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Composition of the "Organic Matter- clay Mineral" Aggregates and Occurrence of Shale Gas on the Lower Cambrian Black Shale in Guizhou, China

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Abstract. Analyses by X ray diffraction analysis (XRD) indicate that the main mineral composition of the Lower Cambrian black shale in Guizhou is quartz, clay minerals, albite, dolomite and pyrite, the clay minerals are mainly composed of illite. The characteristics of organic carbon in the black shale are discussed. The content of original organic carbon is between 3.024% and 8.22% with an average of 5.63%, and the organic matter is mainly type I. Analyses show that trace elements such as As, Mo and Pb of the black shale in this study area are obviously enriched, which are correlated with the organic matter content. Organic matter mineral aggregates and organic matter gelatinous mineral aggregates are generally existed in the black shale, indicating that there is a trade-off relationship between organic matter and mineral. In the black shale, organic matter illite mineral aggregates are produced. The pores are developed in clay minerals which are filled with organic matter, constituting the organic matter clay mineral aggregates. Organic matter clay mineral aggregates, organic matter mineral aggregates and various pores and fractures in organic matter provide space for shale gas occurrence. The experimental results show that the organic matter clay mineral aggregates have a greater methane adsorption capacity than the pure clay minerals, which affects the occurrence of shale gas in black shales.

Brief Features of the Black Shale

The study area mainly includes three districts in Guizhou Province, China: Fenggang in Zunyi and Cengong in Qiandongnan; their strata have different characteristics. The upper strata of the Cambrian Niutitang Formation black shale in Fenggang is the Mingxinsi Formation; the Niutitang Formation includes the upper, middle and lower sections, and the black thin-medium layered carbonaceous mudstone in the lower section is the thickest, about 73.14 m. The upper strata of the Niutitang Formation black shale in Qiandongnan is the Jiumenchong Formation dark grey marl and gray black mudstone mudstone interbed, and the lower strata is the Laobao Formation black siliceous mudstone; the thickness of the dark gray mudstone of the Niutitang Formation is approximately 59.4m.

The common black shale consists mainly of brittle minerals and clay minerals. The brittle minerals are mostly quartz, carbonate minerals, feldspar and pyrite; the clay minerals are mostly illite, kaolinite, montmorillonite and chlorite. The mineral identification results by microscope show that the main mineral composition of the black shale in Fenggang is organic matter, fine-crystalline siliceous minerals, fine-grained dispersed, aggregates-like and fine-grained pyrite, and clay minerals are mainly the basal minerals; the main mineral composition in Cengong is yellow-brown carbonate minerals, light gray particulate siliceous minerals and fine vein quartz, aggregates

granular, fine-grained and strawberry-like pyrite, and organic matter in the shape of an amorphous shape [2-4]. Results of microscopic identification show that the three research areas contain organic matter. The organic matter is black under a single polarized light, gray and taupe under the reflected light. Light gray siliceous minerals are found in black shales.

The representative black shale samples were analyzed by XRD, and the test results are shown in Table 1.1. XRD analysis shows that the black shale in Fenggang is mainly composed of quartz, clay minerals and albite. The quartz content is 27.4% to 47.2%, with an average of 37.3%; its clay minerals are all illite, accounting for 17% to 42.6% of the total minerals, with an average of 29.8%; the albite is 18.4% to 23.9%, with an average of 21.15%. It also contains minerals such as pyrite, potassium feldspar and dolomite, and the content of potassium feldspar and dolomite is relatively small. In the Lower Cambrian black shale in Cengong, the content of quartz is the highest, ranging from 38.6% to 72.8%, with an average of 55.7%; followed by clay minerals, accounting for 8.9% to 27.9% of the total minerals with an average of 18.4%, which are mainly illite and contains a bit of kaolinite. And, it contains a small amount of minerals such as pyrite, albite, potassium feldspar, dolomite and calcite.

These analysis results show that the Lower Cambrian black shale in the study area is mainly quartz and clay minerals, the minor minerals pyrite, dolomite, potassium feldspar, albite and calcite, and the clay minerals are mainly illite.

Table 1.1 Analysis results of black shales by X-ray diffraction /%

Sample	The mineral type and content						The total content of clay minerals	The relative content of clay minerals			
	Quartz	Potassium feldspar	Albite	Calcite	Dolomite	Pyrite		illite smectie etmixed layer	Illite	Kaolinite	Chlorite
FG(Fenggang)	27.4	-	18.4	-	5.8	5.8	42.6	-	100	-	-
FG-4(Fenggang)	47.2	2.8	23.9	-	-	9.1	17	-	100	-	-
Tm-2(Cen'gong)	38.6	1.8	12.7	-	4.3	14.7	27.9	-	99	1	-
Tm-4(Cen'gong)	72.8	1.0	5.3	4.8	2.6	4.6	8.9	-	100	-	-

Note: Tested by Research Institute of Petroleum Exploration and Development

Characteristics of Organic Matter in Black Shales in the Study Area

Organic Matter Content and Type Characteristics of Black Shales

Total organic carbon content (TOC) is a common index to measure organic matter abundance. The TOC test results of the black shale in Fenggang and Cengong are shown in Table 2.1:

Research shows that there is a certain proportional relationship between the original organic carbon content and the measured organic carbon value, and the conversion coefficient is 1.2. TOC values after recovery are shown in Table 2.1.The original organic carbon content in the study area is between 3.024% and 8.22%, with an average of 5.63%. The TOC in general is high, and it is much higher than that of shale gas development in North America (>2%). The original organic carbon content of the black shale in Fenggang is 3.024% to 7.86%, with an average of 5.442%; the content in Cengong is 4.2% to 8.22%, with a mean of 5.76%. There is no significant difference in the original organic carbon content between Fenggang and Cen'gong. The original organic carbon content of the black shale in Cen'gong increases first and then decreases with increasing depth. All organic carbon content of the black shale in the study area is greater than 2%. Based on the data from previous researches, it is considered that the kerogen type of organic matter is sapropelic (typeI) that at over-mature stage.

The organic carbon contents of black shales in Fenggang, Cengong and their neighboring areas are shown in Table 2.2. The content of organic carbon in the study area and its adjacent area is between 5.0% and 6.5%. The organic matter is high in abundance and has good gas generation potential.

Table 2.1 TOC of the black shale in Fenggang and Cengong (/%)

Sample	TOC	TOC after recovery
FG-1	2.52	3.024
FG-4	6.55	7.86
Average value	4.535	5.44
Tm-2	4.04	4.848
Tm-4	6.85	8.22
Tm-7	3.5	4.2
Average value	4.80	5.76

Note: Tested by Coal Mine Exploration of Guizhou Province, China

Table 2.2 TOC of black shales in Fenggang, Cengong and their neighboring areas

Well location / measured section	Sample	TOC/%	Location
Well FS1	FG	5.756	Liujiazhai Villag, DangwanTown, Fenggang County
Well TM1	Tm	5.442	Tianxing Town, Cengong County
Well SY1	SY1-65	6.5	Houcao Village, QinggangtangTown, Suiyang County
Well ZY1	ZY1-34	5.48	DaqianVillage, ShipingTown, Zhengan County
Well MY1	MY1	5.61	Sanlian Village, Gaotai Town, Meitan County
Well ZK2	ZK2-24	5.92	Mawandong in Fenggang County
Juhe Section	FG-9	1.6	Juhe Village, Fenggang County
Zhangjiaba Section	ZJB-2	5.76	Zhangjiaba Village, Yongyi Town, Yinjiang County
Miaoziwan Section	MZW-5	4.82	Miaoziwan Village, Maoshi Town, Bozhou District
Zhongnan Section	ZNC-7	5.31	Zhongnan Village, Songlin Town, Bozhou District
Dawan Section	DW-1	2.15	Dawan Village, Zhongshu Town, Renhuai City

Note: Data from reference [4] except for Well FS1 and Well TM1.

Characteristics of TOC and Related Element Enrichment in Black Shales

A large number of studies have shown that organic matter plays an important role in migration, transformation, enrichment and metallogenesis of metal elements. Black shale contains many organics mainly from lower algae, zooplankton and bacteria. In the course of life activities, these organisms may accumulate and absorb metal elements highly. In the process of sedimentation and diagenesis of black shales, with the increase of buried depth, the temperature of the sedimentary environment gradually increases due to the effect of geothermal heating. Then, organisms such as algae and zooplankton die, and metal elements in organisms enter into the sediments. During the physical and biochemical processes of biological organisms such as decay, decomposition and reduction, a large amount of organic acids such as fulvic acid and humic acid were produced. Metal elements are enriched by complexation or chelation [5]. Organic matter directly or indirectly participates in the initial enrichment of metal elements and forms the source bed. During the evolution of organic matter, organic matter will be degraded at higher temperature and pressure, and

a large number of alkanes and free radicals are generated. The newly formed active organic compounds are easily combined with the metal components in the sediments under the effect of hydrothermal processes, forming a large solubility organic metal complex which is eventually immobilized due to adsorption by organic matter [6].

In this study area, the contents of trace elements such as As, Mo, Pb in black shales are obviously enriched, which may have a certain relationship with organic matter. The contents of organic carbon and metal elements in the research area are shown in table 2.3. According to the relationship diagram of the content of each metal element and organic carbon content, it can be concluded that the content of Mo, V and Ni has a certain linear correlation with the content of organic carbon, and the content of Mo, V and Ni increases with the increase of organic carbon content. However, the content of As, Cr and Pb is less related to the content of organic carbon. The study shows that the concentration coefficient of U in the Lower Cambrian black shale in North Guizhou Province is 3.98, and there is a positive correlation between organic matter and U element due to strong adsorption of organic matter [7-9].

Table 2.3 Contents of some metal elements in black shales(μg/g)

Sample	As	Cr	Mo	Pb	V	Ni
FG-1	14	99	44	15	516	92
FG-4	35	88	71	14	554	141
Tm-2	95	86	80	28	411	129
Tm-4	65	65	155	24	454	257
Tm-7	61.7	110	56.4	132.5	290.1	53.2

Note: Tested by ALS Analysis and Testing (Guangzhou) Co., Ltd.

"Organic Matter - Clay Mineral" Aggregates Characteristics

“Organic matter- clay mineral” aggregates are generally distributed in black shales, using Energy spectrum analysis of field emission scanning electron microscope∑IGMA with energy spectroscopy to analyze the occurrence of organic matter in black shales, which have certain controlling effect on shale gas occurrence. The analysis results were verified by scanning electron microscopy and energy spectrum analysis.

Characteristics of Organic Matter Mineral Aggregates

The results of the study show that organic matter mineral aggregates are commonly found in the black shale in the study area. In addition to sample A with sulfide (pyrite), the rest of the samples are mainly composed of illite clay mineral and a certain amount of SiO_2 by spectrum. According to the XRD analysis, the main clay mineral in black shale is illite, and it can be concluded that the organic matter mineral aggregates mainly present as organic matter illite mineral aggregates.

The main morphology of the "organic matter clay mineral" assemblage shows the pore development in clay minerals, which fill organic matter and form an "organic clay mineral" aggregate. It is also found that the strawberry pyrite is filled with clay and organic matter, surrounded by mineral shrinkage cracks and a small amount of mineral pores, forming a "organic clay mineral - pyrite" aggregate. The existence of mineral and mineral aggregates in organic matter, forming a "organic matter mineral" aggregate.

Pore Characteristics of "Organic Matter - Clay Mineral Aggregates"

The pores in organic matter clay mineral aggregates are mainly divided into several categories:

(1) There are intercrystalline micropores and micro-cracks in the clay minerals, which are intercrystalline pores and corrosion pores, mostly macropores and mesopores; in organic matter, the pores are also developed, mainly mesopores.

(2) There are many organic matters in the black shale, and pores are developed. The organic matte pores with size about 20 nm, are mostly mesopores.

(3) Mineral pores and intercrystalline pores, with size about 100 nm to 200 nm.
(4) There are mineral shrinkage cracks and mineral pores around the mineral.
(5) Organic matter clay mineral aggregates, Organic matter mineral aggregates and various types of pores and cracks developed in organic matter provide space for the occurrence of shale gas.

Experiment and Result Analysis of Methane Adsorption by "Organic Clay Mineral" Aggregate

In water, muddy sediments and mudstones, clay minerals are closely associated with organic matter. Most of the organic matter in nature is combined with clay, existing in the form of complex, called organic-clay complexes [13-15]. The formation of organic clay complexes is bound to affect the occurrence of shale gas, in order to analyze the effect of organic clay complexes on shale gas occurrence, high pressure isothermal adsorption experiments of methane of the Lower Cambrian black shale and its organic clay complexes from gas exploration well in northern Guizhou were conducted. The experimental results are shown in table 4.1.

From the experimental results, at 30°C, the maximum adsorption capacity of methane of the organic-clay complexes in the black shale of the Lower Cambrian in northern Guizhou is 3.42751303 cm3/g, while the maximum adsorption capacity of methane in the black shale is 2.21826574 cm3/g. Results indicate that the organic-clay complexes have a good ability to absorb methane. From the previous analysis, it is known that the clay minerals in the Lower Cambrian black shale in northern Guizhou are almost illite, while the maximum adsorption capacity of methane for the pure illite at 35°C is 1.0892 cm3/g [16]. By comparison, the organic-clay complexes have greater methane adsorption capacity than pure clay minerals. The characteristic of the organo-clay complexes will affect the occurrence of shale gas in black shales.

Table 4.1 Methane adsorption capacity for various samples

Sample	Pressure(MPa)	CH_4(cm^3/g)
Black shales	1.540970443	1.04490071
	2.541646912	1.87521648
	3.657537648	1.96363702
	5.689648426	2.10773285
	7.133893474	2.13938232
	8.975804741	2.20201458
	11.0948691	2.21826574
	12.98104734	1.7972684
Organic matter -clay complexes	1.038407208	2.12685623
	2.151418554	2.42391821
	3.272292801	2.58038148
	5.063961944	2.44589371
	6.763901241	2.81488985
	8.627518075	3.32904802
	10.6411724	3.36831759
	12.70592352	3.42751303

Conclusions

(1) XRD analysis of the representative black shale samples shows the black shale is mainly quartz and clay minerals, the minor minerals pyrite, dolomite, potassium feldspar, albite and calcite, and the clay minerals are mainly illite.

The content of quartz of the Lower Cambrian black shale in Cengong is the highest, with an average of 55.7%. The quartz content average of the black shale in Fenggang is 37.3%, and its clay minerals are all illite with an average of 29.8%. The clay minerals average content of the black

shale in Cengong is 18.4%, and the clay minerals are mainly illite with a bit of kaolinite. The average content of the clay minerals of Zhijin is 49.23%, which are mainly illite, with minor illite smectite mixed layer, kaolinite and chlorite. The average content of albite in the black shale of Fenggang is 21.15%, and it also contains minerals such as pyrite, potassium feldspar and dolomite, and the content of potassium feldspar and dolomite is relatively small. The black shale of Cengong contains a small amount of minerals such as pyrite, albite, potassium feldspar, dolomite and calcite. The black shale of Zhijin contains some pyrite and dolomite.

(2) The original organic carbon content of the black shale in Fenggang is 3.024% to 7.86%, with an average of 5.442%; the content in Cengong is 4.2% to 8.22%, with a mean of 5.76%. All organic carbon content of the black shale is greater than 2%. It is considered that the kerogen type of organic matter is sapropelic (type I) that at over-mature stage. The organic carbon content of the black shale in Zhijin is between 0.79% and 3.01%, with an average of 1.83%. The average content of original organic carbon after recovery is 2.20%, which is also higher than that of shale gas development in North America (>2%). The kerogen type of organic matter is also type I.

(3) Organic matter mineral aggregates are distributed in the black shale. Pores in the clay mineral are developed, filled with organic matter, and constitute the organic matter clay mineral aggregates. Organic matter clay mineral aggregates, Organic matter mineral aggregates and various types of pores and cracks developed in organic matter provide space for the occurrence of shale gas.

(4) From the experimental results, at 30°C, the maximum adsorption capacity of methane of the organic-clay complexes in the black shale of the Lower Cambrian in northern Guizhou is 3.42751303 cm^3/g, while the maximum adsorption capacity of methane in the black shale is 2.21826574 cm^3/g. Results indicate that the organic-clay complexes have a good ability to absorb methane. From the previous analysis, it is known that the clay minerals in the Lower Cambrian black shale in northern Guizhou are almost illite, while the maximum adsorption capacity of methane for the pure illite at 35°C is 1.0892 cm^3/g . By comparison, the organic-clay complexes have greater methane adsorption capacity than pure clay minerals. The characteristic of the organic-clay complexes will affect the occurrence of shale gas in black shales.

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