Oil generation character of Mesoproterozoic Xiamaling formation during stepwise pyrolysis

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Abstract. The exploration potential of Mesoproterozoic petroleum system has getting increasingly attention and the oil generation character of Mesoproterozoic source rock is still uncertain. To solve the problem, this study choose sample from Mesoproterozoic Xiamaling formation from north China, using the stepwise gold tube pyrolysis method to study the oil generation character and the composition of liquid pyrolysates, and choose sample from Mesozoic Yanchang formation in middle China as a comparison to study their differences in oil generation character. The results showed that oil generation window of Mesoproterozoic Xiamaling sample in this research was earlier and narrower, with an earlier oil generation peak, this maybe the result of the single source of organic matter and its labile chemical bound. Furthermore, mainly source of organic carbon, like cyanobacteria and acritarchs, were lack of lipid compounds, perhaps this could make the relative concentration of saturated hydrocarbon in liquid pyrolysates of Mesoproterozoic Xiamaling sample much lower than the Mesozoic Yanchang sample with the same kerogen type, nonpolar fraction of liquid pyrolysates in the oil generation window were mainly aromatic hydrocarbon. Maybe the results mean that although Mesoproterozoic Xiamaling formation is still in low maturity stage, it may has already started oil generation, and type of oil generated by Mesoproterozoic source rock in oil generation window may have significant difference from the Phanerozoic source rock.

1. Introduction
Recently, oil and gas exploration potential of Mesoproterozoic has become academic and industrial focus, several Neoproterozoic oil or gas field has been found and increasing study has focused on Mesoproterozoic source rock, several excellent source rock has been found in China, North America, Africa and Australia, showing good exploration prospect[1]. Depositional environment, control factor, source of organic matter and the preservation pathway of organic matter in Mesoproterozoic has received widespread attention and acquired many findings. However, hydrocarbon generation characteristic of Mesoproterozoic source rock has not gained enough attention.

Studies have shown that although eukayote had emerged, it only played minor role in Mesoproterozoic biosphere, prokaryote(like cyanobacteria) still dominated the Mesoproterozoic biodiversity and it is the mainly source of organic matter in Mesoproterozoic source rock, structure and chemical composition difference between prokaryote and eukaryote can influence the composition of sedimentary organic matter(kerogen)[2]. Meanwhile, previous study has shown that, because of the size and structure difference between prokaryote and eukaryote, they showed obviously different degradation level and preservation pathway in the water column, prokaryote would be degraded by
heterotrophic bacteria more severely in the water column, making lipid compounds became harder to be preserved\textsuperscript{[3]}, these differences all can influence the hydrocarbon generation characteristic of Mesoproterozoic source rock. However, present researches on the hydrocarbon generation of Mesoproterozoic source rocks mainly concentrates on the biomarker composition in pyrolysates gained from hydropyrolysis\textsuperscript{[4]} or PY-GC-MS\textsuperscript{[5]}, few concentrations has focused on the oil yield, oil generation period and the characteristic of oil generated, which has important meaning on source rock evaluation, studying the oil generation period of source rock and estimate the hydrocarbon generation amount of source rock. To focus on these problems, this research choose low maturity source rock sample from Mesoproterozoic Xiamaling formation, north China, using stepwise gold tube pyrolysis to obtain liquid pyrolysate at different maturity, using composition quantitate to study composition of pyrolysates of different maturity to study the oil generation stage and composition of oil generated during this stage, meanwhile, we choose sample from Mesozoic Yanchang formation in the Erdos basin, China as a comparison to study difference of oil generation characteristic between Mesoproterozoic and Mesozoic sample which has the same kerogen type, finding the geological significance of these characteristics.

2. Sample & method

| Sample        | TOC  | HI  | Tmax | H/C | Total liquid yield |
|---------------|------|-----|------|-----|-------------------|
| Xiamaling     | 4.01 | 487 | 431  | 1.24| 338.5             |
| Yanchang      | 5.20 | 385 | 433  | 1.15| 218.5             |

Samples used in this study were chosen from a Mesoproterozoic drilling core in Xiahuayuan, Hebei province, China and a Mesozoic drilling core in Erdos basin, Shanxi province, China separately. The two samples are both type II\textsubscript{1} organism in low maturity, specific geochemical data is shown in Table 1. Kerogen is concentrated via HCl-HF treatment, and stepwise gold tube pyrolysis is used to obtain liquid pyrolysates generated in each stage, the detailed method is that, the initial pyrolysis temperature was 320\textdegree C, and the final temperature was 490\textdegree C. A total of 9 temperature steps were used for the stepwise pyrolysis, with temperature intervals of 20\textdegree C for the temperature range from 320\textdegree C to 440\textdegree C, and 25\textdegree C for the temperature range of 440\textdegree C to 490\textdegree C, the temperature ramp was 20\textdegree C/h, in the first step, the temperature was increased from room temperature to 300\textdegree C in 2 hours and then to 320\textdegree C at a rate of 20 \textdegree C /h, then the gold tubes were cooled to room temperature, use dichloromethane(DCM) to clean the outside of tubes and then cut the tubes, then use DCM to extract kerogen residual to obtain liquid pyrolysates of this stage. After that, the residual was loaded into gold tubes again for the next step pyrolysis, with temperature increased from room temperature to previous temperature(320\textdegree C) and then to 340\textdegree C ramp 20\textdegree C/h and repeated the above procedure until all steps was finished. For the extraction of kerogen residual, use nitrogen flow to dry the solvent and then weight the pyrolysate to calculate yield of liquid pyrolysates in each stage, after that, use IATROSCAN MK-5 TLC/FID analytical instrument to quantify the four composition(SARA) of pyrolysates to study pyrolysate composition of each stage.

3. Result

3.1 Liquid hydrocarbon pyrolysates yield and stage characteristic of Xiamaling and Yanchang sample

The accumulated liquid hydrocarbon yield of two samples are shown in Table 1, the accumulate yield of Xiamaling sample is a bit higher than Yanchang sample, which is consistent with the higher HI and kerogen H/C atomic ratio of Xiamaling sample. Fig 1 shows the liquid pyrolysate yield of each stage and its evolution trend, the oil generation window of Xiamaling sample starts earlier than the Yanchang sample, it begun to generate large amount of liquid hydrocarbon since 340\textdegree C stage, and the
oil generation window region was 340-380°C, the oil generation peak was 360°C stage, with a yield of 147.3mg/g TOC. Liquid hydrocarbon yield decreased sharply after the 380°C stage, stage yields between 400-490°C were all lower than 10mg/g TOC. However, extent of oil generation window of Mesozoic Yanchang sample was wider than the Xiamaling sample, ranged from 340°C to 420°C, and its oil generation peak was also later than the Xiamaling sample, it reached oil generation peak until 380°C, and in accord with the Xiamaling sample, stage yields of Yanchang sample after oil generation window were as well lower than 10mg/g TOC.

![Stage yield](image)

**Figure 1.** Stage yield of liquid pyrolysates from pyrolysis experiment

### 3.2 Fracture composition characteristic of liquid pyrolysates

As saturated and aromatic fraction(nonpolar fraction) are the two most economic valuable fractions in crude oil, especially the saturated fraction, this research mainly concentrate on the relative concentration of saturate fraction in nonpolar fraction. As the liquid pyrolysates of the two sample after 400°C are insufficient for the analysis and the fraction composition can hardly be analyzed, this study only choose liquid pyrolysates in stages between 320 to 400°C.

The liquid pyrolysates in early stages(320 and 340°C) of Xiamaling sample contains abundant saturated fraction(Fig 2.), proportion of saturated fraction in the nonpolar fraction was 36.2% and 42.6% respectively. However, as the pyrolysis temperature increased, relative concentration of saturated fraction decreased sharply after the Xiamaling sample came into the oil generation window, proportion of saturated fraction in the nonpolar fraction was only 7.7%, 4.7% and 4.4% in the 360, 380 and 400°C stage, and on the other side, proportion of aromatic fraction increased sharply in the the liquid pyrolysate after the Xiamaling sample came into the oil generation window, aromatic fraction contains most of the nonpolar fraction in the pyrolysates during the oil generation window.
Figure 2. Relative proportion of saturated and aromatic fraction in liquid pyrolysates of Xiamaling Formation sample

Figure 3. Relative proportion of saturated and aromatic fraction in liquid pyrolysates of Yanchang Formation sample

Composition of nonpolar fraction in the early stage liquid pyrolysate of Yanchang sample showed a similar characteristic as the Xiamaling sample(Figure.2.), saturated fraction contained considerable proportion of the nonpolar fraction in the 320°C liquid pyrolysate, 31% of the nonpolar fraction was saturated fraction. However, different from the Xiamaling sample, when came into the oil generation window, proportion of saturated fraction did not show the decrease trend as the Xiamaling sample, relative concentration of saturated fraction in pyrolysates during the oil generation window was 49.8%, 26.1%, 26.7% and 37.6% respectively, relative concentration of saturated and aromatic
fraction showed similar character as the 320 °C liquid pyrolysate, did not showed a decreasing trend as the pyrolysis temperature increased.

4. Discussion
4.1. Reason for period difference of oil generation window between Xiamaling and Yanchang sample
As shown in Figure 1., oil generation window of Xiamaling sample is earlier than the Yanchang sample, and the range of its oil generation window is much more concentrated than the Yanchang sample, this may be caused by different source of organic matter this two samples have. In the Mesoproterozoic period, prokaryote like cyanobacteria dominated the biosphere and it was the main source of the Mesoproterozoic source rock, source of organic matter was single and this made the oil generation period of Xiamaling sample concentrated. Nevertheless, in the Mesozoic period, biodiversity level was much higher than the Mesoproterozoic period, source of organic matter of Mesozoic source contains prokaryote, eukaryote, higher plant and several kinds of other organisms, composition of source of Yanchang sample and its kerogen maceral was much more complex, different maceral showed different hydrocarbon generation character, this may made the Yanchang sample had a wider oil generation window. Meanwhile, because of the weaker chains in the cyanobacteria resistant biopolymer(PRS), the thermo stability of PRS is weaker than resistant biopolymers(PRB) in eukaryotes, this may cause the oil generation window and oil generation peak of XML sample becomes much earlier than the Yanchang sample.

4.2. Composition differences of liquid pyrolysates of XML and Yanchang sample
Relative concentration of saturated fraction in the liquid pyrolysates of Xiamaling sample decreased sharply as the pyrolysis temperature came into the oil generation window, and its relative concentration was much lower than the Yanchang sample at the same stage, this may caused by the special chemical composition of Mesoproterozoic organisms, different from the composition of algae that rich in lipid, which is the main source of organism in Phanerozoic, concentration of lipid in cyanobacteria, the main source of organism in Mesoproterozoic, is much lower, it is mainly formed by compounds like proteins and polysaccharide, and other sources like acritarchs, its chemical composition is also different from algae, it shows a highly condensed, polyaromatic structure that lacks of lipid compounds, these differences may together caused the low relative concentration of saturated fracture in liquid pyrolysates of Xiamaling sample.

5. Conclusions
Using stepwise gold tube pyrolysis method and TLC/FID fracture quantify analysis to study the composition of liquid pyrolysate of Mesoproterozoic Xiamaling sample, comparing with characters of Mesozoic Yanchang sample, this paper draws the following conclusions:

1. It seems that compared to source rock with the Mesozoic source rock with same kerogen type, oil generation window of Mesoproterozoic Xiamaling source rock was earlier and narrower, and its oil generation peak was also earlier, this may caused by the single source of organic matter and its labile chemical bound, this perhaps indicates that although Mesoproterozoic Xiamaling formation is still in low maturity stage, it may has already started oil generation.

2. May be because of the mainly source of organic carbon, like cyanobacteria and acritarchs, were lack of lipid compounds, relative concentration of saturated hydrocarbon in liquid pyrolysates of Mesoproterozoic Xiamaling sample were in low level, and it seems that they were much lower than the Mesozoic sample with the same kerogen type, nonpolar fraction of liquid pyrolysates in the oil generation window were mainly aromatic hydrocarbon, this character may cause the type of oil generated by Mesoproterozoic source rock in oil generation window may be different from the Phanerozoic source rock.

References
[1] Wang T.G, Han K.Y 2011 On Meso-Neoproterozoic primary petroleum resources Acta Petrolei Sinica 32(1) 1.
[2] Vandenbroucke M., Largeau C. 2007 Kerogen origin, evolution and structure *Organic Geochemistry* 38(2007) 719.

[3] Logan GA, Summons RE, Hayes JM 1988 An isotopic biogeochemical study of Neoproterozoic and Early Cambrian sediments from the Centralian Superbasin, Australia *Geochimica et Cosmochimica Acta* 61(24) 5391.

[4] Brocks JJ, Love GD, Snape CE, Logan GA, Summons RE and Buick R 2003 Release of bound aromatic hydrocarbons from late Archean and Mesoproterozoic kerogens via hydropyrolysis *Geochimica et Cosmochimica Acta* 67(8) 1521.

[5] Imbus SW, Engel MH, Elmore RD and Zumberge EZ 1988 The origin, distribution and hydrocarbon generation potential of organic-rich facies in the Nonesuch Formation, Central North American Rift System: A regional study *Advances inorganic Geochemistry* 13(1) 207.

[6] Brocks JJ, Jarrett AJM, Sirantoine E, Hallmann C, Hoshino Y and Liyanage T 2017 The rise of algae in Cryogenian oceans and the emergence of animals *Nature* 7669(2017) 578.

[7] Chalansonnet, S., C. Largeau, E. Casadevall, Berkaloff C, Peniguel G and Couderc R 1988 Cyanobacterial resistant biopolymers. Geochemical implications of the properties of Schizothrix sp. resistant material. *Organic Geochemistry* 13(4-6) 521.

[8] Arouei KR, Greenwood PF, Walter MR 2000 Biological affinities of Neoproterozoic acritarchs from Australia: microscopic and chemical characterisation *Organic Geochemistry* 31(2000) 75.