

## EVOLUTION CHARACTERISTICS OF SHALE ORGANIC PORES UNDER DIFFERENT THERMAL SIMULATION SYSTEMS

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### Introduction

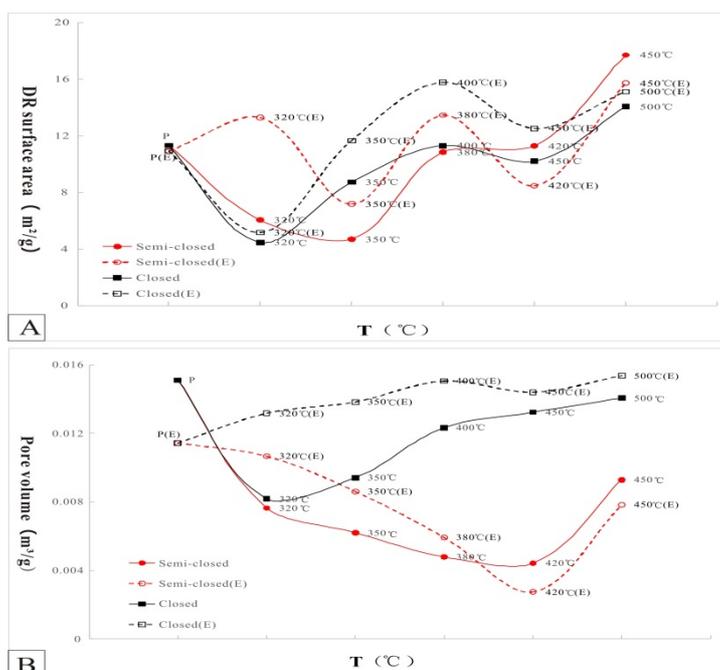
The organic pore structure of organic-rich shale is an important factor affecting the enrichment of shale gas. Many studies suggested with increase of maturity, nanopores are widely developed in organic-rich shale (Milliken et al., 2013; Katz et al., 2018). There also exists some difference when different organic matters develop organic pores, the relationship between organic conversion products and conditions of hydrocarbon's expulsion with shale pore structure during the thermal evolution still remains some controversy. We use the high-temperature and high-pressure semi-enclosed pyrolysis equipment and the glass tube thermal simulation experiment of enclosed system to conduct thermal simulation experiments from low-mature to high-mature stage. Discussing the relationship between different hydrocarbon releasing mode with shale pore evolution to explore occurrence mechanism of organic pores under different thermal simulation systems.

### Results

In semi-closed system, the thermal evolution products can be discharged in time, cracking and releasing of unstable hydrocarbons in the kerogen, resulting shrinkage of kerogen, the shrinkage of kerogen itself leads to the formation of organic nanopores. Therefore, the semi-closed system is more likely to develop organic pores in low-mature to mature stage, but the higher extra pressure may compact the mesopore and macropore in kerogen. In closed system, the hydrocarbons cannot discharge timely, resulting the block of some pores, but the retention of a large amount of liquid hydrocarbons leads to an increase in fluid pressure, which has a protective effect on organic pores. So, pore volume of closed system is higher than semi-closed system in low-mature to mature stage, and pore volume of samples extracted by dichloromethane shows the same trend, which suggested the compaction has great influence on organic pores in low-mature to mature stage. In mature to high-mature stage, we combined with pore volume and specific surface area of extracted and un-extracted samples to explore the development of pore. Pore volume and specific surface area of extracted samples in semi-closed system are significantly lower than un-extracted samples, which mainly concerned with the expansion of kerogen and the destruction of its pore structure, owing to the interaction of kerogen with extractant (DiStefano et al., 2019). Therefore, in semi-closed system, kerogen generates more organic pores with increase of maturity, because residual organic matter in kerogen is gradually cracked and transformed, leading to the space in kerogen is further released. While in closed system, extracted sample's pore volume and specific surface area are increased relative to the un-extracted samples, we reckon that the extractant may extracts part of the adsorbed gas adsorbed in pores of solid bitumen and pyrobitumen. Thus, solid bitumen and pyrobitumen develop more organic pores in the closed system. On the one hand, cracking products of residual organic matter in kerogen cannot be discharged in time, which has an inhibitory effect on the development of pores in the kerogen in some degree, on the other hand, the primary evolution production of kerogen retained in the shale later converted to solid bitumen, pyrobitumen, etc.

## Conclusions

Through the thermal simulation experiments of different systems, we think that development of organic pores is closely related to mode of hydrocarbon's expulsion during thermal evolution of shale. When the thermal evolution products of kerogen can be discharged timely, kerogen will develop more organic pores than solid bitumen and pyrobitumen; when the thermal evolution products of kerogen cannot be discharged, a large number of thermal evolution products are converted into solid bitumen, pyrobitumen, etc., the organic pores developed in solid bitumen and pyrobitumen are dominant.



**Figure 1** Pore volume and Specific surface area change with pyrolysis temperature (extracted and un-extracted). (A) Micropore specific surface area changes with temperature. (B) Pore volume of mesopore and macropore changes with temperature. Note: P is the original sample and P(E) is the original sample after extraction.

## References

- DiStefano, V. H., McFarlane, J., Stack, A. G., et al, 2019. Solvent-pore interactions in the Eagle Ford shale formation. *Fuel*, 238, 298–311.
- Katz, B.J., Arango, I., 2018. Organic porosity: A Geochemist's View of the Current State of Understanding. *Organic Geochemistry*, 123:1-16.
- Milliken, K.L., Rudnicki, M., Awwiller, D.N., et al, 2013. Organic matter-hosted pore system, Marcellus Formation (Devonian), Pennsylvania. *AAPG Bulletin*, 97, 177–200.