

GEOCHEMISTRY OF DISSOLVED ORGANIC MATTER IN THE LOWER SILURIAN MARINE SOURCE ROCKS FROM BALTIC BASIN AND SICHUAN BASIN

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Abundant shale oil and gas resources have been shown in the marine sedimentary regions of southern China, and the marine excellent source rocks have great contribution to these unconventional resources. However, the maturity of most marine source rocks in the area reaches high-over mature stage, with the vitrinite reflectance value (R_o) over 2%, which results in similar developing pattern of conventional geochemical indices and losing their original significations. The geochemistry study of dissolved organic matter (DOM) in these high-over mature marine source rocks is relatively less and restricted, which is also a critical issue in the studied Lower Silurian Longmaxi Formation shale in Sichuan Basin, characterized by high contents of total organic carbon ($TOC > 3\%$), low amounts of free hydrocarbons ($S_1 < 0.15$ kg HC/t rock) and chloroform bitumen A ($< 60 \times 10^{-6}$), in which saturated hydrocarbon and aromatic hydrocarbon are generally absent.

Previous investigation has demonstrated that the Lower Silurian source rocks in Baltic Basin and Sichuan Basin have strong contrast, which can be confirmed in the composition of graptolite and lamalginite through the identification of hydrocarbon-forming organisms, and the kerogen type (type II, mainly composed of benthos, fungi and bacteria) in this study as well. These source rocks in Baltic Basin have low maturity ($R_o < 1.0$) and high content of DOM (up to 7.26×10^{-3}), of which the percentage of total hydrocarbon is over 70% and much higher than that of nonhydrocarbon and asphaltene. Saturate fractions compounds are dominated by n -alkanes in the range from n -C₁₁ to n -C₁₈ carbon atoms in the molecule with one maximum. Abundant alkyl cyclohexane and aromatic hydrocarbon are present but absence of hopanoids and steroids, which is different from the distribution in the source rocks from the same area in the previous report (Zdanavičiūtė and Lazauskienė, 2009). Therefore, further analysis of DOM through using a new method (Zhang et al., 2016) is required to get more information about the geochemistry characteristics of these samples.

All the DOM of these marine excellent source rocks from both basins were subjected to sequential stepwise pyrolysis at 50 °C intervals from 310 to 610 °C. The results indicated that a wide range of n -alkenes/alkanes pairs (C₇ to C₃₀) occurred after 410 °C in all samples. In the high-over mature marine source rocks from Sichuan Basin, saturated hydrocarbons dominated at different temperature stages with the change in carbon atoms. The distribution of alkane products with the increasing temperature is much the same as the process of hydrocarbon generation and expulsion. At 310 °C, n -C₁₄ to n -C₁₈ were predominant and the percentage of

higher molecular weight alkanes ($>C_{20}$) increased with increasing temperature till 410 °C. Then the percentage of higher molecular weight alkanes decreased, whereas the percentage of lower molecular weight alkanes increased (C_8 to C_{20}) till 560°C, which decreased again at 610 °C and dominant $n-C_{17}$ to $n-C_{20}$ alkanes were left. However, the situation is more complicated in the low mature source rocks from Baltic Basin. Due to the pyrolysis of nonhydrocarbon and asphaltene, many hopanoid, steroids and aromatic hydrocarbon occurred, such as tri-aromatic sterane and tetramethylbenzene, derived from some certain acritarch, bacteria or algae (Hoefs et al., 1995; Koopmans et al., 1996; Moldowan et al., 1996; Pedentchouk et al., 2004), which could possibly be present in the source rocks in the Sichuan Basin when they were still in the low maturity stage. The stepwise pyrolysis of DOM in these excellent marine source rocks from Baltic Basin will provide us a hint to interpret the source of organic matter and geochemistry process in the marine sedimentary regions of southern China.

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