the No. 2 coal varies between 15.47% and 90.89% and between 0.48% and 68.79% for CH_4.

The gas content and gas compositions of the samples are plotted against the distance from the F19 fault (Fig. 8). The CO_2 content decreases and the CH_4 content increases along the distance from the

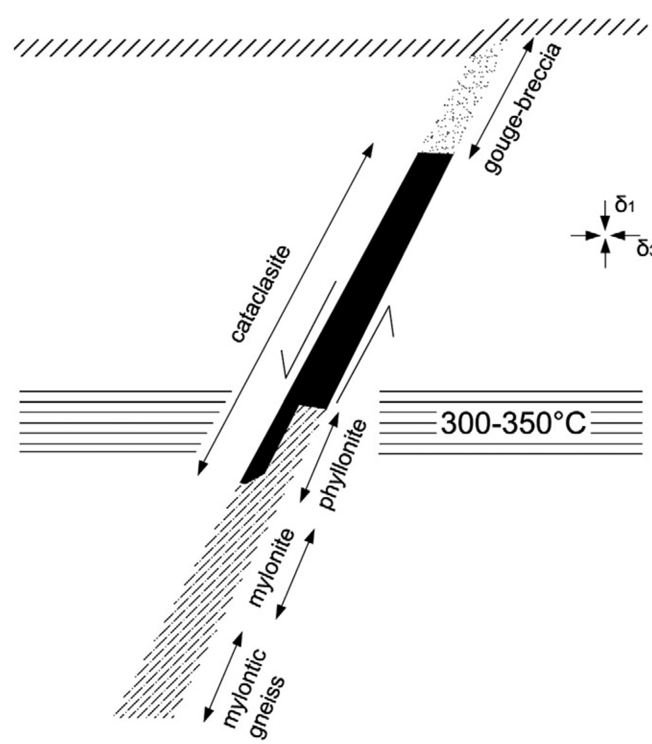

Fig. 6. The fault rock distribution for an optimally oriented crustal-scale normal fault (Sibson, 2000).

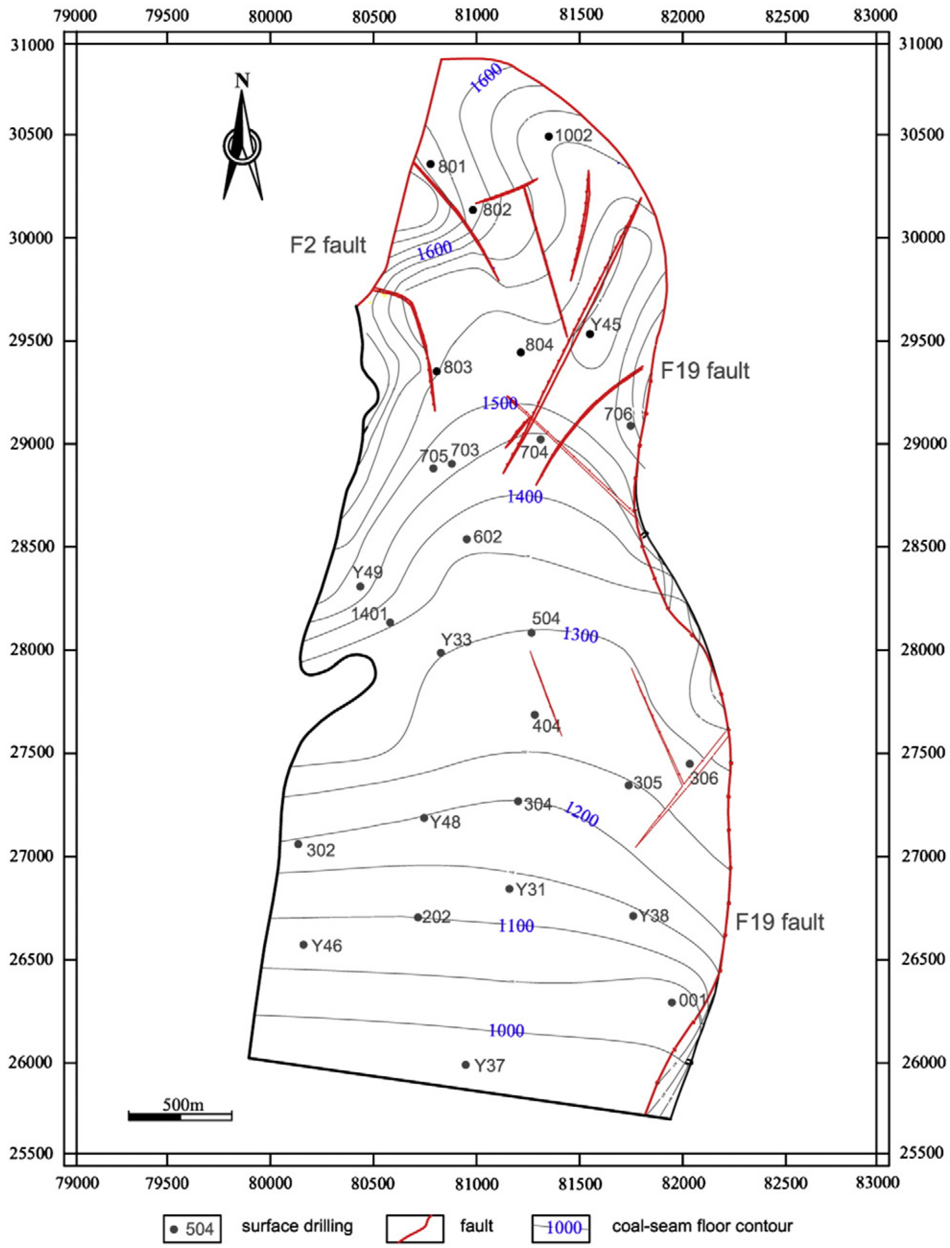

Fig. 7. Arrangement of exploration boreholes in the Haishiwan coalfield. The altitude of ground ranges from 1900 to 2300 m from the valley and mountain covering.

F19 fault. The CO_2 and CH_4 composition show the same trend as the distance from the F19 fault. The CO_2 gas content does not change and the CO_2 balance of the reservoir gas injection direction is related to change in this imbalance and preserves for a long period in geological history.

The identification of the general direction of CO_2 migration also constrains the timing of the CO_2 input relative to CH_4. Assumed by simple filling, the samples closest to the CO_2 source might be expected to have the highest CO_2 concentrations and contents after CH_4 production (Ballentine et al., 2000). CO_2 can be sequestrated into coal seams while CH_4 is recovered from the depleted coal seams by CO_2 injection. The distribution of CO_2 and CH_4 is consistent with an initial input of CO_2 from the east of the F19 fault with subsequent CH_4 generation in the No. 2 coal seam.

The $\delta^{13}C_{CO_2}$values (−20.0‰ to −0.35‰) vary with increasing distance from fault F19. $\delta^{13}C_{CO_2}$ is lighter at greater distances from the fault (Fig. 9). Using a simple isotopic fractionation is difficult to explain this phenomenon (Horita, 2001; Strąpoć and Schimmelmann, 2006), indicating a situation of multi-source CO_2. Coal-generated CO_2 in the process of metamorphism, and CO_2 derived from thermo-catalytic transformation of kerogen or soluble organic matter in coals are recognizable by ^{13}C depleted isotopic signatures (Clayton, 1998), with increasing distance from F19 fault, the volume of inorganic CO_2 decreases and organic CO_2 increases due to longer migration distance. Two secondary causes of the deviation in carbon isotope are also proposed: 1) a finite reservoir effect accompanying the precipitation of carbonates: since carbonates are enriched in ^{13}C at temperatures less than 200 °C, their precipitation will cause the residual CO_2 to become depleted in ^{13}C; and 2) coal seam's preferential adsorption to $^{13}C_{CO_2}$ and easier desorption and migration with regard to $^{12}C_{CO_2}$ may result in a migration of organic-origin CO_2 featured with relatively light carbon isotope.

Determination of mineral content during exploration drilling demonstrates that carbonate mineral accounts for 0.2–9.6%. Carbonate contents are calculated according to the given formula (2). Higher carbonate mineral content is closer to the F19 fault, as shown in Fig. 10. Carbonate mineral, consisting primarily of calcite and siderite, is distributed in pore and crack in the Haishiwan No. 2 coal seam. The

Table 3
Composition of natural gas and the No. 2 coal seam samples determined from boreholes in the Haishiwan coalfield. Measured gas contents in the mine are greater than the boreholes due to the sampling process. However, the gas contents measured through the borehole may suggest the relative distribution of gasses in the coalfield.

Boreholes	Gas concentration (%)		Gas content (m^3/t)		Carbonate content (%)	R_o (%)	$\delta^{13}C_{CO_2}$ (‰, PDB)
	CO_2	CH_4	CO_2	CH_4			
1002	74.25	0.48	6.5	0.05	3.4	0.79	−3.66
801	43.56	1.20	0.85	0.01			
802	89.65	6.26	7.78	0.51		0.69	−0.35
803	71.98	18.58	5.16	1.32	2.7	0.83	−11.69
804	88.84	6.00	9.65	0.79	3.9	0.90	
Y45	90.89	8.96	10.0	1.00			
706	90.67	3.76	9.82	0.42	6.2	0.95	
704	79.26	7.32	7.05	0.69	6.6	0.87	
703	50.69	34.95	4.25	2.93	3.7	0.90	
705	43.01	36.25	2.00	1.96	5.2	0.92	
602	47.43	11.58	2.60	0.74	2.6	0.86	
Y49	18.71	68.79	0.30	1.24			
1401	15.47	67.12	0.82	3.82	1.6	0.96	−13.9
504	63.7	21.66	5.16	1.76	9.6	1.04	
Y33	46.59	39.12	4.10	3.99	1.3	0.95	
404	72.04	9.06	8.86	1.30	2.0	0.99	
306	82.38	2.02	7.58	0.17	6.6	1.03	
305	58.13	16.92	5.68	1.73	5.1	1.03	
304	71.58	16.14	8.24	2.02	7.0	0.97	
Y48	18.97	52.61	1.41	4.16		0.95	−14.72
302	34.26	21.36	1.31	1.15	0.2	0.89	
Y38	66.33	23.52	6.87	3.13	1.6	0.93	
Y31	55.85	25.52	7.21	3.41			−3.79
202	78.48	12.56	4.96	1.06	2.1	1.03	
Y46	23.18	64.44	0.86	2.20	0.7	0.93	−20.0
001	49.51	39.58	3.9	3.36	3.9	1.06	
Y37	23.12	60.48	2.48	6.22	0.6	0.96	

direction of carbonate distribution is consistent with CO_2 influx and migration. The antigenic minerals, such as dawsonite, siderite, ankerite, kaolinite, calcite, and quartz, were determined from experimental and geological studies (Watson et al., 2004; Xu et al., 2005; Worden, 2006; Liu et al., 2006; Gaus, 2010). The ^{13}C content for calcite and siderite in the second coal seam of the Yaojie No. 3 coal mine are −3.19‰ to +3.11‰ and −1.96‰ to +2.66‰(Tao, 1993), respectively, consistent with the ^{13}C content for the inorganic CO_2 in the coalfield (Fig. 4). The values for $\delta^{13}C$ and $\delta^{18}O$ and development of calcite could be eventually derived from CO_2 dissolution and precipitation (Li et al., 1992; Tao, 1993). Carbonate can be used as a tracer mineral of inorganic CO_2 migration by indicating water existence, ph value, pressure, temperature, and the original mineral (Hellevan et al., 2005; Fischer et al., 2006). The distribution of

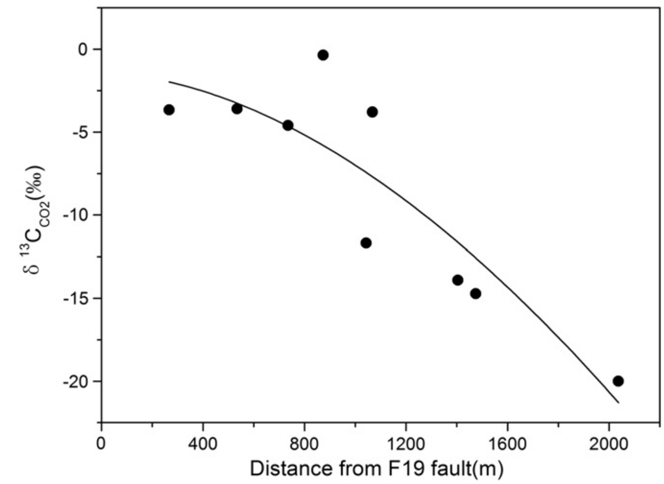

Fig. 9. Decreases in the CO_2 carbon isotope ratio as the distance from F19 increases.

carbonate in the Haishiwan minefield illustrates that CO_2 could alter carbonate within the range of the F19 fault.

$$\mathit{Carbonate\ content}(\%) = \frac{\text{Carbonate}}{\text{Organic maceral} + \text{Mineral impurities}} \quad (2)$$

A series of physical and chemical effects occurred after active CO_2 gas was injected into the coal seam, and controlled CO_2 migration and reservoir formation.

(i) The injection of a higher adsorbing gas, such as CO_2, would be preferentially sorbed and displace CH_4 from coal;
(ii) The $^{13}CO_2$ adsorption on coal and organic CO_2 migration preferentially leads to slight changes in the CO_2 carbon isotope in the migration direction;
(iii) The CO_2 migration distance is limited to the coal seam during geological time.

The solution and adsorption of CO_2 in the coal seams results in a significant expansion effect of coal, such that the permeability of coal decreased (Mazumder and Wolf, 2008), which hinders CO_2 flow to the coal bed (Hildenbrand and Krooss, 2003). Experimental results have demonstrated when permeability is low than flow is nearly impossible even at high pressure. Thus, diffusion is the main form of transport under this condition.

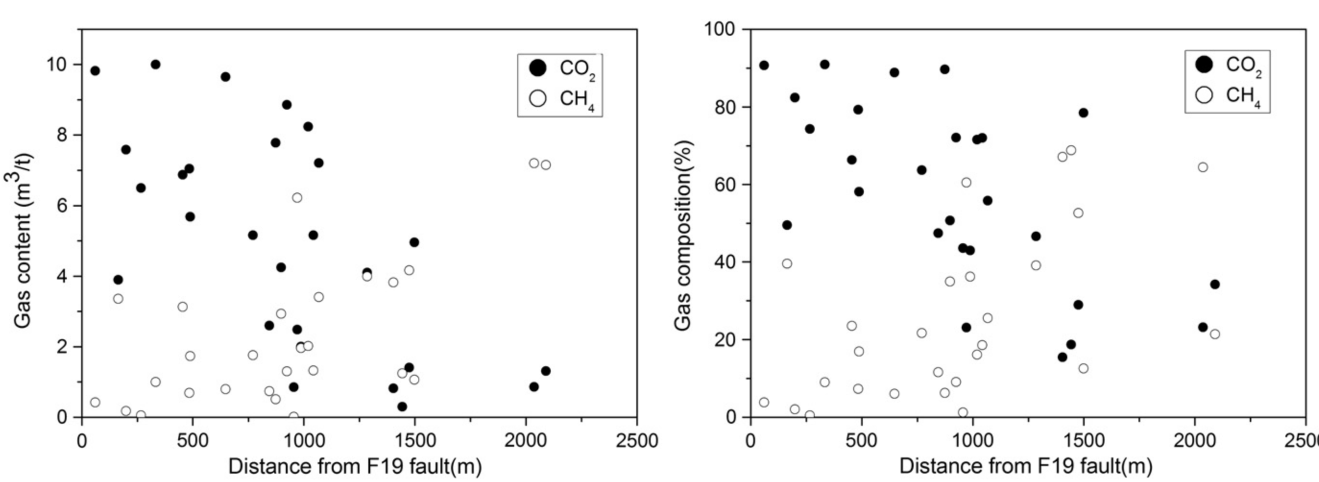

Fig. 8. Graph showing that the CO_2 content/concentration decreases and CH_4 content/concentration increases as the distance from F19 increases.

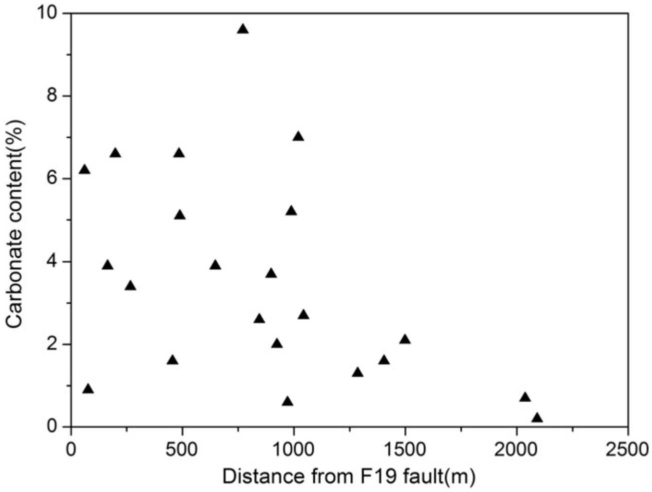

Fig. 10. Carbonate content decreases as the distance from F19 increases for the No. 2 coal seam samples.

(iv) Under the appropriate conditions, CO_2 rapidly evolved into carbonate minerals in coal blocked pore fissures forming the geological storage of trapped minerals.

4.4. The entrapment and accumulation of CO_2

4.4.1. The role of the F19 fault in CO_2 accumulation

The F19 fault zone is located at the eastern boundary fault of the Yaojie Coalfield and comprises of a major fault and a set branch fault that is 100 to 400 m wide extending over 17 km in length, with depth range of 300–1000 m. Currently, the characteristics of the F19 fault are normal with the Cretaceous strata exposed in hanging wall and the Jurassic exposed in footwall. The fault strikes in the SN direction and ends in the E direction. Due to strong compression, a thick coal zone of Jurassic stratum near the F19 fault was created. According to the evolutionary history of the Minhe basin, Tao et al. (1995) divided the formation of the F19 fault into five phases. The F19 fault exhibits seesaw-type tectonic movement because of a periodic variation in the tectonic stress field characteristics. Zhu and Geng (2007) proposed that at least three times the magnitude of the F19 fault tectonic movements occurred during different periods. The different movement types of the F19 fault are the primary factors that control CO_2 generation, migration, and aggregation processes.

The F19 fault zone belongs to the third deformation style. According to Annunziatellis et al. (2008), fault zones consist of two main compartments: a central core surrounded by lateral damage zones. The fault core is the interval in which various mechanical and chemical processes have destroyed the fabric of the host rock. The system has evolved a cataclastic/gouge fault core that is relatively impermeable and a wider interval of fractures and smaller faults of damage zones provide the conduits for CO_2 lateral migration to coal seam. Fault development, along strike or in time, can also substantially influence secondary permeability due to changes in fracture interconnectivity and self-sealing processes.

There is no definitive evidence for the geological time scale of the CO_2 release in the ductile-brittle shear zone from the F19 fault. The isotopic age (K-Ar method) of chlorite thermal alteration is 15.87 Ma in the F19 fault, and the fission track age of the calcite veins in ultrabasic is 18.19 Ma ($\pm$1.62) (Tao, 1993; Wei et al., 2007). These results have demonstrated that CO_2 from hydrothermal activities occurred during this period. The upward movement of fluids in growth faults is proposed to be periodic. When the faults are active, fluid flow can be concentrated, but flow is restricted during inactive periods. Higher flow rates may be the result of fault-zone permeabilities and increases in fluid potential at shear stresses close to the shear strength of the rock (Hooper, 1991; Uehara and Shimamoto, 2004). Simultaneously, hydrothermal flow and precipitation may dramatically reduce existing fault-rock permeability over short time periods (Moore et al., 1994). The activities of the F19 faults in the Himalayan movement and the closed state of the NE principal stress in Quaternary are the primary factors that control CO_2 migration and dissipation. The CO_2 gas pool formation through the F19 fault zone is shown in Fig. 11.

4.4.2. The entrapment system of CO_2 pools

During the Neogene (2.6–23.5 Ma), dynamic-thermal metamorphism of the F19 ductile-brittle shear zone proposed CO_2 to release from basement marble regions. In the early Neogene (15.87 Ma), there was hydrothermal vertical migration of CO_2 along the F19 fault. Calcite fission track ages in coal stratum (8.37–9.81 Ma) (Tao, 1993) demonstrated that during the late Neogene, there was lateral migration of CO_2 to the coal strata until certain pressure conditions in the F19 fault.

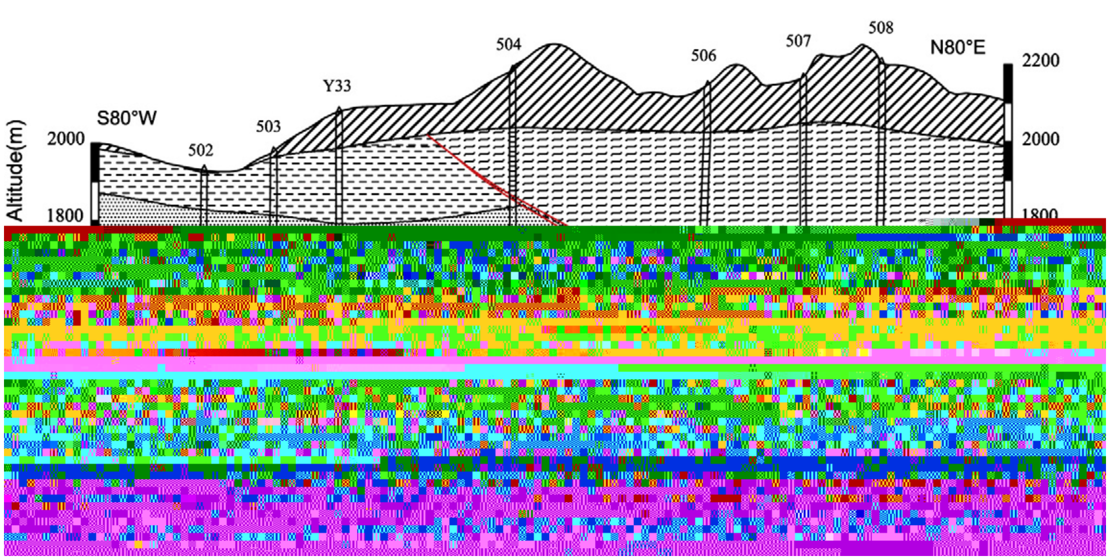

Fig. 11. Formation of the CO_2 gas pool through the F19 fault zone. The fault zones consist of a central core and damage zones. The fault core is impermeable, and the damage zone is the primary route of CO_2 migration.

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The F19 fault, the roof and floor of the No. 2 coal seam constitute a CO_2 trap system, which seals the CO_2 in the coal seam effectively over geological time. The F19 fault coupled to the precipitation and cementation of carbonates that plugs fault pores results in a decrease the fracture zone permeability, which constitute a vertical trap. The mudstone permeability of the Xiangtang group is primarily in the range of 0.03×10^{-3} to 0.76×10^{-3} μm^2. The permeability of glutenite of the Tandonggou group is less than 1×10^{-3} μm^2, which prevents CO_2 dispersion. The interaction between the coal seam and the CO_2 at reservoir temperature, pressure, and in situ stress levels will change CO_2 sorption capacity, permeability, and pore structure of the coal seam to control the diffusion and flow of CO_2 into the coal seam.

The strong affinity between the coal seam and CO_2 heighten the coal sequestration capacity. However, the CO_2 sequestration capacity in the Yaojie coalfield remains unclear. The CO_2 Langmuir volumes of Haishiwan coal samples are mainly in the range of 33 to 36 m^3/t. The typical drainage volume of CO_2 in the Haishiwan mine is not less than 45 m^3/t. The phase state of CO_2 in the coal seam may affect the physical appearance. CO_2 has potential as a supercritical fluid when reservoir temperature exceeds 31.1 °C and pressure exceeds 7.38 MPa. Under typical pressures of a fresh water system, critical pressure is reached at a depth of 756 m. Indirect evidence suggests that supercritical CO_2 is likely to exist in the No. 2 coal seam of the Haishiwan coalfield since:

– The mining depth of the Haishiwan Mine coal is 800 m, where the coal reservoir temperature is 40 °C on average;
– The measured mixture gas pressure is not less than 7.3 MPa;
– The typical drainage volume of CO_2 is much larger than the expected langmuir volume;
– Strong jet phenomena with mist gas emission frequently appear during the seam drilling.

5. Conclusions

High CO_2 contents are observed in the No. 2 coal seam of the Yaojie coalfield. Gas composition reveals $\delta^{13}C$ values for methane in the range of−32.76‰ to−44.08‰, which indicate an organic origin. However, the mainly $\delta^{13}C_{CO2}$ values of the gasses (−5.0‰ to +1.0‰) suggest an inorganic origin for the CO_2. The $^3He/^4He$ ratios of associated helium in these gasses are 0.0042–0.185 times greater than the atmospheric ratio, indicating that the helium is crust-derived.

The generation of CO_2 was controlled primarily by the deep F19 fault. During the late Jurassic to the early Cretaceous, dynamic-thermal metamorphism of the F19 ductile-brittle shear zone resulted in CO_2 release from basement carbonate regions, which are the inorganic sources of CO_2 in the Yaojie coalfield. The regional geological evolution and multi-periodical F19 fault movement control the formation, migration, and accumulation of CO_2 and result in the development of CO_2 gas pools in the Yaojie coalfield. The F19 fault played multiple roles in the generation, transportation, and trapping of gas during CO_2 formation, while the damage zone of the F19 fault is the primary route for CO_2 migration**.** The displacement of CH_4, carbonation generation, and the pore structure transformation of coal occurrence due to a series of physical and chemical effects occurred after CO_2 flux into the coal seams.

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