

# Impact of pyrite on shale gas enrichment—a case study of the Lower Silurian Longmaxi Formation in southeast Sichuan Basin

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**Abstract** Pyrite is one of the important components of shale and plays a crucial role in shale gas enrichment. However, currently there are just a few studies on this subject matter. Therefore, the characteristics of pyrite in organic-rich shale section of the Longmaxi Formation and its impact on shale gas enrichment was studied in this paper by using outcrops, drilling cores, thin sections and test data. Result shows that pyrite occurred in different forms (macro-micro scale) in the Longmaxi Formation in the southeast Sichuan Basin. The formation and content of pyrite has a close relation with TOC content. Pyrite may catalyze the hydrocarbon generation of organic matter. Interparticle pores within the pyrite framboids and organic matter pores in the pyrite-organic matter complex are well-developed in the Longmaxi Shale, which serves as a major reservoir space for shale gas. Pyrite can promote shale gas enrichment by absorbing shale gas on its surface and preserving free gas in the interparticle pores and organic matter pores. In addition, as a kind of brittle mineral, pyrite can improve the brittleness of shale reservoir and increase the micro-nano pore system in shale reservoir, thereby improving the transmission performance of shale reservoir and boosting shale gas recovery.

**Keywords** shale reservoir, pyrite, Longmaxi Formation, southeast Sichuan Basin

## 1 Introduction

In recent years, the shale gas exploration and development

have been quite successful in North America and areas in and around China's Sichuan Basin, and these achievements have attracted worldwide attention (Hao et al., 2013; Zou et al., 2016; Ma et al., 2018). Numerous geologists have conducted researches on shale gas formation conditions, enrichment mechanism, reservoir characteristics and gas-bearing property, demonstrating that the main controlling factors for shale gas enrichment include organic matter type, maturity, TOC content, shale lithofacies, sedimentary environment and preservation conditions (Curtis, 2002; Zou et al., 2010; Hao et al., 2013; Cao et al., 2015; Chen et al., 2015; Xiong et al., 2017; He et al., 2018; Chen et al., 2019; Shu et al., 2020). Pyrite is a common authigenic mineral and one of the typical minerals in shale, usually occurring in the form of irregular aggregates, idiomorphic crystals and framboid (Grimes et al., 2002). Scholars found that pyrite usually develop in marine shale reservoirs (Loucks and Ruppel, 2007; Loucks et al., 2009; Wang et al., 2014a; Wu et al., 2018; Tang et al., 2019). However, due to the low content of pyrite, its impact on shale gas enrichment was ignored and so far only a few studies have been dedicated to this subject matter.

The current researches on pyrite in shale mainly focus on the following aspects. First is the correlation between pyrite and shale sedimentary environment. As the form and size of crystalline and pyrite framboid vary in different sedimentary environment, understanding the sedimentary environment according to the grain size of the pyrite framboid in shale (Wilkin et al., 1996) could have great application significance. Secondly, some scholars have started to study the relationship between pyrite and shale gas (Berner et al., 1985; Love and Amstutz, 1966; Cui et al., 2013; Xu et al., 2015; Liu et al., 2016). They found that pyrite may have huge impact on shale gas enrichment.

It has been shown that pyrite significantly influences hydrocarbon generation and expulsion of organic matters (Hunt et al., 1991; Mango, 1992; Cui et al., 2013; Wang et al., 2014b; Sun et al., 2019), quality of shale reservoirs, as well as organic matter enrichment and gas content (Berner et al., 1985; Love and Amstutz, 1966; Xu et al., 2015; Liu et al., 2016; Zhang et al., 2016; You et al., 2017; Cao et al., 2018; Li et al., 2018). Although some scholars have realized that pyrite has an obvious impact on shale reservoirs, current researches on pyrite characteristics and their impacts on shale gas are limited, and more studies are needed to form a more systematic and clear knowledge structure.

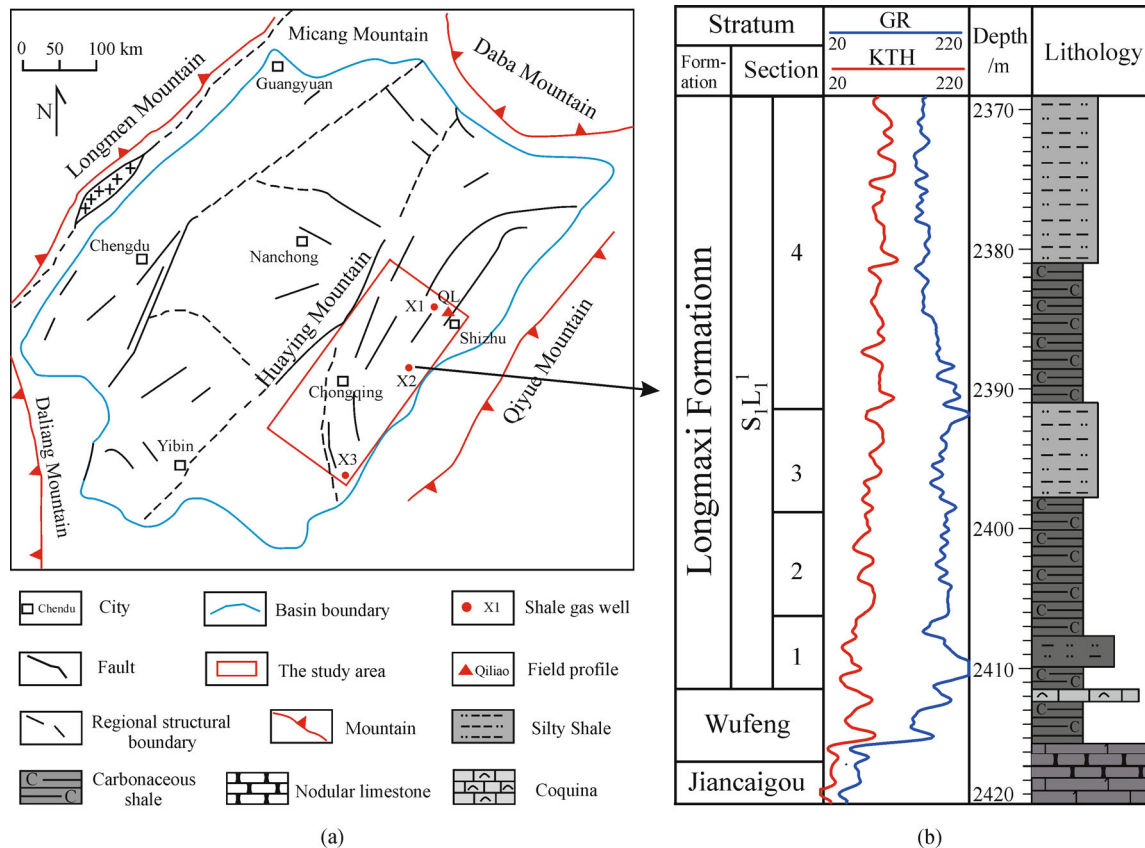
To figure out the characteristics of pyrite, especially pyrite framboid and its geological significance in relation to shale gas, we studied the characteristics of pyrite in the Longmaxi Formation marine shale and its impact on shale gas enrichment in the southeast Sichuan Basin.

## 2 Geologic setting

Under the convergence of the Cathaysia Block and Yangtze Block during the late Upper Ordovician to early Lower Silurian, the Sichuan Basin was formed with a basin pattern restricted by a series of uplifts (Wang et al., 2015; Nie et al., 2017; Zheng et al., 2019). Affected by the paleo-

uplift, southeastern Sichuan developed into a semi-occluded stagnant basin, with a shallow-deep shelf environment that dominated the whole area, leading to the deposition of a set of thick organic-rich marine shale in the area (Zou et al., 2014). High-quality organic-rich shale developed in the Upper Ordovician Wufeng Formation to the First Member of the Longmaxi Formation in the southeast Sichuan Basin. In the southeast Sichuan Basin, organic-rich shale is widely distributed with burial depth mainly ranging from 1500 to 3500 m, thickness of 20–40 m, high TOC (generally,  $TOC \geq 3\%$ ) and high maturity (usually,  $R_o > 2\%$ ) (Zou et al., 2014; Guo, 2015).

The southeast Sichuan Basin is geographical located in the central-southern part of the Yangtze Block, and structurally speaking, it is mostly located in the high-steep structure belts of eastern Sichuan. The study area is situated in the east of the Huayingshan Fault Zone and the west of the Qiyaoshan Fault Zone, and it is a narrow and long area running in a NE direction (Fig. 1). Under the crushing stress of snow peak structure to the southeast in the span from the late Yanshan to Himalayan Period, the structure lifted, strata suffered from denudation and formed a NE-SW “baffle type” construction with residual anticline and residual syncline distributed in alternation. Local adjustment and deformation during the Himalayan Period generated the present structural configuration (Huang et al., 1997; Yu et al., 2013).



**Fig. 1** (a) Location of the study area and (b) stratigraphic column of the Longmaxi Formation, and the gamma-ray log of the X1 Well (After Wang et al., 2002).

### 3 Samples and methods

To study the characteristics of pyrite in the Longmaxi Formation shale in the southeast Sichuan Basin and its impact on shale gas enrichment, core samples were obtained from Well X1, Well X2, and Well X3, and outcrop samples were obtained from Qiliao section in the southeast Sichuan Basin (Fig. 1). A series of analysis and tests including FIB-SEM (Focus Ion Beam-Scanning Electron Microscopes analysis), XRD (X-ray diffraction) test, TOC (Total organic carbon) content test, rock pyrolysis analysis, and total gas content test have been carried out.

#### 3.1 FIB-SEM (Focus Ion Beam-Scanning Electron Microscopes analysis)

First, the core samples were grounded into standard 1 cm × 1 cm samples. Second of all, we used IB-09010CP ion section polishing instrument for argon ion polishing to process the surface of samples. Thirdly, we used FEI Quanta 650 FEG field emission scanning electron microscope for image collection at 10 KV acceleration voltage and 10 μA beam current.

#### 3.2 XRD (X-ray diffraction) test

The shale rock samples were first dried, then crushed into powder with grain size less than 40 μm, and prepared for subsequent testing. As each type of mineral crystal has its own specific X-ray diffraction spectrum, we were able to acquire qualitative and quantitative results because the characteristic peak strength in spectrum is related to the mineral content of sample. The XRD test was conducted using a Panalytical X'Pert PRO MPD X-ray diffractometer.

#### 3.3 Total organic carbon (TOC) test

The shale sample was crushed into powder with grain size of roughly 150 μm, and about 0.5 g samples were prepared for testing. Before heating and combustion, the inorganic carbon, in the form of carbonate, in the samples were removed with acid. After washing and drying, the powder

samples were fully burned. The amount of CO<sub>2</sub> produced was measured by infrared detector, and the total organic carbon content of each sample was calculated. In this study, the TOC content was measured by using a LECO CS400 carbon sulfur analyzer.

#### 3.4 Rock pyrolysis analysis

To begin, surface pollutants of shale sample were removed with purified water, then absorb the water with filter paper, samples were crushed to about 150 μm. Next, accurately weigh 1 to 2 g of samples for testing and then put the sample into a clean porcelain bottle and seal it with purified water. Heat the shale samples to 560°C in pyrolysis furnace with programmed temperature increase, so that hydrocarbons in the rocks evaporate into gases, and organic matters (i.e., kerogen, asphaltene) show thermal cracking reaction and produce volatile hydrocarbon products. With carrier gas carrying gaseous hydrocarbon, it is directly detected by hydrogen flame detector (FID), so as to analyze the hydrocarbon content in rock samples. In this study, YQ-VII oil and gas display evaluation instrument was used to obtain S1 and S2 data under the temperature of 25°C to 28°C, and humidity of 55%–65% RH.

#### 3.5 Isothermal adsorption experiment

First, the shale samples were crushed to 150 μm, and then the iso-200 isothermal adsorption instrument was used to measure the volume of methane adsorbed when the samples reached the adsorption dynamic equilibrium at the same temperature (30°C), humidity about 1% and different pressure conditions. Then, according to Langmuir monolayer adsorption theory, VL (methane adsorption gas volume) was calculated.

Analysis of the test data shows that: Pyrite content in the study area is between 1.3% and 7.5% (3.21%), and the TOC content ranges from 0.83% to 6.67% (2.60%). The content of S1 is 0.66 to 3.0 × 10<sup>-2</sup> mg/g, with an average of 1.45 × 10<sup>-2</sup> mg/g; the content of S2 is 2.63 to 7.59 × 10<sup>-2</sup> mg/g, with an average of 4.21 × 10<sup>-2</sup> mg/g; and the content of methane adsorption gas ranges from 1 to 3.35 m<sup>3</sup>/t, with an average value of 1.97 m<sup>3</sup>/t (Table 1).

**Table 1** The number of samples and data of the test results

Well	Pyrite content (mean)/%	TOC content (mean)/%	Adsorbed gas content (mean)/(m <sup>3</sup> ·t <sup>-1</sup> )	Rock pyrolysis parameters	
				S1 (mean)/(0.01 mg·g <sup>-1</sup> )	S2 (mean)/(0.01 mg·g <sup>-1</sup> )
X1	1.3–6.6 (3.33)	0.83–5.62 (2.60)	1.0–3.01 (1.84)	0.66–2.3 (1.32)	2.63–7.59 (4.21)
X2	1.4–7.5 (2.81)	0.75–4.97 (2.46)	1.42–3.35 (2.21)	1.0–3.0 (1.89)	/
X3	2.0–7.0 (4.06)	0.86–6.67 (3.17)	/	/	/
Total	<u>1.3–7.5 (3.21)</u> n = 177	<u>0.83–6.67 (2.60)</u> n = 177	<u>1–3.35 (1.97)</u> n = 21	<u>0.66–3.0 (1.45)</u> n = 93	<u>2.63–7.59 (4.21)</u> n = 62

## 4 Discussions

### 4.1 Morphological characteristics of pyrite in the Longmaxi Formation shale

According to observations of the drilling cores, outcrop section and thin section, pyrite is well-developed in the Longmaxi Formation shale, and mainly exists in the form of pyrite strips (Fig. 2(a)), with thickness ranging generally between 0.2 cm and 3 cm. Pyrite strips in some regions have aggregated into nodules (Fig. 2(b)). Pyrite nodules are lenticular in shape and randomly distributed in the shale, with size ranging from 0.5 cm  $\times$  2 cm to 1 cm  $\times$  3 cm (Fig. 2(c)). In addition, dispersed granular pyrite (Fig. 2(d)) and pyrites in bedding fractures have also been observed in the shale.

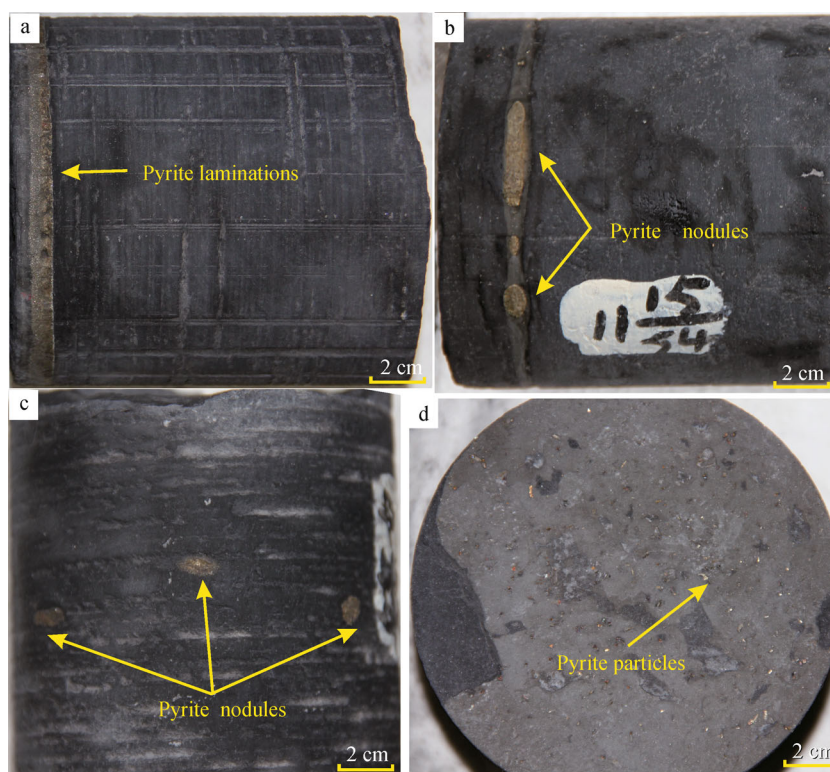
Micro morphology of pyrite in the Longmaxi Formation shale includes the following specific types: 1) normal spherical pyrite framboids (Fig. 3(a)), which have near-spherical or ellipsoidal shape with an average diameter between 2  $\mu$ m and 10  $\mu$ m and a maximum of 14–18  $\mu$ m, and are composed of massive 0.1–1  $\mu$ m pyrite microcrystalline grains with well-developed intercrystalline nanopores; 2) elliptical or nearly spherical pyrite framboid shadows without intergranular nanopores (Fig. 3(b)); 3) pyrite framboid aggregations (Fig. 3(c)), formed when

pyrite framboids aggregated into pyrite framboid aggregation, with the size of single pyrite framboid grain ranging from 3 to 5  $\mu$ m; 4) irregular allotriomorphic-subhedral pyrite clumps (Fig. 3(d)); 5) allotriomorphic-subhedral pyrite grains (Fig. 3(e)); 6) subhedral-euhedral pyrite particles (Fig. 3(f)), with euhedral pyrite grains generally rectangular, triangular, quadrilateral or hexagonal in shape.

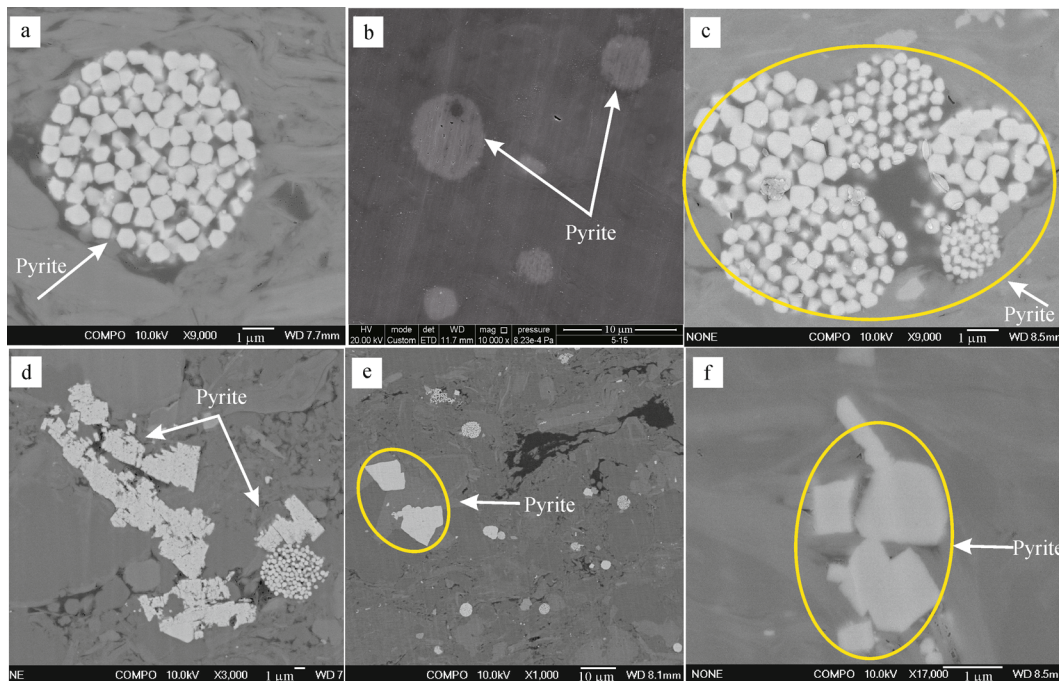
Pyrite shows a variable microcosmic occurrence in the Longmaxi Formation shale in the southeast Sichuan Basin, mainly in the form of normal spherical pyrite framboid (Figs. 3(a) and 3(d)), followed by partially recrystallized pyrite framboid and Allotriomorphic-subhedral pyrite. The ratio of pyrite aggregation is relatively low.

### 4.2 Correlation between pyrite and TOC content

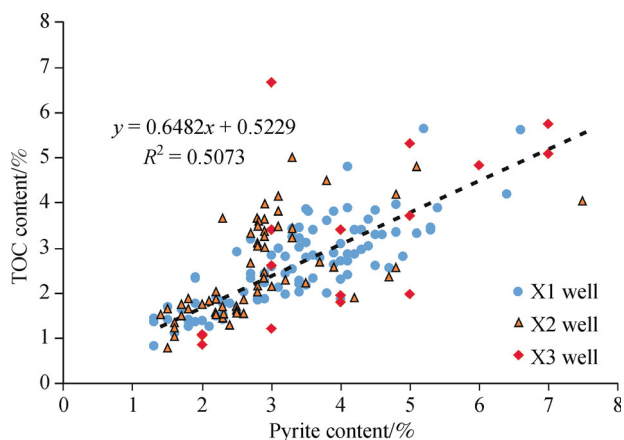
According to the study, there is an obvious and positive correlation between pyrite content and TOC content in the Longmaxi Formation shale in the southeast Sichuan Basin (Fig. 4). The correlation coefficient is about 0.51, which means the higher the pyrite content, the higher the TOC content. Previous studies have shown that pyrite and organic matter are relatively developed in the lower part of Longmaxi Formation (Tan et al., 2015; Chen et al., 2016a; Li et al., 2018). As an essential nutrient, iron may promote biological growth (He et al., 2020). The lower part of



**Fig. 2** Photos of drilling cores showing macroscopic characteristics of pyrite in the Longmaxi shale in the southeast Sichuan Basin. (a) Pyrite laminations, X2 well, 2412.5 m; (b) pyrite nodules developed within the pyrite laminations, X2 well, 2396.85 m; (c) pyrite nodules, X2 well, 2358.62 m; (d) dispersed granular pyrites with particle size less than 0.5 mm, X2 well, 2370.46 m.



**Fig. 3** Microscopic photos showing pyrite characteristics in the Longmaxi Formation shale in the southeast Sichuan Basin. (a) Normal spherical pyrite framboid; (b) pyrite framboids shadows without intragranular nanopore; (c) pyrite framboid aggregation; (d) irregular allotriomorphic-subhedral pyrite clump; (e) allotriomorphic-subhedral pyrite grains; (f) subhedral-euhedral pyrite particles.



**Fig. 4** Relationship between pyrite content and TOC content of the Longmaxi Formation shale in the southeast Sichuan Basin.

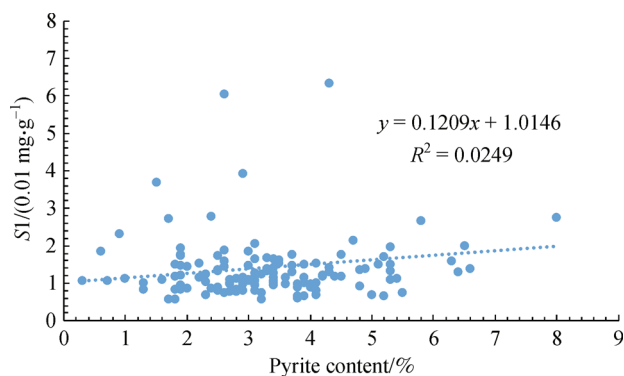
Longmaxi Formation has many ancient organisms and high paleoproductivity, and therefore, organic matters are developed rather well (Li et al., 2018; He et al., 2019). In addition, Love and Amstutz (1966), Kaplan et al. (2012), Nie and Zhang (2012) pointed out that iron plays an important role in organic matter deposition. High content of iron is conducive to the enrichment of organic matter. Pyrite is a stable polymorph of  $\text{FeS}_2$ , which is why iron in pyrite may promote the enrichment of organic matters.

This positive correlation is commonly found in black shale, which is conducive to the development and

preservation of organic matters and pyrite (Cui et al., 2012; Wu et al., 2014; Tan et al., 2015; Xu et al., 2015; Chen et al., 2016a, 2016b; Liu et al., 2016; Sun and Guo, 2017), but not all shale has such a close correlation. For the Permian coastal swamps-shallow shelf shale in the Lower Yangtze area in China, the redox environmental condition in water body is worse than deep-water shelf, which is not conducive to the development and preservation of pyrite and organic matters. In addition, the content of pyrite is low, so there is no correlation between pyrite content and TOC content (Cao et al., 2018). Therefore, when the depositional environment is in reduction conditions, pyrite content has a positive correlation with TOC content. The Longmaxi Formation shale is mainly deposited in the shelf under anoxic conditions in the southeast Sichuan Basin, which results in clearly positive correlation between pyrite content and TOC content in this area.

#### 4.3 Impact of pyrite to hydrocarbon generation of organic matters

The content of pyrite is weakly positively correlated to S1 (content of residual hydrocarbon in rock) in the Longmaxi Formation shale in the southeast Sichuan Basin. The best guess is that pyrite might had catalyzed and promoted the decomposition of organic matters in shale. Thus, the higher the content of pyrite, the higher the content of residual hydrocarbon (Fig. 5). Previous study shows that inorganic mineral in matrix (e.g., clay and carbonate) can also

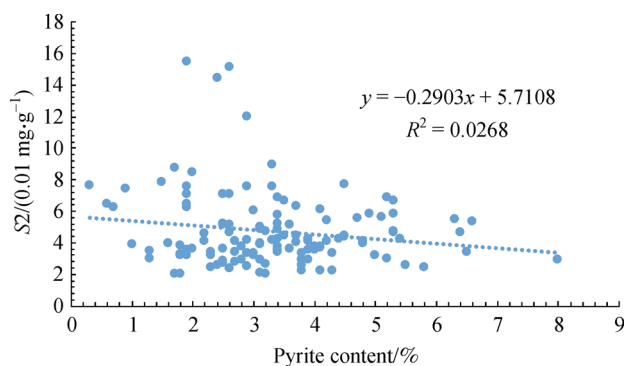


**Fig. 5** Relationship between pyrite content and S1 content in the Longmaxi Formation shale in the southeast Sichuan Basin.

catalyze and promote the decomposition of the kerogen in shale (Tannenbaum and Kaplan, 1985). Therefore, the correlation between the contents of S1 and pyrite cannot fully reflect the catalytic action of pyrite in the generation of organic hydrocarbon.

$T_{\max}$  of the Longmaxi Formation shale is mostly between 375°C and 400°C in the southeast Sichuan Basin. In general, pyrite usually enters the fast decomposition stage at about 485°C (Zhao et al., 2015). In experiment data processing, samples with  $T_{\max}$  higher than 500°C are expected to ensure the relatively accurate correlation between S2 (content of pyrolysed hydrocarbon) and pyrite content. Results show that pyrite content is weakly negatively correlated with S2, as in an increase of pyrite content accompanied by decrease in S2 content, indicating that pyrite might have a catalytic effect on the formation of hydrocarbons under certain conditions, which may increase the content of gaseous hydrocarbon (Fig. 6).

Previous studies show that transition metal and sulfide are ideal catalysts for organic matter evolution in the process of thermal evolution of organic matters (Hunt et al., 1991; Mango, 1992; Cui et al., 2013; Wang et al., 2014b; Sun et al., 2019). Content of pyritic sulfur is negatively related to the reaction activation energy. The increase of sulfur content can reduce the content of



**Fig. 6** Relationship between pyrite content and S2 content in the Longmaxi Formation shale in the southeast Sichuan Basin.

activation energy and promote reaction rate. Iron content in transition metal element can significantly affect electron cloud distribution of cracked organic matter, and promote hydrocarbon generation in organic matters. Large content of pyrite (large S content and sufficient transition element like  $\text{Fe}^{2+}$ ) can reduce activation energy and lower C-S bond energy. At low temperatures, C-S bond would break and generate hydrocarbon in advance. Therefore, pyrite is a good catalyst for organic matter evolution.

#### 4.4 Influence of pyrite on shale gas enrichment

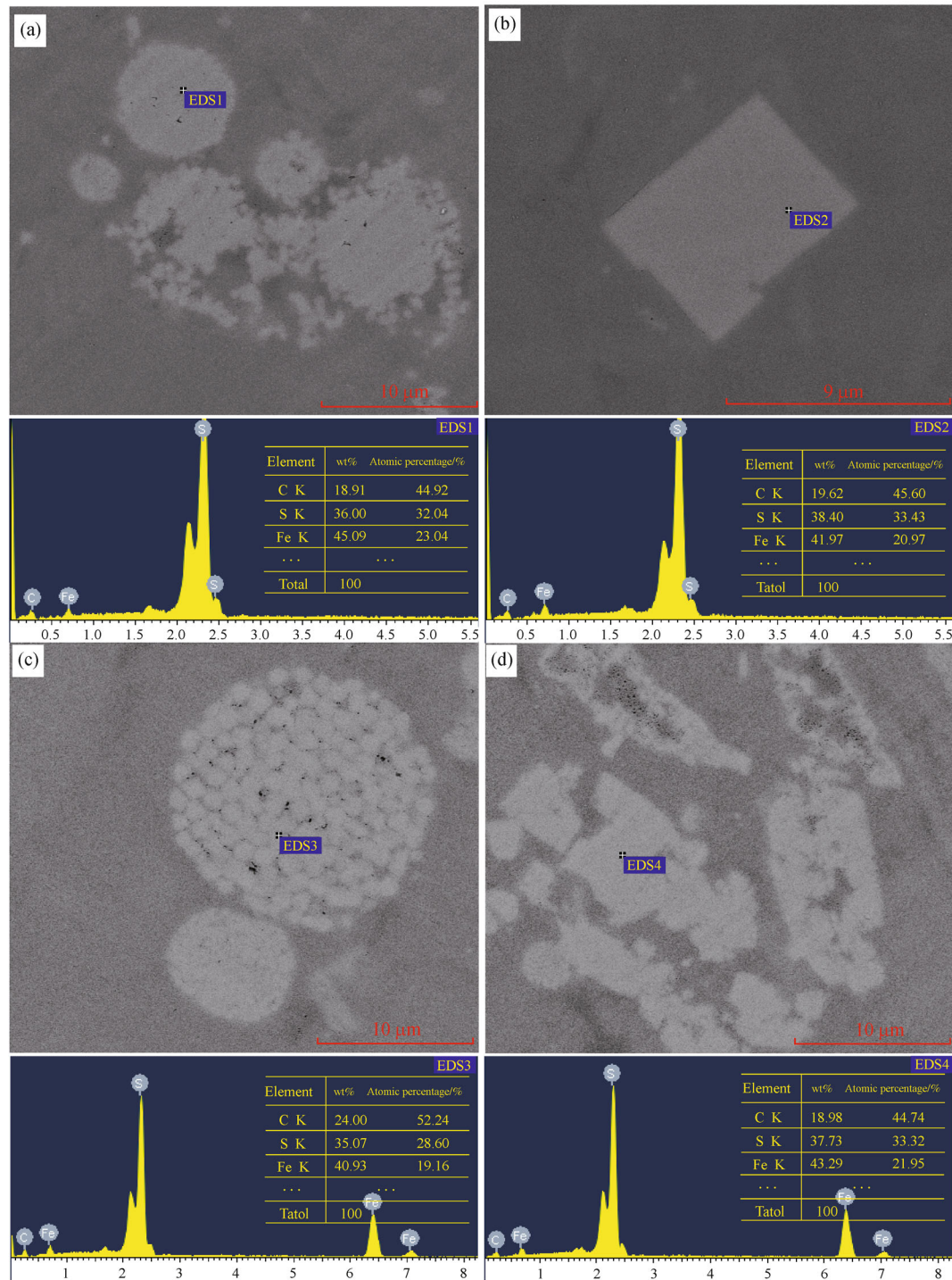
Pyrite can promote the accumulation of shale gas. The surface of pyrite and pores within the pyrite serve as important spaces for shale gas accumulation (Cui et al., 2013; Cao et al., 2018; Li et al., 2018). EDS energy spectrum test of 24 pyrite samples from the Longmaxi Formation shale shows that the weight percentage of carbon element in samples ranges from 17.77% to 28.47%, with an average of 21.56%, and the percentage of carbon atom is 44.02% to 54.97%, with an average of 48.34%. Wherein, the weight percentage of carbon element and percentage of carbon atom of pyrite framboids are higher than other forms of pyrite (Fig. 7(c)), which means that pyrite is rich in hydrocarbon (Fig. 7).

The content of pyrite has a clearly positive correlation with the content of methane adsorption gas in the Longmaxi Formation shale in the southeast Sichuan Basin, which means that the higher the pyrite content, the more the methane adsorption gas content (Fig. 8). Nie and Zhang (2012), Chen et al. (2016b), Zhang et al. (2020) also discovered this positive correlation in the Longmaxi Formation shale. This phenomenon is also found in the shales of the Upper Permian Dalong Formation and the Lower Permian Gufeng Formation in the Lower Yangtze area in China, as well as shale in the Sinian Doushantuo Formation in the Upper Yangtze area in China, which means that pyrite is obviously capable of absorbing shale gas and promotes shale gas enrichment.

The pores associated with pyrite mainly include 1) massive organic pores in pyrite-organic matter complex, which are the most common type of pores closely related to pyrite in the Longmaxi Formation shale (Figs. 9(c) and 9(d)); and 2) a small number of irregular intercrystalline pores within the pyrite framboids (Figs. 9(a) and 9(b)). The intercrystalline pores within pyrite framboids together with organic pores in the pyrite-organic matter complex not only increase shale reservoir space and shale specific surface area, but also provide space for free gas (Fig. 9). Ardakani et al. (2017) already have shown framboidal pyrite's capacity for storing hydrocarbon.

#### 4.5 Influence of pyrite on brittleness and permeability of shale reservoir

Shale reservoir characterized by self-generation and self-

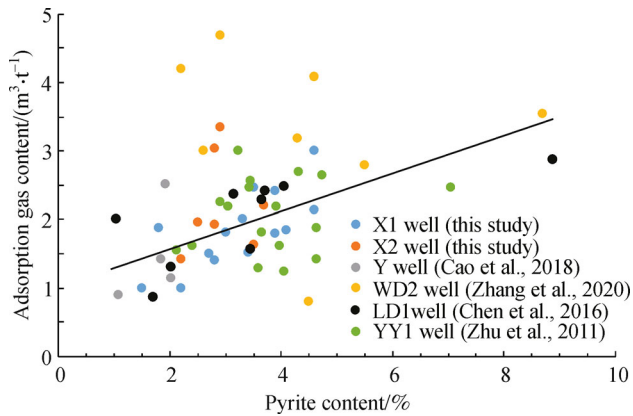


**Fig. 7** Energy dispersive spectrum (EDS) analysis of pyrite in the Longmaxi Formation shale in the southeast Sichuan Basin. (a) Energy dispersive spectrum for pyrite framboid, X1 Well, 1998.21 m; (b) Energy dispersive spectrum for euhedral pyrite, X1 Well, 1997.34 m; (c) Energy dispersive spectrum for pyrite framboids, X1 Well, 2044.17 m; (d) Energy dispersive spectrum for irregular pyrite, X1 Well, 2049.11 m.

storage, ultra-low porosity and ultra-low permeability may have tremendous economic and industrial benefits through artificial fracturing in later stage. As a kind of brittle mineral, pyrite can improve reservoir permeability and

increase the brittleness index of reservoir to some extent, providing favorable conditions for subsequent hydraulic fracturing (You et al., 2017; Li et al., 2018).

Pyrite is a brittle mineral, and its influence on the

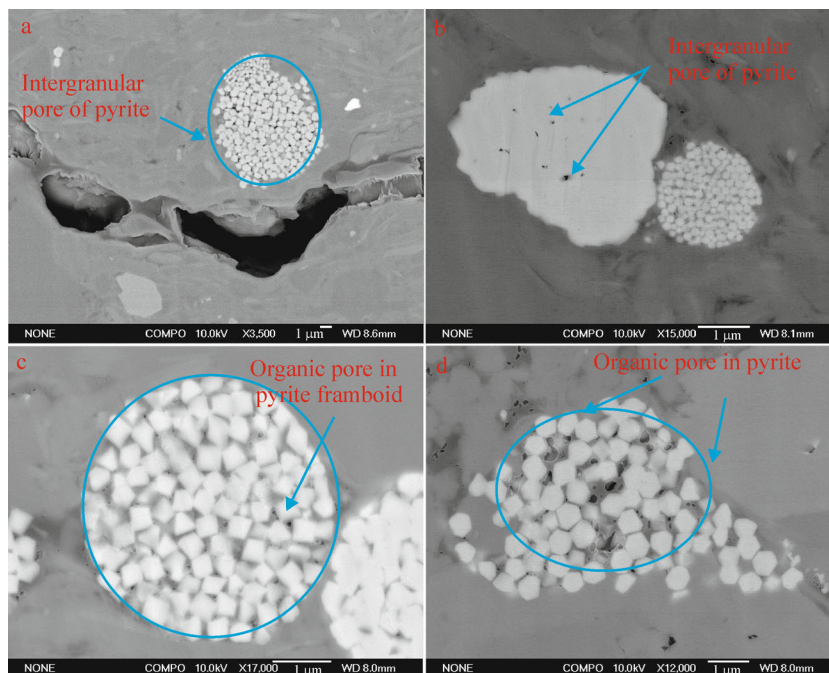


**Fig. 8** Relationship between pyrite content and adsorption gas content in the Longmaxi Formation shale in the southeast Sichuan Basin.

brittleness index of shale reservoir can be explained from the following aspects. First, the physical property of pyrite determines the high brittleness index of shale reservoir. Young modulus of pyrite is about 300 GPa, much greater than quartz, while the Poisson's ratio of pyrite is about 0.15, close to quartz. Mechanical brittleness index of pyrite is apparently higher than organic matters and clay mineral components. Second of all, pyrite can catalyze hydrocarbon generation, thereby promoting the development of pore system in shale reservoirs after hydrocarbon generation and expulsion of organic matters in shale, which would further increase the ease of fracturing shale. The

Longmaxi Formation shale reservoirs in the southeast Sichuan Basin have pyrite content in the range of 1.7% to 6.3%, which can improve the brittleness index of shale reservoir by 2% to 6%. Therefore, pyrite can improve the brittleness of shale reservoir, decreases difficulty in subsequent hydraulic fracturing, and ultimately achieve the purposes of transforming the shale fracturing process and boosting shale gas production.

During acid-fracturing, pyrite and carbonate minerals in shale reservoirs can be quickly decomposed by solution-oxidation. A large number of micro-nano pores-fractures can be produced, which would improve porosity and permeability of shale reservoirs, and in turn enhance shale gas recovery (Harrison et al., 2017; You et al., 2016, 2017; Tan et al., 2018). You et al. (2016) invented a method to increase the fracture network density of shale gas well fracturing. Outcome from a shale fracturing test with hydrogen peroxide fracturing fluids indicates that most organic matters and pyrite can be oxidized and dissolved to burst rock formation.  $\text{Fe}^{3+}$  concentration increases while sulfur content decreases by up to about 98%, and the porosity of the treated core can be raised by about 10%. Therefore, pyrite can increase the micro-nano pore system in shale reservoir, improve the flow within shale reservoir, stimulate the decomposition of adsorbed gas, mitigate reservoir damage and boost shale gas recovery, because when pyrite is dissolved and oxidized under the action of acid-oxygen compound fracturing fluid in later period, it releases heat to produce pores and micro-fractures.



**Fig. 9** Common pore types associated with pyrite in the Longmaxi Formation shale in the southeast Sichuan Basin. (a) Intergranular pore of pyrite, X2 well, 2330.46 m; (b) Intergranular pore of pyrite, X2 well, 2346.50 m; (c) Organic pore in pyrite framboid, X2 well, 2366.74 m; (d) Organic pore in pyrite, X2 well, 2402.65 m.

## 5 Conclusions

Pyrite is well-developed and varies in occurrence in the Longmaxi Formation shale in the southeast Sichuan Basin. On a macro scale, pyrites mainly exist as strips and pyrite nodules, while on the micro scale, pyrites mostly occur as allotriomorphic-euhedral granular pyrite and single spherical pyrite framboid.

As a good catalyst for organic matter evolution, pyrite can promote hydrocarbon generation of organic matter. Inter-particle pores within the pyrite framboids and organic pores in the pyrite-organic matter complex are developed in the Longmaxi Formation shale. These pores not only increase shale reservoir space and shale specific surface area, but can also provide reservoir space for free gas. In addition, pyrite can promote shale gas enrichment by absorbing shale gas.

As a kind of brittle mineral, pyrite in shale reservoir can improve the brittleness of shale reservoir, which is favorable to later hydraulic fracturing. Furthermore, pyrite can increase the pore system in reservoir, improve the flow within shale reservoir, stimulate the decomposition of adsorbed gas and boost shale gas recovery, because when pyrite is dissolved and oxidized under the action of acid-oxygen compound fracturing fluid in later period, it releases heat to produce pores and micro-fractures.

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## References

- Ardakani O H, Saneii H, Ghanizadeh A, McMechan M, Ferri F, Clarkson C R (2017). Hydrocarbon potential and reservoir characteristics of Lower Cretaceous Garbutt Formation, Liard Basin Canada. *Fuel*, 209: 274–289
- Berner R A, De Leeuw J W, Spiro B, Murchison D G, Eglinton G (1985). Sulphate reduction, organic matter decomposition and pyrite formation. *Philos Trans R Soc Lond*, 315(1531): 25–38
- Cao T T, Deng M, Song Z G, Liu G X, Huang Y R (2018). Study on the effect of pyrite on the accumulation of shale oil and gas. *Nat Gas Geosci*, 29(03): 404–414 (in Chinese)
- Cao T T, Song Z G, Wang S B, Xia J (2015). A comparative study of the specific surface area and pore structure of different shales and their kerogens. *Sci China Earth Sci*, 58(4): 510–522
- Chen K, Zhang J C, Tang X, Yu J D, Liu Y, Yang C (2016b). Main controlling factors on shale adsorption capacity of the Lower Silurian Longmaxi Formation in western Hunan-Hubei area. *Oil & Gas Geol*, 37(1): 23–29 (in Chinese)
- Chen L, Lu Y C, Jiang S, Li J Q, Guo T L, Luo C (2015). Heterogeneity of the Lower Silurian Longmaxi marine shale in the southeast Sichuan Basin of China. *Mar Pet Geol*, 65: 232–246
- Chen Q, Zhang J C, Tang X, Li W J, Li Z M (2016a). Relationship between pore type and pore size of marine shale: an example from the Sinian-Cambrian Formation, Upper Yangtze region, south China. *Int J Coal Geol*, 158(3): 13–28
- Chen L, Wang G, Yang Y, Jing C, Chen M, Tan X (2019). Geochemical characteristics of bentonite and its influence on shale reservoir quality in Wufeng-Longmaxi Formation, south Sichuan Basin, China. *Energy Fuels*, 33(12): 12366–12373
- Cui J W, Zhu R K, Wu S T, Bai B (2013). The role of pyrite on organic matter enrichment, hydrocarbon generation and expulsion and shale oil accumulation. *Geol Rev*, 59: 783–784 (in Chinese)
- Cui J W, Zou C N, Zhu R K, Bai B, Wu S T, Wang T (2012). New advances in shale porosity research. *Adv Earth Sci*, 27(12): 1319–1325 (in Chinese)
- Curtis J B (2002). Fractured shale-gas system. *AAPG Bull*, 86(11): 1921–1938
- Grimes S T, Davies K L, Butler I B, Brock F, Edwards D, Rickard D, Briggs D E G, Parkes R J (2002). Fossil plants from the Eocene London Clay: the use of pyrite textures to determine the mechanism of pyritization. *J Geol Soc London*, 159(5): 493–501
- Guo T L (2015). The Fuling shale gas field — a highly productive Silurian gas shale with high thermal maturity and complex evolution history, southeastern Sichuan Basin, China. *Interpretation (Tulsa)*, 3(2): SJ25–SJ34
- Hao F, Zou H Y, Lu Y C (2013). Mechanisms of shale gas storage: implications for shale gas exploration in China. *AAPG Bull*, 97(8): 1325–1346
- Harrison A L, Jew A D, Dustin M K, Thomas D L, Joe-Wong C M, Bargar J R, Johnson N, Brown G E Jr, Maher K (2017). Element release and reaction-induced porosity alteration during shale-hydraulic fracturing fluid interaction. *Appl Geochem*, 82: 47–62
- He T H, Lu S F, Li W H, Tan Z Z, Zhang X W (2018). Effect of salinity on source rock formation and its control on the oil content in shales in the Hetaoyuan Formation from the Biyang Depression, Nanxiang Basin, Central China. *Energy Fuels*, 32(6): 6698–6707
- He L, Wang Y P, Chen D F, Wang Q X, Wang C (2019). Relationship between sedimentary environment and organic matter accumulation in the black shale of Wufeng-Longmaxi Formations in Nanchuan area, Chongqing. *Nat Gas Geosci*, 30(02): 203–218 (in Chinese)
- He T H, Lu S F, Li W H, Sun D Q, Pan W Q, Zhang B S, Tan Z Z, Ying J F (2020). Paleoweathering, hydrothermal activity and organic matter enrichment during the formation of earliest Cambrian black strata in the northwest Tarim Basin, China. *J Petrol Sci Eng*, 189: 106987
- Huang J Z, Chen S J, Song J R, Wang L S, Gou X M, Wang T D, Dai H M (1997). Hydrocarbon source systems and formation of gas fields in Sichuan Basin. *Sci China Ser D Earth Sci*, 40(1): 32–42
- Hunt J M, Lewan M D, Hennt J C (1991). Modelling oil generation with time-temperature index graphs based on the Arrhenius equation. *AAPG Bull*, 75(4): 795–807
- Kaplan I R, Bird K J, TAILLEUR I L (2012). Source of molten elemental sulfur and hydrogen sulphide from the Inigok well, northern Alaska. *AAPG Bull*, 96(2): 337–354
- Li D, Ou C H, Ma Z G, Jin P P, Ren Y J, Zhao Y F (2018). Pyrite-shale interaction in shale gas enrichment and development. *Geophys Prospect*, 57(3): 332–343 (in Chinese)
- Liu Z Y, Zhang J C, Liu Y, Yu W W, He W, Li B W (2016). The particle size characteristics of pyrite in Western Hunan and Hubei areas' Wufeng-Longmaxi Formation shale. *Sci Tech Eng*, 16(26): 34–41 (in Chinese)

- Chinese)
- Loucks R G, Reed R M, Ruppel S C, Jarvie D M (2009). Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale. *J Sediment Res*, 79 (12): 848–861
- Loucks R G, Ruppel S G (2007). Mississippian Barnett shale: lithofacies and depositional setting of a deep-water shale-gas succession in the Fort Worth Basin, Texas. *AAPG Bull*, 91(4): 579–601
- Love L G, Amstutz G C (1966). Review of microscopic pyrite from the Devonian Chattanooga shale and Rammelsberg Bandersz. *Fortschr Mineral*, 43: 273–309
- Ma Y S, Cai X Y, Zhao P R (2018). China's shale gas exploration and development: understanding and practice. *Pet Explor Dev*, 45(4): 589–603
- Mango F D (1992). Transition metal catalysis in the generation of petroleum and natural gas. *Geochim Cosmochim Acta*, 56(1): 553–555
- Nie H K, Zhang J C (2012). Shale gas accumulation conditions and gas content calculation: a case study of Sichuan Basin and its periphery in the Lower Paleozoic. *Acta Geol Sin*, 86(02): 349–361 (in Chinese)
- Nie H K, Jin Z J, Ma X, Liu Z B, Lin T, Yang Z H (2017). Graptolites zone and sedimentary characteristics of Upper Ordovician Wufeng Formation-Lower Silurian Longmaxi Formation in Sichuan Basin and its adjacent areas. *Acta Petrol Sin*, 38(2): 160–174 (in Chinese)
- Shu Y, Lu Y C, Chen L, Wang C, Zhang B (2020). Factors influencing shale gas accumulation in the lower Silurian Longmaxi Formation between the north and south Jiaoshiba area, southeast Sichuan Basin, China. *Mar Pet Geol*, 111: 905–917
- Sun C L, Liu H, Ge J W, Zhang Y N, Han B, Qin M (2019). Changes of functional groups and gas species during oil shale pyrolysis with addition of pyrite. *Energ Sourc Recov Util Environ Effects*, 41(10): 1242–1252
- Sun Y S, Guo S B (2017). Characteristics of microscopic pores of shale from Upper Sinian Doushantuo Formation in the western of Hunan and Hubei, China and the main controlling factors. *J Earth Sci Env*, 39(1): 114–125 (in Chinese)
- Tan M J, Mao K Y, Song X D, Yang X, Xu J J (2015). NMR petrophysical interpretation method of gas shale based on core NMR experiment. *J Petrol Sci Eng*, 136(12): 100–111
- Tan P, Jin Y, Han L, Shan Q L, Zhang Y K, Chen G, Zhou Y C (2018). Influencing mechanism of acidification pretreatment on hydraulic fracture for deep fractured shale reservoirs. *Chinese J Geotechn Eng*, 40(2): 384–390 (in Chinese)
- Tang L, Song Y, Li Q W, Pang X Q, Jiang Z X, Li Z, Tang X L, Yu H L, Sun Y, Fan S C, Zhu L (2019). Quantitative evaluation of shale gas content in different occurrence states of the Longmaxi Formation: a new insight from Well JY-A in the Fuling Shale Gas Field. *Acta Geol Sin*, 93(02): 400–419
- Tannenbaum E, Kaplan I R (1985). Role of minerals in the thermal alteration of organic matter—I: generation of gases and condensates under dry condition. *Geochim Cosmochim Acta*, 49(12): 2589–2604
- Wang Q T, Lu H, Shen C C, Liu J Z, Peng P A, Hsu C S (2014b). Impact of inorganically bound sulfur on late shale gas generation. *Energy Fuels*, 28(2): 785–793
- Wang Y M, Dong D Z, Yang H, He L, Wang S Q, Huang J L, Pu B L, Wang S F (2014a). Quantitative characterization of reservoir space in the Lower Silurian Longmaxi Shale, southern Sichuan, China. *Sci China Earth Sci*, 57(2): 313–322
- Wang X J, Yang Z R, Han B (2015). Superposed evolution of Sichuan Basin and its petroleum accumulation. *Earth Sci Front*, 22(03): 161–173 (in Chinese)
- Wang Z C, Zhao W Z, Zhang L, Wu S X (2002). Structural Sequence and Natural Gas Exploration in Sichuan Basin. Beijing: Geological Publishing House (in Chinese)
- Wilkin R T, Barnes H L, Brantley S L (1996). The size distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. *Geochim Cosmochim Acta*, 60(20): 3897–3912
- Wu C J, Zhang M F, Ma W Y, Liu Y, Xiong D M, Sun L N, Tuo J C (2014). Organic matter characteristic and sedimentary environment of the Lower Cambrian Niutitang Shale in southeastern Chongqing. *Nat Gas Geosci*, 25(8): 1267–1274 (in Chinese)
- Wu J, Hu Z Q, Xie J, Liu Z B, Zhao J H (2018). Macro-micro occurrence mechanism of organic matters in Wufeng-Longmaxi shale in the Sichuan Basin and its peripheral areas. *Nat Gas Indust*, 38(08): 23–32 (in Chinese)
- Xiong J, Liu X, Liang L, Zeng Q (2017). Methane adsorption on carbon models of the organic matter of organic-rich shales. *Energy Fuels*, 31(2): 1489–1501
- Xu Z X, Han S M, Wang Q C (2015). Characteristics of pyrite and its hydrocarbon significance of shale reservoir of Doushantuo Formation in middle Yangtze area. *Lithologic Reservoirs*, 27(02): 31–37 (in Chinese)
- You L J, Kang Y L, Yang P F (2016). A method of increasing fracture network density in shale gas well fracturing. *CN105626028A*, 2016–06–01 (in Chinese)
- You L J, Kang Y L, Chen Q, Fang C H, Yang P F (2017). Prospect of shale gas recovery enhancement by oxidation-induced rock burst. *Nat Gas Indust*, 4(6): 449–457 (in Chinese)
- Yu K H, Jin Z K, Su K, Dong X D, Zhang W, Du H Y, Chen Y, Zhang W D (2013). The Cambrian sedimentary characteristics and their implications for oil and gas exploration in north margin of Middle-Upper Yangtze Plate. *Sci China Earth Sci*, 56(6): 1014–1028
- Zhang G R, Nie H K, Tang X, Du W, Sun C X, Chen S (2020). Pyrite type and its effect on shale gas accumulation: a case study of Wufeng-Longmaxi shale in Sichuan Basin and its periphery. *Petrol Geol & Exper*, 42(3): 459–466 (in Chinese)
- Zhang C C, Wang Y M, Dong D Z, Li X J, Guan Q Z (2016). Evaluation of the Wufeng-Longmaxi shale brittleness and prediction of “sweet spot layers” in the Sichuan Basin. *Nat Gas Indust*, 36(9): 51–60 (in Chinese)
- Zhao L C, Sun C B, Zhang S T, Xie W Q, Zheng X Y, Liu K (2015). Characteristic of thermal decomposition kinetics of main gold-bearing sulfides pyrite. *Chinese J Nonferrous Metals*, 25(08): 2212–2217 (in Chinese)
- Zheng Y L, Mou C L, Wang X P (2019). Sedimentary geochemistry and patterns of organic matter enrichment of Wufeng-Longmaxi Formations in the southern margin of Sichuan Basin, China—a case study of Tianlin Profile in Xuyong Area. *J Earth Sci Env*, 41(05): 541–560 (in Chinese)
- Zou C N, Dong D Z, Wang S J, Li J Z, Li X J, Wang Y M, Li D H, Cheng K M (2010). Geological characteristics and resource potential of shale gas in China. *Pet Explor Dev*, 37(6): 641–653

Zou C N, Dong D Z, Wang Y M, Li X J, Huang J L, Wang S F, Guan Q Z, Zhang C C, Wang H Y, Liu H L, Bai W, Liang F, Lin W, Zhao Q, Liu D, Yang Z, Liang P, Sun S, Qiu Z (2016). Shale gas in China: characteristics, challenges and prospects (II). *Pet Explor Dev*, 43(2): 182–196

Zou C N, Du J H, Xu C C, Wang Z C, Zhang B M, Wei G Q, Wang T S, Yao G S, Deng S H, Liu J L, Zhou H, Xu A, Yang Z, Jiang H, Gu Z (2014). Formation, distribution, resource potential, and discovery of Sinian-Cambrian giant gas field, Sichuan Basin, SW China. *Pet Explor Dev*, 41(3): 306–325