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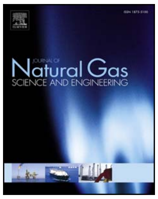

Characterization of organic matter pores in typical marine and terrestrial shales, China

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ABSTRACT

Organic matter (OM) is a significant component in shale and controls gas storage and transportation. Typical marine (JLD sample, NTT sample, WF sample and LMX sample) and terrestrial (C7 sample) OM-rich shale samples from the Sichuan Basin and Erdos Basin in China were investigated using X-ray diffraction and scanning electron microscopy (SEM) to study their mineralogy and OM pore network properties. The X-ray diffraction results indicated that the content of brittle minerals (quartz, plagioclase, calcareous dolomite, dolomite and pyrite) in each shale sample was higher than 60%, providing material in which original matrix pores and microfractures formed during an early stage of diagenesis. The types and contents of clay minerals vary among the shale samples. The main clay mineral in most of the marine shale samples is illite, but the primary clay in the terrestrial shale is an illite–smectite mixed layer. The maturity data of the OM in the marine shale samples suggested a moderate to high stage of maturity, while the terrestrial shale was collected at a relatively low stage of thermal evolution. The SEM observations suggested that the OM was either tight or porous, and the former was the dominant state. The OM pores preserved in the shale consisted of pores within, between and at the interfaces of the OM particles. For the OM pores within the OM particles, the most dominant pore type, type I, exhibits honeycomb-like pores formed by hydrocarbon generation; this type of pore is most developed in the marine LMX shale and NTT shale. Pore type II is related to biogenic residue and is more developed in the JLD shale and LMX shale. Pore type III includes mainly elliptical pores or microcracks related to the volume loss of bitumen. The OM pores between the OM particles are narrow and laminar; these structures were inherited from the previous clay mineral structures. The OM pores at the interfaces of the OM particles and the mineral grains are usually observed as microfractures and are more developed in the C7 shale. The lack of pores within the OM in the terrestrial C7 shale was due to low maturity. A combination of SEM results, mineral compositions and carbon analyses indicated a positive correlation between the development of OM pores and the organic carbon content, as well as the thermal maturity. With increasing burial and maturity, migrated OM was squeezed into mineral matrix pores and appears to be continuous, especially along the bedding planes, forming an effective network due to the interconnectivity of the OM.

1. Introduction

The type, abundance, maturity and burial depth of organic matter (OM) are significant factors that influence shale gas accumulations (Loucks et al., 2009; Milliken et al., 2013; Pommer and Milliken, 2015; Zhang et al., 2016a). As a common constituent in shale, OM acts as a host and creator of OM pores, which have a positive influence on shale gas occurrence as OM pores not only offer the main storage space for absorbed shale gas but also form either the dominant or subsidiary pore network in shale gas or oil migration pathways (Loucks et al., 2012; Loucks and Reed, 2014; Ko et al., 2017). Since the size of the OM pores in shale are mostly at the nanometer scale, the equations describing the macroscale flow in conventional pores are no longer applicable due to the microscale effect (Wu et al., 2015a; 2017; Mozaffari et al., 2017). A model for shale gas transport in nanometer OM pores needs to consider the impacts of the volume and distribution of the OM pores themselves (Jiang et al., 2017; Cao et al., 2017). Hence, investigating the occurrence of OM and OM pore structures in shale is necessary for understanding the permeability pathways and surface diffusion mechanisms in shale gas-oil migration pathways.

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Loucks and Reed (2014) suggested seven criteria to separate depositional OM (kerogen) and migrated OM (bitumen, oil, gas, solid bitumen, and pyrobitumen) based on their many observational results using Ar ion-milling scanning electron microscopy (SEM). The migrated OM was expelled into mineral matrix pores by a pressure differential caused by the thermal decomposition of the OM (Lewan, 1991). The mobility of the OM, together with the increase in thermal maturity, was responsible for the occurrence of the OM. The final connectivity of the OM pore network relied on the distribution of the depositional OM and migrated OM. Migrated OM-hosted pores mimic the distribution of the original shale mineral pore network, which is more likely to provide a more effective three-dimensional OM pore network than that of isolated depositional organic matter (Loucks and Reed, 2014). Studies in recent years have indicated that understanding the evolution of OM pores would help to predict the porosity and related petrological properties (Passey et al., 2010; Milliken et al., 2013; Loucks et al., 2012, Loucks and Reed, 2014; Sun et al., 2014; Milliken and Curtis, 2016). Recently, ongoing work has partly focused on the description and identification of the diagenetic processes related to OM pore formation (Mastalerz et al., 2013; Loucks and Reed, 2014; Pommer and Milliken, 2015). Pommer and Milliken, 2015 studied the pore types and pore-size distributions across different thermal maturities in the Eagle Ford Formation and proposed that OM pores related to migrated OM would increase from the early oil window to the gas window. For high-maturity shale samples dominated by OM-hosted porosity, the development of OM pores and their size distributions are correlated with both OM and brittle mineral content. Larger OM pores occur with increasing brittle mineral content, and larger OM pores preferentially form in migrated OM rather than depositional OM. However, the occurrence of OM and the controls of OM pore evolution are still ambiguous.

OM-rich shale in China consists of marine shale, marine-terrestrial shale and terrestrial shale. Compared with the North American marine shale, marine shale in south China, in particular, is characterized by a deeper burial depth and higher thermal maturity. In addition, the target reservoirs have undergone multiple periods of tectonic uplift during their depositional and burial history (Zou et al., 2014, 2015, 2016). Pores related to the OM in the shale in China have gained increasing research attention, and a host of OM types and OM pore networks have been identified (Ma et al., 2015; Wang et al., 2015, Wang et al, 2016a,b; Wu et al., 2015b; Yang et al., 2016; Zhang et al., 2016b). These studies generally focus on the description of a specific horizon of OM and lack a systematic comparative analysis of shale from different depositional environments. In addition, the factors controlling the OM pore types across a range of burial-diagenesis stages are incompletely studied. In this study, the occurrence of OM and OM pore types in a typical marine shale and terrestrial shale in China are identified using SEM. Based on the research results, this paper discusses the controls on OM pore development in organic-rich shale at various maturation stages and at various burial-diagenesis stages.

2. Samples and experiments

2.1. Geological background and samples

In recent years, studies have confirmed that South and Northwest China, including the Sichuan Basin, Ordos Basin and other nearby basins, are the most favorable regions for shale gas exploration. Across these regions, the Paleozoic has the largest reserve of shale gas, while the Mesozoic ranks second (Zou et al., 2010, 2014). Therefore, five shale samples from within the Paleozoic or Mesozoic strata from the Sichuan Basin and Ordos Basin are investigated herein (Fig. 1). Details of each sample are presented in the following sections.

The Cambrian Jiulaodong (JLD) formation shale was from the Weiyuan 201 well (W201), Weiyuan block, Sichuan Basin. The sample was collected at a depth of approximately 2756 m and mainly contains dark shale mixed with siltstone. As a favorable horizon that was first produced as an industrial gas flow by the China National Petroleum Corporation in 2011, the JLD formation shale is thick, OM-rich formation with a high gas-generating potential. The natural gas that has generated throughout its geological history has not been affected by deep faulting or strong denudation, ensuring that no gas has escaped to the surrounding environment (Chen, 2012). Another advantage of the Weiyuan block is that the well-developed microfractures facilitate hydraulic fracturing and gas migration.

The Niutitang (NTT) formation shale sample was collected in the Ciye 1 well (CY1), Cili area, northwestern Hunan Province. The study area is located in the southeastern margin of the Yangtze platform, straddling the Jiangnan-xuefeng uplift belt and western Hunan-Hubei fold belt. The northwestern Hunan area has experienced multistage tectonic movements, resulting in complex geological structures. The CY1 is the first shale gas exploration well in Hunan Province that was deployed by the Oil and Gas Resources Research Center of the China Geological Survey Bureau, and the target horizon is the lower Cambrian NTT formation. The NTT black carbonaceous-siliceous shale was formed in an anoxic sedimentary environment on a deep-water continental shelf-margin slope; this shale is thick and has a high organic carbon content and high thermal maturity (Li et al., 2015). In addition, most of the kerogen is in the mature to over-mature stage and is type I kerogen.

The Wufeng (WF) and Longmaxi (LMX) shale samples were from the Dafengao outcrop, Shizhu area; this tectonic location belongs to the middle Sichuan Basin of the central upper Yangtze platform. The Ordovician WF formation and Silurian LMX formation in this area are stable suites of marine clastic deposition that resulted from filling of the cratonic basin and foreland basin during the Caledonian (Wang et al., 2016b). The WF and LMX shale at the Shizhu outcrop mainly consists of dark carbonaceous shale with pyrite and quartz veins; the bedding planes are well developed due to the thin and thick layers of parallel intergrowth, resulting in a small cohesion and susceptibility to weathering along the bedding planes. In contrast, the WF shale is weathered more intensely.

The Yanchang 7 (C7) member shale sample was collected in the Triassic Yanchang formation from the Yaoke 1 (YK1) well, Tongchuan city. The location of the YK1 well is in the tectonic area of the Weibei uplift in the southern Ordos Basin. The C7 member shale records the largest expansion period of the terrestrial lake basin. During this period, the retrogradational deltas surrounding the lake basin were widely developed and rapidly subsided, forming the preferred target stratum in the Ordos Basin at the bottom of Chang 7 member shale (Wang et al., 2014; Jiang et al., 2014). Core observations confirm that the C7 shale mainly consists of a black shale and tuff mixed with fine sandstone and carbonatite.

2.2. Experimental methods

2.2.1. Mineralogy tests

The XRD analysis was performed using a Japan Rigaku Rotaflex XRD instrument with JADE software. Mineral contents were determined from the intensity of the maximum peak of each mineral. XRD analyses of the bulk samples were used to determine the content of the granular minerals and the total amount of clay minerals. In addition, the types of clay minerals and their relative contents were determined from three XRD analyses on non-treated samples and samples that underwent ethylene–glycol and heat treatments following the Chinese Oil and Gas Industry Standard SY/T5163-2010; in these analyses, particles less than approximately 2 μm in size were used. The test conditions were as follows: Cu-target and Kα radiation, X-ray tube voltage of 40 kV, and electric current of 100 mA.

2.2.2. Carbon analysis

The total organic carbon (TOC) content analyses were done using a America Leco CS230HC analyzer. First, the total carbon contents were