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Original research paper

An insight into the mechanism and evolution of shale reservoir characteristics with over-high maturity☆

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Abstract

Over-high maturity is one of the most vital characteristics of marine organic-rich shale reservoirs from the Lower Paleozoic in the south part of China. The organic matter (OM) in shale gas reservoirs almost went through the entire thermal evolution. During this wide span, a great amount of hydrocarbon was available and numerous pores were observed within the OM including kerogen and solid bitumen/pyrobitumen. These nanopores in solid bitumen/pyrobitumen can be identified using SEM. The imaging can be dissected and understood better based on the sequence of diagenesis and hydrocarbon charge with the shape of OM and pores. In terms of the maturity process showed by the various typical cases, the main effects of the relationship between the reservoir porosity and organic carbon abundance are interpreted as follows: the change and mechanism of reservoirs properties due to thermal evolution are explored, such as gas carbon isotope from partial to complete rollover zone, wettability alteration from water-wet to oil-wet and then water-wet pore surface again, electrical resistivity reversal from the increasing to decreasing stage, and nonlinearity fluctuation of rock elasticity anisotropy. These indicate a possible evolution pathway for shale gas reservoirs from the Lower Paleozoic in the southern China, as well as the general transformation processes between different shale reservoirs in thermal stages.

Keywords: Over-high maturity; Shale gas reservoirs; Solid bitumen; Property

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1. Introduction

In the progressive process of thermal evolution, the physical and chemical properties of organic matter are thought to vary [1]. Today, with the evaluation, exploration, and exploitation of shale reservoirs in the world, new evidence related to thermal maturation have been noticed gradually; evidence include organic matter pores, carbon isotope rollover, electrical resistivity reversal, and Thomsen parameters [2−6]. For the Lower Paleozoic marine shale reservoirs in South China, organic matters are involved in a wide range of thermal evolution steps from the early diagenesis through catagenesis, even into metamorphism. They are prominently characterized by an extremely high degree of thermal maturity in dry-gas window rank. Therefore, organic matter and inorganic minerals, theoretically, are subjected to intense transformation in this situation; as kerogen is turned into well-ordered structural materials through polymerization, condensation, and rearrangement reaction, maceral vitrinite gained a strong anisotropy, and an

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amount of natural gas along with solid bitumen is generated when the vitrinite reflectance (*R*o) is more than 2% [7,8]. At the time, the processes of inorganic mineral precipitation, cementation, dissolution, recrystallization, and replacement take place, as well as the ordered alteration and preferred orientation of clay minerals occur. The matrix pore size and structure of shale reservoirs have also changed. Nevertheless, the questions associated with how thermal maturity at different stages influence shale properties and reservoir quality, and further makes them specific targets, are yet to be understood and answered.

On the basis of the entire maturity path observed from the incorporated international outstanding cases through the key reservoir parameters, this paper presents the combined effects produced by thermal maturity on shale porosity, wettability, resistivity, elastic anisotropy, and isotopic reversal of natural gas. In the meantime, the research shows intrinsic signatures for shale reservoirs with over high thermal maturity, that is called thermal maturity effect, in order to determine the dynamic features and processes of the Lower Paleozoic marine shale reservoirs from the southern China.

2. Reservoir pore space and carbon isotope for shale gas

2.1. Porosity and nanopores in shale cores

For core samples, conventional core test, mercury injection capillary pressure (MICP), surface area, GRI method, digital imaging technique, and other new means can be used for the laboratory analysis and interpretation of shale porosity. Nevertheless, data from multiple sources are unworkable since they are not interchangeable. For example, MIP results from the examined amount of Hg injected during the testing of the Barnett shale is 20%–50% less than the measurement of the He porosity, because mercury cannot enter the pores connected with 3.6 nm, as well as those with less pore throat. The GRI method, which is recognized internationally, might deviate due to non-unified processing procedures and quality control standards in laboratories. Generally, the difference is 0.5–1.5p.u. [9]. In this study, GRI method data available from mature shale reservoirs of international major areas and strata is still selected to introduce a linear cross-plot between helium (He) porosity and organic matter abundance (Fig. 1). These porosity data chiefly ranges 2%–10%, and 10%–17% in the minority group, and that the amplification of He porosity is different in distinct sections of the organic matter abundance even though the general relationship is positive. In the less abundant area (TOC $< 5\%$), the amplification is great. For example, the correlation coefficient of the Marcellus shale is 0.82–0.86 [10]. However, the correlation in a greater abundant area (TOC $> 5\%$) is usually relatively poor, or even completely irrelevant, regardless of the level of shale maturity. This indicates that the organic matter pore is only one of the important parts of reservoir pore system and that other factors should also be considered.

First, the mineral compositions of organic-rich shale vary. Some are clastic rocks that are constituted mainly by clay mineral and quartz, such as the Longmaxi shale, Marcellus shale, Barnett shale, and Haynesville shale. Some are carbonate rocks with a small amount of quartz, feldspar, clay minerals such as the Green River shale, Eagle Ford shale, Niobrara shale, and Shahejie shale from the Liaohe Depression. In addition to a lot of pores in organic matter, mineral matrix intergranular pore, and intragranular pore are also well developed. For instance, the Eagle Ford shale is characterized by intergranular dissolved pores and cracks, and the Longmaxi shale presents a number of residual intergranular pores (Fig. 2).

Secondly, the kerogen patches are composed of various microscopic compositions without any unified structure. Since kerogen types are different, the relative proportions of chitin group, lipid group, vitrinite group, inertinite group, and others as well as the ability to form organic matter pore also varies. The micro component of the congenital inert is associated to the dead carbon material caused by the reduction of hydrogen in the thermal evolution process. Although they lack the activity and the hydrocarbon generation potential is in limited condition [12], the contribution of these two to organic matter pores are entirely different. Under the microscope, it is common to see organic matter with poor pore development (Fig. 3a–d). By setting the gray level threshold of the SEM images, the delimitated area is extracted. The surface porosity of organic-rich Longmaxi shale with an over high thermal maturity is 24.7% (Fig. 3e and f). Based on more samples from the Longmaxi shale, the porosity value is commonly 7%–30% [4]. For the Barnett shale from the core area, the distribution density and shape of micro and nano-organic pores are inferior than those of the classic style in the published literature (Fig. 3c) [4]. For one of the Woodford mature shale (*R*o $= 1.23\%$), there are no organic matter pores adjacent to the porous area on the micrometer scale. The former may be pyrobitumen, and the latter may be kerogen patches (Fig. 3d) [5]. Noticeably, the same can be observed in the intergranular and intragranular pores in the mineral matrix; additionally, the distribution of organic pore is also heterogeneous.

Third, in the late stage of oil generation, crude oil starts cracking to generate a lot of organic matter pores. Some cavities are connected with narrow throats to form a larger pore network. Even if shale samples come from a larger burial depth, the organic pore morphology remains intact without any deformation (Fig. 3e). It seems that the porosity development in the mineral matrix is considered to be primarily related to the compaction, dissolution, cementation, recrystallization, etc. The creation of organic matter pores has a closer connection to the evolution of thermal decomposition of organic matter during the burial diagenesis and catagenesis.

If it is presumed that the kerogen converted the liquid or gaseous hydrocarbon, organic matter pores produced are controlled dominantly by the maturity, the secondary pores and their specific surface area does not maintain fixed value, which depends on the rearrangement degree of the kerogen structure and expulsion efficiency of hydrocarbon [1]. Thus the required migration pathways for oil and gas inside or nearby source rock would be inseparable with the key parameter. That is to say, in addition to the presentation of pore size, shape, density, and others, the mineral matrix pores well developed in shale