Sedimentary Geology 342 (2016) 180–190

Contents lists available at ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

Micro and nano-size pores of clay minerals in shale reservoirs: Implication for the accumulation of shale gas

Chen Shangbin [a,b,*], Han Yufu [b], Fu Changqin [b], Zhang han [b], Zhu Yanming [a,b], Zuo Zhaoxi [b]

[a] Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process of the Ministry of Education, China University of Mining and Technology, Xuzhou 221116, China
[b] School of Resources and Earth Science, China University of Mining and Technology, Xuzhou, 221116, China

ARTICLE INFO

Article history:
Received 25 April 2016
Received in revised form 27 June 2016
Accepted 29 June 2016
Available online 9 July 2016

Editor: Dr. B. Jones

Keywords:
Clay minerals
Micro-nano pore
Reservoir adsorption effect
Shale gas

ABSTRACT

A pore is an essential component of shale gas reservoirs. Clay minerals are the adsorption carrier second only to organic matter. This paper uses the organic maturity test, Field-Emission Scanning Electron Microscopy (FE-SEM), and X-ray Diffraction (XRD) to study the structure and effect of clay minerals on storing gas in shales. Results show the depositional environment and organic maturity influence the content and types of clay minerals as well as their structure in the three types of sedimentary facies in China. Clay minerals develop multi-size pores which shrink to micro- and nano-size by close compaction during diagenesis. Micro- and nano-pores can be divided into six types: 1) interlayer, 2) intergranular, 3) pore and fracture in contact with organic matter, 4) pore and fracture in contact with other types of minerals, 5) dissolved and, 6) micro-cracks. The contribution of clay minerals to the presence of pores in shale is evident and the clay plane porosity can even reach 16%, close to the contribution of organic matter. The amount of clay minerals and pores displays a positive correlation. Clay minerals possess a strong adsorption which is affected by moisture and reservoir maturity. Different pore levels of clay minerals are mutually arranged, thus essentially producing distinct reservoir adsorption effects. Understanding the structural characteristics of micro- and nano-pores in clay minerals can provide a tool for the exploration and development of shale gas reservoirs.

1. Introduction

Shale gas occurs in three distinct phases in the reservoirs: 1) free phase, 2) adsorption phase and, 3) dissolved phase (Jarvie et al., 2007). The free and adsorption phases constitute the principal occurrences of shale gas (Kang et al., 2010). The proportion of adsorbed gas in shale gas reservoirs is 20% to 85% (Curtis, 2002). The gas is mainly adsorbed on the surface of organic particles and clay minerals (Curtis, 2002; Bowker, 2003; Jarvie et al., 2007). The content of organic matter is only 3% in shale gas reservoirs, but is essential for generating adsorption. The formation of other minerals depends on the chemical composition of the reservoir rocks in which the clay minerals constitute 37% to 48% (Dong et al., 2010). The main clay minerals are variously layered chained-structure silicates. The special structure and physicochemical properties of clay minerals control in part the reservoir structure, its adsorption capacity and gas enrichment.

Clay minerals create important connections between inorganic and organic pores. Clays are important to the process of pore evolution and maturation in petroliferous basins. Clay minerals contain a massive amount of nano-pores (Nelson, 2009; Curtis et al., 2012; Yao et al., 2012), which mostly develop in interlayer and particle inter-cleavage surfaces to produce space in the shale reservoir. Micro-cracks formed by the recrystallization of montmorillonite into illite, provide massive reservoir space and effective channels for shale gas transport and enrichment (Zhao and He, 2012). Clay mineral pores are the main contributors to shale gas reservoir space, especially in the low-mature and mature stage of reservoirs containing a low content of organic matter (Schettler and Parmoly, 1990; Hao et al., 2013; Yang et al., 2015). The nature and content of clay minerals varied with diagenesis leading to different pore structures and capacities of adsorption. The pore structures of a clay mineral within shale differ depending on the degree of evolution of the reservoir. Therefore, the clay mineral pores contribute differently to the formation of the reservoir pores. Meanwhile, their impact on the adsorption of methane in the shale reservoirs remains unclear.

Research experiments performed on clay minerals showed illite having the strongest capacity for methane adsorption which decreases rapidly when it contains water, because of the preferential adsorption of water over methane (Ross and Bustin, 2009). Other studies revealed that montmorillonite possess the largest adsorption capacity for methane (Ji et al., 2012a,b; Tang and Fan, 2014). The complex morphology and polytrophic structure of shale can readily produce a strong heterogeneity leading to varied types of clay minerals (Qiu, 1992). The influence of shale gas adsorption and reservoir quality by clay minerals involves characteristics of solid–liquid-gas phase, and the relationship

* Corresponding author at: School of Resources and Earth Science, China University of Mining and Technology, Xuzhou, Jiangsu 221116, People's Republic of China.

http://dx.doi.org/10.1016/j.sedgeo.2016.06.022
0037-0738/

among them remains unclear. This hampers the fine characterization and evaluation of shale gas reservoirs and affects significantly a detailed resource evaluation. It is a key problem that needs to be solved urgently if one wants to understand the enrichment mechanism of shale gas reservoirs.

2. Sampling and analytical methods

2.1. Shale gas reservoirs in China

China is ranked third country in the world for the commercial development of shale gas, after the USA and Canada. In China, there are three types of organic-rich shales classified according to their depositional environments (Zou et al., 2011; Dong et al., 2012). The shales defined a marine facies, a marine-continental transitional facies and a continental facies. China is rich in shale gas resources and a 2012 preliminary assessment made by the Ministry of Land and Resources in China, estimated a recoverable resources exceeding 25×10^{12} m^3 (Development project of shale gas in China, 2012). China has made breakthrough discoveries of shale gas resources in the three abovementioned sedimentary facies in several regions and geological periods. This includes the Paleozoic formations of the Sichuan Bain, Mesozoic formations of the North Sichuan Basin, Triassic formations of the Edors Basin and Carboniferous–Permian formations in Middle North China (Zou et al., 2011; Dong et al., 2012). The Fuling shale gas field in the Chongqing municipality was the first commercially developed shale gas basin in China (Guo and Zhang, 2014).

2.2. Sampling

We selected different types of black shale samples from various sites, namely from the following formations exposed in China: the Qiongzhusi Formation (Fm.) (ϵ_{1q}), the Longmaxi Fm. (S_{1l}), the Taiyuanzu Fm. ($C_2 - P_{1t}$), the Yanchang Fm. (T_{3y}), which are important shale gas reservoirs in China (Fig. 1). The samples were collected from drillcores and outcrops. Eight-one samples were selected from the Qiongzhusi Fm. in the Yangtze area and come from 8 outcrops and one drill site. Another 83 samples were gathered from the Yangtze area, specifically from the Longmaxi Fm. which includes 6 outcrops. Fifty samples were collected from the Taiyuan Fm. within the Qinshui Basin and were sourced from 11 drill sites. Finally, 10 samples from the Erdos Basin (Yanchang Fm.) were selected from 3 outcrops (Fig. 1). The samples collected from outcrops were affected by a certain degree of weathering. The fresh profiles or outcrops were found as far as possible in the process of sample collection, such as some engineering excavation sites. And the test data was suggested that there is no significant difference in the types of clay mineral between drillcores and outcrops in the same formation. Therefore, all samples and results presented were fine and have no effect on the arrival at a conclusion.

2.3. Experimental methods

In this study, the vitrinite reflectance (*R*o) was measured with a Leitz microphotometer, and the analyses were performed at the Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process of the Ministry of Education (CUMT).

X-ray Diffraction (XRD) was used to identify the mineral composition, and this analysis was performed at the Experiment Research Center of East China Brach (SINOPEC). The experimental temperature and humidity were 24 ℃ and 35%, respectively. Quantitative phase analysis was performed by Rietveld refinement, with customized clay mineral structure models (Ufer et al., 2008).

Field-Emission Scanning Electron Microscopy (FE-SEM) was performed with a Quanta 200F equipped with an energy-dispersive spectrometer (EDS) on surfaces prepared by Ar-ion milling. Secondary electron images and BSE images can provide important qualitative information on the general locations of pores throughout the sample. These experiments were also conducted at a temperature of 24 °C and a humidity level of 35%.

3. Results and discussion

3.1. Results

The vitrinite reflectance (*R*o) and clay minerals content of the three types of the reservoirs test results are shown in Table 1. And combined types of clay minerals in the formation are shown in Fig. 2.

3.1.1. Thermal maturity of shale gas reservoirs

The vitrinite reflectance values of Yanchang Fm. were determined between 0.66% and 1.2%, which showed that the thermal maturity was at the low-mature stage (*R*o > 0.5%) and mature stage (*R*o < 1.2%). The *R*o values of Taiyuan Fm. were determined between 1.2% and 2.4%, which showed that the thermal maturity was at the high-mature stage (*R*o > 1.2%) and over-mature stage (*R*o > 2.0%). The *R*o values of Longmaxi Fm. and Qiongzhusi Fm. were determined between 1.5% and 3.5%, 2% and 4%, respectively, which showed that the thermal maturity was at the high-mature stage (*R*o > 1.2%) and over-mature stage (*R*o > 2.0%). The thermal maturity parameters suggest that the marine facies reservoir (Longmaxi Fm. and Qiongzhusi Fm.) and marine-continental transitional facies reservoir (Taiyuan Fm.) are in the (dry) gas generation window. The continental facies reservoir (Yanchang Fm.) is in the gas condensate and (moisture) gas generation window. In over-mature thermal stage, the source rock mainly generates dry gas based on the principle of methane accompanied with a small amount of gas condensate.

3.1.2. Clay minerals of shale gas reservoirs

Clay minerals were also favorable for the formation and development of the shale gas reservoir. A wealth of data was obtained for clay minerals in typical shale reservoirs representing the three types of sedimentary facies in China. Clay minerals present various compositions depending on their different depositional environments (Fig. 2). The results show that the Yanchang Fm., Taiyuan Fm., Longmaxi Fm. and Qiongzhusi Fm. have different clay minerals content, with a mean content of 51.69% (range 36.3%–80.7%), 61% (range 37.3%–98.5%), 40.13% (range 18%–64.5%) and 20.72% (range 3.7%–47.9%), respectively (Table 1). It is suggested that all samples contain clay minerals composed of illite (I), chlorite (Ch) and illite-montmorillonite (I/S) (Fig. 2). Illite–montmorillonite content is the main clay mineral composition in Yanchang Fm. and Taiyuan Fm., with the value of 56.34% and 46.95%, respectively. Illite (I) is the most common of the clay minerals in Longmaxi Fm. and Qiongzhusi Fm., and it has the highest content, with the value of 55.68% and 67.12%, respectively. The samples also contain kaolinite except Longmaxi Fm. and it has the highest kaolinite content in Taiyuan Fm. with the value of 36.42% for the regional geological features.

3.1.3. Morphology and classification of clay mineral pores in the shale gas reservoirs

Fig. 3 shows the clay mineral morphologies in shale reservoirs under the FE-SEM. Illite presents a flake morphology, illite–montmorillonite is sheet-like and kaolinite forms irregular tabular overlays, and chlorite displays granular overlays under the SEM (Fig. 3A, B, C, D).

The shale reservoir pores were divided into intergranular, interparticle and organic matter varieties (Loucks et al., 2012), while the clay minerals develop the first two varieties. For the classification in shale, Chinese scholars substituted the organic matter by the microfissure variety (Yang et al., 2013; Yu, 2013; Wang et al., 2014a,b). The classification of clay minerals pores is too general compared to that established for organic matter pores. It cannot fully appraise the morphology, occurrence and contact relation of clay minerals which