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Pore Characteristics and Gas Released by Crush Methods of Wufeng-Longmaxi Shale in the Northwest of Hubei Province, China

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1 Introduction

Wufeng-Longmaxi organic-rich shale in the Late Ordovician-Early Silurian is widely distributed in South China (Qiu et al., 2013), which is also the target formations of shale gas industry. Until now, the investigations into shale gas reservoirs is mainly conducted in eastern and southern part of Sichuan Basin (Huang et al., 2012; Liu et al., 2011; Zhao et al., 2014), while few research is done in the west part of Hubei and Hunan province (Qiu et al., 2013). The pore characteristics of these organic-rich shale samples from shallow drilling well in Shennongjia area were preliminarily evaluated based on the analysis results of rock-eval, elemental analysis, low pressure nitrogen/carbon dioxide adsorption measurements. Chemical and stable carbon isotopic compositions of gases released by crush methods were also concerned to compare the gas chemistry between the produced gas and crushed-rock gas from these organic-rich mudrocks.

2 Results and Discussion

2.1 Geochemical data and mineral contents of shales

These shale samples with a depth range of 79–116m contain total organic carbon (TOC) of 1.5–3.6% and have equivalent vitrinite reflectances of 2.45–2.87% (Yang, 2015), which is calculated by the Raman spectroscopic parameters (Liu et al., 2013). Their porosity is in the range of 1.8%–5.5%. They are constituted by quartz rich (70–97%), less carbonate (0–40%) and little clays (0–28%) (Table 1).

2.2 Relationship between TOC and porosity of shales

A positive relationship between TOC and porosity

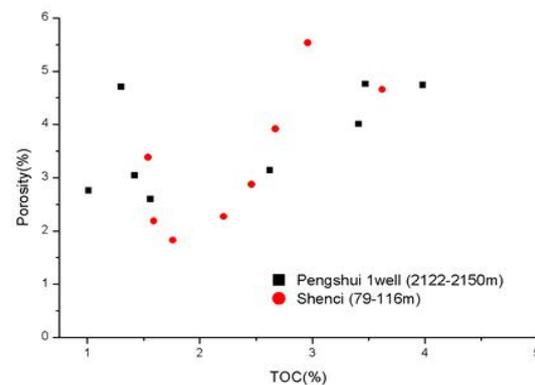


Fig. 1. Relationship between TOC and porosity of shales separately from a shallow drilling well and exploration well in the center of the basin

(Figure 1) is exhibited for the samples from the shallow drilling well of Shenci. For purpose of comparison, the measurement data from another exploration drilling well with deeper depths (Pengshui 1 well, 2122–2150m) are introduced, which implies that pore characteristics of these shales were not influenced by subsurface oxidation and weathering with different burial depth. This also demonstrates that pore characteristics of shale samples from shallow well can partly reflect that of shales in deeper basin. Apparently, porosity in Wufeng-Longmaxi organic-rich shales is dominantly affected by organic matters, which is consistent with the observations of Longmaxi Shale in upper Yangtze region utilizing FESEM–FIB (Jiao et al., 2014).

2.3 Mesopore characteristics

The BJH model for nitrogen adsorption data is widely applied to examine the mesoporosity of shales (Fig. 2),

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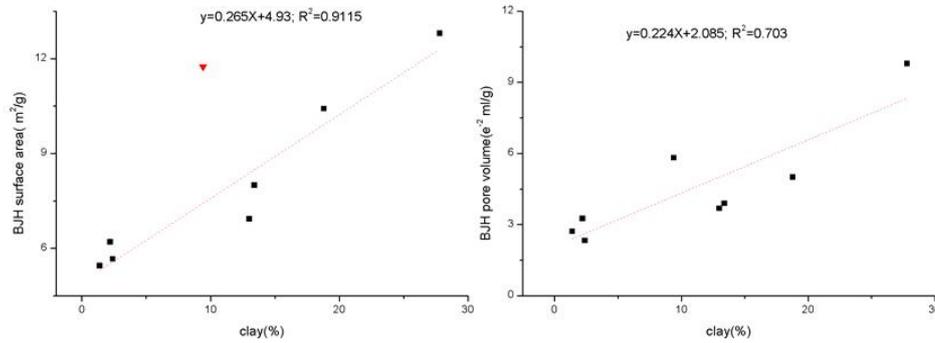


Fig. 2 Relationship between BJH specific surface area/pore volume and clay content in the shale samples from Shenci shallow drilling well

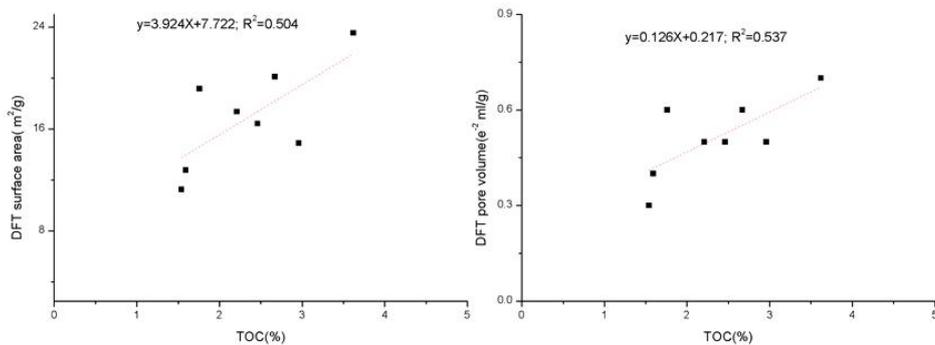


Fig. 3 Relationship between DFT specific surface area/pore volume and TOC in the shales from Shenci shallow drilling well

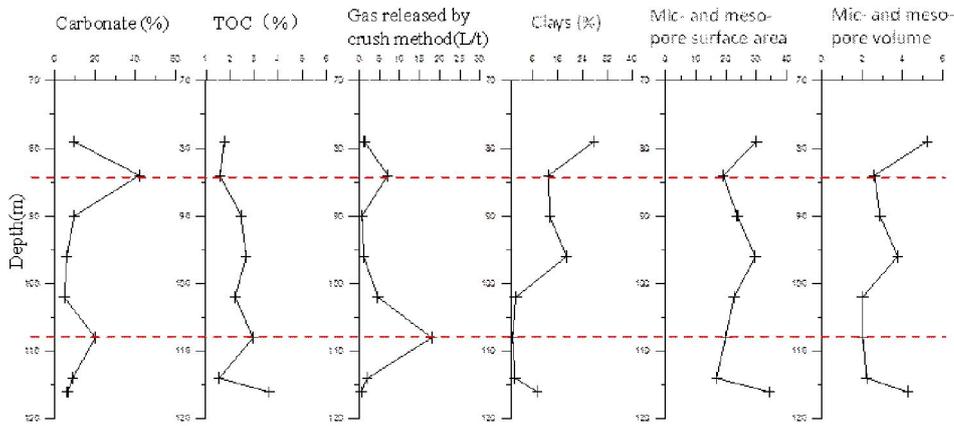


Fig. 4 The interrelations among gas yields released by crush method, mineral compositions, pore characterization and TOC of Wufeng-longmaxi shale

indicating that there is a positive relationship between specific surface area/pore volume and clay content. However, a relatively wider and seemingly unrelated relationship can be found between specific surface area/pore volume and TOC. These indicate that, as previously stated, many of mesopores are located between and within clay minerals (Loucks et al., 2012).

2.4 Micropore characteristics

The micropore volume is determined by the DFT model based on the CO₂ isotherms (Figure 3). The specific surface area/pore volume is plotted against TOC, in which a straight line can be seen as below. This indicates that the micropore is mainly related to organic matters. Organic-matter pores are created during the thermal conversion of organic matters (Hill et al., 2007; Hu et al., 2015), especially due to the secondary cracking of heavy hydrocarbon gases (C₂₋₅) (Chen and Xiao, 2014).

Table 1 TOC, porosity and mineral compositions for the shale samples in a shallow drilling well in Shennongjia area

Depth (m)	TOC (%)	Grain density (cm ³ /g)	Bulk density (cm ³ /g)	Porosity (%)	Relative percent (%)				
					quartz	carbonate	pyrite	feldspar	chlorite
79.49	1.76	2.76	2.706	1.8	55.7		4.2	12.2	7.2
84.84	1.59	2.84	2.778	2.2	32.8	42.2	3.8	8.3	1.3
90.42	2.46	2.7	2.624	2.9	63.2	2.1	4.4	16.9	3.7
96.87	2.67	2.77	2.664	3.9	47.4		11.2	22.6	5.8
102.88	2.21	2.59	2.532	2.3	85.6		3.8	8.2	
108.64	2.96	2.78	2.621	5.5	65.7	19.5	5.9	7.6	
114.85	1.54	2.71	2.62	2.4	62.2	2.1		1.5	

Table 2 The chemical and isotopic compositions of gas released by crush method from shales in Shenci shallow well

Sample NO.	Depth(m)	HCS(L/t)	HCS+CO ₂ (L/t)	¹³ C _{-C₁} (‰)	¹³ C _{-CO₂} (‰)	¹³ C _{-C₂} (‰)
1	79.49	2.3	28	-55.55	-7.47	-39.13
2	84.84	18	88	-36.95	-15.84	-39.11
3	90.42	1.2	21.6	-31.96	-7.84	-31.70
4	96.87	2.8	37	-30.19	-6.40	-28.69
5	102.88	4.9	49	-30.22	-6.17	-36.26
6	108.64	29.4	73	-32.20	-12.35	-38.42
7	114.85	10.5	78.5	-32.84	-7.95	
8	116.07	2.1	25.8	-33.96	-7.15	

2.5 Gas released by crush method from shales

The residual gaseous hydrocarbons in core samples is released by crush method (Zhang et al., 2014) and measured in order to investigate its chemical and stable carbon isotopic compositions (Table 2). The absolute gas yields (include CO₂) are in the range of 21-88 L/T, dominated by CO₂ (60–97%, vol%). This gas yield is about 1% of the produced gas yield (1-5m³/T) from general shale gas play. The yields of released methane of sample 2&6 are much larger than any other sample. Gas yields released by crush method, mineral compositions, pore characterization and TOC shales in the shallow drilling well are plotted in Figure 4. The contrastive analysis states that 1). Methane released by crush method is independent of pore volume/surface area and TOC; 2). Methane released by crush method is in proportion to carbonate content. It is very possible that gas released by crush method is located between or within carbonate crystals.

The stable carbon isotopes of methane varies from -55‰ to -30.2‰. The methane released from the sample at shallow depth (<80m) shows biogenic origin. Other stable carbon isotopic values of methane are much heavier than that of the methane released by crush method from Barnett Shale (-52.8‰--41.3‰) (Zhang et al., 2014). However, these $\delta^{13}\text{C}_{\text{-CH}_4}$ values are in good agreement with that in Jiaoye 6 well (C₁=-30.62‰) in ChongQing City of China, which indicates methane released by crush method may share the same source with the produced gas from gas shales. The $\delta^{13}\text{C}_{\text{-CO}_2}$ values are in the range of -6‰--15.8‰, which is much lighter than that in Jiaoye 6 well (CO₂=4.79‰), showing an organic origin.

3 Conclusion

On the whole, Wufeng-Longmaxi shales in the northwest of Hubei province have moderate contents of organic matters (1.5%–3.6%) and have high thermal maturities (2.45–2.87%, *V*Ro). Mesoporosity mainly located between and within clay minerals while micropores are primarily related to organic matters. TOC and clay contents are important factors to determine the pore characteristics. The very low yields of gas released by crush method cannot be used to evaluate the potential gas in place (GIP) in shale-gas play. The yield of gas released by crush method is in direct proportion to carbonate content, which implies this gas may be located between or within carbonate crystals. Further more, the stable carbon isotopic compositions of methane released by crush method may stand for the corresponding $\delta^{13}\text{C}_{\text{-CH}_4}$ for the produced gas in shale-gas play.

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