Current Status and Challenges of Methyltrimethyltridecylchromans Research in Source Rocks and Crude Oils

Kaixi Jiang,* Chunming Lin,* Chunfang Cai,‡ Xia Zhang,‡ Shuya Huang,‡ and Zuochun Fan§

†State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, PR China
‡Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, PR China
§PetroChina Liaohe Oilfield Company, Panjin, Liaoning 124010, PR China

ABSTRACT: Methyltrimethyltridecylchromans (MTTCs) are structurally similar to tocopherols, which were identified in large numbers of source rocks and crude oils (Pleistocene to Early Cambrian). The occurrence of MTTCs was widely used as a proxy indicator of paleosalinity in the field of organic geochemistry. However, their origin and geological formation pathway still remain greatly debated. Here, we review the progress made over the past 30 years in the distribution and origin of MTTCs and their applications. Furthermore, we discussed several key points for future studies on MTTCs.

INTRODUCTION

Methylated isoprenoid chromans are components that have a methylated 2-methyl-2-(4,8,12-trimethyltridecyl)chroman (MTTC) structure (Figure 1). The structure, origin, and potential application of MTTCs in geological samples were first studied in detail by Sinninghe Damsté et al. in 1987.1 Also, the first ratio of 5,7,8-trimethyl MTTC/8-methyl MTTC (α/δ-MTTC) was established by Sinninghe Damsté et al. as a parameter for paleosalinity reconstruction, which was widely used in a later study although with some modifications.1 Generally, MTTCs consisting of monomethyl (δ-MTTC), dimethyl (β-MTTC, γ-MTTC, ζ-MTTC), and trimethyl (α-MTTC) homologues2−12 were widely found in immature and low-mature source rock/sediment extracts and crude oils.1−15

MTTCs are present in the aromatic fraction of the extract of source rocks and crude oils.1,2 They can be accurately detected on the basis of the mass spectra and relative retention times by using gas chromatography–mass spectrometry (GC–MS) techniques.1 Tulipani et al.16 developed a pyrolysis-gas chromatography-isotope ratio mass spectrometry (PY-GC–irMS) method to measure the 13C values of pyrolysis products generated from α-MTTC. Since MTTCs are easy to be identified, they were found to be widespread in source rocks that were deposited in marine and lacustrine environments.1−15

Studies on the MTTCs in source rocks over the past 30 years showed that paleosalinity is the key factor controlling the distribution and abundance of MTTCs.1−15 Some studies indicated that MTTC parameters might be used as a proxy to indicate freshwater incursion17 or the degree of maturity.18−20 The origin of MTTCs has been a scientific problem affecting applications of MTTC parameters for nearly 30 years. Do MTTCs form via biosynthesis1,4 or condensation reactions of alkylated phenols with phytol?21,22

We review here the progress made in over 30 years in the studies of changes in the abundance and distribution of MTTCs in source rocks and crude oils and their applications. We also discussed several key points for future studies of MTTCs.

ANALYTICAL METHODS FOR MTTCS

MTTCs are present in the aromatic fractions of source rock extracts and crude oils. The source rock extracts can be acquired by multiple methods such as Soxhlet extraction. The extracts were separated using a silica/alumina column, and the aromatics were analyzed by gas chromatography–mass spectrometry (GC–MS).1 MTTCs were identified by comparing their mass-to-charge ratios (m/z) of 121, 135, and 149.1 Biomarker ratios were calculated using the peak areas in the appropriate molecular ion chromatograms. The percentages of the ions in the total MTTC ion intensities were used to calculate the relative abundances of MTTC homologues. The quantitative analysis of MTTCs could use synthesized MTTCs as the internal standard, which were synthesized by a condensation reaction of phytol with phenol derivatives.1,2

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MTTCs were mainly identified in the evaporite-related source rocks and crude oils (Figure 2a). The evaporite-related source rocks contain varying lithology types including mudstone, black shale, marl, halite deposits, etc. The organic matter abundances of these evaporite-related source rocks vary greatly from organic-rich to organic-lean and contained type I, type II, and type III kerogens. Based on previous studies, we found that source rocks containing MTTCs were not widely distributed globally; they were found mainly in salt-bearing sedimentary basins in China and Europe. By comparing Figure 2a and Figure 2b, we found that evaporite-related source rocks were globally distributed, while MTTCs were not detected in most of these evaporite-related organic sediments. There are two possible reasons that may explain this situation. One of the possible reasons is that MTTCs in most of these source rocks have not been studied. The other reason is that some of these source rocks are at the mature to overmature stages, while MTTCs were present only in immature and low-mature source rocks and not detected in mature and high-mature source rocks (Table 1). The thermal stability of MTTC is weak. The geochemical features and geological significances of MTTCs in evaporite-related source rocks still need to be further researched.

The MTTC parameters were commonly used as important organic geochemical indicators to reconstruct paleosalinity. MTTCs have been detected in the Early Cambrian to Quaternary source rocks (sediments) or crude oils, except for Carboniferous, Silurian, and Ordovician source rocks or crude oils (Table 1 and Figure 3a). Among the source rocks and crude oil samples from which MTTCs were detected, the Cretaceous, Paleogene, and Neogene samples were the most common (Table 1). This may be related to the development of the saline sedimentary environments during the Cretaceous, Paleogene, and Neogene period and the low degree of thermal maturity of these samples (Table 1, Figure 3b). MTTCs were mainly enriched in rock/sediment extracts and crude oils with a low degree of thermal maturity.

Statistics on source rocks and crude oil samples from which MTTCs were detected showed that α-MTTC was detected in almost all source rocks and crude oil samples, while (β + γ)-MTTCs and δ-MTTCs were detected in most samples (Table 1). ζ-MTTC was only detected in individual source rock samples (Table 1).

The origin and formation mechanisms of MTTCs remain unclear. There are two hypotheses for the origin of MTTCs. δ-MTTC was probably synthesized through non-photosynthetic bacteria that was first proposed by Sinninghe Damsté et al. in 1987, suggesting later that MTTCs were biosynthesized via primary photosynthetic producers, although the direct precursors of MTTCs have not yet been identified. However, Li et al. suggested that MTTCs may derive from a nonbiosynthetic path by the condensation reaction of alkylated phenols with phytol during early diagenesis. Jiang et al. suggested that MTTCs were likely derived from photosynthetic organisms and originated in euxinic portions of the photic zones (PZE) not in the upper parts of water columns or bottom waters. The variations in paleosalinity that occur in the PZE perhaps have an important impact on the growth of MTTC-producing organisms and abundance of MTTCs (Figure 4). Previous studies focused on searching evidences for the biogenetic hypothesis of MTTCs by comparing the geochemical parameters obtained from MTTCs and other biomarkers (e.g., distribution, relative abundance, quantitative concentrations, and δ13C values) and the lack of positive studies on whether microorganisms contain MTTCs living in saline environments today.

In the previous research work, stable carbon isotope analysis was suggested to be a facile and reliable way to investigate the origin of MTTCs. Tulipani et al. suggested that MTTCs may originate from condensation reactions by comparing the stable carbon isotope values in pyrolysis products generated from α-MTTC by pyrolysis-gas chromatography-isotope ratio mass spectrometry (PY-GC-irMS). The similar stable carbon isotope ratios among monomethyl (δ-MTTC), dimethyl (β-MTTC, γ-MTTC, ζ-MTTC), and trimethyl (α-MTTC) isomers and comparison with other biomarkers likely suggest that MTTCs may originate from the same biological source, most likely from photosynthetic bacteria. While, Hong et al. and Zhang et al. suggested that δ-MTTC and dimethyl-MTTCs were of algal biogenesis origin instead of bacterial origin. The above controversial conclusions show us that we may need to pay more attention to the research of the stable carbon isotope of MTTCs and develop new analytical methods. We suggested that the precise analysis of the stable carbon isotope of MTTCs would still be an approach to shed new light on the origin of MTTCs.

Tulipani et al. proposed that MTTCs in Devonian rock samples from the Canning Basin form via condensation reactions of phytoplankton derived from phytol with high organic geochemical indicators to reconstruct paleosalinity. This may be related to the development of the saline sedimentary basins in China and Europe. By comparing Figure 2a and Figure 2b, we found that evaporite-related source rocks were globally distributed, while MTTCs were not detected in most of these evaporite-related organic sediments. There are two possible reasons that may explain this situation. One of the possible reasons is that MTTCs in most of these source rocks have not been studied. The other reason is that some of these source rocks are at the mature to overmature stages, while MTTCs were present only in immature and low-mature source rocks and not detected in mature and high-mature source rocks (Table 1). The thermal stability of MTTC is weak. The geochemical features and geological significances of MTTCs in evaporite-related source rocks still need to be further researched.

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plant phenols (Figure 5). However, Dutta et al.\textsuperscript{39} found that MTTCs in Neoproterozoic to Early Cambrian crude oil samples were derived from the Bikaner-Nagaur Basin. The high plant began to appear in the Late Silurian,\textsuperscript{49} so there are no high plant phenols in Neoproterozoic to Early Cambrian source rocks. The MTTCs in Neoproterozoic to Early Cambrian crude oils cannot be explained by the condensation reaction of phytoplankton-derived phytol with high plant phenols (Figure 5). Hence, the controversy over the origins and formation mechanisms of MTTCs will continue.

### PALAEOSALINITY RECONSTRUCTION

The paleosalinity was suggested as the most important factor influencing the changes in the relative abundances of MTTCs,\textsuperscript{3} especially the relative abundance of $\alpha$-MTTC and $\delta$-MTTC.\textsuperscript{50,51} Hence, the $\alpha/\delta$-MTTC ratio and the MTTCI value were established to indicate paleosalinity.\textsuperscript{1} Low $\alpha/\delta$-MTTC ratios (<2) or low MTTCI values (<0.5 or 0.4) reflect high-salinity condition, while high $\alpha/\delta$-MTTC ratios (>100) or high MTTCI values (>0.5 or 0.4) reflect the relative low-

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**Figure 2.** Worldwide distribution of MTTCs in (a) sediments and crude oils and (b) evaporite-related source rocks (modified by Warren\textsuperscript{34}).
Variations in the abundance of δ-MTTC and α-MTTC show a high sensitivity to paleosalinity changes compared to (β+γ)-MTTC. Therefore, the controlling factors of changes in the abundance of (β+γ)-MTTCs may

Table 1. Occurrence of MTTCs in Sediments and Crude Oils

| Location                                      | Sample        | Age     | Lithology                      | Maturity         | δ   | β   | γ   | ζ   | α   | References |
|-----------------------------------------------|---------------|---------|--------------------------------|------------------|-----|-----|-----|-----|-----|------------|
| Rozel Point Oil, northwestern part of Utah    | ▲             | Miocene | /                              | /                | +   | +   | +   | -   | +   | 1          |
| Sicily Seep Oils from Sicily, Italy           | ▲             | Miocene | /                              | /                | +   | -   | +   | -   | +   | 1, 32      |
| Jianghan Basin, China                         | ▲             | Paleogene | /                              | immature         | +   | +   | -   | +   | -   | 3          |
| Taragona Basin, Spain                         | ▲             | Miocene | /                              | immature         | +   | +   | -   | +   | -   | 2          |
| Xiangcheng Sag, Henan Province, China         | ▲             | Paleogene | /                              | immature         | +   | +   | -   | +   | -   | 33         |
| Zhengia-Wangzhuang Oilfield in Jiyang Depression, Bohai Bay Basin, China | ▲             | Paleogene | /                              | marginally mature | +   | +   | -   | +   | -   | 36         |
| Dongying Depression, Bohai Bay Basin, China   | ▲             | Paleogene | /                              | immature to low maturity | +   | +   | -   | +   | -   | 37         |
| Qintong Sag, Subei Basin, China               | ▲             | Paleogene | /                              | immature         | +   | +   | -   | +   | -   | 38         |
| Jizhong Depression, China                     | ▲             | Eocene  | /                              | low maturity      | +   | -   | -   | +   | -   | 3, 32      |
| Bakker-Nagar Basin, Western India             | ▲             | Neoproterozoic–Early Cambrian | /                              | low maturity      | +   | +   | -   | +   | -   | 39         |
| Mazagan Escarpment (DSDP, site 545)           | ●             | Late Miocene-Late Aptian | /                              | /                | -   | +   | -   | +   | -   | 1          |
| Mazagan Escarpment (DSDP, site 547)           | ●             | Late Eocene-Albian | /                              | /                | -   | +   | -   | +   | -   | 1          |
| Angola Basin (DSDP, site 530A)                | ●             | Cretaceous | /                              | /                | -   | -   | -   | -   | +   | 2          |
| Walvis Ridge (DSDP, site 532)                 | ●             | Late Cretaceous–Paleogene | /                              | /                | -   | -   | -   | -   | +   | 4          |
| northwestern part of the Montana, USA         | ●             | Permain marlstones | /                              | /                | +   | +   | -   | +   | -   | 3          |
| Sachrang sample from the southwestern part of the Germany | ●             | Early Jurassic black shale | /                              | /                | +   | +   | -   | +   | -   | 2          |
| Renqiu Oil Field in Hebei Province, China     | ●             | Paleogene mudstone | /                              | /                | +   | +   | -   | +   | -   | 2          |
| Perticara Basin, Italy                        | ●             | Miocene bituminous marl | /                              | /                | +   | +   | -   | +   | -   | 3          |
| Jiangban Basin, China                         | ●             | Paleogene mudstone | low maturity                   | /                | +   | +   | -   | +   | -   | 4, 12      |
| Fushun Open Coal Mine, Liaoning Province      | ●             | Eocene cannel coal | /                              | /                | -   | +   | -   | +   | -   | 41         |
| Jinhu Sag, Subei Basin, China                 | ●             | Paleogene mudstone | low maturity                   | /                | +   | +   | -   | +   | -   | 42         |
| Monterey Formation outcrop, California        | ●             | Miocene claystone, mudstone, muddy limestone | /                              | immature         | +   | +   | -   | +   | -   | 2          |
| Jurf Ed Darawish Oil Shale in Jordan          | ●             | Cretaceous bituminous limestone | /                              | immature         | +   | +   | -   | +   | -   | 3          |
| Huanghua Depression, Bohai Bay Basin          | ●             | Eocene mudstone | low maturity                   | /                | +   | +   | +   | -   | -   | 43         |
| Lower Rhine Basin, NW Germany                 | ●             | Permian marly shale | low maturity                   | /                | -   | -   | -   | +   | -   | 8, 25, 29  |
| Mulhouse Basin, France                        | ●             | Oligocene marl | /                              | +                | +   | +   | -   | +   | -   | 4          |
| Kailu Basin, China                            | ●             | Early Cretaceous mudstone | marginally         | +                | +   | +   | -   | +   | -   | 44         |
| Nördlinger Ries, Southern Germany             | ●             | Miocene shale | /                              | +                | +   | +   | -   | +   | -   | 33         |
| Eastern Bavarian Carbonate Platform, Germany  | ●             | Jurassic Malm limestone | low maturity                   | /                | +   | +   | -   | +   | -   | 8          |
| Dead Sea Basin, Israel                        | ●             | Miocene/Pliocene halite deposits | /                              | /                | +   | +   | -   | +   | -   | 28         |
| Western Qaidam Basin, China                   | ●             | Oligocene mudstone, marl | marginally mature               | +                | -   | -   | -   | +   | -   | 23         |
| Northern Calcareous Alps, Austria             | ●             | Late Triassic carbonate | low maturity                   | -                | +   | +   | -   | +   | -   | 27         |
| sediment samples from the Cismon locality, Italy | ●             | Early Cretaceous limestone | mature                      | -                | +   | +   | -   | +   | -   | 45         |
| Chezhen Sag and Jiyang Depression, Bohai Bay Basin, China | ●             | Paleogene mudstone | low maturity                   | /                | +   | +   | -   | +   | -   | 46         |
| Songliao Basin, China                         | ●             | Late Cretaceous mudstone | marginally mature               | +                | +   | +   | +   | +   | -   | 5, 10, 13, 47 |
| Hungarian Paleogene Basin                     | ●             | Early Oligocene mudstone | low maturity                   | -                | +   | -   | -   | +   | -   | 31         |
| Canning Basin, Australia                      | ●             | Devonian mudstone | low maturity                   | -                | +   | +   | -   | +   | -   | 6, 16      |
| Eastern Azerbaijan                            | ●             | Oligocene claystone | immature                      | +                | +   | +   | -   | +   | -   | 26         |
| Maoming Basin, China                          | ●             | Paleogene oil shale | immature                      | -                | +   | +   | -   | +   | -   | 48         |
| Belaya River, North Caucasus                  | ●             | Oligocene to Early Miocene mudstone | low maturity | +                | +   | +   | -   | +   | -   | 7          |
| Bohai offshore area, Bohai Bay basin, China   | ●             | Paleogene mudstone | immature to marginally mature | /                | +   | +   | -   | +   | -   | 3          |
| Shangsi, Guangyuan, Sichuan Province, China   | ●             | Early Triassic marlstone, mudstone | low maturity                   | /                | /   | /   | /   | /   | +   | 12         |

“Note: ‘+’: detected; ‘−’: not detected; ‘/’: unknown; ‘▲’: crude oils; ‘●’: source rocks or sediments.”
require further research. Also, the rule of the variation in the abundance of ζ-MTTC in source rocks is still poorly understood. MTTCs are very rare in normal marine sediments. Therefore, the occurrence of MTTCs, particularly δ-MTTCs, may indicate higher salinity than the normal marine sedimentes.

In immaturity and low-maturity source rocks or crude oils, except for organic sources, the pristane/phytane (Pr/Ph) ratio is mainly affected by the redox conditions in the sedimentary environments. The Pr/Ph ratio is commonly used to reflect redox conditions in the sedimentary environments. Low Pr/Ph ratios (<0.8) reflect anoxic conditions and the increased probability of high salinity in the sedimentary environments, while high Pr/Ph ratios (>3.0) reflect oxic to suboxic conditions and the increased probability of low salinity. However, Pr/Ph ratios ranging from 0.8 to 3.0 are not proposed for directly indicating redox conditions. A diagram of MTTCI values versus Pr/Ph ratios was built to estimate the salinity levels in the depositional environments. According to Schwark et al. and Wang et al., the paleosalinity can be divided into four grades: the hypersaline environments have salinities of >120‰; mesosaline environments have salinities of ~40 to 120‰; normal marine-like saline environments have salinities from ~30 to 40‰; and semi-saline to freshwater environments have salinities from ~1 to 30‰. As shown in Figure 6a, a positive correlation was observed between MTTCI values and Pr/Ph ratios, which further confirms that the paleosalinity is the main factor for the low Pr/Ph ratio.

In addition to the abovementioned chart that has been widely used (Figure 6a), the ternary diagram of mono-, di-, and trimethyl-MTTCs was established to indicate the variation in the paleosalinity (Figure 6b). The differences in the paleosalinity of the rock samples obtained from the Western Qaidam, Jianghan, and Northern Bohai Bay Basins were clearly illustrated by the ternary diagram (Figure 6b), which were deposited in hypersaline, mesosaline to hypersaline, and normal marine to semi-saline environments, respectively. Therefore, the ternary diagram of the relative abundance of MTTCs can also be used to reconstruct paleosalinity.

■ OUTLOOK

There are still many challenges in the study of the origin and paleosalinity significance of MTTCs. Among these, the research of the origin of MTTCs is the most difficult, and there have been no new breakthroughs in recent years. In future research works, we may need to focus more on integrated research, such as a closer integration with paleontology and inorganic geochemistry, and new ideas are needed. The paleosalinity significance of MTTCs is also worthy of further research. For example, the validity and applicability of MTTC parameters in paleosalinity reconstruction will be further clarified by the study of the correlation between MTTC parameters and inorganic geochemical parameters. Previous studies have demonstrated the effectiveness of the MTTC parameters in paleosalinity reconstruction by comparing MTTC parameters with other organic geochemical parameters but with lack of comparison with inorganic geochemical parameters. Therefore, the lack of the

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**Figure 3.** (a) MTTCs were detected in the Early Cambrian-Quaternary sediments or crude oils, except for the Carboniferous, Silurian, and Ordovician sediments or crude oils. (b) MTTCs were mainly detected in samples with a low degree of thermal maturity.

**Figure 4.** Conceptual model illustrating the biosynthetic origin of MTTCs. MTTCs were suggested derived from photosynthetic organisms and originate in euxinic portions of photic zones (PZE). The organisms that produce MTTCs thrive under the conditions of PZE. Algae and terrigenous organisms occur in the upper part of the water column (modified after Tulipani et al. and Jiang et al.). Reprinted with permission from Jiang, Lin, Zhang, Cai, Xiao, He, and Peng (2018). Copyright 2018 Elsevier

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**Table 1.** Occurrence of MTTCs in different geological periods.

| Era      | Period | Ma     | Occurrence of MTTCs |
|----------|--------|--------|---------------------|
| Cenozoic | Quaternary | 2.58  |                     |
|         | Neogene   | 23.03  |                     |
|         | Paleogene  | 66.0   |                     |
| Mesozoic | Cretaceous | ~145.0|                     |
|         | Jurassic   | ~201.3|                     |
|         | Triassic   | 251.902±0.024 |               |
| Paleozone | Permian   | 298.9±0.15 |              |
|         | Carboniferous | 358.9±0.4 |              |
|         | Devonian   | 419.2±3.2 |                     |
|         | Silurian   | 443.8±1.5 |                     |
|         | Ordovician | 485.4±1.9 |                     |
| Precambrian | Cambrian | 541.0±1.0 |                     |
comparison study may reduce the reliability of MTTC parameters in paleosalinity reconstruction.

**CONCLUSIONS**

From this review, it is clear that MTTC parameters have become important indicators for paleosalinity reconstruction in the field of organic geochemistry. This is particularly encouraging in view of the outstanding issues, which remain with respect to the origin and paleosalinity significance of MTTCs. For example, more in-depth research of paleosalinity significance of MTTCs by way of comparing MTTC parameters with inorganic geochemical parameters will probably reveal more paleoenvironmental information than presently known. As the increase in comprehensive research centered on MTTCs, opportunities will arise to gain new understandings about the origin and formation mechanism of MTTCs. Finally, an improved understanding of the organic geochemistry of MTTCs will further promote their application as paleoenvironmental proxies.

**AUTHOR INFORMATION**

*Corresponding Authors*

*E-mail: haokaisi5535553@163.com (K.J.)*

*E-mail: cmlin@nju.edu.cn (C.L.)*

**ORCID**

Kaixi Jiang: 0000-0001-5137-0747

**PRESENT ADDRESS**

School of Earth Sciences and Engineering, Nanjing University, No. 163, Xianlin Road, Qixia District, Nanjing, China.

**NOTES**

The authors declare no competing financial interest.

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