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Pore characterization of organic-rich Late Permian Da-long Formation shale in the Sichuan Basin, southwestern China

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ABSTRACT

The Late Permian Da-long Formation shale in southern China is regarded as a shale gas reservoir target. However, the lack of fundamental data for shale gas reservoirs increases the difficulty of gas exploration. To understand the pore structure characteristics of these shales, a series of experiments was conducted on Da-long Formation samples collected from the Shangsi Section in the Guangyuan area in the Northwest Sichuan Basin, southwestern China, including total organic carbon (TOC) content, X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and low-pressure N_2 adsorption-desorption analyses. The results show that TOC contents vary greatly between the Da-long Formation samples, ranging from 0.14% to 14.40% with an average value of 3.60%. A black shale layer occurs near the middle of the section with a relatively high TOC content ranging from 1.20% to 14.40%. The major components of the mineral matrix are carbonate and quartz minerals. A weakly positive trend between the TOC content of organic-rich shales and the quartz content was observed, indicating that the quartz in these Da-long shale samples is at least partially of biogenic origin. Both mineral matrix and organic matter pores are developed in Da-long black shales, as observed by FE-SEM, along with a few interP and intraP pores and fracture pores. Additionally, with increasing TOC content, the pore size distribution (PSD) curves of organic-rich shale gradually decrease as a result of OM ductility. Bimodal PSD versus surface area and unimodal PSD versus pore volume were measured in the shale samples, indicating that surface area is mainly associated with micropores and fine mesopores (< 10 nm) and larger pores are the dominate contributor to pore volume. Therefore, the pore network in this gas shale reservoir is predominantly associated with organic matter, especially small pores, and the mineral compositions are expected to be responsible for larger pores.

1. Introduction

Shale gas has become one of the most important energy resources in recent years due to the global demand for energy [1]. Unlike conventional oil and gas, the shale gas system is a continuous self-contained source-reservoir petroleum system. Shale gas is generated from biogenic and/or thermogenic process and stored in situ, mainly as both adsorbed gas (i.e., on organic matter) and free gas (i.e., in pores and fractures) [2,3]. Shales are referred to as complex and heterogeneous porous media. Understanding the geometry, size, and distribution of the pores is important for characterization of the shale pore structure [4–6,1] and is of practical significance when investigating the gas storage capacity and gas flow mechanisms in shale reservoirs [7]. Therefore, improving knowledge of the complex pore structure of shales is of great importance.

Pores in a shale matrix can be classified into three groups, according to the pore classification system of the International Union of Pure and Applied Chemistry (IUPAC): macropores (> 50 nm), mesopores (2–50 nm) and micropores (< 2 nm) [8]. Pore structure is one of the major factors that control the gas capacity of shales and therefore is the key element in shale gas formation characterization and potential assessment [4,5,9,10]. Moreover, field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) and helium ion microscope provide high-resolution (~5 nm) images make it possible to observe nanopore geometries in shales [11]. Loucks classified individual nanopores into one of four groups: intra- and interparticle pores within minerals, pores in organic matter (OM) and microfractures [12]. Organic pores are regarded as a significant component of the pore system in shales [2,13,12,14,5], as demonstrated by the positive correlation between total porosity and TOC content

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[14–16]. The fine-grained mineral matrix also influences the size, distribution and arrangement of pore spaces as evidenced by the large amounts of microporosity found in clay platelets [5,17] or in the organo-clay complex [17]. Various techniques have been borrowed from material science to illustrate the complexity of pore networks in shales. Total porosity can be determined by helium pycnometry and mercury porosimetry [18,19,5], while surface area and pore size distribution can be calculated from N_2/CO_2 adsorption [20,16,21], mercury injection capillary pressure [22,23,5,17], and small/ultra-small angle neutron scattering [11,24,25].

Most shale gas exploration in China is conducted in the southern part of the country where thick marine shales are widely distributed. Four shale formations are regarded as targets: the Doushantuo Shale Formation of the Late Sinian, the Niutitang/Qiongzhusi Shale of the Early Cambrian, the Longmaxi Shale of the Early Silurian, and the Da-long/Longtan/Gufeng Shale of the Late Permian [17,26,27]. Large volumes of shale gas have already been produced from the Lower Silurian Longmaxi Formation in the Sichuan Basin in SW China. However, the TOC of black shale and sapropelite in the Late Permian Da-long Formation of the Sichuan Basin is very high, averaging 5.86%. The thickness of the Da-long Formation in the trough facies region is approximately 10–30 m. The hydrocarbon source of the Da-long Formation has the advantages of gas formation and short migration paths to reef and beach reservoir rocks [27]. The detailed pore structure of the Late Permian Da-long Formation shales is not fully characterized. To provide a fundamental understanding of the pore structure in Late Permian Da-long Formation shales, we employed FE-SEM and low-pressure N_2 adsorption to characterize the surface area, pore type and pore-size distribution of the Late Permian Da-long Formation shales and aim to provide new data for further OGIP (original gas in place) evaluation of the Da-long Formation shales in this region.

2. Geological background

The Sichuan Basin in eastern Sichuan province, southwestern China, is one of the most important onshore gas producing areas in China (Fig. 1a). The organic-rich shales in the Sichuan Basin are abundant, with six regionally extensive organic-rich shale units; from bottom to top, these units are the Upper Sinian Doushantuo Formation, the Lower Cambrian Qiongzhusi Formation, the Upper Ordovician Wufeng-Lower Silurian Longmaxi Formation, the Upper Permian Longtan Formation, the Upper Triassic Xujiahe Formation, and the Lower Jurassic Ziliujing Formation (Shaximiao Formation) [28]. The Doushantuo Formation is 15–120 m in thickness, in which a shale with a TOC content greater than 2% is 10–70 m thick. The Qiongzhusi Formation is 400–600 m thick in the southern and southeastern parts of the basin and includes a 60–150 m-thick shale with a TOC content greater than 2%. The Wufeng-Lower Silurian Longmaxi Formation is 300–600 m thick in the southern, northeastern and northern parts of the basin and includes a shale with TOC greater than 2% between 80 and 120 m thick. The Longtan Formation, composed of transitional coal-bearing carbonaceous shale ranging from 20 to 125 m in thickness, contains a 20–52 m-thick shale with a TOC content greater than 2%. The Xujiahe Formation limnetic coal-measure shale is 100–800 m thick and includes a 25–60 m-thick shale with a TOC content greater than 2%. The Ziliujing Formation has shale with moderately deep to deep lacustrine facies, ranges from 40 to 180 m in the central, northern, and eastern Sichuan Basin, and includes shale with a TOC content greater than 2% between 20 and 40 m thick [29].

In Permian strata, there are 4 major source rocks in the Sichuan Basin, the Longtan Formation, the Wujiaping Formation, the Changxing Formation and the Da-long Formation. Those formations have different depositional environments. The Longtan Formation, consisting mainly of mudstone with a small amount of coal, was deposited in a paralic environment. The Wujiaping Formation and the Changxing Formation were deposited in marine environments [30]. The Da-long Formation was deposited in typical deep-water environments, as evidenced by sedimentary features lacking wave action or bioturbation and many Late Permian open marine organism fossils or fossil fragments, such as ammonites, brachiopoda, foraminifera and spicules, radiolarian, microbody foraminifera and ammonite shells [27]. The Da-long Formation consists of interbedded marine dark siliceous shale and mudstone and mainly occurs in the Guangyuan-Wangcang trough and the Western Hubei-Chengkou trough [27–32]. The TOC content of the black shale and sapropelite of the Da-long Formation is 1.44%–24.31% with an average of 5.86%, and the thickness ranges from 10–30 m with an average of approximately 20 m; the thickest deposits are in the Jiulong Mountain-Shejianhe region and the Shaguanping region, where they can be greater than 30 m [27] (Fig. 1c).

3. Materials and methods

3.1. Samples

A total of fourteen samples were collected from the Shangsi Section in the Guangyuan area in the Northwest Sichuan Basin (Fig. 1a, b), with an average sampling interval of ~2 m. As the samples were collected from outcrop sections, the possible effects of surface weathering and recent contamination on the analyses were minimized; weathered surface material on the samples was cut away, and the samples were thoroughly cleaned using ethanol to remove possible surface contamination. Each of the shale samples was divided into two aliquots. The first aliquots were crushed to 200 mesh (< 0.075 mm) and then subjected to X-ray diffraction analysis for mineralogical composition. The second aliquots of the shale samples were crushed to 80 mesh (< 0.25 mm) and then subjected to low-pressure nitrogen adsorption measurements for pore structure characterization and thermal pyrolysis for organic content characterization.

3.2. Organic geochemistry and mineralogy

Total organic carbon (TOC) was measured by a LECO CS-344 analyser after the samples were treated with hydrochloric acid to remove the carbonates. The thermal pyrolysis of the shale samples was performed using a Rock-Eval 6 pyrolyser. The detailed procedures used in these analyses were described by Wang et al. [33].

X-ray diffraction (XRD) analyses of shale powders were carried out on a Bruker D8 Advance X-ray diffractometer at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5406 for CuKα1). Stepwise scanning measurements were performed at a rate of 4°/min in the range of 3–85° (2θ). Relative mineral percentages were estimated semi-quantitatively using the area under the curve for the major peaks of each mineral, with correction for Lorentz Polarization [34].

3.3. Low-pressure nitrogen adsorption measurement

The low-pressure nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 HD88 apparatus. Shale samples weighing approximately 0.3 g were automatically degassed at 110 °C in a vacuum for 20 h to remove adsorbed moisture and volatile matter. Degassed samples were exposed to liquid nitrogen at a temperature of −196 °C according to a series of precisely controlled gas pressures. Nitrogen adsorption volumes were measured over the relative equilibrium adsorption pressure (P/P_0) range from 0.0001 to 0.995, where P_0 is the condensation pressure of nitrogen at laboratory conditions and P is the actual gas pressure. Nitrogen adsorption data collected on shale samples were interpreted using the Brunauer-Emmett-Teller (BET) analysis for surface area and the Barrett-Joyner-Halenda (BJH), Dubinin-Astakhov, and density functional theory (DFT) methods for pore volume and pore size distributions. These analyses and calculations have been described before [35–37] and were generated automatically by the instrument's computer software.