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Geological and Geochemical Characteristics of Black Shale in Yanxi Formation of Middle Ordovician in Central Hunan

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The Middle Ordovician Yanxi Formation (O_2y) in the central area of Hunan province with a set of organic-rich marine shales is having great potential for prospecting of shale gas. Through lots of fieldworks and laboratory tests, this paper has concluded the geological characteristics of Yanxi Formation in this area by comprehensively investigation and analysis on the distribution and geochemical characteristics of the organic-rich marine shales and the features of reservoir. In the study area, it is found that the black shales of Yanxi formation are characterized by widely distribution, great thickness (ranging from 40 to 60m) and high level of organic carbon (ranging from 0.87% to 6.20%, generally higher than2%), the thermal maturity is at the mature to over mature stage. All of these characteristics of the black shares are benefit for generating gas. Mineral composition of black shales include quartz, feldspar, calcite, dolomite, clay minerals and small amounts of pyrite etc., the brittle minerals percentage is ranging from 47% to 87%. The pore types include intergranular pore, intracrystalline pore, mould pore, dissolved pore and organic pore etc, the aperture size of pores varies. Above all, O_2y in Hunan province is a new horizon with great potential for shale gas, especially the area along with Xingning-Qingtong-Ningyuan has been defined as an exploration target with priority.

1. Introduction

Shale gas as a kind of unconventional natural gas with the characteristics of self-generating and self-preserving, is existing in the black shale, in the form of adsorption or free state. With the developement of society and aincreasing wareness of environmental conservation (Bayatia et al., 2009; Simone et al., 2009; Ruiz et al., 2015), the consumption of global energy is developing towards to the cleaner energy direction (Semache et al., 2015; Barkaoui et al., 2013). As a newfound replenishment to the conventional fossil fuels, shale gas which is clearner has become an important energy source of petrol industry. In recent years, China has made a great breakthrough in the exploration and development of shale gas. The Lower Paleozoic marine sediments in south China have been identified as the main source rocks of the shale gas in China. The most favorable gas bearing shales are the Niutingtang Formation ($Є_1n$) of the Lower Cambrian and the Longmaxi Formation of the Lower Silurian (S_1l) (Zhang et al., 2008). The first shale gas field which reached the production of one million cubic meters per day is Jiaoshiba gas field of Fuling area, where more than 100 billion cubic meters of shale gas field have been proven in S_1l (Guo et al., 2014). In addition, Shale gas with industrial value also have been discovered in periphery areas of SiChuan basin, including $Є_1n$ in Weiyuan, Changning etc.

Over 40 years of successively exploration work have been done by precursors in Hunan province, However, the work focus on $Є_1n$ and S_1l of the Lower Paleozoic are merely confined to Northwest Hunan province, whereas it only subject to Devonian, Carboniferous and Permian of the Upper Paleozoic but not the Lower in Central area of Hunan province (Ma, 2013). A extensive transgression hit south China in the Middle Ordovician, massive black shales which contain the shale gas exploration potential deposited on the downslope of Yangtze platform in returns. Confined by the comprehensive tectonic conditions, few evaluation

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work has been done in the Yanxi Formation of the Middle Ordovician (O_2y) by the relative department. As for a better understanding of O_2y and a breakthrough of natural gas exploration in Hunan province, the writer of this paper assessment the exploration potential of the black shale of O_2y via field survey, sampling and analysis.

2. Geological setting

The central part of Hunan province, was belongs to the middle Yangtze platform of south China block before its isolation from the southeastern depression of Hunan by the Hengshan uplift. Structurally, it is located in north of Caledonian fold belt of south China and south to the southeast edge of Xuefeng mountain. It (E: 110°15′~113°, N: 26°~28°20′) covers nearly 9400 km^2. The structural deformation mainly is NE trending tight folds which are comprised by the Upper Paleozoic formation and interspersed by a few the Proterozoic and the Lower Paleozoic domes and somebranchy anticlines. And it deformed and overlapped by the Mesozoic-Neozoic tectonic basins. According to the features of the s palaeo- present tructures, geomorphic features and outcrops, this area can be divided into 5 second-level structural units as follows: Lianyuan sag, Longshan uplift, Shaoyang sag, Guandimiao uplift and Lingling sag (Zhang et al., 2014) (Figure 1).

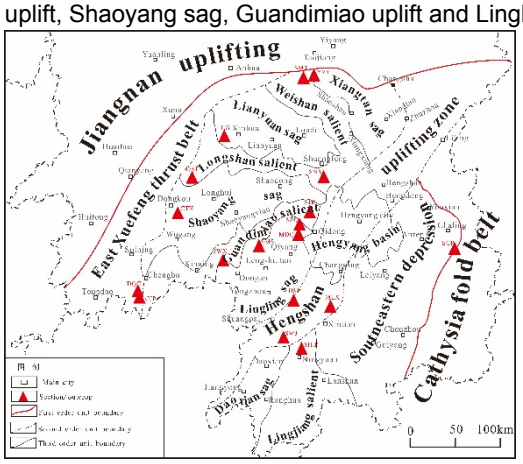


Figure 1: The regional location and structural map

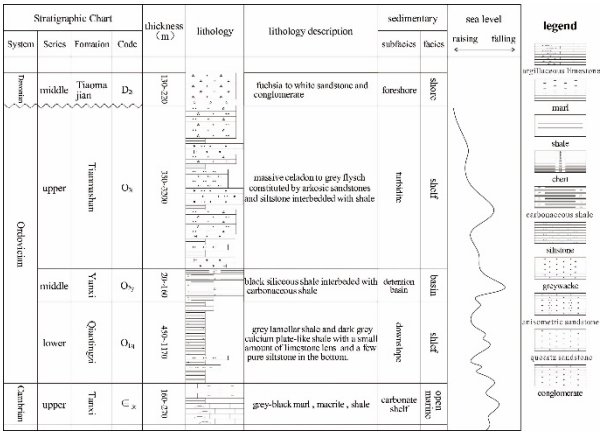


Figure 2: Stratigraphic column of Ordovivian in Central Hunan

The red letter "MDQ" "MHP"and"DST" ect. is the acronym of the name of the village where the sampled section located, such as "MHP" represent the Mianhuaping village of the Ningyuan.

The boundaries between Ordovician and its overlying and underlying strata are obvious. Although the Ordovician Formation is in community with the underlying Cambrian, their lithology are totally different, the underlying Cambrian is limestone, while the Ordovician is clastic rocks. The overlying Devonian is unconformity with the Ordovician Formation and is totally divergent in the types and color of rocks (Figure 2). The stratigraphy of Ordovician comprised of Qiaotingzi Formation (O_1q), Yanxi Formation (O_2y) and Tianmashan Formation (O_3t). The lower segment rock assemblage of O_1q are composed by grey lamellar shale and dark grey calcium plate-like shale with a small amount of limestone lens and a few pure siltstone in the bottom. The upper segment is greyish-green silty shale with graptolites. The O_2y is consist of black carbonaceous shales, siliceous shale and a lot of interbedded cherts, and is rich in graptolites and pyrite nodules. The O_3t is a stable massive celadon or grey flysch which was constituted by arkosic sandstones and siltstone interbedded with shales. The components of the Middle Carboniferous Tiaomajian Formation (D_2t) are thick sandstone and conglomerate with the color of fuchsia to white.

3. Geological characteristics of O_2y

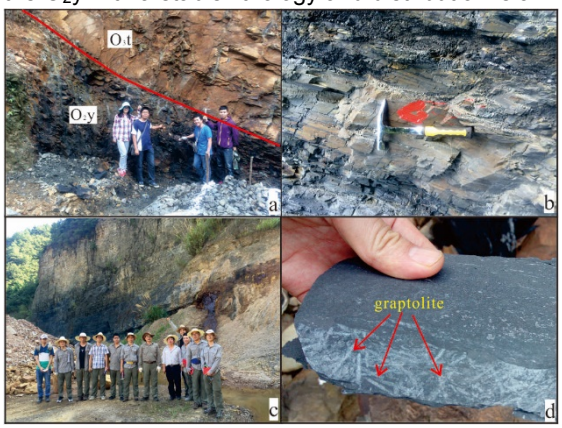
3.1 Sedimentary background

Hunan province is located in the convergence part of Yangtze plate and Cathaysia plate. Its sediments which has been impacted fiercely by the tectonism can be divided into 3 sedimentary subregions, such as platform region (Northwestern area of Hunan province), transitional region (Central area of Hunan province) and south China region (Southeastern area of Hunan province) accordingly. After the transgression of the Early Cambrian, the research area entered into stable subsidence period during the Middle to Late Cambrian. On account of abundancy and rapidity of sedimenting, the carbonate platform of the northwestern region gradually

subsided southwards. Affected by the consistent uplifting of the Cathysia, the transitional region was dwindled gradually. The sea level slowly rose in the Early Ordovician. Though inherited the structural framework from the Later Cambrian, the sedimentary assemblage was changed. The platform region still is mainly composed by carbonate rocks, the biota includes lots of cephalopod and a few trilobite, and also contains some graptolite and brachiopoda. The transitional region was composed of clastic rocks and casually sandwiched by carbonate rocks, the biota was comprised by graptolite and a few trilobite. The amounts and species of the graptolite are much more than the northwest area. The south China region almost are silty shales interbedded with siltstones, the amount of graptolite is rather small. The sea level rapidly rose in the Middle Ordovician again, however, it could not match the extent of the Early Cambrian. The northwest area deposited a thick polygonal marking limestone, nodular limestone and some shale with some siltystones interbeded in it, in where the biota was slightly changed. The transitional region became a basin with thick water column, and here the sediments (O_2y) are mainly composed by black shales, siliceous shale and cherts, they were very thin but rich in organic matters and graptolite. Infected by the uplifting, the Middle to Lower Ordovician of the south China region were eroded out. The tectonic activity intensified in the Late Ordovician. Along with the rising of the sea level and tectonic sinking, the carbonate sediments in the platform region were substituted by black shale and flourishing graptolite of the deep anoxic basin. However, the relative sea level was declined in the transitional region and the south China region. Lithic sandstone, siltstone, graywacke and interbedded shale comprised of the massive flysch which enventually emerged from the water at the end of the Late Ordovician.

3.2 Distribution of the O_2y

The O_2y widely distributed in the uplifts of the central area of Hunan (Figure 3). Its middle and lower part is composed by black carbonaceous shale with abundant *graptolite* while the thin bed siliceous shale exists in the top part in northern regions like Anhua, Taojiang and Yiyang of the research area. In south of the research area along with Lingling, Ningyuan, Chengbu etc., the bottom of the O_2y is formed by black siliceous shale interbedded with carbonaceous shale, the middle and lower part is consisted of black carbonaceous shale interbedded with siliceous shale and lots of *graptolite*, and the top part consists pure chert. Above all, the O_2y with a stable lithology and distribution is an important maker bed of central Hunan.



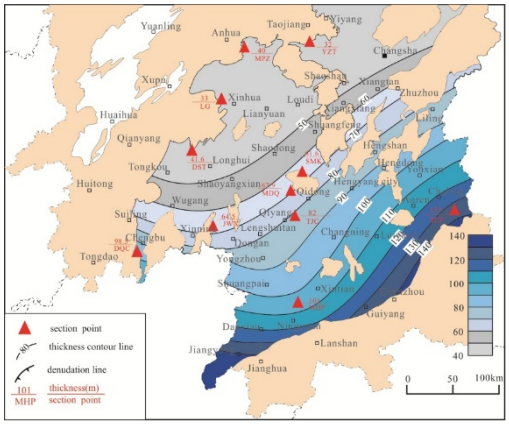


Figure 3: The field observation in Central Hunan *Figure 4: Shale thinkness isoline of O_2y in Central Hunan*

(Figure3: a. the boundary between O_2y and O_3t in CTX; c. O_2y of JWX; d. graptolite of O_2y in DST)

Thickness of the shale is the principal index for evaluation of resource potential. The effective thickness means the total thickness of the high quality shale in acontinuous shale section. Only if the effective thickness of the shale is enough (>30m), an industrial gas reservoir can formed in the shale. The sedimentary extent of the O_2y was confined in the paleo-Xianggui sea. And the shale of the south area is thicker than the north. The thickness of the north part like Xinhua, Anhua, Yiyang etc. is less than 40m, while the thichness of the south areas surrounding the Lingling, Qidong, Hengyang is range from 60 to 90 meters. and it thicker than 80 m in the Chengbu, Ningyuan and Chaling etc. areas, among which the thickness reached 135 m in Shichangpin area of Chaling county (Figure 4). Covered by a thick Upper Paleozoic and lacked of drilling data in the Liabyuan Sag and Shaoyang Sag as well as the large scale of hiatus, it can be deduced from the outcrops that the depocenter of the paleo-Xianghui sea is located in the southward of Chengbu, Ningyuan and Chaning area while the provenance is come from the Cathysia block.

4. Organic geochemical characteristics

4.1 Organic matter abundance

Total organic carbon (TOC) is used for characterising the abundance of organic matters (Yang and Yi, 2005). It shows a positive correlation with the gas-bearing properties and determines the amount of organic pores and the adsorption capacity of the shale. It is the another key index of whether the shale gas can accumulate to a reservoir. As for evaluating the potential of the O_2y, the TOC of 139 samples in O_2y has been assayed (table 1). It is found that the TOC of the black shale in O_2y with an average value of 2.12% is general high, the maximum value of which can reach 8.17%. The heterogeneity of the Toc mainly caused by the sedimentary facies distribution and eustacy. That is to say the O_2y belongs to the high-quality source rock. However, its Toc value is diverse form north to south. The favorable areas with highest value of Toc located in Longhui, Dongkou, Qidong and their vicinity. Another favorable area is along with the Lingling, Ningyuan and Chengbu, where the TOC value ranges from 1.97 to 2.94%. Above all, the black shale in O_2y of the research area which rich in organic matters and highly in Toc value is good source rock for the shale gas.

4.2 Thermal evolution degree

The thermal evolution of the organic matters is a decisive factor of the ratio of hydrocarbon generation. Whereas the thermal evolution is in a close relation with the burial history and the regional structural and thermal events. The residual thickness of the Paleozoic amounts to 5000~10000 m, the structural activities and thermal events were very active in the Late Paleozoic. As the graphite deposite formed both in the Lower Devonian of Huangcai county of Ningxing in the north and the Heye county of Guiyang in the south of the research area and the metallogenic temperature were above 1200 °C, the burial and preserve condition and the thermal evolution degree of the O_2y in this area are unpromising for shale gas judging from the appearance.

The research area undergone and re-deformed by the Caledonian, Hercynian, Indosinian and the later movements. The diversity of structural sink and uplift existed in different tectonic divisions. The heterogeneity was obvious since the burial depth was not too deep or the burial time was not too long in many areas. Based on the test of bitumen reflectance (Rob) of 45 outcrops, the Rob of the samples of O_2y are range from 2.27 to 5.46% with an average value of 4.62 %. According to the correlation between bitumen reflectance and vitrinite reflectance (Ro) (Jacob, 1985) , the Ro value of the O_2y in this area is from 1.83 to 3.77% and the average value is 3.15%. It is much lower than the former cognition. The Ro of the shale in the American shale gas fields is generally >1.3%, among which it reached 4.0% in the southern West Virgina of the Appalachian basin. What's more, the gas only produced in the over-matured areas. High thermal evolution degree (Ro>3.0%) is not the principal factor for restricting the accumulation of the shale gas (Montgomery et al., 2005). Provided keeping a certain distance with the sags and intrusions, the Ro of this area was below the ceiling. Xinning, Qidong etc. areas are relatively good for exploration.

Table 1: Statistics of TOC and Ro of outcrops of O_{2y} in central Hunan

Section	CJP	DJC	CTX	SKC	DST
TOC%	$\frac{2.32}{0.75-4.05}(20)$	$\frac{1.38}{0.55-2.77}(20)$	$\frac{4.42}{1.16-8.17}(3)$	$\frac{1.58}{1.58-1.58}(1)$	$\frac{6.20}{3.79-7.57}(5)$
Ro%	$\frac{3.13}{3.06-3.22}(4)$	$\frac{3.10}{3.04-3.14}(4)$	$\frac{2.27}{1.83-3.30}(3)$	$\frac{3.16}{3.16-3.16}(1)$	$\frac{3.71}{3.66-3.77}(5)$
Section	SNX	MDQ	SJK	SMS	JWX
TOC%	$\frac{1.96}{1.85-2.13}(3)$	$\frac{4.46}{3.28-5.79}(7)$	$\frac{3.14}{3.02-3.25}(2)$	$\frac{1.97}{1.96-1.97}(2)$	$\frac{1.15}{0.15-2.14}(31)$
Ro%	$\frac{3.16}{3.07-3.26}(4)$	$\frac{3.62}{3.39-3.84}(6)$	$\frac{2.93}{2.75-3.10}(2)$	$\frac{2.93}{2.75-3.10}(2)$	$\frac{3.06}{3.00-3.15}(5)$
Section	WSP	MHP			
TOC%	$\frac{2.94}{2.90-2.97}(2)$	$\frac{1.96}{0.69-3.44}(43)$			
Ro%	$\frac{3.21}{3.14-3.28}(2)$	$\frac{3.15}{3.02-3.27}(6)$			

label: $\frac{average\ (value)}{\min imun - \max imum\ (value)}(number)$

5. Reservoir characteristics

5.1 Minerals properties

Analysis of whole rock and clay mineral composition (X Ray Diffraction) of outcrop samples from O_2y black shale in central Hunan area shows that the brittle mineral (quartz, feldspar and pyrite) percentage ranges from 47% to 87%, the average content is about 60%, among them, the content of the quartz is between 40% and 80%, with an average of 55%; feldspar content is as low as 1% to 13%. The content of clay mineral is basically ranging from 13% to 52%, the average percentage is 30% which is roughly the same as S_1L in Sichuan basin. Given the certain content of organic carbon, the higher the content of brittle minerals is, it is more conducive to production and development. Chlorite, illite and illite-smectite of clay minerals are respectively 3~16%, 36~95%, 5~55%, but there are no montmorillonite in samples. In the mixed layer of illite and illite-smectite, the intergranular micropores are quite developed that can provide adsorption sites and storage space for methane produced by organic matter pyrolysis.

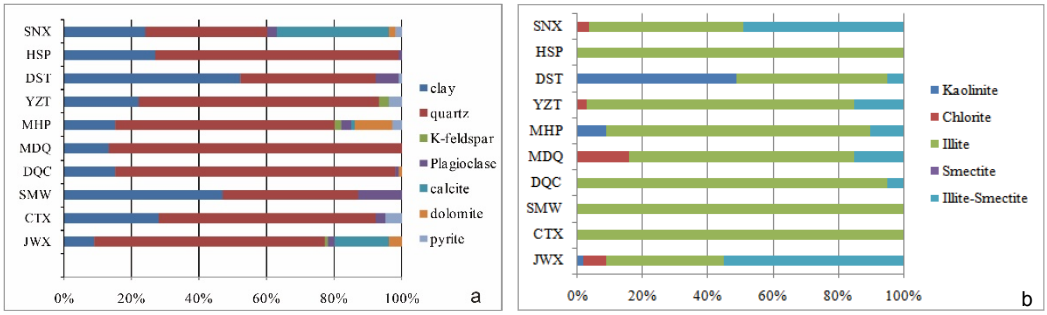


Figure 5: The shale mineral composition statistic (%) of O_{2y} in Central Hunan

5.2 Physical properties

The porosity directly determines the amount of free gas in the shale, thus affecting the occurrence of shale gas (Zhang, 2012), the permeability is the parameters that reflects the effective porosity of shale and the connectivity with the pore throat. By polished section microscope observation, it was found that the porosity of the sample was rather good. The main types of porosity were organic pores, intergranular pores, dissolved pores and mould pore etc. According to a widely used classification of pore size, which classified the size of the micropore of the arillaceous rocks as ultramicropore, micropore, mesopore, macropore, capillary pore and super-capillary pore according to their correponding diameter as <0.6nm, 0.6~2nm, 2~50nm, 50nm~2μm, 2~50μm and >50μm (Keller and Staudt, 2005). The diameter of most pores is 0.11~ 5.1μm, a small amount of is >5.1μm, accordingly they can be typed in the range of macroporous to capillary pores. The morphology of residual intergranular pore has little relation with mineral particle morphology, the pore size is generally 1.4~5.1μm; the morphology of organic pore is mostly round and oval, pore size is generally 0.14~0.42μm. These micron-sized pore throats not only provide the space for shale gas, but also pipelines for the shale gas flowing in the shale.

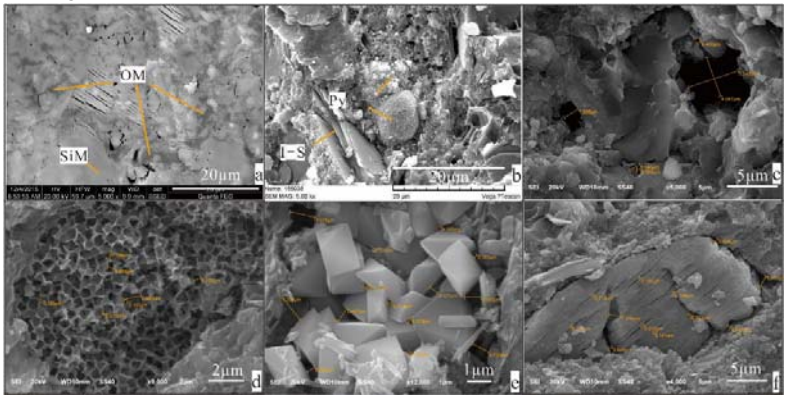


Figure 6: Microscopic pore characteristic O_{2y} in MDQ

(a. OM= organic matters; b. Py=pyrite, I-S=Illite-Semectite; c. dissolved and mould pores; d. organic pores; e. intergranular pores; f. intercrystalline pores)

6. Conclusions

Based on the analysis of the geological characteristics of the black carbonaceous shale in the Yanxi Formation in the central areas of Hunan and the comparison them with the surrounding area of the Sichuan Basin, it is found that: 1) The black carbonaceous shales in O_2y in Central Hunan are widely distributed with big thickness, its average TOC is up to 2.23%, the average Ro is 3.15%. It is considered that the formation has good potential for shale gas exploration, it is a new reservoir for shale gas in southern China. 2) The content of brittle mineralite in black shale of Yanxi Formation is up to 47~87%. The pore type is dominated by intergranular pores and organic matter pores. The pore size is about 0.1~5.1μm, and the highly developed microporosity is favorable for shale gas enrichment. 3) In consideration of the thickness, organic geochemical characteristics and geological features of shales comprehensively, the areas along Xinning - Qidong - Ningyuan are favorable for shale gas exploration in O_2y.

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