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Research paper

Composition and pore characteristics of black shales from the Ediacaran Lantian Formation in the Yangtze Block, South China

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The Ediacaran period was critical in the evolution of the biosphere and ocean in the history of the Earth. Shales rich in organic matter (OM) are well developed for this period in the Yangtze Block, China, and have recently been related to shale gas exploration in South China. To date, detailed characterisation of the Ediacaran shales is not available. The present work sets out a detailed investigation of the composition and pore characteristics of samples from a shallow drill core in the Ediacaran Lantian Formation in the Lower Yangtze area, and the effects of shale composition on the pore growth are discussed.

The 90-m-thick Lantian black shales are highly over-mature (equivalent vitrinite reflectance (EVRo) value approximately 4.0%) with a total organic carbon (TOC) content up to 12%. They are dominated by quartz (33–72%), generally with low clay or feldspar content (<20%) and highly varied carbonate content (up to 60%). The Lantian shales are also notable for their high pyrite content (up to 19%), suggesting a depositional environment of an anoxic water body rich in sulphates; greatly enriched OM is facilitated in deep-water environments.

Bulk porosities of the shales range from 1.0% to 7.9%, and are positively correlated with TOC content. High-magnification scanning electron microscopy (SEM) images support the crucial importance of OM content on pore development. Generally, pore volume shows excellent, positive correlation with TOC content for micropores, good correlation for mesopores, and relatively poor correlation for macropores. Two samples with mostly high TOC content showed very low macropore volume and medium mesopore volume. These results suggest a close relationship between OM with relatively small pores, and enhanced compaction effect on large pores in highly OM-enriched shales.

1. Introduction

It is thought that the second step of oxygenation of the Earth's oceans and atmosphere occurred during the late Neoproterozoic era (ca. 800–542 Ma: Canfield and Teske, 1996; Marais et al., 1992). The Ediacaran Period (ca. 635–542 Ma) was a critical transition for the evolution both of biosphere and ocean (Canfield et al., 2007, 2008; Fike et al., 2006; McFadden et al., 2008; Narbonne, 2005, 2011). Strata deposited in various environments during the Ediacaran are well-developed and preserved in the Yangtze Block, South China, and numerous investigations of their sedimentology, palaeontology and geochemistry have been performed in the past 10 years (Condon et al., 2005; Guan et al., 2014; Jiang et al., 2011; Li et al., 2010; Wang et al., 2012; Yuan et al., 2011; Zhou and Xiao, 2007; Zhu et al., 2007; among others). The Ediacaran strata in the Yangtze Block are highly significant for petroleum exploration in China. Continuous exploration for conventional gas since the 1960s has demonstrated high gas productivity for the upper Ediacaran Dengying Formation (ca. 551–542 Ma, Wei et al., 2008; Zou et al., 2015). Moreover, intensive efforts have begun in the past few years in China to evaluate and explore gas shales (Wang, 2015; Zou et al., 2011, 2015), inspired by the great success of exploration and production of unconventional shale gas in North America (Curtis, 2002; EIA, 2014; Jarvie et al., 2007). Marine shales are widespread in the Yangtze Block, mainly in the Ediacaran Doushantuo Formation, the Lower Cambrian Niutitang Formation and the Lower

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Silurian Longmaxi Formation. These are some of the most promising strata for shale gas exploration in China (Dong et al., 2014; Tan et al., 2014a, 2014b; Zou et al., 2011). Stratigraphic studies have indicated that the black shales in the Ediacaran Doushantuo Formation were mainly deposited in deep-water slope and basin settings (Jiang et al., 2011; Zhu et al., 2007); however, unlike the Cambrian and Silurian shales (Chen et al., 2011; Han et al., 2013; Jiao et al., 2014; Liang et al., 2014; Ma et al., 2015; Tang et al., 2015; Tian et al., 2013, 2015; Wang et al., 2015), the Ediacaran shales have not been described in great detail (Tan et al., 2014a).

Pore networks in shales are of critical importance to gas storage and migration, and porosity and pore distributions are therefore key parameters in the evaluation of gas potential and production (Bustin et al., 2008; Dong et al., 2015; Ross and Bustin, 2009a; Wang and Reed, 2009). Numerous studies have been performed to shed light on the porosity and pore structures of shales and the impact of shale composition on the pore development (Chalmers and Bustin, 2007; Chalmers et al., 2012a; Clarkson et al., 2013; Mastalerz et al., 2013; Milliken et al., 2013; Ross and Bustin, 2007, 2009a; Tan et al., 2014a). Since shales comprise fine-grained particles and abundant organic matter (OM), they commonly possess very low porosity and permeability due to continuous compaction and heating in the sedimentation process. Unlike conventional gas reservoirs dominated by micron-scale pores, shale-gas reservoirs contain a large proportion of nanometre-size pores (Loucks et al., 2009, 2012; Nelson, 2009). Growing evidence of the pore development associated with OM transformation in shales is emerging from a large body of geological evidence (e.g., Bernard et al., 2012a, 2012b; Cardott et al., 2015; Curtis et al., 2012; Mastalerz et al., 2013; Valenza et al., 2013). The complexity of the transformation of OM in shale (hydrocarbon generation, expulsion and retention, secondary cracking and consolidation) has made it a challenging task to characterise its “organoporosity” (Cardott et al., 2015; Mastalerz et al., 2013; Milliken et al., 2013). Pores in shales are also related to mineral content (Loucks et al., 2009, 2012; Slatt and O’Brien, 2011). The large degree of the heterogeneity of shales, both in their pore content and their composition, has also produced unique characteristics in individual shale gas plays (Curtis et al., 2012), and therefore necessitates the use of techniques from several disciplines to describe individual shale plays (Ross and Bustin, 2009a).

The present work focused on the characteristics of the black shales of the Ediacaran Lantian Formation in the Lower Yangtze Block. The Lantian black shales are distinguished by the presence of abundant pyrite and preservation of macroscopic eukaryotes (Guan et al., 2014; Shen et al., 2008; Yuan et al., 2011). An integrated approach combining several methods (geochemical and mineral analysis, field-emission scanning electron microscopy (FE-SEM) coupled with argon-ion beam milling, low-pressure gas adsorption (LPA) and high-pressure mercury intrusion porosimetry (MIP)) was used to investigate the composition and pore characteristics of the Lantian shales. The effects of the composition of the shale on its porosity and pore structure are also discussed. This work aims at providing references for evaluating the Ediacaran gas shale in the Yangtze Block.

2. Geological background and lithostratigraphy

The South China Block consists of the Yangtze and Cathaysia blocks, which were amalgamated during the Sibao-Jinning Orogeny in the early Neoproterozoic (Zhu et al., 2007). The Yangtze Block is mainly located in the northern and south-western parts of the South China Block. Neoproterozoic strata preserved in the Yangtze Block occur in three major divisions, from lower to upper: the pre-Cryogenian siliciclastic units, the Cryogenian glacial and interglacial deposits, and the Ediacaran carbonate-siliciclastic units (Jiang et al., 2011). The Ediacaran strata in the Yangtze Block, comprising the Doushantuo and Dengying Formations, were developed at a passive continental margin between 635 and 542 Ma following the end of global glaciation (Condon et al., 2005; Jiang et al., 2011). The Ediacaran strata in this region are ascribed to various depositional environments, including shallow-water platform, slope, and deep-water basin settings extending from north-west to south-east of the Yangtze Block (Fig. 1a; Guo et al., 2007a; Jiang et al., 2011). The overall sequence of the Doushantuo Formation (ca. 635–551 Ma) in the Yangtze Gorges area, which was deposited on a shallow-water carbonate shelf, typically consists of four members: from bottom up, cap carbonate overlying the glacial diamicite at the base, alternating organic-rich shales and carbonates, carbonates, and a black shale interval at the top. The Dengying Formation (ca. 551–542 Ma) consists mainly of dolostones or limestones (Jiang et al., 2011; Zhu et al., 2007). In the deep-water slope or basin environments in the south-eastern Yangtze Block, the black shales are more developed than the carbonates, and the equivalent of the Dengying Formation is dominated by black chert (Jiang et al., 2011; Wang et al., 2012).

Southern Anhui Province (Fig. 1a) is located in the eastern part of the Yangtze Block and in one part of the Southern Anhui–Northern Zhejiang sub-basin (Zhou and Xiao, 2007). The Ediacaran sediments in this region, consisting of the Lantian Formation and Piyuanchun Formation, were deposited in slope-to deep-water basin settings. The Lantian Formation is the equivalent of the Doushantuo Formation in the Yangtze Gorges area, and the Piyuanchun Formation is correlated to the Dengying Formation. The Lantian Formation in the study area, in Xiuning County, southern Anhui Province (Fig. 1b), has been classified into four members in previous field studies (Guan, 2014; Yuan et al., 2011), and was penetrated by the shallow core in this work (Fig. 1c). The lowest Member I is siliceous dolostone approximately 4 m thick, overlying a Marinoan-age glacial diamictite of the Leigongwu Formation. In ascending order, Member II consists of about 20 m of greyish to black siltstones, 70 m of black shales and 30 m of alternating shale and carbonate layers. The Lantian biota consisting of macroscopic and morphologically differentiated eukaryotes occur in the middle-upper part of this member (ca. 600 Ma, Yuan et al., 2011). Member III consists of approximately 50 m of thick grey argillaceous limestone. The uppermost Member IV is characterised by about 10 m of black or dark grey shale overlain by the dark chert of the Piyuancun Formation.

3. Samples and methods

3.1. Samples

Ninety-seven samples were collected from a shallow drill core obtained in the town of Lantian, southern Anhui Province (Fig. 1a, b). Disseminated fine pyrite crystals, discontinuous fine pyrite laminae and centimetre-size pyrite clusters are very common in the black shales of this region (Guan et al., 2014). Following geochemical analysis, including measurements of TOC content and the carbon isotope value of OM, 22 samples were selected for determination of mineral composition and total sulfur (TS). Pore characterisation of 15 samples was also carried out using a variety of physical methods.

3.2. Organic geochemical analysis

About 100 mg of −200 mesh powder from each sample was placed in a crucible with 5% HCl at 80 °C to remove carbonates, and the TOC content was measured using a Leco C230 carbon analyser. The TS of each sample was analysed using an Elementar vario EL