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Original research paper

Probable mechanism of organic pores evolution in shale: Case study in Dalong Formation, Lower Yangtze area, China☆

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Abstract

Organic pores structures and their probable evolution mechanisms were analyzed by an Ar-ion milling (SEM) after a thermal simulation experiment. Several kinds of organic pores including girdle pores, circular pores, and spongy pores appeared during the thermal simulation process. The result shows that there are different possible mechanisms in organic pores evolution. Girdle pore is a typical pore structure in a particular period of hydrocarbons generation, and the girdle structure is an organic matter—mineral complex where the hydrocarbons generate. This phenomenon made it possible to observe the organic matter—mineral complex for the first time.

Keywords: Organic pores; Evolution mechanism; Organic matter-mineral complex; Thermal simulation; Shale

1. Introduction

In the recent years, South China has become one of the sought-after regions for shale gas exploration and development [1—5]. This area has many kinds of shale pores that can be divided into two types [6]: inorganic pores and organic pores. From the successful experience in Jiaoshiba, the organic pores occupy the majority of pore volume, which means that the organic pores play a crucial role in shale gas occurrence.

The development of analysis technology in micro-nano scale, such as Ar-ion milling, FIB-SEM, TEM, and nano-CT, have promoted the study of pore structure in shale. Behar reported the pore structures from 5 to 50 nm were determined by the types of kerogen [7]. The average apertures of organic pores were less than that of inorganic pores [8]. Chalmers studied the indentations about 2.5 nm within the pore wall, which might be related to micropore structures [9]. However, these research were limited to a static state, and it's seldom focused on dynamic processes including formation of pores in shale. Thermal simulation is an efficient method to study the organic pores evolution process in long geological periods.

A thermal simulation experiment is based on the theory of time-temperature compensation in organic matters degradation process [10]. Consequently, the result that organic matters degrade under high temperature and pressure condition can reappear the long geological process. In this study, the pore structures before and after thermal simulation were compared, not to mention, the possible mechanisms of organic pores evolution in shale were also analyzed.

2. Experimental section

The samples used in the thermal simulation experiments had varying maturities from immature to low mature, but most shale in South China is on a high thermal maturation level. Hence, a sample was preferred to be extracted from the Dalong Formation, specifically in the Lower Yangtze area,

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Table 1
Experiment conditions of thermal simulation.

Sample no.	Time/h	Temperature/°C	Lithostatic pressure/MPa	Fluid pressure/MPa
1	48	350	35	14
2	48	375	40	16
3	48	400	45	18
4	48	425	50	20
5	48	450	55	22

which has a low R_O value (1.56%) with its characteristics being organic rich (TOC 3.23%). The simulation experiment conditions are shown in Table 1. The solid residues were milled by an Ar-ion beam and were further analyzed by a SEM to obtain images of the pore structures in shale.

3. Results and discussions

Fig. 1 shows several typical pore structures in shale after the thermal simulation experiment: (1) one or few macro pores developed in bulk organic matters, and there were girdle structures which could be distinguished by the SEM significantly; (2) some pyrite particles which coexisted with organic matters in geological samples were isolated by pores; (3) pores with high roundness in organic matters; (4) spongy organic pores. This phenomenon meant that there might be various mechanisms in organic matters evolution process. In this work, authors chose the girdle pore (Fig. 1a) to analyze the possible mechanism in organic pores evolution process.

It is observed that the girdle pores also existed in geological samples (Fig. 2a), therefore, it can be inferred that it was not a special product under thermal simulation conditions. The girdle pores were seldom observed in geological samples ($R_O = 1.56\%$), which meant those samples were in the initial development stage. By means of the improvement of thermal evolution degree (R_O from 1.56% to 3.12%), the pores in the center of organic matters progressively grew bigger. Simultaneously, the girdle structure expanded gradually. The shapes of the girdles were irregular, they had no crystal structure, and they were limited by organic matter particles. Additionally, several cracks could be seen in Fig. 2b, thus, the girdle structure was not a single mineral.

The elemental composition of girdle was determined by an EDS. The results showed that the girdle structure contained various types of elements, including C, O, Si, Al, K, Fe, Ca, and S. It is observed in 1–3 of Fig. 2b that the carbon content decreased, whereas the element types increased gradually. Except for carbon, the main elements contained O, Si, and Al, which were the constituents of clay (Table 2). Meanwhile, the value of Si/Al remained constant, which meant this structure might play a catalyst role in the thermal evolution process. In addition, the mineral composition of the girdle should be a mixture of silicon and clay, because the Si/Al value was about 3.5, which was higher than the normal value in clay.

The girdle structure might originate from biogenic silica and clay, this could have higher catalytic activity and promote organic matters degradation. This complex is where hydrocarbons are generated to contain organic matters and minerals. By the development of the evolution degree, CO_2 and carbonate ion ensued from the decarboxylic reaction, which is probably the reason why some elements (Ca, Mg, and Fe) appeared inside of the girdle.

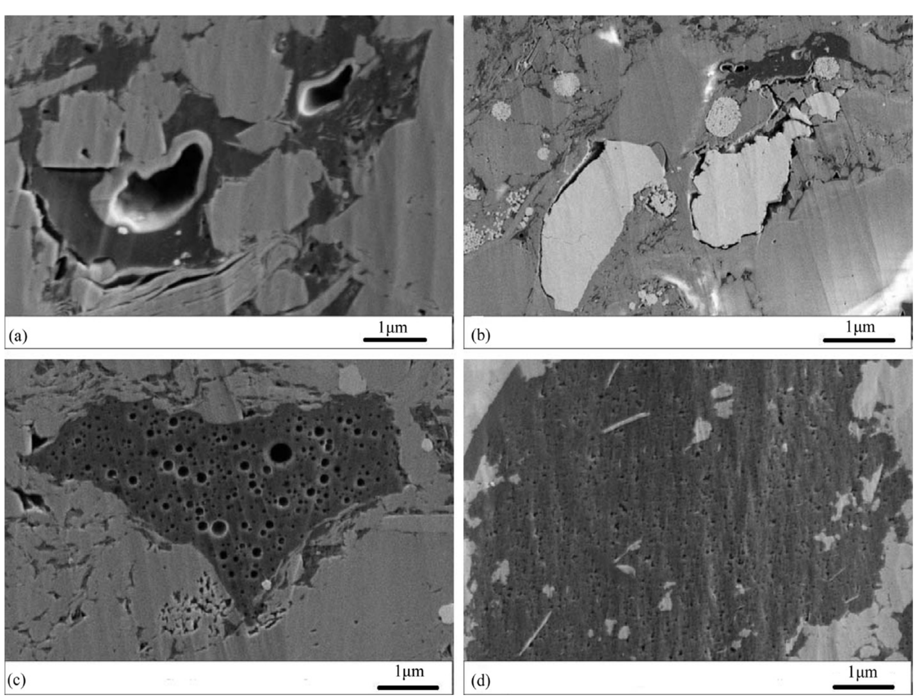

Fig. 1. Typical organic pores in shale after thermal simulation experiment. (a) Girdle pores; (b) Pores around pyrite; (c) Pores with high-roundness; (d) Spongy pores.

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